THE ELECTRON MOBILITY IN INDIUM PHOSPHIDE

BY

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Hall effect and resistivity measurements have been carried out as a function of hydrostatic pressure and temperature on a number of samples of indium phosphide ranging from exceptionally pure to highly doped.

In the case of pure and lightly doped InP an iterative solution of the Boltzmann Equation has been used successfully to describe the temperature and pressure dependence of mobility over the helium temperature range.

Measurements on the highest mobility samples of InP ever grown suggest that the conduction band deformation potential is 6.7eV.

For the case of highly doped material it was found that a theory of scattering from a correlated distribution of impurities describes both the temperature and pressure dependence of mobility well.

pressure dependent mobility measurements on a sample having an impurity density close to the Mott transition suggest that the inclusion of impurity band conduction in the analysis is necessary even at nitrogen temperatures and above. Such an analysis is used successfully to describe the temperature and pressure dependence of both mobility and Hall carrier concentration.
ACKNOWLEDGEMENTS

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I would also like to thank Mr. E.J. Thrush of S.T.C. Technology for supply of the high purity samples studied.

At Surrey special thanks are due to Mr. C.G. Crookes and Dr. D. Lancefield for their help with the experimental work and to Dr. M.A. Fisher for our many interesting arguments. I would also like to thank Mr. B.J. Gunney and Mr. K. Dinan for their technical assistance and Miss J.E. Boud for her assistance with the preparation of the manuscript. Finally I would like to thank the remaining members of the O.D.M. group for their assistance.
PUBLICATIONS

The following papers and presentations are based on the work in this thesis

"Low temperature electron transport properties of exceptionally high purity InP" GaAs and Related Compounds: Heraklion (1987)


Accepted for publication in Semiconductor Science and Technology


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\( r_B \) Boltzmann's constant

\( l \) linear coefficient of thermal expansion

\( m^* \) electron effective mass

\( M \) mass density

\( n \) electron concentration

\( n_i \) intrinsic electron concentration

\( N_A \) acceptor concentration

\( N_C \) effective density of states at conduction band edge

\( N_D \) donor concentration

\( N_I \) density of localised potential centres

\( N_N \) density of neutral impurities

\( N_S \) density of space charge regions

\( N_v \) effective density of states at valence band edge

\( p \) hole concentration

\( P \) piezo-electric constant

\( q \) electronic charge

\( Q \) number of equivalent minima in conduction band

\( r \) Hall factor

\( R \) total correlation length

\( R_0 \) Thomas Fermi screening length

\( R_S \) Debye length

\( S_{ij} \) element of strain tensor

\( S(k,k') \) differential scattering rate involving states at wave vector \( k \) and \( k' \)
<table>
<thead>
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<th>Meaning</th>
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<td>Varshni coefficient</td>
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<td>( \alpha_1 )</td>
<td>non-parabolicity factor</td>
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<td>( \beta )</td>
<td>Varshni coefficient</td>
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<td>correlation length for correlated potential fluctuations</td>
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<td>spin split off energy</td>
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<td>( \Delta E_{Fi} )</td>
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<td>scattering-in probability flux</td>
</tr>
<tr>
<td>( \nu_o )</td>
<td>scattering-out probability flux</td>
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<td>mass density</td>
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<td>( \tau )</td>
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<td>longitudinal optic polar phonon frequency</td>
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<tr>
<td>( \omega_{to} )</td>
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deformation potential tensor
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The first detailed experimentation on InP was carried out by Welker (1953). After an initial period of evaluation interest in the material waned (presumably because of its similarity to the more established GaAs).

Interest in InP was rekindled, first by the discovery of the Gunn effect, later by interest in the material for solar cell applications and most recently in semiconductor layer structures.

InP in conjunction with the alloys InGaAs and GaInAsP is important as a component of emitters and detectors for use in optical fibre communications where it is invaluable as both an active component and as a substrate.

The development of new growth techniques has led to both new applications and improved material quality with the achievement of previously unprecedented purity.

In this thesis the electron transport properties of InP are investigated as a function of both temperature and pressure. Variation of temperature has long been used as a method of studying the mechanisms controlling the electron mobility in semiconductors, whilst the effect of pressure on band energies and consequently on the effective mass enables further studies of each mechanism. The recent development, at Surrey, of a high pressure/low temperature cell now enables both variables to be altered simultaneously. In particular the effect of temperature
variation on a very high purity sample of InP, having the highest
mobility ever measured has produced information about acoustic
phonon deformation potential scattering. Pressure variation at low
temperature on samples close to the Mott transition has shown the
importance of the impurity band on conduction in these samples. In
the case of highly doped samples the high pressure/low temperature
cell has enabled investigation of the effects of correlation of
impurities on electron transport.

The thesis is organised as follows. Chapter two describes the
crystal structure, band structure and other intrinsic material
properties. Chapter 3 discusses the Boltzmann equation and
mechanisms affecting the electronic transport properties of the
material. Conduction at low temperature in an impurity band is
described in chapter 4. The experimental apparatus and techniques
used in the course of this work are dealt with in chapter 5. In
chapter 6 results of temperature and pressure investigations of
high purity and nominally undoped InP are presented and discussed.
Chapter 7 deals with electron transport in doped InP. Finally
chapter 8 is reserved for concluding remarks and suggestions for
further work.
2.1 CRYSTAL STRUCTURE

InP like all the well known III-V semiconductors crystallises into the sphalerite (zinc blende) structure. This is illustrated in figure 2.1 where the heavier (In) atoms are shaded black. It is similar to the diamond structure of group IV semiconductors with the obvious difference of two types of atom. The structure is often pictured as two interpenetrating face centred cubic structures displaced one from the other by 1/4 of the body diagonal.

From the diagram it is clear that the bonding is tetrahedral. The outer electrons of the Indium having an $s^2p^1$ configuration and those of Phosphorous having $s^2p^3$ form. The favoured form of bonding is thus covalent with the formation of $sp^3$ hybrid bonding orbitals.

The first Brillouin zone is illustrated in figure 2.2. The most important symmetry points are labelled and correspond to those in figure 2.3 which will be discussed later. From the symmetry of the figure it is clear that, where as there is only one $\Gamma$ point there are 6 equivalent X and 8 equivalent L points.

2.2 BAND STRUCTURE

The band structure of InP is shown in figure 2.3. This structure was calculated by Chelikowski and Cohen(1976). As far as
Figure 2.1 Unit Cell of zinc blende structure

Figure 2.2 First Brillouin for zinc blende lattice.
FIGURE 2.3 InP BAND STRUCTURE

Band structure of InP from Chelikowsky and Cohen (1976)
our studies go the most important point is the Γ point at the Brillouin zone centre. Both the conduction band minimum and the valance band maximum occur at this point. It is thus a direct gap semiconductor. The valence band maximum consists of two degenerate bands; the light and heavy hole bands and a third close band; the spin split-off band.

The conduction band minimum is fortunately less complicated consisting of a single band, the next highest minimum L being approximately 0.5eV above it. The X and L satellite minima are sufficiently far displaced in energy to contain an insignificant quantity of electrons at room temperature and below but become important at high temperatures, electric fields or pressures. Values of the important energies and their temperature and pressure coefficients are tabulated later in table 2.1.

At points in k space very close to k=0 the conduction band energy follows a parabolic relationship in k. Where the energy can be written:

\[
E = \frac{\hbar^2 k^2}{2m}
\]

Here E is measured from the conduction band edge. At larger values of k non parabolicity is taken into account by writing:

\[
E(1+\alpha_1 E) = \frac{\hbar^2 k^2}{2m}
\]

Where \(\alpha_1\) is the non-parabolicity factor describing the degree of non-parabolocity.
2.3 CARRIER CONCENTRATION

2.3.1 INTRINSIC CASE

The carrier concentration \( n \) is governed by the number of occupiable conduction band states \( N(E) \) and a function representing the probability of each state being full.

For the total conduction band:

\[
N(E) = \frac{Q \sqrt{2}}{\pi^2} \left( \frac{E^2 - E_T^2}{h^3} \right)^{1/2} \left( \frac{m_de}{\hbar^2} \right)^{3/2}
\]

\[
F(E) = \frac{1}{1 + \exp((E - E_f)/K_B T)}
\]

Where \( Q \) is equal to the number of equivalent minima in the conduction band. For InP at atmospheric pressure electrons are at the \( \Gamma \) point and \( Q = 1 \).

Substituting 2.3.3 and 2.3.2 into 2.3.1 and performing the integration gives:

\[
n = 2 \left( \frac{2\pi Q K_B T}{h^3} \right)^{3/2} \frac{M_c F_1/2}{\sqrt{2}} \left( \frac{E_f - E_c}{K T} \right)
\]
Where \( F \) is the Fermi integral which is a function of the reduced Fermi level \( \eta = E_f/K_B T \):

\[
F_{1/2} = \int_0^\infty \frac{\eta}{1 + \exp(\eta - \eta_f)} \, d\eta \tag{2.3.5}
\]

For a non-degenerate semiconductor under the condition \( KT \ll E_c \):

\[
F_{1/2} = \sqrt{\pi} e^{\eta_f/KT} \tag{2.3.6}
\]

and

\[
n = N_c \exp\left\{-(E_c-E_f)/KT\right\} \tag{2.3.7}
\]

for holes:

\[
p = N_v \exp\left\{-(E_f-E_v)/KT\right\} \tag{2.3.8}
\]

In the case of an intrinsic semiconductor each conduction band electron has a corresponding valence band hole. In this case:

\[
n = p = n_i \quad \Rightarrow np = n_i^2
\]

and hence:

\[
n_i = \sqrt{N_c N_v \exp(-E_g/2K_BT)} \tag{2.3.9}
\]

At room temperature even in the purest samples of InP the carrier concentration is dominated by carriers supplied by impurities. However at high temperatures intrinsic carriers dominate and the band gap energy can be obtained as the slope of the \( \log(n) \) versus \( 1/T \) plot.
2.3.2 EXTRINSIC CASE

The inclusion of either donor or acceptor impurities into the semiconductor leads to extrinsic conduction. Donor or acceptor impurity levels with binding energies corresponding to a small fraction of the band gap and sufficiently small that ionization can occur at normal temperatures are termed shallow. Calculation of the binding energies was originally considered by Mott and Gurney (1940) for the case of groups III and V impurities in silicon and germanium.

The impurity is considered simply as an electron having the effective mass of the semiconductor band to which it is tied moving in the field of the charged impurity ion. The problem is then reduced to that of the hydrogen atom giving:

\[
E_d = \frac{m^* n^4}{32\pi^2 E_h^2 n^2}
\]

This gives for InP donor levels of 7meV and acceptor levels at about 50meV.

Strictly this expression is only true for very low impurity activation energy concentrations. At higher concentrations the donor \( A \) (assuming n-type) reduces and eventually disappears as a result of two effects. First the large number of free electrons at high impurity concentrations will tend to screen the potential due to the impurity atom and secondly an increase in impurity concentration will result in reduced spacing between impurities and increased overlap of wave functions associated with electrons on donor levels. This will cause energy level spreading and the formation of an impurity band in a similar way to the formation of bands in a solid as individual atoms come together. This effect becomes particularly significant when the inter-impurity spacing is
reduced to few Bohr radii. In InP this happens at around $10^{16}$ cm$^{-3}$.

By consideration of the conditions for charge neutrality,

$$n + N_A^- = p + N_D^+$$

$$n + \frac{N_D}{1 + g \exp[(E_d - E_f)/KT]} = N_D - N_A \quad 2.3.11$$

Where $g$ is the degeneracy factor = 1/2 for donors. A similar expression is obtained for holes with $g = 1/4$ due to double degeneracy of the valence band. The binding energies $E_d$ and $E_a$ manifest themselves in the so called "freeze-out" region at low temperature in light and averagely doped semiconductors.

Another effect which can occur as a result of the presence of impurities is band tailing. This only becomes noticeable at high impurity concentrations ($\approx 10^{18}$ cm$^{-3}$ for InP). If the impurity distribution is not uniform then the attraction of areas of higher concentration (where impurities are clumped together) for electrons will cause local distortion of the conduction and valence band. There will then be spatially separated tail states below the average position of the conduction band edge.

2.4 TEMPERATURE DEPENDENCE OF THE DIRECT BAND GAP

To apply the preceding expressions to a semiconductor at finite temperature it is necessary to know the temperature dependence of $E_g$. This can be accounted for in terms of two effects. Lattice dilation, which accounts for only about one third of the total shift in energy and electron-phonon interactions. In the presence of phonons local disturbances in the band energy produce "dips" in the conduction band edge into which electrons "gravitate". The overall result being the accumulation of electrons in areas of narrower band gap producing a decrease in
energy gap at higher temperatures.

Ehrenreich (1957) gives the following expression for the effect of dilation on the band gap:

\[ E_g(T) = E_g(0) - 3lT \frac{\partial E_g}{\partial P} \frac{1}{K} \]

2.4.1

Where \( l \) is the linear coefficient of thermal expansion and \( K \) is the compressibility.

The temperature dependence of the band has been fitted empirically by Varshni (1967) using:

\[ E_g(T) = E_g(0) - \frac{\alpha T}{T+\beta} \]

2.4.2

The values for \( E_g(0) \) and the Varshni coefficients \( \alpha \) and \( \beta \) are included in table 2.1.

2.5 EFFECTIVE MASSES

Effective masses are related to the curvature of the bands. The \( k.p \) method uses second order perturbation theory to provide a way of evaluating the band energies and hence the effective...
masses in the region of a relative minima in $k$ space. The following expression for the effective mass has been derived by (Roth et. al. (1959):

$$\frac{1}{m^*} = \frac{p^2}{E_0} \left\{ \frac{2}{E_0} + \frac{1}{E_0 + \Delta_0} \right\} \quad 2.5.1$$

Where $p^2$ is the interband squared matrix element describing the coupling between bands.

The above expression gives a clue as to the temperature and pressure dependence of the effective mass if the dependence of $E_0$ is known. The temperature dependence of $m^*$ may be described in terms of the above expression by including the dilation effect on $E_0$ in the Ehrenreich expression (equation 2.4.1). This is discussed by Woods and Stradling (1968,1970).

The pressure dependence of $m^*$ can again be understood by 2.5.1 since it is clear that $m^*$ increases with $E_0$.

### 2.6 OTHER MATERIAL PARAMETERS

Apart from a knowledge of the effective mass and band energies a number of additional parameters are required to quantitatively analyse data using the expressions in subsequent chapters. Several reviews of the properties of InP are available including Bachmann (1981) and Adachi(1982), who reviews a number of III-Vs and their alloys.

The lattice constant, mass density, sound velocity and elastic constants are all closely inter-related and have a bearing on phonon scattering.

The lattice constant and mass density are related to temperature through the thermal expansion coefficient. The thermal
expansion coefficient can be regarded as linear for the region of interest to this thesis although there is some deviation from linearity at higher temperatures (>750K)(Glazov (1977)).

The lattice constant quoted is for 291K and atmospheric pressure. At approximately 130 Kbar a phase transformation takes place with the InP taking up the NaCl structure (Jamieson (1963)).

Sound velocity measurements (Hickernell Gayton (1966)) reveal the elastic constant from which a compressibility or bulk modulus may be obtained.

2.6.1 PHONONS

The phonon dispersion curves for InP are shown in figure 2.4. The experimental points were obtained by Borcherds et. al.(1975) using inelastic neutron scattering techniques. In the case of optical phonons the frequencies \( \omega_{lo} \) and \( \omega_{to} \) can be regarded as approximately constant throughout the zone.

2.6.2 DIELECTRIC CONSTANTS

The dielectric constant is a measure of the amount of polarization that can be induced by an electric field. At low frequencies dipoles present in the material can follow the field, however at higher frequencies such that \( 1/\omega \gg \tau_d \) where \( \tau_d \) is the characteristic time constant for the dipole response they will be unable to follow. Two dielectric constants are quoted \( \varepsilon_s \) and \( \varepsilon_\infty \).
figure 2.4 Phonon Dispersion Curves for InP

Phonon Dispersion Curves for InP from Borcherds et al. (1975)
representing the low frequency and high frequencies respectively.

These are related by the Lyddane Sachs Teller relationship.

\[
\frac{\varepsilon_S}{\varepsilon_{\infty}} = \left( \frac{\omega_1}{\omega_{\infty}} \right)^2
\]

2.6.3 DEFORMATION POTENTIALS

The deformation potential is defined as the shift in energy of the band edge per unit elastic strain.

The deformation potential tensor \( E \) is of rank two. If the strain tensor \( S_{ij} \) is defined as:

\[
S_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)
\]

Where \( u \) is the displacement of the unit cell. Then the change in energy can be written:

\[
\Delta E = \sum E_{ij} S_{ij}
\]

Herring and Vogt (1956) show that for cubic crystals such as the III-Vs the number of independent deformation potential components reduces to two which they label \( E_d \) and \( E_u \) relating to pure dilation and pure shear respectively. The \( \Gamma \) valley is unaffected by shear strains (Herring and Vogt (1956)) and for this case a deformation potential may be related to the pressure coefficient of the band. It may then be defined simply as:

\[
E_1 = \frac{1}{K} \frac{dE}{dP}
\]

where \( E \) in this case refers to the value of the band energy at the \( \Gamma \) point with respect to some pressure independent reference.

It should be noted that it is normally impossible to separate
conduction and valence band deformation potentials and where a measurement is made by optical techniques it is the whole direct band gap deformation potential that is measured. That is to say the $E$ in the above expression is replaced by $E_g$. There is evidence to suggest that the valence band deformation potential is small in which case such a measurement will be of the conduction band deformation band. This will be discussed further in chapter 5.

2.6.4 PIEZOELECTRIC CONSTANT

The dimensionless piezoelectric constant $P$ is isotropic for the zinc blende structure. Rode(1975) writes, for zinc blende:

$$P^2 = e_{14}^2 \varepsilon_0 \left[ \frac{12}{c_1} + \frac{16}{c_t} \right] \frac{1}{35}$$

2.6.3

Where $e_{14}$ is the one independent element of the piezoelectric stress tensor and $c_1$ and $c_t$ are the spherically averaged elastic constants for longitudinal and transverse modes.

Zook (1964) writes:

$$c_1 = \frac{(3c_{11} + 2c_{12} + 4c_{44})}{5}$$

$$c_t = \frac{(c_{11} - c_{12} + 3c_{44})}{5}$$

The elastic constants have been measured by Hickernell and Gayton (1966). Substituting these into the above expressions shows (Rode (1975)) that for sphalerite structures the transverse mode scattering is approximately four times greater than longitudinal.

2.6.5 PRESSURE COEFFICIENTS OF ENERGIES AT CONDUCTION BAND MINIMA

Of the three types of minima the $\Gamma$ minimum is the most
important to this work. It is also the easiest to measure and consequently is the best catalogued. A comparatively large number of measurements of its pressure dependence have been made.

The higher minima are less well documented. The figures quoted in table 2.1 suggest that the X minima do not cross the \( \Gamma \) minimum until pressure in the region of 100 kbar is reached. Thus in all the work discussed here the band gap remains direct.
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<th>SYMBOL</th>
<th>Value</th>
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<td>Å</td>
<td>a</td>
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<td>gcm$^{-3}$</td>
<td>b</td>
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(d) Hickernell and Gayton (1966)  
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(w) This work chapter 5
3.1 INTRODUCTION

In a real semiconductor the motion of an electron under applied electric field is impeded by intrinsic mechanisms, (lattice scattering), by extrinsic effects (impurity and defect scattering) and by the presence of other carriers.

In this chapter the influence of various scattering mechanisms is discussed. Expressions for the effect of each mechanism are given in terms of partial mobilities, the mobility an electron would have if the mechanism under discussion were the only scatterer present. A method of combining all the effects to produce a total mobility - the iterative solution of the Boltzmann equation - is discussed. This method does not involve a knowledge of the partial mobilities and instead requires a wave vector dependent relaxation rate for each mechanism. These relaxation rates are tabulated in appendix (i). The partial mobilities are quoted in this chapter because they lead more readily to simple comparison with experimental results.

3.2 THE BOLTZMANN EQUATION

If a quantity \( f_k(r) \) is defined so that it represents the concentration of carriers in the state \( k \) at position \( r \) in space then there are three ways in which \( f_k(r) \) can change with time. These are: by diffusion, by the effects of external fields and by scattering.

The rate of change of the distribution due to diffusion can
be written as follows:

\[
\frac{\partial f}{\partial t} \bigg|_{\text{diff.}} = -v_k \nabla f_k 
\]

3.2.1

The effects of both electric and magnetic fields can be included by means of the Lorentz equation:

\[
\dot{k} = \frac{q}{\hbar} \left[ \mathbf{F} + \mathbf{v}_k \times \mathbf{B} \right] 
\]

3.2.2

If \( k = \frac{\partial k}{\partial t} \)

\[
\frac{\partial f}{\partial t} \bigg|_{\text{fields}} = \frac{\partial f}{\partial k} \frac{\partial k}{\partial t} = -\frac{q}{\hbar} \left[ \mathbf{F} + \mathbf{v}_k \times \mathbf{B} \right] \frac{\partial f}{\partial k} 
\]

3.2.3

The effects of scattering can be included by the following:

\[
\frac{\partial f}{\partial t} \bigg|_{\text{scatt}} = \int \left\{ S(k,k') f_k (1-f_{k'}) - S(k',k) f_{k'} (1-f_k) \right\} dk 
\]

3.2.4

In the above the electron is scattered from state \( k \) to state \( k' \) and vice-versa. \( S(k',k) \) is the probability per unit time that an electron initially in the state \( k' \) makes a transition to the state \( k \). \( S(k',k) \) is known as the differential scattering rate.

The integral states that the rate of change of \( f \) with \( t \) due to scattering processes depends on the product of the basic transition probability, the density of electrons in state \( k \) and the number of vacancies in the state \( k' \) integrated over all possible states.

Combining 3.2.1, 3.2.2, 3.2.4:

\[
0 = -(e/\hbar)F \cdot \mathbf{v}_k f(k) + \int dk \left[ S(k,k') f(k) - S(k',k) f(k') \right] 
\]

3.2.5
Where it has been assumed for the time being that $B = 0$.

3.2.2 DRIFT AND HALL MOBILITIES

Initially the drift mobility $\mu_d$ is defined as the average electron velocity per unit field measured as the field $F$ tends to zero. It can be written:

$$\mu_d = \frac{\int v_k E f(k) \, dk}{\hbar F \int f(k) \, dk} \quad 3.2.6$$

$$= \frac{e \langle \tau \rangle}{m} \quad 3.2.7$$

Where $\langle \tau \rangle$ is the scattering relaxation time,

The Hall mobility is written:

$$\mu_H = \frac{e \langle \tau^2 \rangle}{m \langle \tau \rangle} \quad 3.2.8$$

If $\tau$ is energy dependent then in general the ratio $r = \langle \tau^2 \rangle / \langle \tau \rangle$ will not be equal to unity and the drift and Hall mobilities will differ by a multiplicative factor $r$ which normally varies between one and two. This quantity is often known as the Hall factor.
3.2.2 MATTHIESEN'S RULE

This result from the relaxation time approximation which assumes that the distribution of electrons emerging from collisions is independent of the distribution immediately prior to the collision. Then the rate at which the distribution \( f \) relaxes back to \( f_0 \) the Fermi Dirac distribution can be written:

\[
\frac{\delta f}{\delta t} = -\frac{(f-f_0)}{\tau(k)}
\]

Where the relaxation time \( \tau \) is written:

\[
1/\tau(k) = \sum_1 1/\tau_1(k)
\]

If it is also assumed that \( \tau \) is \( k \) independent then a direct consequence of 3.2.10 is:

\[
1/\mu = \sum_1 1/\mu_1
\]

This is known as Matthiessen's rule and has been used in this work in a few cases where approximate evaluations of theoretical mobilities are required. All the accurate calculations have been performed using the Iterative Solution of the Boltzmann Equation described in the next section.

3.2.3 THE ITERATIVE SOLUTION OF THE BOLTZMANN EQUATION

This is a technique first used by Rode (1970). This method does not involve the assumption connected with Matthiessen's rule that the electron distribution is known prior to combining the partial mobilities. The distribution function is calculated from a knowledge of individual \( k \) dependent relaxation rates before the
effects are combined to produce an overall mobility. Secondly the problem of defining a single relaxation rate for the inelastic process of polar optic phonon scattering is avoided by the inclusion of separate scattering-in and scattering-out rates.

Rode (1970) writes the total distribution function for the low applied field case as:

$$f_t = f_o + xg$$

3.2.12

The function is divided into two parts an equilibrium part $f_o$, which is the Fermi-Dirac distribution, and a perturbation part $g$. $x$ is the cosine of the angle between $k$ and the driving force (in this case electric field $F$). The induced drift current is entirely contained in $g$.

Substituting 3.2.12 in 3.2.5, multiplying by $x$ and integrating over $x$ produces (according to Rode(1975)) the following equation:

$$\frac{eF \delta f_o}{\hbar \delta k} = \frac{\nu_i - \nu_o}{x}$$

3.2.13

Where the $\nu_i, \nu_o$ are the scattering probability fluxes due to the unbalanced part of the distribution $g$.

$$\nu_i = \int dk \left[ s(k,k')xg(k) \right]$$

3.2.14

$$\nu_o = xg(k) \int dk \left[ s(k,k') \right]$$

3.2.15

If the differential scattering rates $s(k,k')$ are known then it is possible to obtain the distribution $g(k)$ from 3.2.13. in the following way.

For acoustic phonon deformation potential, piezo-electric and ionised impurity a scattering rate including both $\nu_i$ and $\nu_o$ can be
Where all scattering mechanisms have been combined into $S_o$. For the case of polar optic phonons the scattering-out rate can also be included in $S_o$. However the inelastic nature of this scattering mechanism requires that $g(k)$ be evaluated at different wavevectors $k^+$ or $k^-$ for scattering-in depending on whether phonon emission or absorption has taken place.

\[ S_{i^{+}} = \frac{\nu_{i^{+}}}{xg(k^+)} \quad 3.2.17 \]

\[ S_{i^{-}} = \frac{\nu_{i^{-}}}{xg(k^-)} \quad 3.2.18 \]
Putting equations 3.2.18, 3.2.17 and 3.2.16 into 3.2.13 results in.

\[ g(k) = \frac{S^+_{ip} g(k^+) + S^-_{ip} g(k^-) - eF \frac{\partial f}{\partial k}}{h \frac{\partial k}{\partial k}} \]  
3.2.19

\[ S_0 \]

In practice a more sophisticated form is used which allows additionally for the perturbing effects of finite magnetic field.

The total distribution is written:

\[ f_t = f_o + xg(k) + yh(k) \]  
3.2.20

Where \( h(k) \) is the distribution due to the magnetic field effect alone and \( y \) is the cosine of the angle between \( B \) and \( k \). The other parameters are the same as in the previous expression. Rode (1973) shows that the problem then becomes one of solving the following two coupled differential equations:

\[ g_{I+1} = \frac{S I_i(g_i) - eF \frac{\partial f}{\partial k} + \beta S I_i(h_i)}{(S I_o + S e_1)(1 + \beta^2)} \]  
3.2.21

\[ h_{I+1} = \frac{S I_i(h_i) - e\beta F \frac{\partial f}{\partial k} + \beta S I_i(g_i)}{(S I_o + S e_1)(1 + \beta^2)} \]  
3.2.22

Where \( \beta = eB(S I_o + S e_1) \)

In this case \( S I_i \) and \( S I_o \) represent inelastic scattering into and out of the volume element in question. \( S e_1 \) is the sum of all elastic scattering rates. This is the form used in our I.S.B.E.. The inclusion of the effect of magnetic field allows Hall mobilities to be calculated.
SCATTERING MECHANISMS

The rest of this chapter describes a number of scattering mechanisms which need to be considered with respect to InP. It is divided into two sections. The first deals with those intrinsic mechanisms which are a direct property of the material. The second deals with extrinsic factors resulting from impurities and imperfections. Those mechanisms which are included in the I.S.B.E. are tabulated in appendix (i) in the form of relaxation rates.

3.3 LATTICE SCATTERING

At temperatures above OK the atoms of the lattice will vibrate about their equilibrium positions. There are a number of different ways they can do this. The wave of vibrations passing through the crystal can be either of the longitudinal type or of the transverse type. In addition for crystals containing two atoms per unit cell the two types of atoms can form separate chains vibrating in anti-phase with one another. It is clear that these vibrations can be paired in four ways; longitudinal and transverse with neighbouring atoms in phase, and longitudinal and transverse with neighbouring atoms in anti-phase. The in-phase vibrations are known as acoustic as they can propagate no faster than the speed of sound. The anti-phase vibrations are known as optic. Looking at the acoustic phase first. There are two ways these can scatter electrons.

3.3.1 DEFORMATION POTENTIAL ACOUSTIC MODE SCATTERING

Rarefaction and dilation of the lattice atoms associated with
longitudinal acoustic waves cause local changes in the band gap and distortion of both conduction and valence bands. An electron moving in the conduction band sees a potential produced by this atomic displacement, the magnitude of which is associated with the deformation potential. The energy shift in the conduction band (in ev) is equal to the product of deformation potential and strain due to the acoustic vibration.

Bardeen and Shockley (1950) give the following expression for deformation potential limited electron mobility.

\[
\mu_{dp} = \sqrt{2\pi} \frac{h^4 \rho u_T^{3/2} m^{-5/2}}{3eK_B^{3/2}E_1^2}
\]

3.3.2. PIEZO-ELECTRIC SCATTERING

This mechanism occurs if the atoms constituting the crystal are partly ionised. The displacement of electrons from their equilibrium positions causes a redistribution of charge and change in potential. Zook (1964) gives the following expression for Piezo-electric limited electron mobility;

\[
\mu_{pe} = \frac{1.714(10)^{-58}}{\varepsilon s T^{-1/2} m^{-3/2}} e_{14}^2 \left(\frac{4}{C_t} + \frac{3}{C_1}\right)
\]
This mechanism is of some importance to InP at low temperatures. However even in the purest material it is still obscured at low temperatures by ionised impurities and at high temperatures by both polar phonons and deformation potential scattering.

Electrons can be scattered by optical phonons in two ways also.

3.3.3 OPTICAL MODE DEFORMATION POTENTIAL

Optic vibrations can also produce a perturbing potential which in this case is proportional to the strain induced by the optic phonon. The magnitude of the electron interaction with this optic potential is highly dependent on band structure symmetry and tends to be weak for electrons at the \( \Gamma \) point or at the \( <100> \) minima (Conwell (1967)). The strongest interactions are with \( <111> \) minima. It is consequently unimportant for most compound semiconductors.

The mobility limit for this mechanism is discussed by Conwell (1959), (1967).
3.3.4 Polar optic phonon scattering.

For materials containing two or more different atoms e.g. all compound semiconductors this is an important scattering mechanism.

Scattering occurs via electric fields which are set up by LO phonons. Transverse optic phonons do not produce macroscopic fields and do not take part in this scattering process.

This is the dominant mechanism in InP at room temperature. The early work of Ehrenreich (1959) has been extended by Fortini et. al. (1970) to produce the following expression for polar optic phonon limited mobility:

\[
\mu_{po} = \frac{16\hbar e_0 (2\pi K_b^{1/2}) G(z)(\exp(z)-1)T^{1/2}}{3e\omega_1 (1/\epsilon_\infty - 1/\epsilon_0)}
\]

In this expression \( z \) is the reduced phonon energy \( (\hbar \nu_1/K_B T) \) and \( G(z) \) is a function of \( z \) which varies between .6 and 1.5 over the range of interest.

The previously mentioned processes of lattice scattering may be further sub-divided into more classes: intravalley and intervalley scattering.

In a lattice scattering event the total energy of the electron and phonon are conserved. If an electron travelling in the lowest minimum near the \( \Gamma \) point is scattered by a low wave vector phonon it will not, because of momentum conservation, be scattered out of this minimum. Scattering in which the carrier remains in the same valley is known as intravalley scattering and is the process considered so far.

In materials where there are several equivalent minima close in energy it may be possible for an electron to be scattered by a large wave vector phonon to another valley. This is particularly
likely in the case of indirect semiconductors. At high fields an
electron may gain enough energy whilst travelling in a low valley
to be scattered at constant energy to higher valleys. Scattering
from one valley to another in this way is termed intervalley
scattering.

In InP intervalley scattering will become significant at high
pressures when the material is close to becoming indirect. Our
experiments here have been limited to 8Kbar and therefore such
effects are not included in the analysis. A full discussion of
scattering in many valley semiconductors is given by Herring and
Vogt (1956).

3.4 EXTRINSIC SCATTERING

3.4.1 IONISED IMPURITY SCATTERING

Impurities are included in a semiconductor either by accident
due to limited purity of source materials and cleanliness of
growth equipment or deliberately in an attempt to dope the
material to create free carriers of the chosen type. In general
these impurities will be ionised at temperatures above a few
Kelvin. The Coulomb potential of the ion will scatter the
electron. It can be thought of in a way similar to Rutherford
scattering. If a scattering cross section is defined as :

\[ \sigma(\theta)\,d\omega \propto \text{cosec}^4(\theta/2)\,d\omega \]  

3.4.1

Where the electron is scattered through an angle \(d\omega\) into a
solid angle \(\theta\).
The conduction cross section is defined as:

\[ \sigma_c = 2\pi \int_0^1 (1 - \cos\theta) \sin\theta \, d\theta \quad \text{3.4.2} \]

Then upon integration an infinite conduction cross section is obtained. It is the fact that the Coulomb field of the charged centre does not extend to large distances because it is modified by the presence of carriers and by the neighbouring impurities that prevents this occurrence in reality. There have been various attempts to modify this expression. Conwell and Weiskopf (1950) defined a radius equal to \(1/2(N_i)^{1/3}\) (half the mean distance between impurities) beyond which the Coulomb field is assumed to be ineffective.

Dingle (1955) has modified the above by approaching the problem from the fact that the field of the charged centre modifies the carrier distribution in its vicinity so the electrostatic potential decays as \((1/r)e^{-r/d}\) where \(r\) is the distance from the centre and \(d\) is the debye length.

The theory of Brookes and Herring (1955) has made an attempt to modify Dingle's theory further to include screening by neighbouring impurities including (for n-type materials) compensating acceptors.
Brookes Herring theory gives the ionised impurity limited mobility as:

$$\mu_{BH} = \frac{128\sqrt{2\pi}}{m} \frac{\varepsilon_o \varepsilon_s}{N} \frac{2}{Z} \frac{q^2}{q^3} \ln(1+b) - \frac{b}{1+b}$$

3.4.3

Where \( b = \frac{4k^2}{\beta_s^2} \)

$$n d \beta_s = \frac{q}{\varepsilon_o \varepsilon_s K_B T} \left\{ \frac{n F_{-1/2}}{F_{1/2}} + \frac{(N_D - N_A - n)(N_A + n)}{N_D} \right\}$$

3.4.4

Where \( F_{1/2} \) and \( F_{-1/2} \) are Fermi integrals of order 1/2 and -1/2 respectively. These are tabulated in appendix (ii). The ratio of Fermi integrals in equation 3.4.4. varies between 1 and 2 for cases of interest.

A simpler, slightly more readily understandable form of equation 3.4.3. may be derived by making the approximation \( b \gg 1 \) in which case the term in brackets reduces to \((\ln(b))^{-1}\). If high temperature is assumed \((n \approx N_D)\) and no compensation \((N_A = 0)\). Then writing:

$$k^2 = \frac{2m \varepsilon}{h^2}$$

The \( \ln \) term becomes:

$$\left\{ \ln \left[ \frac{24m \varepsilon_o \varepsilon_s (K_B T)^2}{nq^2 h^2} \right] \right\}^{-1}$$
3.4.2 NEUTRAL IMPURITY SCATTERING

This mechanism gives rise to a small effect and only begins to become significant at low temperatures when carrier freeze out occurs. Two formulism exist. The earlier expression Erginsoy (1950) gives an energy independent scattering rate:

\[ \mu_{NI} = \frac{q^3 m^*}{80N_n \pi \varepsilon_o \varepsilon_s h^3} \]

Where \( N_n \) is the neutral impurity density.

The work of Sclar (1956) has produced a slightly more complicated expression which has a weak temperature dependence but produces low temperature mobilities of essentially the same order. The effect of this mechanism is very small even at low temperatures. In our analysis the Erginsoy expression is used.

3.4.3 SPACE CHARGE SCATTERING

This form of scattering was first suggested by Weisberg (1962) as a way of explaining anomalously low mobilities observed in certain semiconductors.

The assumption is that locally inhomogeneous areas of semiconductor give rise to large regions of surrounding spacecharge. Weisberg suggest that the inhomogeneous distribution of coulombic centres produces scattering cross sections over an order of magnitude greater than that of a single impurity. The region surrounding, say, an impurity cluster will be depleted of carriers and hence create an "insulating void". The work of Gossick (1959) assumes that the area of inhomogeneity is such as to cause inversion of conductivity type but is however flexible
enough to be extended to more general cases.

Weisberg (1962) gives the mobility limit due to space charge scattering as:

\[ \mu_{sc} = q(N_s (2m^*_B T)^{1/2} A)^{-1} \]  \hspace{1cm} 3.4.6

Where the space charge regions are assumed to be totally impenetrable to the carriers, \( A \) is the effective scattering area of the regions of inhomogeneity and \( N_s \) is the concentration of space charge regions. Gossick (1959) has considered two types of region. For spherical regions and for cylindrical viewed perpendicular to the axis where \( r \) is the effective radius of the space charge region.

For the cylindrical case \( r \) is found to vary as \( (T/N)^{1/3} \) and for the spherical as \( (T/N)^{1/6} \) hence conveniently for both cases the mobility can be written as:

\[ \mu_{sc} = C n^{1/3} T^{-5/6} \]  \hspace{1cm} 3.4.7

Where \( N \) is the carrier concentration and \( C \) is a multiplicative constant.
3.4.3 CENTRAL CELL SCATTERING

This is scattering due to the core potential of an impurity. Such potentials are screened at large distances and will only effect the mobility of an electron passing close to its centre.

Recent work by Stringfellow and Kunzel (1980) on the high temperature transport properties of GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has shown that a partial mobility with a $T^{-1/2}$ dependence similar to that of space charge scattering is required to explain low high temperature mobilities. However constant illumination has no effect on the mobility. Further more intentional compensation using Ge and Zn has no effect on the additional partial mobility. For this reason they suggest that the additional mechanism is due to scattering from the central cell of the substitutional impurity carbon which replaces arsenic in the lattice. (N.B. carbon has a much larger electronegativity than arsenic.)

The partial mobility has the form:

$$\mu_{cc} = \frac{3q}{16(2\pi^{3/2})N_I \hbar^2} \left[ \frac{15}{8} \left( \frac{K_B T}{E_I} \right)^{1/2} + \frac{E_I}{(K_B T)^{1/2}} \right] m^{*1/2}$$  \hspace{1cm} 3.4.8

In the above $E_I$ is the localised scattering potential and $N_I$ is the density of localised potential centres.

Chattopadhyay (1980) has determined a relaxation time for scattering by localised potentials and applied it to an iterative solution of the Boltzmann equation. Good agreement with experimental results for GaAs has been obtained using a localised scattering potential of 95mev.
3.5 SCATTERING BY POTENTIAL FLUCTUATIONS

In the case of heavily doped semiconductors (for InP \( n > 5(10)^{17} \)) it has been suggested (Yanchev et. al.(1979)) that it is no longer reasonable to consider scattering from individual impurities.

Coulomb interactions between free carriers and ionized impurities in the melt will result in correlation of the distribution which will be frozen in upon solidification at a temperature \( T_0 \) where impurity diffusion becomes insignificant.

For highly doped material several impurities lie within a screening length and scattering can be considered as being due to a smooth randomly fluctuating potential rather than due to individual impurities. For a randomly fluctuating potential obeying Gaussian statistics a relaxation time has been derived (Yussouf and Zittartz(1973)):

\[
\tau^{-1} = \frac{\alpha \gamma^2}{\hbar k_f R E_f}
\]

\[3.5.1\]

\( E_f \) and \( k_f \) are the Fermi energy and Fermi wave number respectively, \( \gamma \) is the rms. potential energy and \( R \) is the correlation length (ie. the potential changes by \( \gamma \) in a distance \( R \)).
The numerical factor $\alpha$ is given by Yanchev et al. (1979) for the cases of a random distribution $\alpha_1$ and a correlated distribution $\alpha_2$:

$$\alpha_1 = \frac{1}{8} \int_0^\infty dy \frac{y}{(1 + y)^2} \text{erfc} \left( \frac{E_S y}{4\gamma_1} - \frac{E_F}{\gamma_1} \right)$$  \hspace{1cm} 3.5.2

$$\alpha_2 = \frac{1}{16} \int_0^\infty dy \frac{\text{erfc}(E_S y/4\gamma_2 - E_F/\gamma_2)}{1 + y + (R_S/R_0)^2}$$

$$+ \frac{1}{16} \int_0^\infty dy \frac{\text{erfc}(E_S y/4\gamma_2 - E_F/\gamma_2)}{y[1 + y + (R_S/R_0)^2]}$$  \hspace{1cm} 3.5.3

The $\gamma_1$ and $\gamma_2$ are given by:

$$\gamma_1^2 = 2 \int \frac{d^3 q}{(2\pi)^3} D_1(q) = N_1 R_S e^{4/4\pi\varepsilon_0 \varepsilon_r^2}$$  \hspace{1cm} 3.5.4

$$\gamma_2^2 = \frac{2N_1}{\varepsilon_0 \varepsilon_r^2} \left\{ 1 + \frac{2}{\pi} \frac{R}{R_S} \left[ \frac{R_S - \pi}{R} + \text{artan} \left( \frac{R}{R_S} \right) \right] \right\}$$  \hspace{1cm} 3.5.5

The correlation length is equal to the Thomas-Fermi screening length $R_S$ for a random distribution and, for the correlated distribution is dependent on both the Thomas-Fermi screening length and the Debye length of the ionized impurities at temperature $T_0$.

$$R = (R_0^{-2} + R_S^{-2})^{-\frac{1}{2}}$$  \hspace{1cm} 3.5.7

The quantity $T_0$ varies with the donor and acceptor concentration and varies upwards as the compensation ratio $K$ changes from 0, (Yanchev and Evtimova (1985)).

When performing these calculations at such high impurity levels it is necessary to include corrections to the fermi level
due to the interactions of electrons with each other and with the ionised impurities. To this end the fermi level is written:

$$E_F = E_F - \Delta E_{FT} - \Delta E_{Fe} - \Delta E_{Fi}$$  \hspace{1cm} 3.5.8

The correction due to finite temperature:

$$\Delta E_{FT} = \left(\frac{\pi k_B T}{E_F}\right)^2/12E_F[1 + (12/\pi^3)k_F a]$$  \hspace{1cm} 3.5.9

a is the effective Bohr radius.

The correction due to exchange interactions is written:

$$\Delta E_{Fe} = \frac{e^2 k_F}{4\pi \varepsilon_0 \varepsilon}$$  \hspace{1cm} 3.5.10

and the impurity interaction effect (band tailing) is:

$$\Delta E_{Fi} = \frac{\chi^2}{8E_{F0}}$$  \hspace{1cm} 3.5.11
3.6 SCATTERING BY CHARGE CARRIERS

3.6.1 ELECTRON-ELECTRON SCATTERING

Electron-electron scattering results in exchange of energies between electrons and, because momentum is conserved it is not obvious how this form of scattering would result in changes of mobility. However the resulting equalisation of energies between electrons modifies the electron distribution and ultimately the scattering mechanisms.

A number of authors have published their theoretical findings including Appel(1961) and Luong and Shaw (1971). Bate et. al.(1965) have produced expressions for corrections to various scattering mechanisms. The reduction of the mobility is greatest for ionised impurity scattering. Consequently the effects are largest in intermediateley doped material where ionised impurity scattering is significant but where the material is not degenerately doped.

3.6.2 ELECTRON-HOLE SCATTERING

This type of scattering is important in narrow gap semiconductors or at high temperatures where there are significant quantities of both electrons and holes present. Taking the hole as an immobile point charge it is possible to use a modified form of B-H theory to describe the behaviour. This is reasonable if the hole mobility is small compared to that of the electron.
4.1 INTRODUCTION

Impurity band conduction was first observed by Hung and Gleissman (1950) in silicon and germanium and has since been studied in a range of semiconductors including GaAs and InP (Emel'yanenko et al. (1974)). At temperatures such that the majority of carriers have trapped out of the conduction band it would be expected for the resistivity to grow large exponentially as temperature is decreased further. It is in fact found experimentally that at these low temperatures a new conduction mechanism with a much weaker exponential dependence becomes apparent.

4.2 HOPPING CONDUCTIVITY

A thorough study of the temperature dependence of resistivity at low temperature has been made for germanium by (Fritzsche and Cuevas (1960)). A number of samples were included showing variation over a large range of carrier concentrations with a constant compensation ratio.

The resistivity was found to have the form:

\[ \rho^{-1} = \rho_3^{-1} \exp(-\epsilon_3/KT) \]
The activation energy $\varepsilon_3$ is usually of the order of a factor of ten less than the impurity binding energy resulting in a shallower slope in the impurity conduction regime.

It has been shown (Miller and Abrahams(1960)) that $\rho_3$ has the form:

$$\rho_3 = \rho_c \exp\left(\frac{\alpha}{N_d^{1/3}} a_B\right)$$

where $\rho_c$ is a constant and $a_B$ is the effective Bohr radius for the material in question. $\alpha$ is a constant ($= 1.75$) which has been calculated by Shklovskii and Efros (1984).

The currently accepted mechanism is of phonon assisted tunnelling between impurity centres (Mott (1956))(Conwell (1956)). This is illustrated in figure (4.1). The presence of acceptors is necessary for this type of conduction to occur. At low temperatures there will be very few electrons in the conduction band. In a compensated semiconductor there will be both charged (empty) donors and neutral (full) donors. Conduction can then occur by tunnelling of electrons from full donors to empty donors. The acceptors will all have "accepted" electrons and therefore will be positively charged. The random field of the charged acceptors will then produce fields giving rise to a small energy spread of the donor levels. The tunnelling process can only then occur under the assistance of a phonon. This is the origin of the activation energy $\varepsilon_3$. 
The presence of acceptors results in "empty" donor allowing tunnelling between impurity levels.

The results of Fritzshe and Cuevas have shown that $\varepsilon_3$ is independent of impurity concentration at lower impurity levels. At high impurity levels the activation energy gradually dissappears with the conduction ultimately becoming metallic as $\varepsilon_3 \rightarrow 0$.

To discuss this effect it is helpful to divide doped semiconductors into three categories. If $a_B$ is the Bohr radius of the impurity atom and $N_I$ is the impurity concentration then the three regimes are:

- lightly doped \( N_I a_B^3 \ll 1 \)
- moderately doped \( N_I a_B^3 \approx 1 \)
- heavy doped \( N_I a_B^3 \geq 1 \)

At very low concentrations the wavefunctions of electrons on impurities do not overlap and as the temperature goes to zero the resistivity goes to infinity. At high concentrations there will be considerable overlap and a band will be formed, which at a high impurity concentration will extend into the conduction band. For this case there will be finite conductivity as the temperature
tends to zero. Metallic conduction then occurs in the impurity band.

4.3 THE MOTT TRANSITION

Mott(1949), (1961) first suggested that the change from insulator to metal is not a gradual process and in fact occurs as a sharp transition.

The process can be thought of in a semiconductor in the following way. At low temperature in a lightly doped semiconductor electrons are strongly bound to donor impurities by the coulomb interaction. At these low carrier concentrations the material is on the insulator side of the Mott transition with the carriers being strongly localised. According to Mott increasing the impurity concentration will not give rise to electrons in extended states until the donor density reaches a level where the corresponding electrons can produce sufficient screening of the coulomb potential to allow the electrons to remain unbound.

An approximate expression for the critical number of electrons \( n_{cr} \) required for this transition to take place can be derived in the following way (see for example Zimman(1972).

Any free electrons will tend to screen the ionic charge so that the potential at distance \( r \) from the ion core is reduced by a multiplicative factor \( e^{-\lambda r} \). Where \( \lambda \) is the Debye screening length:

\[
\lambda^2 = \frac{4mq^2n^{1/3}}{\hbar^2}
\]  

4.3.1
If the screening radius is defined as \( r_s = \frac{1}{\lambda} \) and the lowest bound state of the hydrogen atom is \( a_B \):

\[
a_B = \frac{\hbar^2}{mq^2}
\]

Then the electron cannot be bound for the case \( r_s < a_B \) which produces the following condition.

\[
n_{cr} \approx (0.25/a_B)^3
\]
5.1 INTRODUCTION

This chapter describes the preparation and measurement techniques for Hall effect samples.

5.2 SAMPLE PREPARATION

Samples for Hall effect experiments were prepared in a number of different ways. Clover leaf samples were either etched or ultrasonically cut. Metal contacts were produced by evaporation or by alloying tin or indium dots into the material. The preferred method is etching followed by evaporation. However some samples have been prepared by ultrasonically cutting clover leaves. This has the advantage of being simple and quick. However it is not such an economical technique resulting in the loss of comparatively large amounts of material.

5.2.1 ETCHING METHOD

This method was used for the preparation of the majority of samples discussed including the high purity ones. It is used at Surrey as a standard technique. The following is a description of this method of preparation.

Samples are initially cleaned in a variety of solvents
starting with a 10 minute boil in methanol and followed by a similar treatment in trichlorethylene. Finally the sample is cleaned in distilled isopropal alcohol by placing it in a reflux unit so that it comes into contact with the vapour and with drops of distilled liquid.

Three layers of Shipley AZ 1350H photoresist are spun on at 8000 rpm for 1 minute each and the sample is pre-baked for a period of 20 minutes at 80°C. The clover leaf pattern is printed onto the specimen by use of a photographic mask and a Radio Spares UV exposure unit No. 555-279 350mm. The exposure time required has been determined by trial and error to be 15 mins.

The sample is next developed in a mixture of NaOH and de-ionised water until the resist has been totally removed from the exposed areas. Traces of NaOH are removed by an additional wash in de-ionised water and the sample is post baked at 120°C for 30 minutes to harden the resist.

The clover leaf pattern is etched into the sample by using a 3:1:1 mixture of 40% sulphuric acid; 30% hydrogen peroxide and de-ionised water. The etch rate has been estimated to be 1.5μm/min. at 50°C for InP and normally enough time is allowed for a total thickness of about twice the epilayer to be removed. Remaining traces of the etch are washed off using de-ionised water.

Finally the photoresist is removed by soaking the sample in acetone or methanol.
5.2.2 METALLIC CONTACTS

The specimen is again cleaned using the three stage process described above and a single layer of photoresist is spun on again at 8000 rpm for one minute. The sample is then pre-baked in the same way as above. A negative mask of the contacts is used during the U.V. exposure and after development of the resist a shorter, lower temperature post bake is used (90°C for 2 minutes). This keeps the resist softer to ease the lift-off process after the inevitable heating during evaporation.

The surface is lightly etched in a 20:4:1 solution of de-ionised water; hydrogen peroxide and ammonia for 20 seconds to provide a fresh clean surface for metal to adhere to.

For n-type InP gold tin/nickel is evaporated onto the specimen. A shutter is provided so that the sample is protected from the initial evaporant which may be contaminated.

After contact evaporation the resist is removed using acetone or a proprietry resist stripper. The unwanted metal is "lifted off" with the resist.

After a final cleaning the contacts are alloyed in hydrogen/nitrogen flow for 10 minutes at 350°C.

A resin bonded diamond cutting wheel is used to separate individual clover leaves.
5.3 HALL EFFECT APPARATUS AND MEASUREMENT TECHNIQUE

5.3.1 MEASUREMENT TECHNIQUE

Samples produced by the method described above (5.2.) are of the van der Pauw clover leaf variety. The choice of this type of sample is based on work by van der Pauw (1958 a and b). In these papers a method of measuring both the Hall effect and resistivity on flat samples is described. Such a technique overcomes problems such as the requirement that the current flow in bar samples be parallel provided the following conditions are fulfilled:

(a) the contacts are on the circumference of the sample
(b) the contacts are small

If the four contacts to the clover leaf are labelled a,b,c and d and $R_{abcd}$ is defined as the ratio of the potential difference $V_d - V_c$ to the current passed from a to b then according to van der Pauw the following expression is true for the sample resistivity:

\[ R_{abcd} \frac{V_d - V_c}{I_{ab}} = \rho \]

*figure 6.1* The different configurations for Hall effect measurement on Van der Pauw samples
\[ \rho = \pi d \frac{(R_{ab,cd} + R_{bc,de})}{2 \ln(2)} f \left\{ \frac{R_{ab,cd}}{R_{bc,da}} \right\} \]

Where \( f \) is a function of the ratio \( R_{ab,cd}/R_{bc,da} \) only and is given by:

\[ f = 1 - \left( \frac{R_{ab,cd} - R_{bc,da}}{R_{ab,cd} - R_{bc,da}} \right)^2 \frac{\ln(2)}{2} - \left( \frac{R_{ab,cd} - R_{bc,da}}{R_{ab,cd} + R_{bc,da}} \right)^4 \]

The constant \( \varepsilon = \left\{ \frac{\ln(2)}{4} - \frac{\ln(2)}{12} \right\} \)

For perfectly symetric samples \( R_{ab,cd}/R_{bc,da} = 1 \) and \( f = 1 \). As the sample becomes more asymetric \( f \) begins to deviate more greatly from 1.

The Hall mobility is shown to be given by.

\[ \mu = \frac{\frac{d \Delta R_{bd,ac}}{B \rho}}{} \]

Where \( \Delta R_{ab,cd} \) is the change in the resistance \( R_{ab,cd} \) due to the application of magnetic field \( B \).

The Hall effect measuring equipment is fully automated controlled by a BBC microcomputer via an I.E.E.E. instrumentation bus. The heart of the system is a d.c. current source built at Surrey which can source current from \( 1\mu A \) up to 10 mA. Sample voltages are measured using a Keithley 196 digital multimeter, which can measure down to \( \mu V \). The complex switching required to enable all different measurement combinations is performed by a 3D
relay box. Two different magnets have been used; a Newport Instruments magnet capable of producing fields up to 10000 Gauss and a solenoid magnet which can produce up to 1000 Gauss. (The solenoid although producing smaller fields has the advantage, by virtue of the axial field, of permitting easy optical access to samples). The magnets are driven by a Herts series 4000 power supply which can source up to 10 Amps.

5.4 CRYOSTAT SYSTEM

The experiments which go down to 4K have been performed using an Oxford Instruments CF1200 continuous flow cryostat operated with a GFS300 gas cooled transfer tube. This equipment is shown in figure(5.2).

Helium enters the transfer tube through the small needle valve in the base of the leg. The flow of helium is controlled by a control nut near the top of this leg. A flexible section is provided to simplify connection between cryostat and storage vessel. In this section return gas flows concentrically around the inlet tube thus effectively radiation shielding the inlet flow. The gas return is pumped by a Compton diaphragm pump.

Inside the cryostat the coolant is fed down a capillary into the copper heat exchanger at the bottom of the cryostat. This heat exchanger is fitted with a AuFe/chromel thermocouple and a 68Ω heater. Coolant then flows over the sample and is exhausted through a hole about 10cm from the top of the sample tube. It then passes over a second heat exchanger which serves to cool the radiation shield. It is finally returned via the gas transfer
gas return

ring seal

needle valve control

syphon entry arm

exhaust line

feed line

sample space

position of heat exchanger, heater and temperature sensor

Figure 5.2 The continuous flow cryostat system
The heater is controlled via the I.E.E.E bus using an Oxford instruments 3120 controller.

Using this system we are able to routinely perform measurements down to 3.8K.

5.5 HIGH PRESSURE TECHNIQUES

5.5.1 PRESSURE MEDIA

In our pressure experiments the sample to be studied is placed in a medium which is compressed. The choice of the medium is critical to the success of the given experiment. Factors such as compressibility, freezing points, optical transmissivity, electrical properties, corrosivness and ease of pressure sealing have to be taken into account.

The table below lists a range of pressure media used in the course of this work including approximate freezing pressures (Kbar) and freezing temperatures (K) (where known) and their advantages/disadvantages.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Freezing pressure</th>
<th>Freezing temp</th>
<th>Advantages/Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Castor oil</td>
<td>15</td>
<td>200</td>
<td>Easy to seal</td>
</tr>
<tr>
<td>Pentane/Isopentane</td>
<td>20</td>
<td>100</td>
<td>Highly compressible. Hard to seal</td>
</tr>
<tr>
<td>Methanol/Ethanol</td>
<td>&gt;100</td>
<td>40</td>
<td>Can damage electrical insulation. Hard to seal</td>
</tr>
</tbody>
</table>
Experiments using the Hall effect in the 8Kbar piston and cylinder apparatus have employed castor oil only because this seals well and acts hydrostatically up to 8Kb.

Experiments using the high pressure/low temperature cell use a more complicated system of pentane in the intensifier and high pressure capillary with vegetable oil (which has similar properties to castor oil but is slightly less viscous) covering the sample space in the cell. It was found that the two liquid system was necessary to achieve low temperature/high pressure measurements without loss of pressure at the freezing point of pentane. The vegetable oil freezes first around the sample at a constant pressure maintained by the still-liquid pentane. Pentane freezes at a lower temperature giving rise a change in volume of the pentane at the cold end of the capillary. This has a negligible effect on the sample pressure because it is already "frozen-in" by the oil and because there is a relatively small volume of pentane at the cold end of the capillary. Photoconductivity experiments confirm that pressure changes resulting from freezing are negligible.

5.5.2 PISTON AND CYLINDER SYSTEM

*Figure (5.3)* shows a diagram of the piston and cylinder apparatus used to obtain hydrostatic pressures up to 8Kb. The dimensions of the cylinder are approximately I.D. 1.15", O.D. 5" and height 5.25".
figure 5.3 8 Kbar piston and cylinder setup
The cylinder is held in a steel ring which, although not bearing load, provides support and protection from high pressure liquid in case of cylinder failure.

The pistons are made from hardened tool steel. The thrust piston and bottom piston being identicle in all ways except length - the diameter being 29.2mm. The bottom piston is stationary and does not require the travel needed for the top piston. It is therefore often shorter. Electrical lead throughs are provided via hardened steel plugs ground into ceramic sleeves. Wires are connected and passed through a central hole in the piston. Depending on the type of measurements taking place either 0.6 mm insulated copper wire or RG 178/BU coax is used. On later pistons where pentane is to be used as the pressure transmitting fluid it has been found that ceramic is inadequate as a seal and in this case a new type of seal has been developed involving "Vespel" and a slightly larger silver steel plug.

Sealing between piston and cylinder is achieved by means of two sealing rings (figure 5.5). A neoprene "O"-ring provides low pressure sealing (up to ≤ 2 Kbars) and at higher pressures a nylon or phospher bronze ring provides a seal.

Diagrams of a typical piston and of a second type of piston used when the system is to be used as an intensifier are shown in figure 5.5. In the intensifier piston Harwood High pressure capillary is passed through a central hole and sealed by means of "Vespel". The piston has no electrical lead-through and the top is flat. The lead-throughs on the bottom piston are used to accommodate a manganin pressure gauge and a chromel-alumel thermocouple. The manganin gauge consists of a number of turns of
Figure 5.4 Stationary piston showing manganin gauge mounting

Figure 5.5 Two different thrust pistons. (a) is used as a sample mount for measurements inside the cell. The piston in (b) is fitted with high pressure capillary so that the system can be used as an intensifier.
36swg manganin wire giving a total resistance of about 100 Ω. The pressure is directly related to the resistance according to:

\[ P_1 - P_2 = \frac{1}{\varepsilon} \ln \left( \frac{R(P_1)}{R(P_2)} \right) \]  

5.5.1

\( R(P_1) \) and \( R(P_2) \) are the resistance at pressures \( P_1 \) and \( P_2 \) respectively, \( \varepsilon \) is given by Peggs(1983) as \( 2.3(10)^{-3}\text{Kbar}^{-1} \). The above expression is simplified by taking \( P_0 = \text{atmospheric pressure} \approx 1 \) and taking this as equal to zero on a kilobar scale.

Preparation of the manganin gauge is not simple requiring careful winding of the coil in a strain free way followed by careful temperature cycling in castor oil to 120°C and pressure cycling.

The manganin gauge is mounted on the lower piston as shown in figure 5.4.

If used as a straight forward piston and cylinder apparatus with the sample mounted on the cylinder it is possible to use a heater coil which can be mounted on the bottom piston to produce a small temperature variation in the range room temperature to 40°C.

After pressure changes it is necessary to monitor the system until the temperature has equalised. It normally takes around 15 minutes for the temperature inside the cell to return to room temperature after an increase of about 1 Kbar corresponding to a temperature rise of about 2°C. Due to its large thermal mass the system does not fluctuate by more than about 2K during a twelve hour period and thus temperature fluctuations do not present a
A magnet is mounted on the top piston for Hall effect measurements. The toroidal electromagnet consists of a mumetal former having a pole gap of 1.0mm and a pole surface area of $0.5\text{mm}^2$ around which is wrapped about 250 turns of 0.18mm diameter enamled copper wire. It has been found that a 60mA constant current source can produce a magnetic field of about 500 Gauss. At this level of current heating effects in the coil are negligible and the magnetic current is turned off whilst pressure changes are made and during the stabilisation period.

Hall samples are mounted in a C-shaped frame, between sheets of plastic for insulation. The frame is then inserted between the poles of the magnet and then held in place with p.t.f.e tape.

5.5.3 THE HIGH PRESSURE LOW TEMPERATURE CELL

This cell was also developed at Surrey and is described more fully in a paper by Lambkin et. al.(1988).

The cell is shown diagramatically in figure 5.8. The cylinder is double walled made from grade 250 Cu:Be heat treated to a final hardness of 34 Rockwell C. The outer diameter is 19mm allowing access to our cryostat. The inner bore is 5mm diameter allowing ample space for Hall clover leaf samples.

The bottom piston is blank. The top piston has a standard Harwood seal to eighth inch Harwood stainless steel tubing through which high pressure liquid is fed from an intensifier system.

Electrical contacts to the sample are provided via 0.07mm diameter enamled copper wire which is passed down the capillary.
Figure 5.6 The use of the Harwood three way coupler to provide access for both electric wires and high pressure fluid.
Figure 5.7 Two sample mounts for high pressure low temperature cell. (a) Flat mount for use with Newport magnet and (b) a "cage" mount for use with solenoid magnet.

Figure 5.8 The high pressure low temperature cell.
An optical fibre (140/100) provides optical access. The pressure access for fibre and wires is obtained by means of an epoxy/nylon seal in a stub of capillary connected in a Harwood three way coupler. This set up is in figure 5.6. The wires and fibre are fixed into the short length of capillary using a mixture of MgO powder and Araldite grade MY 750 epoxy which is sucked into the tube and freed from air bubbles in a vacuum system. The high pressure end of this stub has a nylon seal which consists of a disc of nylon (diameter 1mm and length 2mm) having a 250 μm hole in the centre. It is threaded over the wires and sits in a counter sunk hole in the stub. If a fibre is to be used as well as the six wires the hole diameter is increased to 300μm.

The third arm of the coupler holds high pressure capillary from the intensifier. Two intensifier systems are available, a small portable system which is described in the paper by Lambkin et.al.(1988) and the piston and cylinder described in section 5.4.

The mini system has been calibrated against load using a manganin gauge in the intensifier. The piston and cylinder has a manganin gauge permanently fitted in the intensifier system. This enables continuous monitoring of the pressure during experiments. It has been shown from photoconductivity measurements on semiconductor samples that, using this system with the two liquid technique discussed in section 5.4., the pressure in the small cell is equal to that in the intensifier system throughout the temperature range 300 - 4K.
CHAPTER 6

TEMPERATURE AND PRESSURE STUDIES OF ELECTRON MOBILITY IN PURE
INP

6.1 INTRODUCTION

In chapter 7 the effect of doping on the transport properties of InP is discussed. Before considering these effects, due to ionised impurity scattering and impurity band conduction, results of measurements on high purity and nominally undoped InP are presented and a comparison with theoretical predictions, using an iterative solution of the Boltzmann Equation, is made. Results from the very pure layers give clear details of the intrinsic transport properties by extending the phonon domination of scattering down to lower temperatures than ever before. Depletion effects peculiar to thin high purity samples are discussed in terms of their effects on transport properties and the measured Hall carrier concentration. The effect of high pressure, up to 8Kb, on the electron mobility throughout the helium temperature range is presented and comparisons with theoretical predictions are given.

6.2 ATMOSPHERIC PRESSURE RESULTS

Figure 6.1 shows Hall Mobility measurements at 2000 Gauss for three nominally pure InP samples.

Sample (c) at \((N_D - N_A)\) around \(5 \times 10^{14} \text{ cm}^{-3}\) represents a typical undoped sample having a 77k mobility in the region of \(8 \times 10^4 \text{ cm}^2\)
**Figure 6.1** Temperature dependence of Hall mobility for three samples. Solid lines I.S.B.E generated fits.

θ = compensation ratio
Figure 6.2 Open circles raw Hall carrier concentration data for samples (b) and (c). Closed circles data corrected for Hall factor and depletion. Solid lines fits using equation 2.3.11.
Samples (a) and (b) have 77k mobilities in the region of $3(10)^5$ cm$^2$ v$^{-1}$s$^{-1}$ and $2.2(10^5)$ cm$^2$ v$^{-1}$s$^{-1}$. The highest purity sample peaks at around $4(10)^5$cm$^2$ v$^{-1}$s$^{-1}$. The measured room temperature Hall carrier densities are in the region of $3(10)^{13}$cm$^3$ for sample (a) and $5(10)^{13}$cm$^3$ for (b). Samples (a) and (b) represent the highest mobilities ever recorded in InP (sample (a) having a 77K mobility of greater than two times the previous highest recorded (Di Forte Poisson et al (1985)) and consequently these are excellent samples with which to test theories of phonon scattering using the I.S.B.E..

The high temperature mobility is limited by optical phonons whilst, at low temperatures ionised impurity effects dominate. In the region where the mobility turns over the characteristic is not dominated by any one mechanism but is a combination of several. It is at this point where acoustic phonon deformation potential effects are most important but by no means dominant. An ideal sample to study acoustic phonon scattering in this material would contain no ionised impurities so that at least one masking effect would be removed.

The experimental results of figure 6.1 have been analysed using the I.S.B.E. including all the mechanisms presented in appendix (i) and using the parameters of chapter 2.

The solid lines in the figure are theoretical fits to the results using the I.S.B.E.. In these cases the unknown acceptor density has been used as a fitting parameter. The carrier concentration has been self consistently corrected for the Hall factor $r_H$ by a recursive process. The carrier concentration is replaced by the $r_H$ corrected value and the program is re-run. It
is usually found that approximately three corrections are needed to determine the correct drift carrier concentration.

Before proceeding with the analysis of less pure samples the two very high purity layers were used to determine the choice of conduction band deformation potential.

This parameter has caused some controversy over recent years. Many workers have analysed their transport results by including the deformation potential as a variable parameter. Values obtained in this way vary considerably from 3.4eV (Takeda and Sasaki(1984)) to 18eV (Nag and Dutta(1978)).

In our analysis we proceed by taking results from the two highest mobility samples and using the I.S.B.E. to obtain the best fit paying particular attention to the characteristic near the peak.

It has been found that good fits to our experimental results can be obtained if a deformation potential of 6.7eV is used with the compensation ratios shown. The fits are excellent below 200K although there is a discrepancy at higher temperatures for the very pure sample which is discussed later. It is important to note that although it is possible to fit to various portions of the curve with higher values of $E_1$ and correspondingly lower values of $N_A$ it is not possible to fit throughout the peak and low temperature region with any other combination. It is at the peak where the curve is most sensitive to values of $E_1$.

This value is considerably lower than many values obtained from transport measurements. It is, however close to values obtained optically from the pressure dependence of the direct band gap (Müller et al (1980)) and to theoretical values (Cardona and
Christensen (1987)). It is also close to values obtained recently by (Nolte et. al. (1987)) where $E_1$ has been measured directly by looking at the effects of strain on deep Ti and V levels associated with the conduction band, which has resulted in the figure 7.0eV.

Optical measurements relate the pressure rate change of band gap to $E_1$ and thus incorporate effects from both conduction and valence bands (this has been discussed in 2.6.3). The fact that our conduction band deformation potential closely agrees with these summed effects must suggest that the valence band moves little with pressure which is the observed case in GaAs where an optically determined deformation potential of around 9eV (Welber et.al.(1977)) also produces good agreement with transport results (Lancefield et. al.(1987)).

In the case of thin pure samples it is important to also include corrections for depletion at the surface and substrate. The raw Hall carrier concentration data (for samples (b) and (c)) as measured assuming a constant layer width is plotted for these samples in figure 6.2. The characteristic for sample (a) will be discussed later. Sample (c) shows an initial apparent trap-out between 300K and 150K. This has the appearance of being due to the presence of a deep level. It can, however be explained in terms of the temperature dependence of the surface and substrate depletion widths. Such an effect has been observed in high purity GaAs (Skromme et al (1985)). The result is to alter the effective thickness of the Hall sample. Methods of correction to the thickness are discussed by Chandra et. al.(1978) where it is applied to the case of GaAs.
The depletion width at the surface/interface $l_{s,1}$ is given by:

$$l_{s,1} = \left[ \frac{2e\varepsilon_0(V_{s,i} - K_BT)}{q(N_D - N_A)} \right]^{1/2}$$  \hspace{1cm} 6.2.1

where $V_{s,i}$ are surface and interface potentials given by:

$$V_s = \phi_s - K_BT \ln \left( \frac{N_C}{N_D - N_A} \right)$$  \hspace{1cm} 6.2.2

$$V_i = (E_c - E_T) - K_BT \ln \left( \frac{N_C}{N_D - N_A} \right)$$  \hspace{1cm} 6.2.3

$\phi_s$ is the surface barrier height.

$E_T$ is the energy level of electron traps in the substrate, ie. the Fermi level is pinned at $E_T$ in the substrate.

$N_C$ is the effective density of states in the conduction band.

If the true "metallurgical" thickness of the sample is $d_r$, then the thickness required for Hall calculations $d_T(T)$ is given by:

$$d_T = d_r - l_s - l_i$$  \hspace{1cm} 6.2.4
The situation is illustrated in figure 6.3 below.

For iron doped substrates the Fe\(^{2+}\) trap level is taken as being 0.64eV below the conduction band (Fung et al. (1979)). Which gives the interface barrier height. The surface barrier presents a few problems. It will depend on the history of the surface, i.e. sample preparation. The work of Spicer et al (1979) shows that the Fermi level position varies from 0.9eV to 1.2eV above the valence band in n-type InP depending on oxygen exposure. The calculation performed here takes the lower of these values giving a surface barrier height of 0.5eV.

The method of correction is as follows. The Hall data does not give a true carrier concentration but instead gives the product of the carrier concentration and the thickness of the conducting layer n.d\(_T\)\(d(T)\). To initially estimate d\(_T\)(T) a value of \(N_D - N_A\) is taken (a figure slightly greater than the apparent room temperature carrier concentration is a good first approximation). The effective sample thickness can then be estimated using 6.2.1
to 6.2.3. and the carrier concentration can be calculated. \( N_D - N_A \)
is then adjusted until an acceptable least squares fit to equation
2.3.11 is obtained. The calculated carrier concentration is then
used to obtain a mobility fit in the I.S.B.E. from which Hall
factor \( r_H \) corrections are made. The process is repeated until the
carrier concentration data gives good fits to both the expression
modelling trap-out to a shallow level 2.3.11 and to the
theoretical mobility given by the I.S.B.E. As would be expected
for non degenerate material, trap-out to a shallow donor level is
observed. The least squares fits to equation 2.3.11 produce a
binding energy of 6.8meV for sample (b) and 6.2meV for sample (c).

The corrected carrier concentration results are plotted
alongside the raw data in figure 6.2. Failure to perform the
correction would result in a maximum error in carrier
concentration of a factor of about two for sample (b) and the
corresponding mobility data would suggest a compensation ratio
somewhat higher than the actual case.

The theoretical donor binding energy is given by (Neumark(1972)):

\[
E_d = E_{do} \left[ 1 - 1.81a_B \gamma (N_D - N_A)^{1/3} + 0.81a_B^2 \gamma^2 (N_D - N_A)^{2/3} \right]
\]

6.2.5

Where the effects of screening by both free electrons and
ionised impurities on \( E_d \) have been taken into account. \( \gamma \) is a
constant determined by Falicov and Cuevas (1967) to be 2.93. \( E_{do} \)
is the hydrogenic donor binding energy and \( a_B \) is the effective
Bohr radius. This expression is plotted in figure 6.4 along with
our experimental results and those of Leloup et.al (1978). The
lowest carrier concentration point extends their work towards the
Figure 6.4 Donor binding energy against \((N_D - N_A)\). Circles samples (b) and (c) this work. Squares experimental points from Leloup et al. (1978). Solid line theoretical from Neumark (1972).
hydrogenic case where there is good agreement with theory.

Clearly depletion effects are important in the case of the very high purity samples.

6.3 PERSISTENT PHOTOCONDUCTIVITY IN VERY HIGH PURITY SAMPLES

In the case of the highest purity sample (sample (a)) low temperature Hall effect measurements could only be performed under constant illumination or, in the dark, after being illuminated. Samples cooled in the dark to below 150K become highly resistive so that current can not be driven through them. (In terms of our equipment this means a resistance between contacts substantially greater than 400 M\(\Omega\).)

Such a rapid change of resistivity with temperature can be explained for this layer in terms of depletion due to surface and substrate interface barrier potentials. The effect of temperature on the carrier concentration in the sample has been modelled using a Poisson Equation solving routine with the following parameters: \(N_D = 3 \times 10^{13} \text{cm}^{-3}\) (determined from electrochemical C-V profiling); sample thickness = 8\(\mu\)m; surface barrier potential = 0.5V. The substrate is taken as containing deep acceptors at 0.64eV below the conduction band edge.

*Figure 6.5* shows the potential/depth profile at two different temperatures and *figure 6.6* shows the corresponding free carrier concentration profile.

At 300K the surface and substrate depletion regions have almost met so that carriers are confined in a relatively narrow central region (90\% of carriers are in the central 2\(\mu\)m). The
Figure 6.5 Potential variation with distance into epilayer calculated for background impurity densities of $3(10)^{13}$ cm$^{-3}$ and $4(10)^{13}$ cm$^{-3}$ at two temperatures.
Figure 6.6 Carrier concentration variation with distance into epilayer for background impurity density of $3(10)^{13}$ cm$^{-3}$ and $4(10)^{13}$ cm$^{-3}$ at two temperatures.
temperature dependence of these depletion regions discussed earlier ensures that by the time the temperature has been reduced to 150K the two regions have merged and significant carrier loss has occurred. It should be pointed out that this "true" carrier loss is different from the "apparent" carrier loss discussed with regard to thicker and less pure layers. In the case of "apparent" loss the carrier concentration in the conducting part of the layer does not change significantly with temperature although it appears to do so if the decrease in the width of this region due to the temperature dependence of the surface and substrate barrier potentials is not taken into account. In the case of the very pure sample the loss is real and results from carriers being swept out of the epilayer as the two depletion regions meet and the sample becomes completely depleted.

The model gives nearly 100% loss in carrier concentration in the conducting region as the temperature is reduced from room temperature to 77K and total carrier loss by 4K. At a temperature such that the depletion regions are close to meeting the carrier concentration is very sensitive to layer width, surface barrier potential and ionized impurity concentration. It is reasonable to suppose that the sample is not exactly uniform and at a given temperature, certain regions of Hall sample might be almost totally depleted whilst others would still contain a significant number of carriers. This is shown by comparing the two graphs in figure 6.5 where the different depletion depths in layers at 3(10)$^{13}$ cm$^{-3}$ and 4(10)$^{13}$ cm$^{-3}$ produces a potential difference (at the centre of the sample) between them $>1$eV at 77K. Figure 6.6 shows the corresponding carrier concentration profile profile
where at 77K the carrier concentration at the centre of the sample differs by a factor of $10^8$ between the two background impurity densities. Then the sample would be expected to take the form of pools of conducting regions filled with charge carriers surrounded by non conducting barriers, which spread and eventually cover the whole space as the temperature is progressively lowered.

In such a system the resistivity would become very large as the conducting regions just become cut off from one another by the barriers. Figure 6.6 shows that (for a sample with background impurity density $3(10)^{13}$ cm$^{-3}$), as the carrier density becomes small at lower temperatures, the loss of conductivity will occur even in a perfectly homogeneous sample and therefore the percolation type argument, although it must occur to some extent if the sample is at all non-uniform, is not necessary to explain the results discussed so far.

To perform temperature dependent Hall effect measurements carriers must first be "put back" into the sample at low temperatures. The Hall effect results measured in the helium range for this sample have been achieved using the persistent photoconductive effect. The temperature dependence of the Hall carrier concentration for this sample is shown in figure 6.7. In this case the sample was illuminated at low temperature and measurements made upon increase in temperature. This gives rise to a rather strange characteristic. Loss of optically generated carriers as temperature is increased gives rise to the drop observed near room temperature.

It is found that samples, when in the high resistance regime, display persistent photoconductive effects. Such effects have been
Figure 6.7 The temperature dependence of the Hall carrier concentration for sample (a). The sample was illuminated at low temperature and the measurement was carried out as temperature was increased.
observed in two dimensional systems (Kastalsky and Hwang (1984) and Kane et.al.(1986) and in "bulk" GaAs (Queiser and Theodorou(1979)) but apparently not in InP. In the case of "bulk" layers the effect is normally put down to the presence of a barrier to recombination to a deep state with a large lattice relaxation. The work of Queiser and Theodorou (1979) on GaAs suggest that the barrier causing charge separation and preventing recombination is in fact the potential barrier at the epilayer/substrate interface. This is based on the fact that the effect is only observed in their case in layers less than 5µm thick. At a first glance it would appear that our InP at 8µm is too thick for such an effect to be important. However it should be noted that for \( N_d - N_A = 3(10)^{13} \text{cm}^{-3} \) and for an iron doped substrate the depletion region at the substrate would extend 5µm from the interface so that electron-hole pairs generated only 3µm from the surface would be separated by the potential gradient and would be able to contribute to persistent photoconduction.

To study the wavelength dependence of the persistent Hall effect, carrier concentration measurements as a function of wavelength of prior illumination have been carried out. Illumination of samples was achieved by means of an optical fibre passed into the pressure cell and illuminated by means of a tungsten bulb and spectrometer. This set up assured that optical power was very low and sample heating did not occur. Illumination at each wavelength was performed for the same period of time to ensure that approximately the same total energy fell on to the sample. The wavelength dependence of the persistent effect is plotted in figure 6.8.
Figure 6.8 Dependence of carrier concentration - layer width product on wavelength of prior illumination for pure InP sample.
The large change in the product of layer width and Hall
carrier concentration corresponding to the band edge energy would
again tend to support the charge separation by macroscopic fields
at depletion regions rather than a microscopic effect involving
D-X centres. From the figure it is clear that there is a reduced
effect from below band gap radiation. This is likely to be due to
carrier generation from levels in the substrate via sub band gap
radiation unlikely to be absorbed in the very pure InP epilayer.

The importance of the substrate is supported by our
experiments on 15μm layers of similar background impurity density
which do not show persistent photoconductivity.

The dependence of the mobility on the apparent carrier
concentration at 77 K has also been recorded and is plotted in
figure 6.9. The point at the lowest value of n.d corresponds to the
first recordable point (ie. that at which current could first be
passed). The curve representing the total effects of screening on
the mobility is also plotted. (This includes screening of ionised
impurities, Brooks-Herring, and screening of polar phonons, which
are still the dominant scattering mechanism in this sample at
77K). To generate this curve it is assumed that all the change in
n.d is due to an increase in carrier concentration and not to an
increase in d and therefore this represents a maximum expected
change.

Clearly the observed characteristic can not be explained in
terms of screening alone - although it may explain the small
increase near saturation. The rapid rise at the low mobility end
is more likely to be a characteristic of the percolation type
arguments discussed earlier. In this case the percolation effect
Figure 6.9 Variation of Hall mobility with measured Hall carrier concentration for pure InP sample. Experimental points obtained utilizing the persistent photoconductive effect.
must result in a reduced mobility. Addition of carriers by illumination will produce a widening of the conduction region and the lowering of potential barriers until the barrier to recombination is reduced to a few $k_B T$ and a further charge separation can not occur. The fact that the mobility saturates suggests that at this point the "Lakes" of conduction have all merged so that the percolation no longer occurs. This is born out by the fact that, at saturation, measurements made under constant illumination produce an increase in the n.d product but no further mobility increase.

An exact analysis is not possible due to the large number of unknowns: we do not know the barrier heights or the true electron concentration in the valleys. Secondly it is not true percolation in that we are not so much "filling up the valleys" by the introduction of charge carriers as "filling down the mountains" by electric fields produced by the accumulation of charge carriers.

It is, however possible to make a few approximations with regard to the fraction of the area which is insulating. The surface and substrate potential barriers effectively confine the electrons to the centre few microns of the epilayer. The electrons then avoid non-conducting areas by moving in the plane of the centre of this layer. Thus the electron is percolating in two dimensions. The work of Adkins(1979) has produced a theory of the Hall effect in a two dimensional effective medium. For an effective medium with two constituents A and B. The Hall coefficient and mobility can be written as linear combinations of those in each of the separate constituents:
If the conductivity of the composite normalised to that of the B component is:

\[
\sigma = (1-x)(0.5-C) + \sqrt{[(1-x)^2(0.5-C)^2+x]}
\]

where \(C\) is the fractional concentration of component A and \(x\) is the ratio of the conductivities of components A and B.

Then the coefficients \(r\) and \(m\) are written:

\[
\begin{align*}
  r_a &= x^2(\sigma^2 - 1)/\sigma^2(x^2-1) \\
  r_b &= (x^2 - \sigma^2)/\sigma^2(x^2-1) \\
  m_a &= x(\sigma^2 - 1)/\sigma(x^2-1) \\
  m_b &= (x^2 - \sigma^2)/\sigma(x^2-1)
\end{align*}
\]

If consideration is limited to the points well away from saturation in figure 6.9 Then the approximation \(x=0\) is not unreasonable. This states that A can be considered an insulator by comparison with B. The results of figure 6.6 show that even for the small inhomogeneity considered the ratio of n and hence of the conductivity in the two regions is \((10)^{-8}\). This approximation gives the following simplified expression for the Hall coefficient and \(\mu_H\):

\[
\begin{align*}
  R_H &= R_{Hb} \\
  \mu_H &= (1-2C)\mu_{Hb}
\end{align*}
\]

A consequence of expression 6.3.8 is that for this extreme case the measured Hall concentration will be equal to that of the
If $\mu_{HB}$ is taken to be equal to the maximum mobility at saturation then it is possible to estimate the fraction of the sample that is insulating. Taking the two lowest mobility points shows that this model would explain the observed mobility change if $C$ varies from $1/3$ to $1/12$.

To put some actual figures into the expression and obtain an idea of whether such a change of $C$ is possible the case of $\mu_H$ changing from zero to $\mu_{BH}$ is considered. Equation 6.3.9 shows that such a change in $\mu_H$ requires $C$ to change from $1/2$ to $0$. If the two regions are taken as having background donor concentrations of $4(10)^{13} \text{cm}^{-3}$ and $3(10)^{13} \text{cm}^{-3}$ as considered in figures 6.5 and 6.6 it is possible to draw an idealised potential profile in the plane of the epilayer for the case $C = 1/2$.

\[ \frac{E_c}{A} \quad \text{V} \quad \text{B} \]

In the above diagram it is assumed that the layer consists of two constituents only each occupying half the total area. Region A has $N_{DA} = 3(10)^{13} \text{cm}^{-3}$ and B has $N_{DB} = 4(10)^{13} \text{cm}^{-3}$.

It should be noted that $V$ is not simply the potential expected at an n-n\textsuperscript{+} homojunction, which for these impurity concentrations is very small ($V = kT \ln(N_{DA}/N_{DB}) = 2 \text{ meV}$ at 77K). It in fact results from potentials at surface and substrate. The results of calculations in figures 6.5 and 6.6 suggest that if each type of region can be considered separately, the electron
concentration for each is \( n_A = 2 \times 10^{13} \text{cm}^{-3} \) and \( n_B = 1 \times 10^6 \text{cm}^{-3} \) with a potential difference between the two (V) equal to .13V at 77K.

Illumination by above band gap radiation will result in the normal charge separation observed at an \( n^+ \) junction or \( p \) \( n \) junction except that although the electrons collect in the valleys the holes are swept out by the band bending discussed earlier. The result is similar to the photovoltaic effect except that the removal of holes leads to persistence after illumination.

The situation is no longer one of equilibrium even after removal of the light source as the system is still trying to return to its original state by recombination.

Upon illumination electrons initially collect in the B region and set up a field tending to repel further electrons from entering thus reducing V. This enables the B region to spread into part of that occupied by A.

Turning again to the profile perpendicular to the plane of the epilayer figures 6.5 and 6.6 and borrowing the following expression from the case of a \( p \) \( n \) junction under illumination (Gossick (1964)):

\[
V_{\text{ph}} = kT \left\{ \ln \left( 1 + \left( n - n_o \right) n_o / n_i \right)^2 \right\} \tag{6.3.10}
\]

Where \( n \) is the electron concentration in the epilayer under illumination and \( n_o \) is the equilibrium concentration.

At 77K \( n_i \) is approximately equal to \( 2 \times 10^{-23} \text{cm}^{-3} \). For such a system, taking \( n_o \) equal to \( 1 \times 10^{13} \text{cm}^{-3} \) (corresponding to the B regions), gives \( V_{\text{ph}} \) of .1V for \( n - n_o = (10)^{-50} \text{cm}^{-3} \) only.
In our system trapping of holes in the substrate means that the electron concentration will remain in this non-equilibrium state for some time and the epilayer/substrate barrier will remain reduced by \( V_{\text{ph}} \). Electrons preferentially fall into the lower potential B regions where accumulation causes a reduction in the epilayer/substrate potential and hence in the potential between A and B regions. This continues until the potential difference between A and B equals zero and the carrier concentrations in A and B are equal.

6.4 HIGH PRESSURE HALL EFFECT RESULTS

In the case of sample (c) trapout of carriers with temperature over a range of about one order of magnitude can clearly be observed and recorded at pressures up to 8Kb. It is possible to use equation 2.3.11 and by performing a least square fit obtain values for the binding energy of the shallow donor. The fits along with the experimental points for atmospheric pressure have already been shown in figure(6.4). The pressure dependence of the binding energies is shown in figure(6.10). The pressure dependence of the binding energy is again analysed in terms of the Neumark expression.

The pressure dependence of \( E_d \) is governed by that of the effective mass and dielectric constant through the hydrogenic shallow donor energy \( E_{d0} \) and the Bohr radius \( a_B \). The pressure dependence of the Neumark expression is plotted alongside the experimental results in figure 6.10. The pressure dependence is small. The absolute values are not in agreement but as can be seen by the dashed line in the figure, which is the Neumark expression transposed for comparison, the theory agrees approximately with
Figure 6.10 Variation of donor binding energy with pressure for 8(10)$^{14}$ cm$^{-3}$ InP sample. Circles experimental points. Solid line predicted using expression from Neumark (1972).
experiment over this pressure range. However a thorough test would require use of much higher pressures.

The results of high pressure transport measurements for sample (b) are shown in figure 6.11 where the ratio of mobility at 8Kbar to that at atmospheric pressure is plotted as a function of temperature. Agreement between results and theory using the I.S.B.E. is reasonable considering the experimental error involved. At high temperatures the pressure dependence goes as the polar phonon limited mobility ($\propto m^{-3/2}$). The mobility goes through an intermediate temperature region where a mixture of mechanisms control the transport properties. At low temperatures $\leq 20K$ the mobility tends to that controlled by the ionized impurities. The ionized impurity scattering is proportional to $m^{-1/2}$ and a small contribution from the screening term.

The screening term in the Brookes-Herring expression is:

$$\left[ \ln(1+b) - \frac{b}{1+b} \right]$$

The change in 8Kbar is 1% for large $b$. For this sample $b>200$ at 20K. Thus the screening term has an effect on the pressure dependence of the ionized impurity limited mobility equal to about 1% at large $b$. At small $b$ when the Born approximation is close to failure ($b\approx 1$) the pressure dependence becomes much larger. This does not effect our sample as the Born approximation is still valid.
Figure 6.11 Temperature dependence of pressure coefficient of mobility for $8(10)^{14}$ cm$^{-3}$ sample. Circles experimental points. Solid line theoretical prediction using I.S.B.E.
A number of nominally pure samples of InP have been studied with background impurity densities varying from the low $10^{13}$ s to $10^{15}$ cm$^{-3}$. An iterative solution of the Boltzmann equation has been used to analyse results of temperature dependent Hall effect measurements down to helium temperatures. Good agreement with theory is obtained for all samples including the highest purity layer which, having a mobility of in excess of 400,000 Vcm$^{-1}$s$^{-1}$ at 40K is the highest mobility measured to date. This sample provides the best test of phonon scattering theories presently available for InP and has enabled the acoustic deformation potential for the conduction band to be pinpointed at 6.7 ± .1eV. Depletion effects due to surface and substrate potentials are important. Failure to incorporate these into the mobility analysis would result in an over estimate of the compensation ratios. In the case of the highest purity samples these effects result in near complete loss of carriers from the epilayer and electrical measurements can only be made under constant illumination or after illumination relying on the persistent photoconductivity resulting from charge separation at the epilayer - substrate interface. The Hall mobility varies with carrier concentration reaching a maximum where the photogenerated carrier density saturates. A suggested cause of this phenomenon is a percolation effect caused by small inhomogeneities in the sample which can result in massively depleted regions at such low carrier concentrations.

Where trap-out of carriers can be observed at low temperatures an activation energy for shallow donors can be
calculated. The relationship between donor binding energy and free electron concentration is in rough agreement, for the $10^{15} \text{cm}^{-3}$ sample, with the theory of Neumark(1972). For purer samples a binding energy close to the hydrogenic case is observed. In this case the small deviation from the hydrogenic case is described well by the Neumark expression.

High pressure experiments reveal a pressure dependence of mobility which can be described well by the I.S.B.E. throughout the helium temperature range. At low temperatures Brookes Herring theory describes the ionised impurity limited mobility well.

A small pressure dependence of the donor binding energy can be measured. This is in agreement with the pressure dependence of the Neumark expression.
7.1 INTRODUCTION

In the last chapter an I.S.B.E. was used with success to accurately describe both the temperature and pressure dependence of the mobility in pure and nominally undoped InP.

In this chapter the experiments have been extended to more heavily doped samples where the I.S.B.E. is shown to be inadequate as a description of the transport properties of the material.

Two additional effects are discussed. The effects of correlation of impurities on the mobility in highly doped samples is considered. At low temperatures conduction in an impurity band is likely to have a considerable effect on transport properties.

*Figures 7.1 and 7.2* show the experimental results for five samples. Two undoped samples from the previous chapter have been included for comparison.

The intermediateely doped sample (c) and the heavily doped sample (e) are discussed individually. Comment on results from sample (d) is reserved until the general discussion section.
Figure 7.1 Mobility temperature characteristics for five samples:
- Solid lines - I.S.B.E. calculated fits for samples (a), (b), (c).
- Dotted line - I.S.B.E. plus impurity band effects for sample (c).
- Dashed line - scattering from a correlated distribution of potential fluctuations appropriate for sample (e).

\[ \eta_H T=300K \ (\text{cm}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ S(10)^{13} \]

\[ S(10)^{14} \]

\[ S(10)^{15} \]

\[ S(10)^{16} \]

\[ S(10)^{17} \]

\[ S(10)^{18} \]
Figure 7.2 Temperature dependence of experimental Hall carrier concentration for samples (c), (d), (e). Solid lines - Hall factor correction.
7.2 INTERMEDIATE DOPING

For the experimental temperature dependence of both the Hall mobility and Hall carrier concentration we refer to figures 7.1 and 7.2. Interesting features of these plots are the extremely low mobility at the low temperature end of the curve for sample (c) and the dip in the carrier concentration between 10K and 300K. An I.S.B.E. predicted curve has been included in figure 7.1 and clearly the Brookes Herring theory is not successful in simultaneously describing both low and high temperature results.

In the low temperature region we have found that it is necessary to include the effects of impurity band conduction. Such effects are negligible in the high purity samples described in the previous chapter. For these (high purity samples) electrons on impurity levels are strongly localised and have not had to be included in the analysis.

An indication that hopping conduction is present would be an activated conductivity at low temperatures. Figure 7.3 shows the resistivity of sample (c) plotted against reciprocal temperature. It is clear that if the resistivity is activated at the low temperature end ( < 10K ) then the activation energy is small and its measurement beyond the accuracy of the present experiment.

As previously discussed in chapter 5 if the donor concentration is above a certain critical concentration \( N_{dc} \) such that \( \left( N_{dc}^{1/3} a_B \right)^{-1} = 4 \) then the Mott transition takes place and conduction becomes metallic. Below this value conduction takes place by a hopping mechanism. The results of Emel'yanenko et al
Figure 7.3 Resistivity as a function of reciprocal temperature for sample (c).
suggest that the critical value for the reciprocal of the product \(N_{dc}^{1/3}a_B\) may be closer to 3. Our sample with \((N_{dc}^{1/3}a_B)^{-1} = 3.2\) is just equal to that expected at the Mott transition. We assume that the hopping expression is valid and that the activation energy is small, which is reasonable this close to the Mott transition.

The low temperature resistivity of both InP and GaAs have been studied by Emel'yanenko et. al (1973). They analyse the resistivity in terms of equation 4.2.1. Where the factor \(\rho_3\) has the form of 4.2.2:

\[
\rho_3 = \rho_c \exp(a/N_d^{1/3}a_B) \quad 7.2.1
\]

From their experiments they are able to obtain a value for \(\alpha = 1.8\) in good agreement with theory \((1.7 \pm .2)\) (Shklovskii and Efros (1984)). We have used 7.2.1 with \(\alpha = 1.75\) (in agreement with both the values of Emelyanenko et. al. and theory) and \(\rho_c = 4(10)^{-4}\) \(\Omega\text{cm}\) in the analysis that follows.

In figure 7.4 the fractional change in mobility in 8Kbars has been plotted against temperature. For clarity the data for sample (c) has been plotted again in figure 7.6 where we have included an I.S.B.E. predicted fit for comparison. The pressure dependence of the mobility at low temperature is very large \((\mu_B/\mu_O = 0.80)\). The pressure dependence of the hopping resistivity can be calculated from 7.2.1 where the pressure dependence of \(N_d\) is negligibly small and the greatest effect will come from the dependences of \(m^*\) and \(\lambda_s\) via \(a_B\). Such an analysis has been used successfully for hydrostatic pressure effects on p-type InSb by Aladashvili et. al. (1986)
Figure 7.4 Percentage change in electron mobility to 8Kbar for four samples of InP.
figure 7.5 Percentage change in electron mobility to 8Kbar for three samples. Solid line I.S.B.E. generated curve for sample (b). Dashed line - scattering from a correlated distribution of potential fluctuations appropriate for sample (e).
Figure 7.6 Percentage change in electron mobility for sample (c). Triangles experimental points: dot-dashed line I.S.B.E. prediction: solid line pressure dependence of effective impurity band mobility: dotted line combined effects of impurity band and conduction band using two band theory.
By suitable algebraic manipulation it can be shown that:

\[
\frac{\rho_8}{\rho_0} = \exp \left\{ \left[ \frac{m^*(P)}{e_s(P)} - \frac{m^*(0)}{e_s(0)} \right] \frac{\alpha}{N_d^{1/3} a_B} \right\} \tag{7.2.2}
\]

The calculated pressure dependence using 7.2.2 above is plotted in figure 7.6 along with the experimental points for the 8Kbar case.

These experimental results are in excellent agreement with the theory for hopping conductivity.

The temperature dependence of the carrier concentration is shown in figure 7.2. The presence of a "hump" in the temperature dependence of the Hall carrier concentration has been used by previous authors as evidence of a two band conduction process (for example Mott and Davis (1971) and Basinski and Oliver (1962)). Included in the diagram is the correction for the Hall factor. As can be seen this factor alone does not explain the characteristic at all well. The use of a two band analysis for our sample would seem justified both as a result of the observed dip in the Hall carrier concentration and the fact that the low temperature resistivity can be represented by the hopping form giving good agreement with experimental pressure dependences.
For a two band system the following two expressions apply (Mott and Davis (1972):

\[ \mu_T = \frac{n_i r_i \mu_i^2 + n_c r_c \mu_c^2}{n_i \mu_i + n_c \mu_c} \]  

7.2.3

\[ n_T = \frac{(n_c \mu_c + n_i \mu_i)^2}{n_c^2 r_c + n_i \mu_i^2 r_i} \]  

7.2.4

These two expressions can be combined to give:

\[ n_T = \frac{n_c \mu_c}{\mu_T} + \frac{n_i \mu_i}{\mu_T} \]  

7.2.5

Where \( \mu_T, n_T \) are the measured Hall mobility and carrier concentration. All other \( n \) and \( \mu \) are drift values. The \( i \) and \( c \) refer to impurity and conduction bands respectively. The expression 7.2.5 is simply a statement that the total conductivity is equal to the sum of the individual conductivities of the two bands.

In the analysis \( \mu_i \) is taken as constant and equal to the low temperature value of the measured mobility. The \( \mu_T \) and \( n_T \) are known for a range of temperatures between 300K and 4K. We write \( n_i = N - n_c \) where \( N \) is the total number of electrons available and is initially taken as the high temperature \( n_T \). This leaves \( \mu_c, n_c \) to be determined at each temperature.

The analysis takes the following form:

1) The I.S.B.E. is used to generate values for \( \mu_c \) throughout the temperature range.

2) Using 7.2.5 and the assumed \( N \) values for \( n_c \) are generated.
3) Using 7.2.5 the $n_T$ are calculated at 8Kbar assuming $n_c$ and $n_i$ are pressure independent and using an I.S.B.E. generated $\mu_c$ at 8Kbar and $\mu_i$ derived from 7.2.2.

4) The value $N$ is adjusted and the process is repeated from stage 2 until the $n_T$ derived from stage 3 represent the best possible fit.

The best fit mobility curve obtained in this manner is plotted in figure 7.1 and the corresponding carrier concentration fit in figure 7.7'. It is clear that such a process will give rise to near perfect agreement with the temperature dependence of both mobility and carrier concentration.

A true test of the quality of the fit will be a comparison of the pressure coefficients of both the mobility and carrier concentration. The theoretical values are obtained using equations 7.2.3 and 7.2.4 and assuming that $n_c$ and $n_i$ do not change with pressure or change very little. This is the usual observed effect, for instance in the case of sample (b) - see last chapter. The pressure dependence of both $\mu_T$ and $n_T$ is then only due to that of $\mu_c$, $\mu_i$ and $r_c$ -the latter of which is very small $<.1\%$. The pressure dependence of $\mu_c$ is determined from the I.S.B.E. assuming the $N_A$ obtained from the temperature fit. The pressure dependence of $\mu_i$ comes from equation 7.2.1 with the appropriate $m^*$ and $\epsilon$ for the required pressure. The dotted curves in figure 7.6 and 7.8 are the pressure dependences derived from these equations. It is clear that both theoretical curves have the right form. The predicted pressure dependence of $n_T$ is rather larger than the experimental result. The room temperature pressure dependence of
Figure 7.7 Hall carrier concentration results for sample (c). Solid line - theoretical dependence assuming two band system.
figure 7.8 Fractional change in Hall carrier concentration to 8Kbar against temperature for sample (c). Circles - experimental points. Solid line - predicted pressure dependence resulting from the pressure dependence of $\mu_c$ and $\mu_i$ in two band theory.
mobility is rather smaller than that predicted. Near room
temperature the majority of electrons must be in the conduction
band ($K_B T = .026eV$ and the energy between conduction and impurity
band must be considerably less than the hydrogenic donor binding
energy = 7meV). Thus the failure to predict the high temperature
pressure dependence lies in the I.S.B.E. calculation for the
conduction band. Similarly the resulting over estimate of the
importance of the impurity band at high temperatures results in an
overestimate of the pressure dependence of the carrier
concentration due to the high pressure coefficient of mobility in
this band. However the true importance is in the fact that the two
band theory is able to describe the characteristic curve shape.
Previously the only quoted evidence for a two-band system at these
doping levels has been the observed hump in the temperature

Returning to the pressure coefficient of the mobility. At low
temperature the mobility clearly tends to that of the impurity
band which must be the case. At high temperatures it would be
expected that nearly all the carriers would be activated into the
conduction band and therefore the mobility must tend to that of
the conduction band. The I.S.B.E. fit for the conduction band
obtained as a result of the above two band fitting process is
plotted on the same diagram and the close agreement near room
temperature suggests that this is indeed the case.
7.3 HEAVILY DOPED MATERIAL

The mobility and carrier concentration results for sample (e) are shown in figure 7.1 and figure 7.2 respectively.

Sample (e) has a room temperature Hall carrier concentration of $1.2(10)^{19}\text{cm}^{-3}$ and is thus far above the Mott transition. The value of $n$ is unchanging with temperature down to 4K and the Hall mobility changes little with no perceivable change below 200K. The sample has all the characteristics of a degenerate doped semiconductor. At 200K the effects of phonons limit the mobility to $20(10)^{4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ so at temperatures below this the mobility can be considered to be due purely to ionised impurity effects.

The scattering due to potential fluctuations predicts a 77K mobility of $1100\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ due to a correlated distribution with a compensation ratio of zero and $T_o=800\text{K}$ (Yanchev and Evtimova (1986)). The random case produces a mobility slightly larger than the I.S.B.E. but in reasonable agreement with it. The correlated case results in a mobility in the region of $1100\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ which is very close to our experimental value $\mu_{77} = 900\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The temperature dependence of the Yanchev model is very weak as can be seen by the dashed line plotted in figure 7.1 giving good agreement throughout the region. It should be noted that to obtain agreement using the I.S.B.E. it would be necessary to use a compensation ratio of $K>0.7$, which would suggest an enormously large acceptor density for a sample which was not deliberately compensated.

It is interesting to note that the Fermi energy is equal to 85meV when the corrections for electron-electron exchange, band
tailing and temperature given in chapter 3 are taken into account. Thus the Fermi level is well into the conduction band throughout the temperature range 4-300K and hence impurity band conduction does not affect the electron mobility even at the lowest temperatures.

Turning now to the pressure results. The temperature dependence of the pressure coefficient is plotted in figure 7.5. The pressure coefficient is almost constant throughout the temperature range considered showing no change-over between conduction band and impurity conduction observed in the lower doped samples.

The pressure dependence derived from the Yanchev model assuming a correlated distribution and the same parameters as for the temperature fit has also been plotted in figure 7.5 and shows very good agreement throughout the whole temperature range.

The carrier concentration for this sample does not change as a function of pressure showing none of the anomalous "dips" that might be associated with a two band system. This is to be expected for such a highly doped sample where the impurity band must have merged with the conduction band.

7.4 GENERAL DISCUSSION

For direct comparison of the samples the percentage change in Hall mobility to 8 Kbars has been plotted as a function of Hall mobility for the three temperature regions (150K, 77K and for the low temperature case). These are shown in figures 7.9, 7.10 and 7.11 respectively. For the high temperature cases there is a
Figure 7.9 Percentage change in Hall mobility to 8Kbar as a function of Hall mobility at 150K. Solid line - I.S.B.E.. Dashed line scattering from a correlated distribution. Circles - experimental points.
Figure 7.10 Percentage change in Hall mobility to 8Kbar as a function of Hall mobility at 77K. Solid line - I.S.B.E.. Dashed line scattering from a correlated distribution. Circles - experimental points.
Figure 7.11 Percentage change in Hall mobility to 8Kbar as a function of carrier concentration at low temperature. Solid line - effective mobility assuming impurity band conduction. Dashed line scattering from a correlated distribution. Circles - experimental points.
general trend to higher pressure sensitivity as the mobility reduces. At low temperature (figure 7.10) the situation is somewhat different with the pressure dependence varying in a less obviously predictable way.

Returning for the moment to higher temperatures. For the high mobility sample (b) agreement with the I.S.B.E. is reasonable at both temperatures. This is within 1% which is equivalent to the estimated experimental error for this case.

As the mobility reduces the deviation from the I.S.B.E. increases until sample (e) where the error is in the region of 4%. At this level of doping $10^{19}$ cm$^{-3}$ the theory of scattering from a correlated distribution of impurities describes the pressure dependence well in all three temperature ranges.

For the two high temperature cases, samples (c) and (d) lie somewhere between that described by a totally random distribution of individual scattering centres (I.S.B.E.) and that described by the correlated distribution of potential fluctuations.

This would perhaps seem obvious: as the mobility decreases and the ionised impurity concentration increases correlation effects of impurities in the melt become more important and the mobility tends away from the random situation to that of a correlated distribution. This may be true at higher temperatures but the theory cannot be extended above 150K to samples with impurity concentrations less than $-5(10)^{17}$ cm$^{-3}$. The theory can, however, be used for sample (d) where agreement is good at 77K and reasonable for 150K.

Below 50K the pressure dependences turn around so that the $6(10)^{16}$ cm$^{-3}$ doped sample has a much higher pressure coefficient
than the others. This contradicts the suggestion of increasing importance of correlation effects for this temperature range.

At these low temperatures ionised impurity scattering completely dominates and one would expect all three samples to have the same pressure coefficients of mobility if the same mechanism is responsible in all three cases.

It has already been established that for sample (c), which is close to the Mott transition the mobility and its pressure coefficient at low temperature can be well described in terms of a mobility derived from hopping conduction.

For the higher doped sample (e) scattering from a correlated distribution of impurities explains the observed pressure dependence well throughout the whole temperature range. In this case the sample is highly degenerate and the fermi-level is well into the conduction band - even at room temperature. There is no separate impurity band.

Sample (d) has a larger pressure dependence than expected from a correlated distribution. It is doped far above the Mott transition so that the hopping conductivity is not strictly applicable.

At these concentrations, states associated with individual impurities would no longer be localised and it might be expected for the impurity levels to form a band of extended states showing a metallic (non-activated) form of conduction. It is unlikely that, at these concentrations such an impurity band would be separate from the conduction band.(Considering for instance the Neumark expression which predicts a zero donor binding energy in the region of $9/(10)^{16} \text{ cm}^{-3}$. There is a dip in the carrier
concentration which occurs at a higher temperature than for sample (c). It is however much smaller and can be explained by variation in Hall factor. (see figure 7.2)

The low temperature mobility for sample (d) is higher than for (c) and (e) whilst its pressure dependence is intermediate between (c) and (e).

The plot in figure 7.10 for the low temperature case includes the pressure dependences of mobility for both the correlated impurity case and the hopping case.

Sample (d) has a pressure dependence close to that of the correlated distribution. It is however slightly larger and tends towards that of hopping conductivity.

In the figure the hopping expression has been extended as a dotted line above the Mott transition.

It would be interesting to investigate the region between samples (c) and (d) to see if there is a discontinuous jump at the Mott transition from the pressure dependence determined by that of hopping conduction and that of the correlated distribution applicable to the conduction band.

The presence of compensation could bring the fermi level down so that it is in the tail states. Such an effect would result in a degree of localisation (obviously states in tails become increasingly more localised with depth).

Although we have no reason to suspect compensation in sample (d) it would be reasonable to suggest that such a degree of localisation might explain the higher pressure dependence than (e).

The effect of compensation has been used by Redfield (1975)
for the case of GaAs where the low temperature conductivity is
governed by hopping between tail states.

To test the region of doping between samples (c) and (d)
adequately would require a number of samples of accurately known
compensation.

7.5 CONCLUSIONS

The major conclusions of this chapter are that, for higher
doped samples a theory of scattering from a correlated
distribution of potential fluctuations describes the temperature
and pressure dependence of mobility well.

For lower doped samples close to the Mott transition the high
temperature mobility can be described by the I.S.B.E. although it
appears to be inadequate as a description of the pressure
dependence.

At low temperatures for the intermediate doped sample the
form of conduction is hopping. This describes both temperature and
pressure dependences well. A two band analysis can explain the
"dip" seen in the large pressure dependence of the Hall carrier
concentration. This is further evidence for the existence of a
separate impurity band in addition to the normally considered
"dip" in the temperature dependence.
CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

The electron mobility in indium phosphide has been measured in a range of samples as a function of both temperature (room temperature down to 4K) and pressure (from atmospheric pressure to 8Kbar) using the high pressure/low temperature cell.

Analysis of mobility measurements on very high purity samples using the I.S.B.E. with standard scattering mechanisms including Brooks Herring ionised impurity scattering produces excellent agreement with theory if a conduction band deformation potential of 6.7 eV is used. This value is a major conclusion of the work. The exceptional purity of the samples measured means that this must be the most clear derivation of the deformation potential from transport measurements.

At higher impurity densities it became clear that the I.S.B.E. including Brooks Herring theory was not capable of predicting either the temperature or pressure dependence of mobility. At an impurity density of around 6(10)$^{16}$ cm$^{-3}$ it was found that the I.S.B.E. could not simultaneously describe high and low temperature characteristics. Secondly the pressure dependence of mobility at low temperature was significantly greater than that predicted by the I.S.B.E.. The low temperature mobility had a pressure dependence characteristic of hopping conductivity. It was
found that by combining conduction and impurity band effects using a two band theory it was possible to describe the temperature dependence of both mobility and carrier concentration. The pressure dependence of the mobility could also be explained well using such a technique. The temperature dependence of the pressure coefficient of the Hall carrier concentration contained a "dip" at intermediate temperatures. This could be explained in terms of the two band analysis. This "dip" in the pressure coefficient is evidence for two band conduction in addition to the normally quoted "dip" in the temperature dependence of the Hall carrier concentration.

In the case of the highly doped sample the I.S.B.E. was not successful in describing either the temperature or pressure dependence of the Hall mobility. It was found that in this case good agreement with theory was obtained by considering scattering from a correlated distribution of potential fluctuations.

A suggestion for further work would be to investigate more thoroughly the low temperature transport properties for samples near the Mott transition. This would require a range of samples over the \((10)^{16}\) to \((10)^{17}\) \(\text{cm}^{-3}\) range. Of particular interest would be a study of the low temperature pressure dependence of mobility for such samples where it would be possible to investigate the change over from hopping type conductivity in an impurity band to the conduction band mobility governed by scattering from a correlated impurity distribution (figure 7.11).
APPENDIX (I)

SCATTERING RATES USED IN THE I.S.B.E.

In the following:

\[ c = \left( 1 - \left( \frac{1 + \frac{x}{2}}{x} \right) \right)^{1/2} \]

where \( a = 1 + \frac{h^2 k^2}{m E_g} \left( 1 - \frac{m^*}{m} \right) \)

and \( d = \frac{1}{\left( 1 + \left( \frac{1}{m^*} - 1 \right) /a \right) \} \}

(i) Piezo electric scattering

\[ \nu_{pe} = \frac{q^2 \varepsilon T P^2 m d \left( \frac{3 + 6c_2 + 4c^4}{3 - 6c_2 + 4c^4} \right)}{6\pi h^3 \varepsilon_0 k} \]

(ii) Acoustic Mode Deformation Potential

\[ \nu_{dp} = \frac{q^2 \varepsilon T E_1^2 m \delta k \left( \frac{3 - 8c^2 + 6c^4}{3 - 8c^2 + 6c^4} \right)}{3\pi h^3 c_1} \]
(iii) Brooks Herring Ionised Impurity Scattering

\[ \nu_{BH} = \left( q^4 N_1 m^* / \beta \pi c^2 \hbar^3 k^3 \right) \ln \left\{ 1 + 4k^2 / \beta^2 \right\} - \frac{4k^2}{(\beta^2 + 4k^2)} \]

(iv) Neutral Impurity Scattering

\[ \nu_{NI} = \left( m^* / 20 \hbar N_N \right) (a_B \epsilon_s / m^*) \]

(v) Polar Optic Phonon Scattering

\[ s(k,k') = q^2 \omega_{lo} \left\{ \frac{1}{\epsilon_s} - \frac{1}{\epsilon_o} \right\} \frac{G(k',k)}{|k' - k|^2} \]

\[ X \left\{ \begin{array}{ll}
\delta(E - E' + \hbar \omega_{lo})(N_{po} + 1) & \text{emission} \\
\delta(E - E' - \hbar \omega_{lo})N_{po} & \text{absorption}
\end{array} \right. \]

Where \( G(k,k') \) is an overlap integral and \( N_{po} \) is the phonon occupation number.
APPENDIX(II)

FERMI INTEGRALS

The Fermi integrals $F_{1/2}$ and $F_{-1/2}$ which occur in the Brooks Herring expression 3.3.5 are calculated and plotted in the following diagrams. The ratio $F_{1/2}/F_{-1/2}$ is plotted in the second diagram.

The Fermi Integral is:

$$F_x(\eta_f) = \frac{1}{\Gamma(1+x)} \int_{0}^{\infty} \frac{\eta_f^x}{1 + e^{(\eta - \eta_f)}} d\eta$$
The dependence of the Fermi Integrals $F_{1/2}$ and $F_{-1/2}$ on the reduced Fermi energy $\eta_F$. 
The dependence of the ratio $\frac{F^2}{F} - \frac{1}{2}$ on the reduced Fermi energy $\eta_F$. 

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