THE EFFECTIVE MASS DEPENDENCE OF ELECTRON TRANSPORT IN GROUP IV
AND GROUP III-V SEMICONDUCTORS.

BY

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A thesis submitted to the Faculty of Science
at the University of Surrey for the Degree
of Doctor of Philosophy.

Department of Physics,
University of Surrey,
September 1985.
For my mother and late father.
The pressure dependence of the electron Hall mobility in a variety of semiconductor materials has been measured. The results, analysed by a number of techniques, indicate that in general very good agreement can be obtained for pure material at temperatures where ionized impurity scattering is unimportant. Thus we obtained good agreement between theory and experiment for relatively pure GaAs, InP, Si, Ge and GaP, using appropriate electron scattering mechanisms and material parameters.

For InSb we find that consistent agreement can only be obtained if the dielectric constants are highly pressure sensitive. For pure Ga$_{0.47}$In$_{0.53}$As the pressure dependence of the mobility is close to that predicted assuming space-charge scattering, rather than alloy scattering, is significant.

When heavily doped samples of LPE GaAs and VPE InP were measured it was not possible to predict the experimental pressure dependence of the mobility using the Brooks-Herring theory of scattering from ionized impurities. The possibility of inaccuracies in analysis have been reduced by using an iterative solution of the Boltzmann equation, phase shift calculations, and also Moore's analysis for dressing and multi-ion corrections. These however, proved to be inadequate and we obtain the best agreement with experiment using the theory of Yanchev et al for scattering from a correlated distribution of impurities in a gaussian fluctuating potential. The important effects of impurity correlation have been verified by studying samples of GaAs grown by MBE, and bulk GaAs subjected to neutron transmutation doping. The inability of impurities to correlate in such material is demonstrated by the close agreement between Brooks-Herring theory and experiment for these samples.
ACKNOWLEDGEMENTS

The work reported in this thesis was carried out in the Department of Physics at the University of Surrey and at the Science and Engineering Research Council (SERC) High Pressure facility at the Standard Telecommunications Laboratories (STL) Harlow. Support was provided by SERC in the form of a CASE studentship with the Royal Signals and Radar Establishment (RSRE) Malvern.

The author would like to thank Dr. A.R. Adams, under whose supervision the work was performed, for his continuous help, guidance and good humour.

Thanks are also due to Dr. M.L. Young, Dr. C. Pickering and Dr. D.A. Anderson of RSRE, Dr. B.T. Debney of Plessey Research Ltd (Caswell), and Dr. P.D. Greene of STL, for supplying the material, the code for the iterative solution of the Boltzmann equation, and for many useful discussions.

I am also grateful for technical assistance and helpful discussions to Dr. A.K. Saxena, Mrs. V. Hinton, Mr. B.J. Gunney, Mr. K. Dinan, Mr. J. Lees and Mr. M.A. Fisher. Finally I'd like to thank the rest of the ODM group for their help and Mr. M.J. Turner for his assistance with programing in Fortran77.
The following papers, based on the work reported in this thesis have been published in the scientific literature.


iii) "Random and Correlated Scattering from Ionized Impurities in GaAs". Proceedings of the 10th International AIRAPT Conference, Amsterdam, Holland. to be published in Physica (b) (1985).
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Effective Scattering Area (m²)</td>
</tr>
<tr>
<td>a₀</td>
<td>Effective Bohr Radius (m)</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic Flux Density (T)</td>
</tr>
<tr>
<td>C</td>
<td>Electronegativity Difference component of Band Gap (eV)</td>
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<tr>
<td>C₁</td>
<td>Longitudinal Elastic Constant (N/m²)</td>
</tr>
<tr>
<td>Cₜ</td>
<td>Transverse Elastic Constant (N/m²)</td>
</tr>
<tr>
<td>C₀</td>
<td>Correction term for additional Momentum Matrix Elements</td>
</tr>
<tr>
<td>D₀</td>
<td>Intervaly Coupling Constant (eV/cm)</td>
</tr>
<tr>
<td>e</td>
<td>Electronic Charge (C)</td>
</tr>
<tr>
<td>e₄</td>
<td>Piezoelectric Constant (C/m²)</td>
</tr>
<tr>
<td>E</td>
<td>Energy (J)</td>
</tr>
<tr>
<td>Eₐ</td>
<td>Acoustic Deformation Potential (eV)</td>
</tr>
<tr>
<td>Eₙ</td>
<td>Shallow donor binding energy (eV)</td>
</tr>
<tr>
<td>Eₚ</td>
<td>Homopolar Energy Gap (eV)</td>
</tr>
<tr>
<td>E₁</td>
<td>Central-Cell Binding Energy (eV)</td>
</tr>
<tr>
<td>Eₙ*</td>
<td>Band Gap at i&lt;sup&gt;th&lt;/sup&gt; symmetry position (eV)</td>
</tr>
<tr>
<td>E₈*</td>
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</tr>
<tr>
<td>E₉,E₉'</td>
<td>Interband Momentum Matrix Elements (eV)</td>
</tr>
<tr>
<td>F</td>
<td>Electric Field (V/m)</td>
</tr>
<tr>
<td>f(k)</td>
<td>Perturbed Electron Distribution</td>
</tr>
<tr>
<td>f₀(k)</td>
<td>Fermi-Dirac Distribution</td>
</tr>
<tr>
<td>g(k)</td>
<td>Perturbed Part of Electron Distribution due to Electric Field</td>
</tr>
<tr>
<td>g₀</td>
<td>Electron spin degeneracy</td>
</tr>
<tr>
<td>h</td>
<td>Planck's Constant/2π (Js)</td>
</tr>
<tr>
<td>h(k)</td>
<td>Perturbed Part of Electron Distribution due to Magnetic Field</td>
</tr>
<tr>
<td>J</td>
<td>Current Density (A/m²)</td>
</tr>
<tr>
<td>k</td>
<td>Wave Vector (m⁻¹)</td>
</tr>
</tbody>
</table>
- k -

$k_B$ Boltzmann's Constant (J/K).
$M$ Primitive Cell Mass (kg).
$m_e$ Electron Rest Mass (kg).
$m^*$ Electron Effective Mass (kg).
$N_a$ Acceptor Concentration (cm$^{-3}$).
$N_e$ Effective Density of States.
$N_d$ Donor Concentration (cm$^{-3}$).
$N_i$ Ionized Impurity Concentration (cm$^{-3}$).
$N_N$ Neutral Impurity Concentration (cm$^{-3}$).
$N_s$ Concentration of Space Charge Regions (cm$^{-3}$).
$n$ Real or "Drift" Carrier Concentration (cm$^{-3}$).
$n_H^P$ Hall Carrier Concentration (cm$^{-3}$).
$P$ Pressure (kbar).
$R$ Correlation Length (m).
$r_H^P$ Hall Scattering Factor.
$R_H^P$ Hall Coefficient (cm$^3$/C).
$R_i$ Sample Resistance in configuration $i$ (ohms).
$S_i(g_x)$ Inelastic Scattering Rate into volume d$k$ (s$^{-1}$).
$S_0(g_x)$ Inelastic Scattering Rate out of volume d$k$ (s$^{-1}$).
$s$ Differential Scattering Rate (s$^{-1}$).
$T$ Temperature (K).
$t$ Sample thickness (µm).
$T_C$ Phonon Temperature (K).
$V_C$ Crystal Volume (m$^3$).
$v$ Electron velocity (m/s).
$W_{IA}$ Intervalley-Acoustic Phonon Coupling Strength.
$\alpha$ Numerical factor dependent on Impurity Correlation.
$\alpha'$ Linear Coefficient of Thermal Expansion (K$^{-1}$).
$\beta$ Inverse Screening Length (m$^{-1}$).
$AU$ Alloy Scattering Potential (eV).
$\Delta_i$ Spin-Orbit splitting at $i^{th}$ symmetry position (eV).
$\delta$ Born Correction.
\( \delta \) & Dressing Correction.
\( \delta_n \) & Multiple Scattering Correction.
\( \xi \) & Augmented Density of States.
\( \eta \) & Reduced Fermi Energy.
\( \Omega \) & Volume of Primitive Cell (m³).
\( \varepsilon_0 \) & Permittivity of Free Space (F/m).
\( \varepsilon_s \) & Static Dielectric Constant.
\( \varepsilon_{\infty} \) & High Frequency Dielectric Constant.
\( \gamma \) & R.M.S. Band Edge Fluctuation (eV).
\( \theta \) & Compensation Ratio \( N_+/N_- \).
\( \kappa \) & Compressibility (kbar⁻¹).
\( \mu_d \) & Drift Mobility (cm²/Vs).
\( \mu_h^p \) & Hall Mobility (cm²/Vs).
\( \nu_{el} \) & Elastic Scattering Rate (s⁻¹).
\( \xi' \) & Fractional pressure dependence of material resistance (kbar⁻¹).
\( \rho \) & Mass Density (kg/m³).
\( \sigma \) & Conductivity (ohms⁻¹cm⁻¹).
\( \tau(E) \) & Relaxation Time (s).
\( \omega_{lo} \) & Longitudinal Polar Optic Phonon Frequency (s⁻¹).
\( \omega_{ta} \) & Transverse Acoustic Phonon Frequency (s⁻¹).
CHAPTER 1.

INTRODUCTION.

As the use of semiconductor electronics becomes increasingly widespread and important, the need to analyse and characterize the variety of material grows in proportion. Accurate characterization allows an increased understanding of the physical systems to be obtained which may, in turn, result in new and novel device structures.

One often used method is to measure the free carrier mobility and concentration, and to analyse the results obtained to determine the impurity content of the material. Clearly to achieve accurate results the effect of impurities must be accurately modelled.

The analysis of data on electron mobility and carrier concentration obtained as a function of temperature has been undertaken for many years and although the methods of analysis have improved recently there have been only minor modifications to the scattering mechanisms used.

A relatively new approach, however, has been to investigate electron transport as a function of hydrostatic pressure\(^1\). This enables parameters other than the temperature to be varied and thus provides a further test of the transport theories for electrons in a number of semiconductors. In this thesis we report the systematic measurement of electron mobility and carrier concentration in a variety of n-type semiconductors, both as a function of temperature and pressure, and analyse the results obtained using a number of techniques. With this information conclusions can be drawn about the transport properties of the materials.

The thesis format is as follows: In Chapter 2 an outline of
the band structure and material parameters is given and their temperature and pressure dependences are discussed. The effect of impurities and their distribution is also described. Chapter 3 reviews the low field transport theory, with particular emphasis on the limitations and approximations applied, while in Chapter 4 the experimental apparatus and sample preparation is described. Chapters 5 and 6 give an account of the results obtained for the binary materials InP and GaAs. Chapter 7 discusses the results obtained in InSb and the alloy Ga_{0.47}In_{0.53}As, while in Chapter 8 the indirect band gap semiconductors Si, Ge, and GaP are investigated. Finally in Chapter 9 some conclusions are drawn and guidelines for the future development of this work are suggested.
CHAPTER 2.

REVIEW OF THE PRESSURE AND TEMPERATURE DEPENDENCE
OF GROUP IV AND III-V MATERIAL PROPERTIES.

2.1 Introduction.

In this chapter a brief review of the material properties of some of the group IV and III-V semiconductors is given. The chapter can be conveniently divided into three sections. The first is concerned with band structure extrema and their curvature, while the second discusses effects associated with the density and distribution of impurities. The final section is predominantly concerned with related material parameters that appear in the scattering mechanisms discussed in the next chapter. Of particular interest are the variations of these properties as a function of temperature and pressure so that an accurate interpretation of the experimental results can be made. In each section, the relevance of changes in pressure and temperature are highlighted. All relevant data, extracted from numerous sources, is given in the tables that follow. However, in a number of instances experimental data is not available. Where this is the case we have either used predicted variations derived from standard theories or interpolated from other, measured properties.

Before proceeding further it is useful to consider the crystal structure and binding of group IV and III-V semiconductors. All the materials discussed here crystallize into the diamond or zincblende structure. This consists of two interpenetrating face-centred cubic (fcc) lattices, labelled A and B in Figure 2.1, where the B-sublattice is displaced by a quarter of the body diagonal with respect to the A-sublattice.
Figure 2.1 Diamond/Zincblende Structure.

Figure 2.2 Brillouin Zone and symmetry points of f.c.c. lattice.
For the group IV semiconductors Si and Ge we can write symbolically that $A=B$, while for the binary III-V semiconductors, such as GaAs $A=Ga$ and $B=As$. For a III-V alloy, such as $Ga_{x}In_{1-x}As_{y}P_{1-y}$, there is a degree of freedom in the location of either the group III or the group V atoms on one type of lattice site which gives rise to so-called alloy disorder.

The first Brillouin zone of such crystals is shown in Figure 2.2 together with the principal symmetry points. The symmetry of the crystal gives useful information about band edge maxima and minima, and their degeneracy. Most important is the $\Gamma$ point at the zone centre, and the $L$ and $X$ points at the zone boundaries along the $(1,1,1)$ and $(1,0,0)$ directions respectively. Clearly any conduction band minimum at the $\Gamma$ point is unique, while there are 4 and 3 equivalent minima at the $L$ and $X$ points respectively. When the minima lie away from the zone edges they are no longer shared by adjacent Brillouin zones so that there are then 8 and 6 equivalent minima at the $A$ and $\Lambda$ points, respectively.

2.2 Band Structure.

2.2.1 Introduction.

As a result of the periodic lattice outlined previously the band structure of a semiconductor consists of regions of allowed electron energy states separated by "forbidden energy gaps". The general arrangement of these bands of allowed energy levels is primarily a function of the crystal symmetry. Consequently, the band structure characteristics of group IV and III-V semiconductors are broadly similar, even though the latter lack the inversion symmetry of the former. The
splitting of band edge degeneracies at certain symmetry points due to the partial ionic bonding character of III-V materials is found to be rather small. Thus it has little effect on electron transport. Spin-orbit splitting is important, but can usually be considered independent of temperature and pressure. Consequently a generalized band structure diagram, such as that shown in Figure 2.3, can be envisaged. Generally all the materials have conduction band minima close to the $\Gamma$, $X$, and $L$ points as well as a rather complex valence band maximum at the $\Gamma$ point. However, symmetry considerations alone do not determine the ordering of the conduction band minima.

To calculate the energy gaps shown in Figure 2.3 a number of theoretical methods are available. However, it is sufficient, for our purposes, to consider a simple semi-empirical method for calculating the band structure which clearly indicates the physical origin of both its temperature and pressure dependence. This is described in the next section.

2.2.2 Band Structure Calculations.

A useful, semi-empirical method of calculating some of the band gaps shown in Figure 2.3 for tetrahedrally bonded semiconductors has been developed by Phillips, Van Vechten, and Van Vechten and Bergstresser. This is described in terms of the chemical bonding description of Pauling, which indicates that valence and conduction bands arise from the anti-bonding and bonding configurations of $sp^3$ hybridised orbitals. Thus the crystal properties depend on the bonding orbitals and thus on the potential seen by the valence electrons localized near the ions. This in turn, is found to depend only on the net ionic core charge.
Figure 2.3 Principal energy gaps of generalized semiconductor.
The major contributions to covalent bonding are the outermost "p" and "s" orbitals, although the presence of d-core electrons has an important effect. More strongly bonded electrons are assumed to be part of the ionic core and to a good approximation play no part in determining the energy levels except through their influence on the lattice spacing. The potential seen by electrons outside the ionic core can be divided into covalent and ionic contributions. For purely covalent materials the ionic contribution is zero and the bonding and anti-bonding levels split by the homopolar energy, $E_h$, due to the covalent potential. For partially ionic materials, such as the III-V semiconductors, the antisymmetric potential causes an additional splitting of the bonding and anti-bonding levels, $C$, related to the electronegativity difference between neighbouring atoms. The bonding anti-bonding separation is then given by,

$$E_b^2 = E_h^2 + C^2.$$  \hspace{1cm} (2.2-1)

The effect of d-core electrons can be separated into two factors, $AE_1$, which depends only on the nearest neighbour distance, and $(D_{av}-1)$, which gives a measure of the coupling strengths between the d-core and valence electrons.

In Appendix A we give the prescriptions and data of Van Vechten and Bergstresser and Camphausen et al. required to calculate the band structure information given in Table 2.1, from which it is clear that the method works remarkably well, particularly at the $\Gamma$ point. We defer further comment until later.
TABLE 2.1. Band Structure Parameters and their Pressure and Temperature Coefficients.

<table>
<thead>
<tr>
<th>Property</th>
<th>Material</th>
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<tbody>
<tr>
<td></td>
<td>Si</td>
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<tr>
<td>d/\alpha</td>
<td>4.444</td>
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<tr>
<td>\gamma</td>
<td>0</td>
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<tr>
<td>D_{av}</td>
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<td>E_{\theta}^T (eV)</td>
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<tr>
<td>(T=0K)</td>
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<td>E_{\theta}^X (eV)</td>
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<td>\Delta_{\theta}^X (eV)</td>
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<tr>
<td>E_{\theta}^X (eV)</td>
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<th>Ge</th>
<th>GaAs</th>
<th>InP</th>
<th>GaP</th>
<th>InSb</th>
<th>GaInAs</th>
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<tr>
<td>$\alpha_n$ [$10^{-4}\text{eV}/K$]</td>
<td>$4.730^b$</td>
<td>$6.05^p$</td>
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<tr>
<td>$E_{\text{ex}}$ (eV)</td>
<td>$0.98^r$</td>
<td>$1.14^r$</td>
<td>$2.07^r$</td>
<td>$2.68^r$</td>
<td>$1.57^r$</td>
<td></td>
<td>$2.07^r$</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>$E_{\text{ex}}$ (eV)</td>
<td>$1.170^b$</td>
<td>$2.015^e$</td>
<td>$2.22^r$</td>
<td>$2.338^b$</td>
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<td></td>
</tr>
<tr>
<td>$\alpha_x$ [$10^{-4}\text{eV}$]</td>
<td>$4.774^b$</td>
<td>$4.60^p$</td>
<td></td>
<td></td>
<td>$5.771^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(T=300\text{K})$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k$ [$10^{-3}$ [meV/kbar$^{-1}$]]</td>
<td>$1.02^d$</td>
<td>$1.33^d$</td>
<td>$1.34^d$</td>
<td>$1.38^d$</td>
<td>$1.13^d$</td>
<td>$2.20^d$</td>
<td>$1.38^d$</td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$3.8^y$</td>
<td>$14.2^y$</td>
<td>$10.9^y$</td>
<td>$9.5^y$</td>
<td>$7.9^y$</td>
<td>$14.3^y$</td>
<td>$12.2^y$</td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$12.7^d$</td>
<td>$11.1^d$</td>
<td>$8.5^d$</td>
<td>$10.5^d$</td>
<td>$14.6^d$</td>
<td>$9.2^u$</td>
<td></td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$-0.2^y$</td>
<td>$-0.2^y$</td>
<td>$-0.1^y$</td>
<td>$-1.1^y$</td>
<td>$-0.9^y$</td>
<td>$-1.1^y$</td>
<td>$-1.0^y$</td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$-1.5^d$</td>
<td>$-1.34^c$</td>
<td>$-2.4^c$</td>
<td>$-1.1^l$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$1.2^y$</td>
<td>$5.3^y$</td>
<td>$3.7^y$</td>
<td>$3.1^y$</td>
<td>$2.5^y$</td>
<td>$5.0^y$</td>
<td>$4.2^y$</td>
</tr>
<tr>
<td>$dE_{\text{ex}}$ [meV/kbar]</td>
<td>$4.8^o$</td>
<td>$5.5^o$</td>
<td>$2.0^o$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No. of Ev. Cond. Band Minima.</td>
<td>6</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta_0$ (eV)</td>
<td>$\sim0.03^i$</td>
<td>$\sim0.19^n$</td>
<td>$0.19^n$</td>
<td>$0.07^n$</td>
<td>$0.05^n$</td>
<td>$0.33^n$</td>
<td>$0.29^n$</td>
</tr>
<tr>
<td>$\Delta_1$ (eV)</td>
<td>$\sim0.22^n$</td>
<td>$\sim0.23^n$</td>
<td>$\sim0.15^n$</td>
<td>$0.08^i$</td>
<td>$0.50^n$</td>
<td>$0.27^n$</td>
<td></td>
</tr>
<tr>
<td>$E_{\text{ex}}$ (eV)</td>
<td>$5.9^i$</td>
<td>$5.51^v$</td>
<td>$6.60^v$</td>
<td>$6.66^v$</td>
<td>$7.17^v$</td>
<td>$5.25^v$</td>
<td>$6.27^v$</td>
</tr>
</tbody>
</table>
Table 2.1. Continued.

<table>
<thead>
<tr>
<th>Property</th>
<th>Material</th>
<th>Bi</th>
<th>Be</th>
<th>GaAs</th>
<th>InP</th>
<th>GaP</th>
<th>InSb</th>
<th>GaInAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dE_1^{\text{Th}}$</td>
<td>[meV/kbar]</td>
<td>$2.7^\gamma$</td>
<td>$7.1^\gamma$</td>
<td>$5.5^\gamma$</td>
<td>$4.7^\gamma$</td>
<td>$4.2^\gamma$</td>
<td>$7.0^\gamma$</td>
<td>$6.1^\gamma$</td>
</tr>
<tr>
<td>$dE_1^{\text{Ex}}$</td>
<td>[meV/kbar]</td>
<td>$5.2^1$</td>
<td>$7.7^1$</td>
<td>$7.3^1$</td>
<td></td>
<td>$5.8^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$dE_2^{\text{Th}}$</td>
<td>[meV/kbar]</td>
<td>$3.6^\gamma$</td>
<td>$4.3^\gamma$</td>
<td>$3.6^\gamma$</td>
<td>$3.1^\gamma$</td>
<td>$3.2^\gamma$</td>
<td>$4.1^\gamma$</td>
<td>$3.7^\gamma$</td>
</tr>
<tr>
<td>$dE_2^{\text{Ex}}$</td>
<td>[meV/kbar]</td>
<td>$3.0^1$</td>
<td>$5.7^1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$2.9^1$</td>
</tr>
</tbody>
</table>

The superscripts refer to the following references,

$^8$ Imil $^{11}$  $^12$  $^10$  $^13$  $^14$  $^15$
$^16$  $^17$  $^18$  $^19$  $^20$  $^21$  $^22$
$^23$  $^24$  $^25$  $^26$  $^27$  $^28$  $^29$

$^\gamma$ Calculated by the author using the prescriptions of Appendix A.

$^*$ Calculated using standard linear interpolation (see ref 30).
2.2.3 k.p Theory and Electron Effective Masses.

Before discussing the temperature and pressure dependence of the band gaps we wish to indicate how the effective mass of electrons is also dependent on the band gap. The development of the k.p perturbation method has been reviewed by Kane. By this technique the interaction between two closely spaced conduction and valence bands is treated exactly through k.p and k-independent spin-orbit interactions. Interactions with higher lying bands are treated by 2nd order perturbation theory. The effective mass of carriers is given by,

\[
\frac{1}{m_i} = \frac{1}{m_0} + \frac{2}{m_0} \sum_{n'} \frac{l_1 \cdot p_{nn'} \cdot l_2}{E_n(k_0) - E_{n'}(k_0)}
\]

where \(l\) is a unit vector in the direction of the \(i^{th}\) principal axis and \(2.1_1 \cdot p_{nn'} \cdot l_2/m_0\) represents the square of the matrix between the \(n\) and \(n'\) bands.

Consequently the effective mass can be calculated provided the band gaps and the momentum matrix elements are known. In principle this approach can completely determine the band structure. However, in reality it is a semi-empirical approach as not all the required energy gaps and matrix elements are available. From equation 2.2-2 it can be shown that at zero temperature the effective mass of an electron is given by

\[
\frac{m_0}{m_i} - 1 = \frac{E_p}{3} \left[ \frac{2}{E_i} + \frac{1}{E_i + \Delta_i} \right] - \frac{E_{p'}}{3} \left[ \frac{2}{E_i'} + \frac{1}{E_i' + \Delta_i'} \right] + C'
\]

where \(i=0,1,\) and \(2\). For \(i=0\) the effective mass is isotropic, while for \(i=1\) and \(i=2\) this is not the case and equation 2.2-3
then describes the effective mass in the conduction band minima at the energy gap $E_s$. The longitudinal effective mass is of order one and is considered independent of temperature and pressure. $E_p$ and $E_{p'}$ are momentum matrix elements describing the interactions of the conduction band with the valence band and with the nearest conduction band respectively. $C'$ is a correction term included to account for interactions between the conduction band and the remaining bands above the next nearest conduction band. Taking the results of Shantharama et al.\cite{18}, and assuming that $E_p$, $E_{p'}$ and $C'$ are independent of temperature and pressure leads to the values quoted in Table 2.2. Values of the low temperature effective mass are also given. The relationship between the electron effective mass and the band gap is then readily apparent.

2.2.4 Pressure Dependence of the Band Gaps.

The prescriptions given in Appendix A indicate clearly how the nearest neighbour distance plays an important role in determining the band gaps. Consequently any external effect which can change this is likely to cause significant changes in the band structure. In this section and the next we describe how changes in hydrostatic pressure and temperature affect the band structure.

The application of hydrostatic pressure, unlike uniaxial stress, does not change the crystal symmetry and consequently does not force any degenerate bands to split. However, via the material compressibility it changes the lattice constant and hence the band gaps via expressions $A_1$-$A_{10}$. Camphausen et al.\cite{10} have shown how the theory of Phillips and Van Vechten can be used to calculate the pressure coefficients of the
TABLE 2.2. Electron Effective Masses and their Pressure and Temperature Dependence.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\frac{m^*}{m_e}$</th>
<th>$E_p$ (eV)</th>
<th>$E_p'$ (eV)</th>
<th>$C'$</th>
<th>$\frac{d m^*}{dT} \cdot 10^{-4}$</th>
<th>$\frac{d m^*}{dP} \cdot 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0.9163</td>
<td>0</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>0.1905</td>
<td>18.4</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
<td>0.21</td>
</tr>
<tr>
<td>Ge</td>
<td>1.55</td>
<td>25.0</td>
<td>25.0</td>
<td>0</td>
<td>-1.9</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>0.082</td>
<td>-25.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.53</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.067</td>
<td>25.0</td>
<td>5</td>
<td>0</td>
<td>-2.2</td>
<td>0.64</td>
</tr>
<tr>
<td>InP</td>
<td>0.082</td>
<td>16.7</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
</tr>
<tr>
<td>GaP</td>
<td>1.5</td>
<td>16.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>InSb</td>
<td>0.0133</td>
<td>23.2</td>
<td>0</td>
<td>0</td>
<td>-4.2</td>
<td>6.2</td>
</tr>
<tr>
<td>GaInAs</td>
<td>0.041</td>
<td>29.8</td>
<td>37</td>
<td>0</td>
<td>-4.1</td>
<td>1.68</td>
</tr>
</tbody>
</table>

The superscripts refer to the following references:

^1Longitudinal Effective Mass.
^2Transverse Effective Mass.
^kCalculated by the author.
direct energy gaps and hence the pressure coefficients of the conduction band edges at the L and X points with respect to the valence band at the $\Gamma$ point. This is also given in Appendix A. Thus the calculated pressure coefficients given in Table 2.1, can be compared with the measured pressure coefficients. At the L and X points there is a compromise between obtaining fits for both the band gaps and their pressure coefficients which generally degrades the band gap agreement, but gives a good prediction of their pressure coefficients. The calculated values agree quite well and follow the general trend first discussed by Paul.\(^{40}\) The band gap at the $\Gamma$ point increases the quickest, while the Er-L$_x$ separation tends to increase at approximately half the rate. The Er-L$_x$ separation tends to decrease slowly.

At sufficiently high pressures the bands may cross resulting in electron transfer. However, for pressures up to 15kbar electron transfer is usually not important, except in certain highly doped samples, and consequently it is likely to have only a small effect on the observed carrier concentration (see section 2.3).

2.2.5 Temperature Dependence of the Band Gaps.

The band structure is expected to vary with temperature from the aforementioned discussion because of thermal expansion. However, this effect is only important at low temperatures where the thermal expansion coefficient varies non-linearly with temperature, and may even change sign resulting in a non-linear temperature dependence of the band gap. At high temperatures it contributes only about 25% of the total change with temperature. The rest is associated with the temperature dependent electron-phonon interaction. Clearly at
low temperatures the density of phonons is low and this effect is less important. At higher temperatures the electron-phonon interaction causes the band gap to decrease with increasing temperature. This is physically reasonable for if one considers, for example, acoustic phonons (discussed later in this chapter), it is apparent that their density increases with increasing temperature. Such phonons correspond to regions in the lattice of alternate compression and rarefaction, which lead to corresponding regions of increased and decreased band gap. Electrons preferentially favour the regions for which their energy is lowered. A similar argument for holes thus leads to an overall decrease in the band gap as observed.

The temperature dependence of the band gap in a number of materials has been measured by a variety of authors. Varshni\(^\text{12}\) found that the results could be described empirically by an expression of the form,

\[
E_g(T) = E_g(0) - \frac{\alpha T^2}{(T + \beta)}
\]

2.2.6 Pressure and Temperature Dependence of the Electron Effective Mass.

Kane's \(k.p\) theory discussed previously applies only at zero temperature, while most of the results discussed later were taken in the range 77-450K, where the band gap has decreased.
However, the temperature dependence of the effective mass is smaller than that predicted using the temperature dependence of the energy gaps discussed above, which are usually called the optical or thermal band gaps in the literature. The band gap used to describe the temperature dependence of the effective mass is called the Effective Mass Band Gap. Following the notation of Ehrenreich\(^\text{11}\) we write its temperature dependence as,

\[
E_i^{\ast}(T) = E_i(0) + \left. \frac{\delta E_i^{\ast}(T)}{\delta T} \right|_{p} T, \tag{2.2-5}
\]

where,

\[
\frac{dE_i^{\ast}}{dT} = -3\kappa' \frac{dE_i}{dp}, \tag{2.2-6}
\]

\(\kappa\) is the compressibility and \(\kappa'\) is the coefficient of thermal expansion. Rode\(^\text{12}\) uses \(E_i^{\ast}\) to determine the band non-parabolicity, which is important in calculating the electron mobility discussed in Chapter 3.

The temperature dependence of the effective mass has been measured for a number of materials\(^\text{37,38}\) and has been found to agree reasonably well with an expression of the form of equation 2.2-3 with \(E_i\) replaced by \(E_i^{\ast}\). Consequently, where no experimental results were available equation 2.2-3 was used.

The pressure dependence of the electron effective mass has been measured by Shantharama et al at Burrey, for GaAs and InP\(^\text{39}\) and for BaInAs/InP of a number of compositions\(^\text{40}\). Their results are given in Table 2.2. For the other materials listed no direct measurements are known, and so the pressure coefficients given in Table 2.2 were calculated using equation 2.2-3 and the data in Tables 2.1 and 2.2. The longitudinal
effective mass was assumed to be independent of pressure.

2.3 Effects of Impurities.

2.3.1 Introduction.

The discussion so far has dealt with a perfect crystal in which there are no impurities. Of course this is never the case, and thus one must include a number of aspects associated with the presence of impurities and extrinsic carriers.

The incorporation of impurities in a semiconductor results in impurity levels, often located in the band gap. Such levels are described as being either "shallow" or "deep". We shall confine the discussion predominantly to shallow levels. In particular we are concerned with two conditions. Firstly the low impurity case, characterized by $N_\text{xa} \ll 1$, where $a_\text{e}$ is the effective Bohr radius and $N_\text{x}$ is the impurity concentration. Secondly when $N_\text{xa} > 1$ and $n \ll N_\text{x}$.

Broadly speaking for $N_\text{xa} \ll 1$, the band structure of the pure material may be assumed to prevail, at least for temperatures greater than 77K, and the impurities can be assumed to be independent. With increasing impurity concentration the impurities start to interact leading to a broadening of the shallow impurity levels, described in terms of a rms potential, $\gamma$, discussed in the next chapter. At sufficiently high impurity concentrations the impurity band merges with the conduction band edge and results in an exponentially decreasing density of states going into the band gap. For heavily doped material with low compensation, the Fermi level lies above these localized states.
2.3.2 Temperature and Pressure Dependence of Extrinsic Carrier Concentration.

A donor impurity is called shallow if its ionisation energy is small compared to the band gap. This implies that the excess electron is weakly bonded and the usual picture is to consider the impurity as a hydrogen atom embedded in a uniform medium of dielectric constant $\varepsilon_\infty$. Its binding energy is then given as \( E_d \)

\[ E_d = \frac{-e^2 m^*}{32\pi^2 \varepsilon_0 \varepsilon_\infty k^2} \]

Thus we would not expect shallow levels to show a large "trap-out" as a function of applied pressure as the increase in $E_d$ due to changes in $m^*$ and $\varepsilon_\infty$ is small compared to $k_B T$.

In extrinsic material, it is necessary to examine how electrons are distributed between the bands and the impurity states in thermal equilibrium. The requirements of electrical neutrality, along with occupation statistics lead to the following expression for the temperature dependence of the carrier concentration

\[ \frac{n(n + N_d)}{N_d - N_a - n} = \frac{N_c \exp(-E_d/k_B T)}{g_0} \]

This assumes one type of impurity level, of concentration $N_d$ and ionisation energy $E_d$, partially compensated by ionised shallow or deep acceptors of concentration $N_a$. $g_0$ is the spin degeneracy and $N_c$ is the effective density of states of the conduction band. Excited states of the donor level have been neglected.
2.4 Material Properties.

2.4.1 Introduction.

To analyse the experimental results the following material parameters were used. Frequently the data given, as well as being a function of both temperature and pressure, is also a function of the impurity concentration/electron concentration. This is discussed as necessary in later chapters. Here we concentrate on the pressure and temperature dependence of some important quantities. All the data required is given in Table 2.3. For the alloy, Gao.47Ino.53As, the quoted material properties were either determined experimentally or interpolated from the values of the binary compounds GaAs and InAs using the commonly used expression\(^{30}\). Further information about each material parameter is given in the following sections and the values obtained were included in the analysis of the experimental results.

2.4.2 Phonon Energies.

The scattering of electrons by phonons is an important mechanism in all the semiconductors considered here. The energy of the ionic vibrations is quantized with an energy \(\hbar \omega\) and a momentum \(\hbar \mathbf{k}\), where \(\omega\) and \(\mathbf{k}\) are the vibrational frequency and the wavevector of the vibration respectively. A typical dispersion relation for the lattice vibrations within the first Brillouin zone in silicon\(^{51}\) is shown in Figure 2.4. The branches whose vibrational frequency increases with increasing wavevector are called the acoustic branches, while the other branches are called the optical branches. For intervalley scattering we are interested in phonons near the
TABLE 2.3. Material Properties and their Pressure and Temperature Coefficients.

<table>
<thead>
<tr>
<th>Property</th>
<th>Si</th>
<th>Ge</th>
<th>GaAs</th>
<th>InP</th>
<th>GaP</th>
<th>InSb</th>
<th>GaInAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho ) (g/cm(^3))</td>
<td>2.328</td>
<td>5.324</td>
<td>5.307</td>
<td>4.787</td>
<td>4.130</td>
<td>5.775</td>
<td>5.449</td>
</tr>
<tr>
<td>( E_{\text{ac}} ) (eV)</td>
<td>6.511</td>
<td>9.01</td>
<td>9.0</td>
<td>11.5</td>
<td>~12</td>
<td>15.0</td>
<td>5.9</td>
</tr>
<tr>
<td>( D_{\text{m}} ) (10(^{\text{eV/cm}}))</td>
<td>0.3</td>
<td>0.32</td>
<td>1.3</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \varepsilon_{\text{m}} ) (T=OK)</td>
<td>~11.70</td>
<td>15.98</td>
<td>12.40</td>
<td>11.93</td>
<td>~10.9</td>
<td>~17.68</td>
<td>13.31</td>
</tr>
<tr>
<td>( \varepsilon_{\text{m}} ) (T=OK)</td>
<td>~11.70</td>
<td>15.98</td>
<td>10.60</td>
<td>9.33</td>
<td>~8.95</td>
<td>15.68</td>
<td>11.08</td>
</tr>
<tr>
<td>( \frac{1}{\varepsilon_{\text{m}}} \frac{d\varepsilon_{\text{m}}}{dT} ) (10(^{-5}) K(^{-1}))</td>
<td>7.8</td>
<td>13.4</td>
<td>12.0</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{\varepsilon_{\text{m}}} \frac{d\varepsilon_{\text{m}}}{dT} ) (10(^{-5}) K(^{-1}))</td>
<td>~14.0</td>
<td>9.0</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{\varepsilon_{\text{m}}} \frac{d\varepsilon_{\text{m}}}{dP} ) (kbar(^{-1}))</td>
<td>~1.2</td>
<td>~1.8</td>
<td>~1.4</td>
<td>~1.1</td>
<td>~13</td>
<td>~13</td>
<td>~1.4</td>
</tr>
<tr>
<td>( \frac{1}{\varepsilon_{\text{m}}} \frac{d\varepsilon_{\text{m}}}{dP} ) (kbar(^{-1}))</td>
<td>~0.28</td>
<td>~1.4</td>
<td>~1.4</td>
<td>~1.3</td>
<td>~0.6</td>
<td>~13</td>
<td>~1.3</td>
</tr>
<tr>
<td>( \varepsilon_{\text{m}} ) (10(^{-1}) cm(^{-1}))</td>
<td>5.431</td>
<td>5.658</td>
<td>5.653</td>
<td>5.869</td>
<td>5.450</td>
<td>6.479</td>
<td>5.869</td>
</tr>
<tr>
<td>( \varepsilon_{\text{m}} ) (10(^{-1}) cm(^{-1})) (T=300K)</td>
<td>5.431</td>
<td>5.658</td>
<td>5.653</td>
<td>5.869</td>
<td>5.450</td>
<td>6.479</td>
<td>5.869</td>
</tr>
<tr>
<td>( \mu_{\text{m}} ) (C/m(^2))</td>
<td>9.06</td>
<td>5.36</td>
<td>5.102</td>
<td>5.032</td>
<td>6.34</td>
<td>~3.76</td>
<td>4.75</td>
</tr>
<tr>
<td>( \mu_{\text{m}} ) (10(^{9}) cm(^2)/V)</td>
<td>9.06</td>
<td>5.36</td>
<td>5.102</td>
<td>5.032</td>
<td>6.34</td>
<td>~3.76</td>
<td>4.75</td>
</tr>
<tr>
<td>( \hbar_{\text{m}} ) (meV)</td>
<td>~55.3</td>
<td>~30.5</td>
<td>~36.5</td>
<td>~42.7</td>
<td>~49.9</td>
<td>23.6</td>
<td>34.12</td>
</tr>
<tr>
<td>( \hbar_{\text{m}} ) (meV)</td>
<td>~57.3</td>
<td>~36.4</td>
<td>~33.8</td>
<td>~37.6</td>
<td>~45.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \hbar_{\text{m}} ) (meV)</td>
<td>~51.0</td>
<td>27.57</td>
<td>~23</td>
<td>18.6</td>
<td>21.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \hbar_{\text{m}} ) (meV)</td>
<td>18.2</td>
<td>7.76</td>
<td>~8.5</td>
<td>7.69</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{\text{m}} ) (10(^{10}) N/m(^2)) (T=OK)</td>
<td>6.88</td>
<td>5.73</td>
<td>4.71</td>
<td>3.65</td>
<td>5.80</td>
<td>2.51</td>
<td>3.95</td>
</tr>
<tr>
<td>( C_{\text{m}} ) (10(^{10}) N/m(^2)) (T=OK)</td>
<td>6.88</td>
<td>5.73</td>
<td>4.71</td>
<td>3.65</td>
<td>5.80</td>
<td>2.51</td>
<td>3.95</td>
</tr>
<tr>
<td>( \frac{1}{C_{\text{m}}} \frac{dC_{\text{m}}}{dP} ) (kbar(^{-1}))</td>
<td>~1.5</td>
<td>~1.6</td>
<td>~3.9</td>
<td>~3.9</td>
<td>2.2</td>
<td>~9</td>
<td>~3.9</td>
</tr>
<tr>
<td>Property</td>
<td>Si</td>
<td>Ge</td>
<td>GaAs</td>
<td>InP</td>
<td>GaP</td>
<td>InSb</td>
<td>GaInAs</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\frac{1}{\omega_0} \frac{d\omega}{dT} [10^{-2}]$</td>
<td>$-4.0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{\omega_0} \frac{d\omega}{dT} [10^{-3}]$</td>
<td>$-5.5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{\omega_0} \frac{d\omega}{dP} [10^{-3}]$</td>
<td>$1.02^a$</td>
<td>$1.49^a$</td>
<td>$1.55^a$</td>
<td>$1.57^a$</td>
<td>$1.24^a$</td>
<td>$2.0^a$</td>
<td>$1.9^a$</td>
</tr>
<tr>
<td>$\frac{1}{\omega_0} \frac{d\omega}{dP} [kbar]$</td>
<td>$1.02^a$</td>
<td>$1.49^a$</td>
<td></td>
<td>$1.91^a$</td>
<td>$1.35^a$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The superscripts refer to the following references:

$^a$14, $^b$44, $^c$45, $^d$46, $^e$47, $^f$15, $^g$48, $^h$49, $^i$39, $^j$30, $^k$24, $^l$50, $^m$20, $^n$42

$^\gamma$Calculated using standard linear interpolation between binary compounds.$^{30}$

$^*$Best fit to data presented in this thesis.
Figure 2.4 Dispersion of [100] directed phonons in Si (after Brockhouse\textsuperscript{(51)}).
zone boundary. The small wavevector dependence of the optical branches near the zone centre allows the optical vibrational frequency to be regarded as independent of the wavevector for small k. Acoustic phonons cause the atoms to vibrate in phase leading to alternating regions of compression and rarefaction, while for optical phonons they vibrate in quadrature.

The characteristic phonon energies are given in Table 2.3. Their temperature dependence is rather small and is generally insignificant in comparison to the temperature dependence of the phonon population. However, the pressure dependence of the phonon energy at constant temperature can be important and these are also given in Table 2.3. For direct band gap III-V semiconductors it is the polar optic phonon which is dominant, while for indirect gap materials a number of phonons can be important, and their relative coupling strengths with electrons must be included. In Be and GaP the conduction band minima are at the zone boundaries, at the L and X points respectively. Consequently intervalley scattering via phonons near the appropriate zone boundaries is important. For Be the similar energies of the non-polar optic and the LO and LA phonons means that in practice electron scattering by the two mechanisms cannot be distinguished. Consequently we follow Rode" and combine the two mechanisms by ascribing an "average" phonon of energy 32.92 meV.

In Si" and GaP", non-polar optical scattering is negligible so that the above problem does not arise. However, in Si we have to describe the effects associated with the conduction minima lying away from the zone boundaries at the A points. This results in two types of intervalley scattering, either along parallel principal axes (g-scattering) or between perpendicular crystal axes (f-scattering). It is relatively easily shown" that both mechanisms involve umklapp
processes in [110]-type directions. Also f-scattering involves phonons which are close to the zone boundary at X, while g-scattering phonons are located approximately one third of the way to the zone boundary. Group selection rules applied between symmetry points limit the phonons involved in intervalley scattering.\(^{(54,55,56)}\)

The ratio of the coupling strengths of the intervalley to acoustic phonons, as used in equation 3.4-4 has been given by Conwell\(^{(57)}\) as,

\[
\frac{w_f}{w_a} = \frac{2D_{ac}^2 \omega_f^2}{E_{ac}^2 \omega_f^2} = -2.4-1
\]

Values of this ratio for the various phonons in Si, Ge, and GaP are given in Table 2.4.

2.4.3 Static and High Frequency Dielectric Constants.

The values of the high and low frequency dielectric constants, \(\varepsilon_\infty\) and \(\varepsilon_\omega\), are given in Table 2.3, along with their temperature and pressure coefficients. The pressure and, less importantly, the temperature dependence of \(\varepsilon_\infty\) is found from the pressure and temperature dependence of the refractive index, \(n\), as \(\varepsilon_\infty = n^2\). The corresponding changes in \(\varepsilon_\omega\) can be calculated from the Lyddane-Sachs-Teller (LST) relation,

\[
\varepsilon_\omega = \frac{\omega_\infty^2}{\omega_\omega^2} = -2.4-2
\]

given the appropriate variations in \(\omega_\infty\) and \(\omega_\omega\). For Si and Ge, which possess an inversion symmetry, \(\omega_\infty = \omega_\omega\) so that \(\varepsilon_\omega = \varepsilon_\infty\). For GaAs and GaP, the LST relation is found to hold very well\(^{13}\). Consequently we have used equation 2.4-2 to
### TABLE 2.4. Intervalley Phonons and Coupling Constants.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phonon Energies, Coupling Ratios and their Pressure Coefficients.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>$\hbar\omega$ (meV)</td>
<td>54.3$^a$</td>
</tr>
<tr>
<td>$W_1/W_0$</td>
<td>2.0$^b$</td>
</tr>
<tr>
<td>$W_0 d(W_1/W_0) \times 10^{-3}$</td>
<td>$\sim 0^d$</td>
</tr>
<tr>
<td>$W_1 dP$</td>
<td>--</td>
</tr>
</tbody>
</table>

The superscripts refer to the following references:

$^a$39  $^b$53  $^c$61

$^d$calculated using equation 2.4-1.
calculate the temperature and pressure dependences of \( \varepsilon \) in the materials for which no measured values are available, although for InSb other interesting effects will be discussed later.

2.4.4 Mass Density, Elastic Constants, and Sound Velocities.

The mass density, \( \rho \), can be found from,

\[
\rho = \frac{M}{\Omega}
\]

where \( M \) is the primitive cell mass, and \( \Omega \) is the volume of the primitive cell. The temperature and pressure dependence of \( \rho \) arises through the thermal expansion coefficient and the bulk compressibility respectively.

We have assumed that the elastic constants are independent of temperature. The pressure coefficients of the elastic constants of Si, Ge and GaAs have been measured by McSkimin et al., from which we calculated the pressure coefficients of \( C_1 \), the "averaged" longitudinal elastic constant, given in Table 2.3. The pressure coefficients of the other compound semiconductors were assumed to be the same as those of GaAs.

The average longitudinal sound velocity, \( u_1 \), is given by,

\[
u_1^2 = \frac{C_1}{\rho}
\]

Using this expression the pressure dependence of \( u_1 \) is easily calculated.
2.4.5 Deformation Potentials.

The deformation potential, \( E_{ij} \), is defined as the shift in absolute energy of the band edge per unit elastic strain. This is a symmetric rank two tensor, which for cubic crystals has two independent components, corresponding to pure dilation and pure shear. For the case of the direct minima at the \( \Gamma \) point only the dilation term is important, and it can be seen that this is given by,

\[
E_{\text{ac}} = \frac{1}{k} \frac{dE_{\text{c}}}{dP}
\]

provided, as is commonly assumed, that the valence band shifts relatively little with pressure. Thus in principle, we can obtain both the atmospheric value of the deformation potential and its dependence on pressure. However, experimentally it has been found by numerous workers that equation 2.4-5 does not give good agreement with electron transport measurements made as a function of temperature, and most prefer to regard \( E_{\text{ac}} \) as an adjustable parameter. We have done likewise, and our values are given in Table 2.3. The relative merits of a number of alternative values will be discussed later. The pressure dependence of \( E_{\text{ac}} \) is quite small and can usually be neglected.
CHAPTER 3.
THEORY OF LOW FIELD ELECTRON TRANSPORT.

3.1 Introduction.

The theory of electron transport is concerned with the description of the movement of electrons under the application of electric and in some cases magnetic fields. In this chapter it is intended to give a brief resumé of the theory of electron scattering as it applies in the limit of low electric fields and to emphasize, where appropriate, the applications and limitations of the theory described. It is not the intention to give a mathematically rigorous account, but rather to highlight the methods used and the approximations made. Its importance, particularly for material characterization and device applications, warrants a critical review of the mathematical methods used and the physical models adopted for a number of scattering mechanisms. The mathematical methods and their relation to measured electron mobilities are discussed initially, while the remainder of the chapter describes the expressions commonly used for a number of the most significant scattering mechanisms. In particular we discuss in some detail the theory of ionized impurity scattering as it is presently used, together with some of the refinements available, because of its relevance to the results described in Chapters 5 and 6.

3.2 Electron Scattering, Hall Mobility and Drift Mobility.

An electron moving in a perfectly periodic potential behaves as a free electron, the periodicity only changing the
electron's effective mass. However, in a real crystal a number of additional effects occur. Thermal vibrations and the presence of alien atoms alters the periodic nature of the lattice, while the presence of other electrons also affects the lattice in their vicinity. As a consequence of these imperfections in the crystal periodicity the electron cannot execute long-range motion without changing its state and these changes of state are said to occur as a result of collision processes. The physical consequence of this is that, when an electric field is applied to a semiconducting sample, the electrons accelerated by the field are retarded by the collision processes so that an equilibrium is obtained. For low electric fields the drift velocity of the electrons is proportional to the electric field, where the constant of proportionality is called the electron mobility. The mathematical techniques used to calculate the mobility are often applied in various guises, but most are concerned with the determination of the electron distribution function \( f(r, k, t) \) in the presence of perturbing fields. The function \( f(r, k, t) \) gives the probability that the state corresponding to the wavevector \( k \) at a point in the crystal \( r \) is occupied by a charge carrier at time \( t \). Having obtained \( f(r, k, t) \), the drift and Hall mobilities may then be calculated.

The electron mobility normally calculated is the drift mobility, \( \mu_d \), which results from the application of an electric field alone. However, most experimental mobility data is obtained from Hall effect measurements where the electron distribution is also perturbed by a magnetic field. The mobility then measured is called the Hall mobility, and is denoted here as \( \mu_H \). The ratio of the two as given by equation 3.2-1 defines the Hall scattering factor,
However, some caution should be observed here. Usually what is meant by the above expression, but not explicitly stated, is that this should be taken in the limit as the magnetic field \( |B| \to 0 \). However, experimentally this is never the case. Indeed, in some experiments, the complete range between high and low magnetic fields can be scanned and consequently, to distinguish between the two, we could adopt the notation,

\[
\rho_{\text{H}} \equiv \frac{\mu_{\text{H}}}{\mu_0}
\]

where the magnetic field dependence of \( \mu_{\text{H}} \) and \( \rho_{\text{H}} \) is clearly emphasized.

To calculate the electron Hall and drift mobilities the perturbed electron distribution is required and this is the subject of section 3.3. Assuming it is known the above mobilities can be calculated as described below.

Following the notation of Rod*\( \text{a}^{14}\), the perturbed electron distribution function in the presence of a small electric field \( F \) maintains axial symmetry about the direction of \( F \) and is given by,

\[
f(k) = f_0(k) + xg(k),
\]

where \( x \) is the cosine of the angle between \( F \) and \( k \), \( f_0(k) \) is the equilibrium distribution and \( g(k) \) is the perturbed part of distribution. The drift mobility is by definition,

\[
\mu_0 \equiv \frac{J_yF_y}{enF.E}
\]
\[ \mu_0 = \frac{1}{n} \frac{V_e}{3m^2} \int_{-\infty}^{\infty} \frac{h k^2 g(k) dk}{F m^2 \zeta} \]

where \( J \) is the current density and \( \zeta \) is the augmented density of states \(^{322}\), which describes the enhanced density of states in a non-parabolic band. The carrier concentration is given by,

\[ n = \frac{(V_e/4\pi^2) f(f_k) dk}{3} \]

Using the definitions,

\[ \langle \ast \rangle = \int_{-\infty}^{\infty} (k^3/\zeta) \ast dk, \]

\[ \langle\langle \ast \rangle\rangle = \int_{0}^{\infty} k^2 \ast dk, \]

it is easily shown that,

\[ \mu_0 = \frac{1}{3m^2F} \frac{<g>}{\langle\langle f_0 \rangle\rangle} \]

The Hall mobility is calculated from the electron distribution perturbed by both an electric field \( E \) and an orthogonal magnetic field \( B \). Rode has shown \(^{322}\) that this can be described for isotropic media by,

\[ f(k) = f_0(k) + pg(k) + qh(k), \]

where \( p \) and \( q \) are the cosines of the angles between \( E \) and \( k \), and \( B \times F \) and \( k \) respectively. Thus, assuming that \( B \) is in the z-direction it can be shown that the \( x \) and \( y \) components of the current are given by,
\[ J_x = \int v_x f(k) dk = \frac{V_e e_n}{3\pi^2 m_F} \langle g \rangle F_x - \langle h \rangle F_y \], \quad -3.2-11

\[ J_y = \int v_y f(k) dk = \frac{V_e e_n}{3\pi^2 m_F} \langle g \rangle F_y + \langle h \rangle F_x \]. \quad -3.2-12

Now for \( J_y = 0 \) we obtain by definition the Hall coefficient,

\[ R_{H0} = \frac{F_y}{J_x B} = \frac{-3\pi^2 m_F}{eV_e B} \frac{\langle h \rangle}{\langle g \rangle^2 + \langle h \rangle^2} \], \quad -3.2-13

and using the definition of the Hall mobility given in equation 3.2-14 we obtain,

\[ \mu_{H0} = R_{H0} \sigma_{PS0}, \quad -3.2-14 \]

\[ \mu_{H0} = \frac{1}{B} \frac{\langle h \rangle \langle g_{PS0} \rangle}{\langle g \rangle^2 + \langle h \rangle^2} \], \quad -3.2-15

where it is important to notice that \( \langle g_{PS0} \rangle \) in the numerator is not the same as \( \langle g \rangle \) in the denominator. The former being the perturbed electron distribution caused by the effect of the electric field alone, and which has already been referred to with respect to the drift mobility. Equation 3.2-15 gives the Hall mobility for an arbitrary magnetic field. It is easily shown that for \( |B| \to 0 \) this tends to,

\[ \mu_{H0} = \frac{1}{B} \frac{\langle h \rangle}{\langle g \rangle} \], \quad -3.2-16

It now remains to describe how the perturbed electron distribution functions are obtained and this is outlined in the next section.
3.3 Mathematical Methods.

3.3.1 Introduction to the Boltzmann Equation.

There are a number of methods of obtaining the electron mobility in, or resistivity of, a specimen\(^{43,44}\). However, the most commonly used method is associated with solving the Boltzmann equation. This equation has been derived using intuitive arguments in a number of texts\(^{45}\) and is given here as,

\[
Df = \frac{\delta f}{\delta t} = -\frac{F \cdot \nabla f}{\hbar} - \frac{1}{\hbar} V \cdot E \cdot \nabla f. \tag{3.3-1}
\]

This equation is itself derivable from the more general Liouville equation of motion\(^{46}\), which on its own gives a complete description of the evolution of a dilute gas system with time under the action of specified forces. However, it is almost impossible to obtain transport coefficients using it and consequently the Boltzmann equation approximation is preferred. This requires that collision processes occur on a time scale which is small compared to the period between collisions. Other approximations\(^{47}\) mean that its validity has been questioned sporadically in recent years, but for the present it is still widely used. Bearing this note of caution in mind, provided that steady state solutions are required and that the material is homogeneous equation 3.3-1 can be simplified to,

\[
\frac{F \cdot \nabla f}{\hbar} = \frac{\delta f}{\delta t} \bigg|_{\text{eq}} \tag{3.3-2}
\]
To solve 3.3-2 we must know how to describe the collision term on the right of 3.3-2 between an initial state \( k \), and a final state \( k' \). This is given in a number of texts as:

\[
\frac{\partial f}{\partial t} = -(V_c/Bn^2) \int_{k'} [f(1-f')s - f'(1-f)s'] dk', -3.3-3
\]

where we have used the abbreviations:

\[
\begin{align*}
    f &= f(r, k, t) \\
    f' &= f(r, k', t) \\
    s &= s(k, k') \\
    s' &= s(k', k).
\end{align*}
\]

\( s \) and \( s' \) are the total differential scattering rates for all the collision processes. It should be noted here that there are some important assumptions associated with 3.3-3. Firstly, that the differential scattering rates, \( s \), are usually derived in the Born approximation. This is valid for short range scattering potentials, and if the carrier energy or the thermal energy is high. Under these conditions the differential scattering rates can be calculated by perturbation theory, cf. Schiff. Secondly that all the scattering mechanisms act independently so that the total differential scattering rate is just the sum of the component differential scattering rates. Equation 3.3-3 just describes the rate of increase in the number of electrons in \( dk \) around \( k \). The presence of the integral in 3.3-3 means that 3.3-2 is an integro-differential equation which cannot be solved analytically. Consequently either numerical techniques or further approximations are required to obtain solutions...and these are discussed in the next section.
3.3.2 Iterative Solution of the Boltzmann Equation.

The iterative technique of solving the Boltzmann equation, hereafter abbreviated as ISBE, is the principal method we shall discuss. Being a numerical technique in which no further approximations are required it provides one of the most rigorous tools for studying electron scattering theory. The cost of this rigour is increased computing time and the inherent ambiguities of a numerical technique, compared with the analytical expressions to be described in section 3.4.

The technique used was initially described in a number of papers by Rode and Knight, and later in the excellent review by Rode. It allows relatively easily for the inclusion of Fermi statistics, energy band non-parabolicity, electron wavefunction admixture, and combines the various scattering mechanisms at the matrix element level. Its limitations, which are usually also true of the relaxation time approximation described in section 3.4, are that each scattering mechanism used is derived in the Born approximation and that it assumes that each mechanism is physically independent of the others.

The technique is based on manipulating the Boltzmann equation into a linear finite difference equation, from which it can be shown, on substituting for the perturbed electron distribution function, that at the $I+1^{th}$ iteration $g_{I+1}$ and $h_{I+1}$ are solutions of the coupled equations,

$$g_{I+1} = S_1(g_I) - \frac{eF \cdot \delta f_{\text{int}} + \beta S_1(h_I)}{\hbar \delta k} \frac{1}{(S_0 + v_{\text{int}})[1 + p^2]},$$

-3.3-4
\[ h_{2+1} = B_1(h_2) - \frac{eB_1 \, \delta f_o + \rho \, B_1(g_2)}{\hbar \, \delta k} \frac{1}{(S_o + v_{-1})[1 + \beta^2]} \]  

where,

\[ \rho = eB_1 \, (S_o + v_{-1}) \]

and we have written the total scattering rate as the sum of the elastic and inelastic scattering rates. \( S_1 \) and \( S_o \) refer to inelastic scattering rates into and out of the volume element \( dk \) respectively. The convergence properties of the technique are good. Depending primarily on the temperature, convergence to better than 1\% occurs for between four and six iterations. For elastic scattering it can be shown that,

\[ g = -eB_1 \, (S_o + v_{-1}) \frac{\delta f_o}{\hbar \, \delta k} \]

where \( \tau(k) \), the relaxation time is given by,

\[ v_{-1} = \frac{1}{\tau(k)} = \int (1 - X) v_{-1} dk' \]

and \( X \) is the cosine of the angle between \( k \) and \( k' \).

It is also apparent that as \( |B| \to 0 \), equations 3.3-4 and 3.3-5 decouple so that each can be solved independently. Expressions for the differential scattering rates appropriate for this formalism have been given by Rode\(^a\) and will not be reproduced here. Instead in the next section we describe how analytical solutions may be obtained.
3.3.3 Relaxation Time Approximation.

Perhaps the simplest, most commonly used and physically instructive approach to solving equation 3.2-4 is to use the relaxation time approximation. This assumes that the rate at which the perturbed electron distribution, \( f \) returns to its equilibrium distribution, \( f_0 \) (Fermi-Dirac Distribution) is proportional to the extent to which it is perturbed, i.e.

\[
\frac{\partial f}{\partial t}
|_{t=0} = - \frac{(f - f_0)}{\tau(k)}.
\]

where \( \tau(k) \) is a measure of the rate at which the distribution relaxes, and is known as the relaxation time. This approach gives accurate results, bearing in mind the approximations already mentioned in section 3.2, provided there are no inelastic scattering mechanisms present and also that the total relaxation time \( \tau(k) \) is calculated from,

\[
\frac{1}{\tau(k)} = \sum_i \frac{1}{\tau_i(k)},
\]

where the \( \tau_i(k) \)'s refer to the relaxation times for individual scattering processes. Under these conditions it is easily shown from 3.2-9 and 3.3-4 that the drift mobility, \( \mu_0 \) is given by,

\[
\mu_0 = \frac{e \langle \tau \rangle}{m^*},
\]

where now,

\[
\langle \tau \rangle = \frac{2 \int_0^\infty \tau(W) W^{3/2} \exp(-W) dW}{3 \int_0^\infty W^{1/2} \exp(-W) dW}.
\]

Similarly it can be shown by using equations 3.2-16, 3.3-4 and
3.3-5 that the Hall mobility, \( \mu_h \), in the limit as \( |B| \to 0 \) is given by,

\[
\mu_{h}^{\infty} = \frac{e}{m} \langle \tau^2 \rangle \tag{3.3-13}
\]

where 3.3-11 and 3.3-13 are the commonly quoted expressions. Clearly \( \mu_{h}^{\infty} \) and \( \mu_0 \) are generally not the same. Notice, from 3.3-12 that it is the energy dependence of the relaxation time that governs the Hall scattering factor at small magnetic fields.

Frequently a further assumption in the relaxation time approximation is also made and this is commonly referred to as "Matthiessen's rule". In this approximation, instead of adding the relaxation times as in 3.3-10 the mobility is calculated using 3.3-11 or 3.3-13 for each individual relaxation time, and the total mobility is then found using the expression,

\[
\frac{1}{\mu_{\text{total}}} = \sum \frac{1}{\mu_i} \tag{3.3-14}
\]

Apparently this is valid provided that the \( \tau_i(E) \)'s have the same energy dependence. Generally this is not the case, although in the degenerate limit the use of Matthiessen's rule is in principle valid.

However, Matthiessen's rule does have the practical advantage of allowing the scattering mechanisms to be investigated independently and their physical nature is then more readily apparent. For this reason we have chosen in section 3.4, when describing the common scattering mechanisms, to quote the mobility components rather than the relaxation times which the interested reader can find elsewhere.\(^{(25)}\)
doing so we neglect the effect of band non-parabolicity, which necessarily complicates the evaluation of 3.3-12, although in the analysis discussed in later chapters it has been included where necessary.

3.4 Scattering Mechanisms.

3.4.1 Introduction.

The scattering mechanisms that are important in a semiconductor can be categorized as being either intrinsic or extrinsic to the crystal lattice. One example of the latter is ionized impurity scattering which is discussed in section 3.5. Here we describe intrinsic scattering associated with the thermal vibration of the crystal lattice, as well as carrier-carrier, neutral impurity, central-cell, space-charge and alloy scattering. However, such a list of mechanisms is not exhaustive. In the expressions that follow the temperature and effective mass dependence of the mobility is emphasized because of its importance in subsequent chapters.

3.4.2 Deformation Potential Scattering.

Electrons can be scattered by acoustic phonons in two distinct ways. The first of these arises as a result of the changing spacing between the ions. We have seen previously that the band gaps of semiconductors are very sensitive to changes in lattice spacing and consequently the acoustic phonons cause the conduction and valence band edges to fluctuate, from which the electrons can then be scattered. Symmetry considerations reveal that only longitudinal (LA) phonons are responsible for such scattering in the \( \Gamma \) minimum.
where shear forces or transverse vibrations are ineffective. However, transverse (TA) phonons may cause scattering away from the zone center and consequently may be significant in indirect materials like Si and Ge. The physical description of this is simplified by regarding the deformed lattice as producing a short range perturbing potential referred to as the deformation potential. The resulting drift mobility limited by this mechanism has been given by Bardeen and Shockley as,

$$\mu_{ac} = \frac{2(2\pi)^{1/2} \hbar^2 q_1^2}{3e_k b^{3/2} E_{ac}^2} T^{-3/2} m^{-3/2}.$$  

3.4.3 Piezoelectric Scattering.

The second acoustic phonon scattering process, known as Piezoelectric scattering, arises from a change in the potential due to the redistribution of electric charge when the ions are displaced from their equilibrium positions. This is only operative in crystals without inversion symmetry. Electrons can be scattered by both LA and TA phonons, although the former tend to dominate. The drift mobility limited by this scattering mechanism is given by Zook as,

$$\mu_p = \frac{1.714 \times 10^{-66} e_1^2}{a_{14}^2 (4/C_1 + 3/C_2)} T^{-1/2} m^{-3/2},$$  

where $e_{14}$ is the Piezoelectric constant and $C_1$ and $C_2$ are the transverse and longitudinal elastic constants respectively. In pure III-V semiconductors, piezoelectric scattering may be significant at low temperatures. However, for material with impurities incorporated, scattering from ionized impurities is
3.4.4 Polar Optical Phonon Scattering.

The optical phonons mentioned previously also scatter electrons in two distinct ways. The first of these mechanisms occurs as a result of the neighbouring atoms vibrating in anti-phase. The electrons are scattered by a long range Coulomb interaction set up by the polarization of the charges on each atom. This occurs only with LO phonons as TO phonons do not produce macroscopic electric fields. The drift mobility limited by such scattering was developed by Ehrenreich\textsuperscript{173} and subsequently by Fortini et al\textsuperscript{174} and is given here as,

\[
\mu_p = \frac{16\pi e (2\pi k_B)^{1/2} G(z) (\exp(z)-1) T^{1/2} m^{-3/2}}{3\omega_l (\varepsilon_m - 1/\varepsilon_m)}
\]

where \(\omega_l\) is the longitudinal polar optical phonon frequency and \(z = \hbar \omega_l / k_B T\). The term \(G(z) (\exp(z)-1)\) has been given graphically by both Ehrenreich\textsuperscript{173} and Fortini et al\textsuperscript{174} and accounts for the effects of electron screening on the scattering by polar phonons, and consequently they are both a function of the electron concentration. Fortini et al, however, have only published a curve appropriate to pure material where screening effects are minimal. We have incorporated free carrier screening into the differential scattering rate for polar phonon scattering given by Rode\textsuperscript{172} in some of the calculations that follow.

For all direct gap polar semiconductors scattering by polar optic phonons is the most important mechanism, particularly at temperatures \(\geq 300K\), and for pure materials the lower temperature range extends well towards liquid nitrogen.
temperatures. However, because of the inelastic nature of the mechanism it is least suited to use in the relaxation time approximation.

3.4.5 Intervalley Scattering.

So far we have considered only phonon scattering process involving long wavelength phonons. Clearly scattering by shorter wavelength phonons may be important for two regimes. Firstly for indirect material where electron scattering between equivalent minima is important, and secondly in material under conditions where scattering between non-equivalent minima, such as between the \( \Gamma \) and \( X \), may be significant.

Herring and Vogt\(^{75}\) have calculated the relaxation time for such processes and with the energy term replaced by \( 3k_B T/2\epsilon^* \), the mobility can be written as,

\[
\mu_{iv} = \frac{NA}{e} \left[ \sum_{i} \left( \frac{T_{ci}}{T} \right)^{3/2} \frac{(T/T_{ci} + 2/3)^{1/2} + (T/T_{ci} - 2/3)^{1/2}}{\exp(T_{ci}/T) - 1 - \exp(-T_{ci}/T)} \right]^{-1}
\]

\[ -3.4-4 \]

where \( w_i/w_A \) is a measure of the coupling strength between the acoustic phonons and the \( i^{th} \) intervalley phonons with characteristic temperature \( T_{ci} \). The second term in the brackets vanishes if \( T/T_{ci} \leq 2/3 \); i.e. the emission of phonons is prohibited.

3.4.6 Electron-Hole and Electron-Electron Scattering.

Obviously another set of scattering mechanisms is comprised
of the scattering of electrons by other mobile charge
carriers, either electrons or holes. In the case of
electron-hole scattering it is common to use the larger
effective mass and consequently reduced mobility of the heavy
holes to simplify the problem. Under these conditions the
holes look like immobile point charges as far as the electrons
are concerned, and thus they can be described using a slightly
modified form of the Brooks-Herring formula for ionized
impurity scattering described in section 3.5.2. So for
electron-hole scattering we use the expression,

\[ \mu_{eh} = 3.131 \times 10^{-4} e_\infty T^{3/2} m^{2-1/2} \left[ \ln(1+b) - \frac{b}{1+b} \right]^{-1} \]

where \( p \) is the concentration of holes and,

\[ b = \frac{4k^2}{p^2} = \frac{1.42 \times 10^{34} e_\infty m^{2} T^2}{n'} \]

\( p_s \) is the inverse screening length discussed in section 3.5.2 and,

\[ n' = n + \frac{(N_a - N_a - n)(n + N_a)}{N_a} \]

The problem of electron-electron scattering however, is
much more difficult to describe. It might be thought that,
because momentum is conserved, such scattering would not
effect the mobility. However, it does affect the perturbed
electron distribution, and consequently affects all the other
scattering mechanisms. Following Bate et al\(^{74}\) we used the
approximate expression,
for a component of mobility with \( \tau(E) \propto E^q \). The calculated corrections to the mobility components as a function of the reduced Fermi energy are shown in Figure 3.1. The corrected mobility is then given by Bates et al. as

\[
\mu_i = \mu_i^0 \left[ 1 + \frac{\mu_i^0 (e-e)}{\mu_i^0} \right].
\]

This clearly shows the carrier concentration/temperature dependence of the electron-electron scattering corrections for a number of mechanisms. Apparently electron-electron scattering corrections may be very important at intermediate carrier concentrations, but become negligibly small in the degenerate limit.

3.4.7 Neutral Impurity Scattering.

Electron scattering from neutral impurities may be important at low temperatures where electron freeze-out occurs or at high impurity concentrations. Two formalisms due to Erginsoy and Sclar are available but we have only considered the former. The neutral impurity scattering limited mobility as given by Erginsoy is,

\[
\mu_n = \frac{e^3 m^*}{80 N_{IMP} \hbar^2}. \quad -3.4-10
\]
Figure 3.1

Ratio of mobility components corrected for electron-electron scattering to the uncorrected mobility, plotted as a function of the reduced Fermi energy (after Bate et al. [7]).
where $N_m$ is the density of neutral impurities.

### 3.4.8 Space-Charge Scattering

When we discuss impurity scattering in section 3.5 it is normally considered that the impurities are distributed randomly in the crystal. However, it may be possible for inhomogeneities to exist, as a result of impurity clustering for example. This results in a charge difference between such a region and the surrounding crystal. To ensure charge neutrality space-charge regions form around the inhomogeneities resulting in distortions in the conduction and valence band edges, which consequently scatter electrons. Weisberg\(^{47}\) has derived the mobility limited by such a mechanism treating it as a simple collision problem and obtains,

$$\mu_{sc} = \frac{e}{N\sigma A (2k_B) \frac{1}{2}} T^{-1/2} m^*=1/2,$$

where $N\sigma A$ is the product of the concentration of space charge regions and their effective scattering cross-section.

### 3.4.9 Alloy Scattering

The essence of Alloy Scattering was proposed in the 1930's by a number of authors (see for example Mott\(^{40}\)) in connection with substitution effects in dilute alloys. The formula for the drift mobility limited by alloy scattering was first derived by Brooks and has been referred to many times although it was never published. Recently, Littlejohn et al\(^{41}\) repeated the calculation of Brooks and found it to be
in error by a factor of \(\frac{\pi}{2}\). The formula as derived by Littlejohn et al.\(^{32}\) is of the form,

\[
\mu_{\text{AL}} = \frac{\pi(2)^{1/2} a^*}{9\Omega n^3/2 k_B^{1/2} S(\alpha) e(\Delta U)^2} \cdot T^{-1/2} \cdot m^{-\delta/2},
\]

where \(S(\alpha)\) describes the degree of randomness and is invariably taken to be unity, i.e., completely random. \(\Delta U\) is the alloy scattering potential in eV and is a measure of the magnitude of the fluctuations in the crystal periodicity caused by the alloy disorder.

3.4.10 Central-Cell Scattering.

The effect of the localized central-cell potential is neglected in the standard theory of scattering from ionized impurities discussed in the next section. As a first approximation in considering scattering from impurities which have a long-range screened coulomb potential and a large short-range central-cell potential, the scattering by the two components of the potential can be considered separately. Using the scattering cross section of Faulkner\(^{35}\), Stringfellow and Künzel\(^{34}\) indicate that the Hall mobility of the central-cell scattering component is given by,

\[
\mu_{\text{cc}} = \frac{3e}{16(2\pi^{3/2})N_i \hbar^2} \left[ \frac{15(k_B T)^{1/2}}{8} + \frac{E_i}{(k_B T)^{1/2}} \right] m^{-1/2},
\]

where \(E_i\) is the ionisation energy for the electron bound to the impurity.
3.5 Ionized Impurity Scattering

3.5.1 Introduction.

The last important mechanism for electron scattering to be discussed is associated with the scattering of electrons by ionized impurities. This is generally important in relatively pure materials at low temperatures and at increasingly high temperatures as the crystal becomes increasingly less pure.

The mechanism is particularly important as a means of characterizing material quality. Thus, if the mobility and carrier concentration of a sample at a specified temperature is known, the concentration of ionized impurities and the compensation ratio may be deduced. The importance of this approach is apparent from the wide use of look-up tables for just such a purpose, particularly those of Walukiewicz et al for GaAs and InP. Clearly, however, for these to be of use they must be accurate and this then means that it is important that the theory of ionized impurity scattering used is equal to the task. It will become clear in this section, however, that this is not always the case. It is unfortunate that, for a range of impurity concentrations, carrier concentrations, and temperatures for which ionized impurity scattering is important, the usual theory discussed in 3.5.2 breaks down. Numerous refinements have been obtained and some are mentioned here, but for more detailed discussion and a comprehensive list of references the review of Chattopadhyay and Queisser is recommended.

3.5.2 Random Impurity Distribution.

The usual description of scattering from ionized impurities
is based on a number of assumptions which will be discussed in the rest of the chapter. One that is frequently overlooked is that impurities are distributed randomly in the crystal, so that the impurity levels present within the band gap arise from fluctuations in the concentration of the impurities. Indeed, if there were no fluctuations this would correspond to the case in which impurities were distributed completely uniformly throughout the crystal. Under these conditions only the periodic nature of the lattice would be altered, resulting in a change in electron effective mass. Under such conditions the electrons would no longer be scattered by impurities.

Also frequently overlooked is the effect of increased impurity concentrations on the density of states. These effects have been reviewed by Abram et al\textsuperscript{109}. As the impurity concentration increases the impurity levels broaden into an impurity band, which at sufficiently high concentrations merges with the conduction band edge. This together with an increased electron-electron exchange interaction causes the band gap to shrink.

The formulation of scattering from ionized impurities in the Born approximation takes account of none of the previously mentioned factors. The results of various workers have been primarily concerned with the form of the scattering potential of the impurity, which is usually assumed to be the difference between that of the host crystal and that of the impurity.

The initial formulation of scattering from ionized impurities was given by Conwell and Weisskopf\textsuperscript{109}, where the impurity potential was modelled by a coulomb potential. However, in this model the relaxation time diverges for small angle scattering, so that collisions were only allowed for electrons that approached within $N_{i}^{-1/3}/2$, half the average.
Impurity separation. This arbitrary cut-off distance was removed by including screening, which, to the first order in powers of the impurity potential over \( k_B T \), results in the well-known screened coulomb potential, which drops off faster than the normal coulomb potential due to the multiplicative exponential screening factor. Dingle's approach\(^{101}\) only included screening by electrons, while the Brooks-Herring theory\(^{101}\) attempts to include screening by neighbouring ionized impurities as well, i.e. in compensated material there is additional screening by electrons trapped on acceptors. The mobility limited by ionized impurity scattering as given in the Brooks-Herring theory is,

\[
\mu_n = \frac{3.131 \times 10^{-4} e_s^2 \pi^{3/2} m^{-1/2}}{N_r} \left[ \ln(1 + b) - \frac{b}{1 + b} \right]^{-1}, \quad -3.5-1
\]

where \( N_r \) is the concentration of ionized impurities and \( b \) is given by \( 3.4-6 \) with \( p_\ast \) given by,

\[
p_\ast = \frac{10^4 e^2}{\epsilon_0 k_B T} \left[ n \Phi_{-1/2} (\eta) + \frac{(N_d - N_a - n)(n + N_a)}{N_d} \right] \frac{F_{\eta/2}(\eta)}{n \Phi_{-1/2}(\eta)}, \quad -3.5-2
\]

The \( F_{\eta}(\eta) \) are Fermi integrals of order \( j \), where \( \eta \) is the reduced Fermi energy, and the methods of calculation of these integrals have been discussed by Blakemore\(^{122}\), although they effectively cancel out in non-degenerate material. Indeed, for \( 3.5-1 \) to be valid it is usually stated that, \( b \gg 1 \) (see ref. 87), which implies non-degeneracy. This is also required because in calculating \( 3.5-1 \) the logarithmic term in the relaxation time is taken out of the integral in \( 3.3-12 \) and the energy replaced by the value at which the integrand is a maximum. At intermediate values of \( b \) this is not valid and the
full evaluation of the integral must be undertaken.

It is interesting that both the Conwell-Weisskopf and the Brooks-Herring theories consider a characteristic length defining the range of the potential, and assume that within a sphere of this radius only one scattering centre is present. Ridley\textsuperscript{(93)} has shown how these formalisms can be linked, so that smooth transitions between the two can be obtained.

3.5.3 Refinements to the Brooks-Herring Theory.

A number of refinements to the Brooks-Herring theory have been made in an attempt to remove some of its simplifying assumptions. All the expressions described in the previous section result from the linearisation of Poisson's equation. This is justified provided the electric potential is small compared to the thermal energy. This is valid for any impurity concentration at high temperatures, and for one kind of impurity at all temperatures. This latter case is true because as T decreases the thermal energy goes down linearly with T while the number of impurities decreases exponentially. However, when this is not the case better approximations\textsuperscript{(94)} and numerical solutions\textsuperscript{(95)} indicate that the Brooks-Herring theory tends to overestimate the scattering. However, Takimoto\textsuperscript{(96)} has shown that the screening included in the Brooks-Herring theory will be lessened by the polarization of the screening cloud by the colliding electron. Various workers\textsuperscript{(77,98)} have tried to incorporate the dielectric response of the valence electrons normally described by the static dielectric constant into the impurity potential. Using this approach Resta and Resca\textsuperscript{(99)} calculate a reduced mobility compared to the Brooks-Herring value, that is particularly significant at high temperatures.
The Brooks-Herring theory also assumes that scattering occurs incoherently from individual impurities. If this is not the case so that electrons are scattered by several impurities simultaneously, multiple scattering is said to take place. Also the perturbing or "dressing" effects of the impurities on the electron wavefunctions and energy levels are also neglected. These two effects have been analysed by Moore and Moore and Ehrenreich, along with corrections associated with higher Born approximations. The corrected mobility can be expressed as,

\[ \mu_{\text{cor}} = \frac{\mu_{\text{BH}}}{1 + \delta_{\text{M}}(k') + \delta_{\text{D}}(k') + \delta_{\text{P}}(k')} \]

where \( k' \) is the wavenumber associated with the energy at which the integrand in 3.3-12 is a maximum. The complicated expressions for each of the corrections have been given by Moore and will not be reproduced here. As an example the corrections calculated for uncompensated InP of two carrier concentrations is shown in Figure 3.2 as a function of temperature. Clearly the corrections are negligible at both low and high carrier concentrations. Also included in this figure is the correction given by Moore for higher Born approximations. The often quoted expression for the Born approximation is that,

\[ b = \frac{4k^2}{\beta} \gg 1, \]

which is usually valid at high temperatures and/or low carrier concentrations. However, Meyer and Bartoli have pointed out that this is too restrictive. They define two parameters, \( \gamma = 10.5 \text{ka}_0 \), where \( \text{a}_0 \) is the effective Bohr radius,
Figure 3.2
Temperature dependence of Moore's corrections \(^{(100)}\) for multiple scattering, \(\delta_M\), dressing effects, \(\delta_D\), and higher Born approximations, \(\delta_B\), calculated for uncompensated InP with carrier concentrations of \(10^{17}\) cm\(^{-3}\) and \(10^{19}\) cm\(^{-3}\).
and $F$ such that,

$$b = 4F^2y^2.$$  \[ -3.5-5 \]

They find that the Born approximation is always valid provided $y \gg 1$. However, they also show that it is valid for $y < 1$, provided $F \ll 1$; i.e., it is also valid when $b \ll 1$. Physically these conditions mean that the wavefunction of the electron in the presence of the scattering potential must be "similar" in form to the unperturbed wavefunction. They have calculated the mobility for ionized impurity scattering using a phase shift analysis and then calculated the drift mobility using Kohler's variational technique. By this method they avoid the Born approximation completely.

An alternative approach to calculating the scattering by ionized impurities has been given by Yanchov et al. for the region of high carrier concentrations. Here, where multiple scattering effects are likely to be important, rather than consider scattering from individual impurities and correct for multiple scattering, they consider scattering from a smooth potential caused by fluctuations in the impurity concentration. In the heavy doping régime this potential obeys Gaussian statistics and is characterized by a pair correlation function. Yussouff and Zittartz have shown that the mobility appropriate to such a scattering mechanism is given by,

$$\mu = \frac{e\hbar k_F R \cdot E_F}{\alpha \gamma^2 m^*}$$  \[ -3.5-6 \]

where $R$ is the screening or correlation length of the potential, $E_F$ is the Fermi energy, $k_F$ is the Fermi wavenumber,
and $\gamma$ is the rms potential such that the potential changes by an amount $\gamma$ over the distance $R$. The term $\alpha$ is expressed in terms of the pair correlation function. Yanchev et al\(^{(10)}\) give $\gamma$ and $\alpha$ as respectively,

$$\gamma^2 = \frac{N_k e^2 R}{4\pi (\varepsilon_0 e)^2},$$  \hspace{1cm} (3.5-7)

$$\alpha = \frac{1}{8} \int_0^\infty dy \frac{y}{(1 + y)^2} \text{erfc} \left[ \frac{E_F + \gamma - E_F}{4\gamma} \right],$$  \hspace{1cm} (3.5-8)

where $E_F = \frac{\hbar^2 p_\gamma^2}{2m^*}$, and $\text{erfc}(x)$ is the complementary error function.

Using the correlation function for a random distribution of impurities, and with $R = \rho = 1/p_\gamma$ in equation 3.5-7 assuming no ionic screening, similar results were obtained to the Brooks-Herring theory. In the analysis of Yanchev et al an attempt was made to correct the Fermi energy for the effects of finite temperature, electron-electron exchange interaction and band tailing. They give the corrected Fermi energy $E_{F^C}$ as,

$$E_{F^C} = E_F + \Delta E_{F_1} + \Delta E_{F_2} + \Delta E_{F_3},$$  \hspace{1cm} (3.5-9)

where the corrections for electron-electron exchange interaction, band tailing and finite temperature are respectively,

$$\Delta E_{F_1} = \frac{-e^2 k_F}{4\pi^2 \varepsilon_0 e},$$  \hspace{1cm} (3.5-10)

$$\Delta E_{F_2} = \frac{-\gamma^2}{8E_F},$$  \hspace{1cm} (3.5-11)
3.5.4 Correlated Impurity Distributions.

In the previous section the importance of the assumption that the impurities were uncorrelated was noted. An alternative approach, and indeed a physically reasonable one is that there is some correlation between impurities in the crystal. This was considered by Falicov and Cuevas with respect to the problem of non-linear screening, and they concluded that the correlation functions were likely to be complicated. Yanchev et al considered correlation between impurities due to the coulomb forces between ionized impurities in the melt and were able to derive the reduced dependence of mobility on carrier concentration at 77K that is observed experimentally in GaAs. In their expression for the screening length they replace the second term in the brackets in equation 3.5-2 by a term describing the ionic screening of a plasma of ionized impurities. The Debye screening length is given by,

$$\Delta E_{rs} = -(\frac{\pi k_{B} T}{2}) \cdot [1 + \frac{12}{\pi^{2} k_{F} a_{0}}].$$

$$[\frac{1}{R_c}]^2 = \frac{e^2 N_i T}{\epsilon_0 \pi k_{B} T T_0}.$$  

**3.5-12**

$$[\frac{1}{R}]^2 = [\frac{1}{R_c}]^2 + [\frac{1}{R_a}]^2.$$  

**3.5-13**

where now the effect of screening by impurities is dependent on the temperature, $T_0$, at which the diffusion of impurities in the melt effectively stops. However, it seems likely that
the correlation effects should also depend on the degree of compensation, as well as the growth technique used. Indeed in a recent paper Yanchev et al. indicate that the compensation can have a marked affect on T0. They give values of T0 in GaAs for compensation ratios, θ, of 0.0, 0.1, 0.2 and 0.3 as 900K, 1025K, 1150K, and 1300K, respectively. The modified expression for the drift mobility limited by scattering from a correlated distribution of impurities is given by Yanchev et al. as,

\[ \mu = \frac{e \hbar \kappa R_0 E_0}{\alpha_1 \gamma_0^2 m^*} \]  

where \( \gamma_0^2 \) is given by 3.5-7 with R replaced by 3.5-14. \( \alpha_1 \) is given by,

\[ \alpha_1 = \frac{1}{16} \int_0^\infty dy \text{erfc} \left( \frac{E - y/4\gamma_1 - E_F/\gamma_1}{1 + y + (R_0/R_0)^2} \right) \]

\[ + \frac{1}{16} \int_1^\infty dy \text{erfc} \left( \frac{E - y/4\gamma_1 - E_F/\gamma_1}{y[1 + y + (R_0/R_0)^2]} \right) \]

where

\[ \gamma_1^2 = \frac{N_e e^2 R_0}{2\pi(\varepsilon_0 \varepsilon_0)} \left[ 1 + \frac{2R_0^2}{\pi R_0^2} \left[ R_0 - \frac{R}{2} + \tan^{-1} \left( \frac{R}{R_0} \right) \right] \right]. \]

The importance of such effects will be discussed in later chapters.
CHAPTER 4.
APPARATUS AND EXPERIMENTAL TECHNIQUES.

4.1 Sample Preparation.

4.1.1 Introduction.

All the experimental work reported in this thesis was obtained from Hall effect and resistivity measurements made on semiconducting samples using the van der Pauw technique. To minimize the errors associated with the position and size of the ohmic contacts clover leaf patterns were usually used. Samples were prepared by two techniques, ultrasonic cutting, for bulk material, and photolithographically defined etching, for epitaxial material. However, some samples prepared in other laboratories have also been measured during the course of this work. Consequently alternative methods, particularly air abrasion, have also been used although they will not be described here. In the next two sections sample preparation by ultrasonic cutting and chemical etching will be described.

4.1.2 Clover Leaf Preparation by Ultrasonic Cutting.

This technique was exclusively used for bulk material. The sample slice to be prepared was fixed, polished side down, to a glass slide with shellac wax and located under the appropriate size cutting tool, which consisted of a bronze cylinder with the sample shape hollowed into one end. This cutting tool was screwed into the arm of an ultrasonic vibrator. A suspension of tungsten carbide granules in water, applied to the sample, acts as the abrasive material. Care
must be taken using this technique to ensure that the cutting is stopped as soon as it is completed, otherwise the sample may be fractured by subsequent vibration within the cutting tool itself.

### 4.1.3 Clover Leaf Preparation by Etching

Clover leaf samples were prepared from epitaxial material by defining photolithographically the area to be etched. Initially the sample slice was cleaned, first in boiling methanol, then in boiling trichloroethylene and finally in iso-propyl alcohol vapour to remove grease and any other deposits that may have accumulated on the surface prior to preparation. Three layers of Shipley AZ 1350H positive photoresist were then applied to the surface, and the slice spun at 8000 r.p.m. for 1 minute. This produces a uniform layer of photoresist approximately 0.7 µm thick. The sample was then prebaked for 20 minutes at 80°C to harden the resist, after which time the negative mask of the clover leaf was placed over the sample and exposed to ultraviolet light for 15 minutes. The resist was then developed in a 100:1 mixture of H₂O and NaDH and then the unexposed photoresist could be washed away.

Subsequently the sample was baked for 30 minutes at 120°C to further harden the resist. The epitaxial layer and about 10 µm of the substrate was then etched away using a mixture of H₂SO₄, H₂O₂, and H₂O in the ratio 3:1:1, which at 50°C gives an etch rate of approximately 2 µm/minute. The sample was then thoroughly washed in deionized water and the photoresistive mask was removed, to reveal the clover leaf sample, by immersing the sample in acetone for a short period.
4.1.4 Contact Fabrication.

Ohmic contacts were made by one of two methods:

i) For some samples wire leads were placed on In dots located at the edges of the four clover leaves and then alloyed into the sample in a hydrogen/nitrogen atmosphere, having previously bubbled the gas through HCl to clean the surfaces. Alloying temperatures just greater than the contact melting temperature were used for a duration of two minutes.

ii) Contact regions on the sample were photolithographically defined, using an appropriate mask and a technique similar to that described in the previous section. The contact surfaces were then etched for 20 seconds in a 20:4:1 mixture of H2O, H2O2 and NH3, and rinsed in deionized water. Contacts, either Au-Sn/Ni or Au-Be/Ni, were then evaporated onto the sample and alloyed in a furnace at 425°C for 5 minutes. As phosphorus has a very high vapour pressure and can thus evaporate from the sample surface at the elevated alloying temperatures, such samples as necessary were alloyed in a glass capsule with an InP-lined interior and with the surfaces covered by an InP layer. Electrical connection to the contacts was made with 1/1000 inch gold wire using a Dage Precima Industries TSB21EH pulse tip bonder.

4.2 Automated Low Temperature Apparatus.

4.2.1 Hall Coefficient and Resistivity Measurement.

The Hall voltage and resistivity of semiconductor samples was measured by the van der Pauw technique using the clover leaf samples describe previously. This has the advantage over the conventional Hall bar of only requiring
four contacts on the perimeter of the sample. This makes possible measurements on small samples of arbitrary shape, but requires an increased number of measurements. It is necessary in the van der Pauw technique to take measurements across different pairs of contacts in order to correct for sample geometry. This requires the interchanging of the current and voltage leads as is shown schematically in Figure 4.1. Only four configurations are essential, but to obtain the maximum information twenty were taken, where these include reversals of both electric current and magnetic field. These are commonly used to eliminate thermally generated voltages produced by the Nernst and Righi-Leduc effects⁽¹⁰⁾. The resistivity, \( \rho \), in ohms-cm is calculated using,

\[
\rho = \frac{\pi t \cdot R_a + R_b \cdot f[R_a]}{\ln 2} \quad \text{[4.2-1]}
\]

where \( R_a \) and \( R_b \) are the resistances as defined in Figure 4.1, \( t \) is the sample thickness in cm and \( f(R_a/R_b) \) is a dimensionless quantity dependent only on the ratio \( R_a/R_b \), and is given by van der Pauw⁽¹⁰⁾ as

\[
f(R_a/R_b) = 1 - \left( \frac{R_a - R_b}{R_a + R_b} \right)^2 \quad \frac{\ln 2}{2} \quad \left( \frac{R_a - R_b}{R_a + R_b} \right)^2
\]

\[
\frac{[(\ln 2)^2 - (\ln 2)^3]}{4} \quad \frac{12}{-4.2-2}
\]

provided \( R_a \) and \( R_b \) are almost equal. The Hall coefficient, \( R_m \), in \( \text{cm}^2\text{C}^{-1} \) is given by,

\[
R_m = \frac{10^9 \cdot t \Delta R_a}{B} \quad \text{[4.2-3]}
\]

where \( \Delta R_a \) is the change in resistance \( R_a \) when a magnetic field
Figure 4.1 Sample connections for van der Pauw measurements.

Figure 4.2 Schematic diagram of electrical connections to sample via switching system.
of B Gauss is applied perpendicular to the sample.

The van der Pauw technique, and hence equations 4.2-1-4.2-3, is only valid if two basic assumptions are satisfied. Firstly that the contacts are infinitely small and secondly that they are located on the periphery of the sample. Errors are incorporated when this is not the case, which may be reduced by using a clover leaf shaped sample\(^{100}\), although even here some shorting of the electric field by the contacts cannot be avoided. For the sample geometries used here \(R_{\text{in}}\) is likely to be \(\approx 3\%\) low and \(\sigma \approx 1-2\%\) low. Even under these conditions it is necessary that, within the conducting region, the sample is homogeneous. Although surface and interface effects, which may be significant for thin epilayers, can be taken into account\(^{111}\), gross inhomogeneities produce anomalous results\(^{112}\).

The current and voltage switching required by the van der Pauw technique is achieved in the automated apparatus by a set of sixteen programmable relays that allow any combination of voltage and current connections to the sample to be made. The system uses reed relays which exhibit \(\approx 20\mu V\) of noise due to thermal and contact resistance effects. This limits the range of samples and temperatures over which accurate measurements can conveniently be taken as signal levels <0.1mV may have significant associated errors.

The arrangement of electrical connections to the sample via the relays is shown in Figure 4.2. A constant current supply was used to give currents in the range 1.0\(\mu A\) to 10.0mA. The current supply was not directly programmable but remained constant to within 0.1% during the course of an experiment. A Keithley 1950 Voltmeter with a resolution of 0.1\(\mu V\) was used to monitor the voltages.

The experimental technique also requires the programmable
switching of the magnetic field. This was accomplished by heavy duty 10A relays which were in turn controlled by two programmable relays. The simple circuit used for this is shown in Figure 4.3 and has the important characteristic that the magnet coils are protected from going open-circuit through both the computer program and through the circuit design. The magnetic field was not monitored during the experiment, but it was checked intermitently, and was found to remain constant to within 3%.

4.2.2 Cryostat and Vacuum System.

Samples were mounted on veroboard and located in a static helium atmosphere exchange gas, within an Oxford Instruments DN704 cryostat. Although pumping cycles for this cryostat of approximately one month were quoted, it was found necessary to pump continuously using a standard rotary and diffusion pump arrangement with a cold trap to ensure the best temperature stability performance, any reduction of the vacuum within the cryostat being detrimental to this.

The temperature of the sample was measured by a gold-iron-chromel thermocouple mounted on the heat exchanger. The cold junction of the thermocouple was immersed in liquid nitrogen, and the output signal from the thermocouple was used by a programmable Oxford Instruments 3120 three term temperature controller to set and maintain the required temperature. Temperature stabilities of ~0.1K were normal, although the switching of the magnetic field did cause transients in the thermocouple output. These however, were found to be insignificant for temperatures down to 77K.
Figure 4.3 Automatic/manual magnetic field switching circuit.
4.2.3 Computer Controlled Data Acquisition.

Using the experimental arrangement outlined previously, fully automated data acquisition of Hall effect and resistivity measurements between 77-450K could be made. A Commodore "Pet" was used to run the experiment using standard IEEE-488 instructions to control the various peripheral devices. Data obtained during the course of an experiment was printed out as the experiment proceeded, while options also allowed for this data to be stored on cassette tape or floppy disc for later retrieval. Graphical output could also be obtained at the end of each experiment. A listing of the computer program is not given here, but a generalized flow diagram of the program is shown in Figure 4.4.

Two blocks shown in Figure 4.4 warrant further comment because of their practical importance. These concern the program's assessment of the stability of the temperature and the acquired data. If the limits set are too strict the experiment will "hang-up", while if they are too lax unnecessarily noisy results are acquired. We used the following criteria. The temperature was monitored at approximately one second intervals during the "Is Temperature Stable?" period, and was required to remain constant to within ±0.2K for five minutes for a set of measurements to be taken. This allows not only for the thermocouple temperature to stabilize, but for the sample temperature in the exchange gas to come into equilibrium with the heater exchange block and typically resulted in a data acquisition rate of three points per hour. The second problem is the accuracy of the acquired voltage data. For each configuration, six measurements of the voltage across a pair of contacts were taken. If the data was either monotonically increasing or decreasing, or if the
Figure 4.4 Generalized flow chart for computer controlled data acquisition.
standard deviation was greater than a specified value for a given voltage range the data was rejected and a new set of measurements taken. These simple tests ensured results with low random errors. Systematic errors are, by their very nature, harder to quantify. Typical uncertainties were associated with sample uniformity, effects of interface and substrate regions where appropriate, and with the accurate calibration of the magnetic field. These problems will be discussed where appropriate in later chapters.

4.2.4 Experimental Limitations.

This experimental arrangement was found to be adequate for all measurements on non semi-insulating samples in the range 77-450K. However, if the temperature range is extended down to liquid Helium temperatures, electric field dependent impact ionisation of donors means that reduced current densities must be used. The reduced signal levels thus obtained require the use of low noise relays, perhaps driven by the relays used presently. Alternatively a system such as the Solatron Minato Scanner could be used, where noise levels as low as ~1μV should be achievable. The effects of thermocouple voltage transients, arising from the magnetic field switching, on the temperature stability of the sample will also require further assessment.

4.3 High Pressure Apparatus.

4.3.1 Introduction.

We have also undertaken Hall effect and resistivity measurements as a function of hydrostatic pressure, at room
temperature using a piston and cylinder apparatus developed at the SERC High Pressure facility at the Standard Telecommunication Laboratories (STL), Harlow. Pressures in the range 0-8 kbar were obtainable at Surrey with this system, while pressures up to 15 kbar were obtainable using the STL system. The technique is non-destructive and consequently has the advantage of enabling a number of experiments to be performed on one sample.

4.3.2 Piston and Cylinder Apparatus.

A schematic diagram of the piston and cylinder apparatus used to achieve pressures in the range 0-8 kbar is shown in Figure 4.5. The cylinder is made of hot-worked die steel and has an outer diameter of 12.7 cm and a height of 11.5 cm. This is located inside a steel ring, of outer diameter 15.8 cm, to confine any cylinder fracture. The cylinder is elastic to 12 kbar, and has been tested to 10 kbar. The cylinder is held down by steel straps to prevent it rising on unloading, and safety spacers are placed between the cylinder and the die to prevent crushing in the event of a sudden leak.

The thrust piston, also shown in Figure 4.5, is made of hardened tool steel and is 29.2 mm in diameter. Leads to contact terminals at the end of the piston are passed out of the pressure chamber via hardened silver steel terminals ground into ceramic sleeves and then through a hole down the piston axis. Piston backing pads separate the pistons from the die set, and U-grooves have been milled into them to accommodate the electrical leads. Extrusion of the silver steel terminals down the holes is expected to be the practical limitation of the pistons compressive strength, but it has not proved a problem in routine measurements in either the 8 or
Figure 4.5 Schematic diagram of piston and cylinder high pressure apparatus.
the 15 kbar systems.

The piston face accommodates eight silver steel terminals, evenly distributed. Four of the terminals are used for electrical connections to the test sample while the remaining four are used to provide electrical connections to a chromel-alumel thermocouple, for monitoring the sample temperature, and the toroidal electromagnet consisting of a coil of ~250 turns of 0.18 mm enamelled copper wire wrapped round a toroid of mumetal with a pole gap of 1.0 mm and a pole surface area of 0.5 cm$^2$. A constant current of 60 mA produces a magnetic field of 500 ± 100 Gauss. For such currents the heating effects due to the coil resistance are negligible and the magnetic field is thought to vary by less than 1% over the pressure range used.

Similar silver steel contacts on the bottom piston provide electrical connections to a heater coil and a manganin gauge. The heater coil allows temperatures up to ~40°C to be achieved, while the manganin gauge allows the direct measurement of hydrostatic pressure to be made using the expression,

$$P = 1.1 \frac{\ln \left[ R(P) \right]}{\xi'} \left[ \frac{R(0)}{R(P)} \right]$$

where $R(P)$ and $R(0)$ are the resistances of the manganin gauge at a pressure of $P$ kbars, and at atmospheric pressure respectively. $\xi'$, the fractional change in the resistance of the manganin wire per kbar, has been given by Peggs as $2.3 \times 10^{-3}$ kbar$^{-1}$ \cite{1174}.

The liquid pressure transmitting medium used was castor oil for pressures in the range 0-8 kbar, and a 1:1 mixture of amyl alcohol and castor oil for the range 0-15 kbar. Significantly
above these maximum working pressures the fluid freezes resulting in non-hydrostatic pressures being applied to the sample. Changes in pressure resulted in changes in temperature which typically required 15 minutes to return to ambient.

Sealing between the piston and cylinder is accomplished by a combination of a neoprene "O-ring" and a phosphor bronze ring. Sealing below ~4 kbar is achieved by the "O-ring", and above ~6 kbar by the phosphor bronze ring. Consequently leakage is most likely in the range 4-6 kbar, where special care was taken although leaks were rare.

The clover leaf samples were mounted between insulating plastic sheets and clamped to a bronze U-shaped frame. The 1/1000 inch gold wire, or 0.18 mm copper wire was fixed to the plastic sheeting with silver dag and insulated copper wire was then laid over the silver dag and the leads sandwiched between the plastic sheeting and clamped in place in the U-shaped frame. The frame was then located between the poles of the toroidal magnet which was fixed by a nylon screw to the top, flat face of the thrust piston. The frame was then secured firmly to the magnet by wrapping PTFE tape around both. It was then possible to solder the insulated copper leads to the silver steel connections and perform an experiment without causing the sample to move.

The sample, thus mounted to the piston was then immersed in the liquid medium by carefully placing the piston into the cylinder bore. The trapping of air was minimized by over filling the cylinder with fluid and allowing some to leak out prior to the initial seal being made. The top die was then lowered slowly onto the piston ensuring that the electrical leads are located correctly in the grooves. Pressure was then applied to the die set by a 60-ton press.
CHAPTER 5.

TEMPERATURE AND PRESSURE DEPENDENCE OF THE ELECTRON MOBILITY IN InP.

5.1 Introduction.

Hall effect and resistivity measurements were made on a set of samples with room temperature carrier concentrations in the range $4 \times 10^{14} - 1.5 \times 10^{19}$ cm$^{-3}$ as a function of temperature, in the range 77-450K, and as as function of pressure, at room temperature, in the range 0-8kbar. The results obtained for the variation of the electron Hall mobility with temperature and pressure are shown in Figures 5.1 and 5.3 respectively. The corresponding variations in the Hall carrier concentration are shown in Figures 5.2 and 5.4.

5.2 High Purity VPE InP.

If we initially consider the temperature dependent results shown in Figure 5.1 we see that in the purest material the electron mobility is limited at all but the lowest temperatures by intrinsic phonon scattering processes. The results are well described theoretically by the solid curves in Figure 5.1. These were obtained using an iterative solution of the Boltzmann equation (ISBE) including piezoelectric, polar-optic, and deformation potential scattering and the material parameters given in chapter 2. The best agreement was obtained with a deformation potential, $E_D$, of 11.5eV. This value must be compared with those frequently quoted in the literature. Rode has used values varying from 6.8eV$^{12}$ to 14.5eV$^{70}$. Potter$^{113}$ using a Matthiessen's rule analysis
Figure 5.1  Temperature dependence of the Hall mobility in five VPE InP samples. Solid curve- ISBE for \( n_H = 5 \times 10^{14} \text{ cm}^{-3} \), \( \theta = 0.13 \) and \( \theta = 0.41 \). Dashed curve- ISBE for sample with \( n_H = 7 \times 10^{16} \text{ cm}^{-3} \), \( \theta = 0.25 \). Dash-dot curve- drift mobility including scattering from a correlated distribution of ionized impurities (\( n_H = 1.2 \times 10^{19} \text{ cm}^{-3} \), \( \theta = 0.0 \)).
Figure 5.2 Dependence of carrier concentration on reciprocal temperature for five VPE InP samples. Solid curve—Hall carrier concentration fits to data. Dashed curve—self-consistent ISBE calculated drift carrier concentration.
Figure 5.3  Pressure dependence of the Hall mobility for samples of VPE InP normalized to atmospheric pressure. Solid curve - ISBE for sample with $n_H = 5 \times 10^{14}$ cm$^{-3}$. Dashed curve - ISBE for sample with $n_H = 7 \times 10^{16}$ cm$^{-3}$. Dotted curve - phase shift analysis for sample with $n_H = 5.3 \times 10^{17}$ cm$^{-3}$. Dot-dashed curve - pressure dependence of the drift mobility limited by scattering from a correlated distribution of impurities ($n_H = 1.2 \times 10^{19}$ cm$^{-3}$, $\theta = 0.0$).
Figure 5.4 Pressure dependence of the Hall carrier concentration of five VPE InP samples normalized to atmospheric pressure.
obtained best agreement to his data with $E_A = 18.5\text{eV}$. Nag and Dutta analysed the same data and found that best agreement was obtained with $E_A = 18.0\text{eV}$ using an ISBE type calculation. Hamilton however, criticized this analysis on the basis of the low electron effective mass used and concluded that $E_A = 14.5\text{eV}$ was more appropriate. Clearly then there is still some uncertainty over the value of $E_A$. This is important as Walukiewicz at have used $E_A = 6.8\text{eV}$ when calculating their widely used "look-up" tables to determine the impurity content of samples. Any error in $E_A$ will thus be manifest in the impurity concentration so determined. There are two, rather different, factors that support a value of $E_A = 11.5\text{eV}$.

Firstly, for the purest samples shown in Figures 5.1 and 5.2, we have self-consistently fitted to both the Hall mobility and the Hall carrier concentration. To do this we determined $\tau^{-1}(T)$ from the ISBE assuming initially that $\tau^{-1}(T) = 1.0$. We can then calculate the temperature dependence of the real or "drift" carrier concentration by correcting the measured carrier concentration using the calculated scattering factors (we call this quantity the "drift" carrier concentration by analogy with equation 3.2-1). Then using the new drift carrier concentration we can recalculate the Hall scattering factor, and proceed cyclically until the results converge. Normally this takes ~4 cycles. Such an analysis has, to our knowledge, not been published previously for InP, although Look and Colter have used a variation of this technique for GaAs. Using this approach we fitted the results for the two lowest carrier concentration samples in Figures 5.1 and 5.2 by the solid curves, where the calculated "drift" carrier concentration is shown by the dashed curve in Figure 5.2. Note that the dip in the measured carrier concentration
is removed by this technique. This analysis has also been applied to mobility and carrier concentration measurements made on VPE InP by Anderson et al.\(^{119}\) over the temperature range 4-300K, where the carrier concentration is thermally activated. Their results for the temperature dependence of the carrier concentration and the Hall mobility of one sample are shown in Figures 5.5 and 5.6 respectively by the circles. The squares in the former figure denote the calculated values of the "drift" carrier concentration obtained by self-consistent calculations using the ISBE. Using equation 2.3-2 we obtained the fits shown to the temperature dependence of both the Hall and the "drift" carrier concentration. The concentrations of donors and acceptors, and the donor binding energies are given in Figure 5.5. Using these values, and now with no further adjustable parameters the temperature dependence of the Hall mobility shown by the full curves, and the drift mobility shown by the dashed curves in Figure 5.6 were obtained. The agreement with experiment is very good when the scattering factor corrections are incorporated, the slight overestimate of the mobility at low temperatures being attributable to the omission of neutral impurity scattering in the ISBE calculations.

From these figures it is apparent that without including corrections for the Hall scattering factor we cannot obtain agreement with both the mobility and carrier concentration. In other samples analysed, as with the one described above, including these corrections results in a modified donor binding energy, \(E_d\), and compensation ratio, \(\theta\). Generally the compensation is slightly reduced, while the donor binding energy is increased.

A second test of \(E_{ac}=11.5eV\) is to fit the pressure dependence of the Hall mobility shown by the solid curve in
Figure 5.5 Dependence of carrier concentration on reciprocal temperature. •— Measured Hall carrier concentration (after Anderson et al. (119)). ■— Drift carrier concentration calculated from self-consistant ISBE. Curves— fits to data using equation 2.3-2 with the parameters indicated.
Figure 5.6  Temperature dependence of the mobility. ● - Measured Hall mobility for VPE InP sample (after Anderson et al.\textsuperscript{119}). Curves—Hall and drift mobility calculated with and without $r_H$ corrections to Hall carrier concentration of Figure 5.5.
Figure 5.3 using an ISBE calculation which now incorporates the pressure dependence of the material parameters discussed in chapter 2. Again consistently good agreement is obtained with the data for the pure samples. Moreover, because the predominant effect of pressure is to increase the electron effective mass we observe that as $\mu_{dp} \propto m^{-2/3}$, while $\mu_d \propto m^{-3/2}$, we can estimate the effect of changes in $E_a$ on the pressure dependence of the mobility, particularly for large values of $E_a$. This is indicated in Figure 5.7. This figure shows the relative change in the Hall mobility in 8kbar as a function of the room temperature mobility at atmospheric pressure. The solid curve is the pressure dependence of the mobility calculated by the ISBE assuming $E_a=11.5$eV. The two dotted curves in the high mobility region, labelled $E_a=6.8$eV and $E_a=14.5$eV, indicate the predicted variation calculated for the deformation potentials used by Walukiewicz et al and Rode respectively. The smaller deformation potential tends to give improved agreement, but the results are not very sensitive to the choice of $E_a$ here as the pressure dependence is dominated by that of polar-optic phonon scattering. However, higher deformation potentials, such as 14.5eV, clearly degrade the agreement with high purity material, and lead to an upper limit for $E_a$ of about 12eV.

5.3 High Carrier Concentration Samples.

For samples with increased doping levels we observe the very well known decrease in the low temperature mobility associated with electron scattering from ionized impurities. More interestingly, we also observe a consistent increase in the pressure dependence of the electron mobility with increasing free carrier concentration. Considering equation
3.5-1 it might be thought that as $\mu_0 \propto m^{-1/2}$, compared to an effective exponent, $\delta$, in $\mu \propto m^{-\delta}$ of $\delta=1.21$ for pure material, that the pressure dependence of the electron mobility would decrease with increasing carrier concentration. Indeed, just such an effect is predicted, as indicated by the solid curve in Figure 5.7. However, the decrease is not as large as the above simple arguments predict and at higher carrier concentrations the pressure dependence of the mobility increases. This effect is due to the varying degeneracy of the electron gas, which at very high carrier concentrations constrains the electrons to scatter within $\sim k_BT$ of the Fermi energy. This results in a value of $\delta^{\alpha 2^{120}}$, which is effectively reduced to that predicted using the ISBE because of the conduction band non-parabolicity.

However, it is apparent from Figures 5.3 and 5.7 that as the carrier concentration increases and the mobility decreases there is an increasingly large discrepancy between theory and experiment, until for the sample with $n_\text{e}=1.2\times10^{17}\text{cm}^{-3}, \mu_\text{e}=890\text{cm}^2/\text{Vs}$, the experimental change in the mobility with pressure in 8kbar is ~50% greater than predicted theoretically. At intermediate and high carrier concentrations there are a number of well known limitations associated with the Brooks-Herring theory of ionized impurity scattering which we have outlined previously, and to which we shall return. It is interesting to note, however, that the deviation between theory and experiment is already apparent for the sample with $n_\text{e}=7\times10^{15}\text{cm}^{-3}$. This sample has a carrier concentration for which the Born approximation is still valid, and is also sufficiently low that multiple impurity scattering should be insignificant\textsuperscript{121}. However, if we use the 77K data of Walukiewicz et al. we find that the sample should have a compensation of ~0.25. Using this impurity content data but
Figure 5.7  Relative change in the Hall mobility in 8kbars at 300K plotted as a function of the Hall mobility at atmospheric pressure. Curves-theoretically predicted dependence using the analysis technique and model for ionized impurity scattering indicated.
our values of $E_A^c$ in the ISBE we calculate the dashed curve shown in Figure 5.1. Clearly the agreement is rather poor toward the higher temperature region. This is not perhaps surprising considering that our values of $E_A^c$ are consistently higher than those of Walukiewicz et al.

It is apparent that whatever value of $E_A^c$ is chosen no consistent agreement can be obtained for the broad range of carrier concentrations considered here. For example, to obtain improved agreement at higher temperatures one option is to reduce the impurity concentration, but this removes the good agreement at 77K. Alternatively decreasing $E_A^c$ would increase the high temperature mobility, while hardly affecting that at 77K. However, a reduced value of $E_A^c$ results in poor agreement with the experimental results obtained for pure material. The only consistent solution could be obtained if $E_A^c$ were to be some function of $n_h$! Even if we were to admit such a possibility the predicted pressure dependence of the mobility shown by the dashed curve in Figure 5.3 indicates that a deformation potential that increases with increasing $n_h$ would be required to give improved agreement with the results in Figure 5.3, as $\mu_{pp} \propto m^{-5/2}$. We therefore conclude that it is not possible to obtain agreement between theory and experiment over the ranges of pressure, temperature and carrier concentration considered if the Brooks-Herring theory of ionized impurity scattering is employed.

An alternative explanation of this discrepancy is that a new extrinsic electron scattering mechanism is important in these samples. Such mechanisms as scattering from space-charge regions and the central-cells of impurities have been invoked previously to account for discrepancies in GaAs (see next chapter) and have also been discussed with respect to InP\(^{122}\). However, for space-charge scattering, $\mu_{sc} \propto m^{-1/2}$,
while for central-cell scattering $\mu_{cc} \propto m^w$. Thus if space-charge scattering were significant the pressure dependence of the mobility would be reduced, while if central-cell scattering was dominant the mobility would increase with increasing pressure. Consequently neither of these additional scattering mechanisms gives improved agreement with our results.

There are a number of alternative possibilities. Firstly we have neglected the effect of electron-electron scattering, which, according to Figure 3.1 can significantly reduce the ionized impurity limited mobility. Furthermore we see from this figure that, $d[\mu_{ion}(e-e)]/d[E_F/k_BT] > 0$, which means that the increase in $m^w$ with pressure leads to a slow lowering of the Fermi energy as the carrier concentration remains unaltered as shown in Figure 5.4. The resulting increase in electron-electron scattering would enhance the pressure dependence of the mobility. However, if this were the case one would expect to see improved agreement again at very high carrier concentrations where $d[\mu_{ion}(e-e)]/d[E_F/k_BT] = 0$. This is not observed as is apparent from Figure 5.7.

Another possibility is that the disagreement is associated with the breakdown of the Born approximation for carrier concentrations $\geq 5 \times 10^{17} \text{cm}^{-3}$. We have calculated the pressure dependence of the mobility limited by ionized impurity scattering using the phase shift analysis of Meyer and Bartoli. This technique does not invoke the Born approximation but even so the predicted pressure dependence of the mobility, shown by the dotted curve in Figures 5.3 and 5.7, although slightly more pressure sensitive, still shows a significant discrepancy with the sample with a carrier concentration of $5.3 \times 10^{17} \text{cm}^{-3}$. Consequently it seems that the failure of the Born approximation is not responsible for the
discrepancy between theory and experiment.

Yet another approach is to consider corrections associated with multiple impurity scattering and impurity dressing effects. Such corrections have been calculated by Moore for GaAs\(^{100,101}\). We have repeated the calculations for InP and the various corrections to the Brooks-Herring theory, as given in equation 3.5-3, were shown in Figure 3.2. It is clear from this figure that such an analysis reduces the ionized impurity limited mobility of the 1.2x10\(^{15}\) cm\(^{-3}\) sample by about 6% at room temperature, this being predominantly due to corrections for higher Born approximations. At lower concentrations, \(\sim 10^{17}\) cm\(^{-3}\), the multiple scattering factor predominates and reduces the impurity limited mobility by \(\sim 50\%\). However, our calculations also indicate that these corrections are relatively insensitive to pressure, and lead to no significant differences from the solid curve shown in Figure 5.7. So again we see no improved agreement with experiment. It thus seems clear that none of the previous arguments alone are sufficient to explain the experimental results obtained for the pressure dependence of the mobility. It is possible that some complex combination of the above mechanisms may provide improved agreement over a limited carrier concentration range; e.g. at intermediate carrier concentrations a combination of electron-electron scattering and Meyer and Bartoli's phase shift analysis may give improved agreement. However, no combination of the above mechanisms is satisfactory over the whole range of carrier concentrations, and in particular none can explain the high pressure dependence of the mobility in the highest carrier concentration sample.
5.4 Impurity Correlation Effects.

All the modifications to the Brooks-Herring theory so far considered assume a random impurity distribution. Yanchev et al.\(^{104}\) have considered the effect of a non-random impurity distribution. They found that it describes well the variation of mobility with carrier concentration in GaAs at 77K, in the régime where several impurities can be found within a screening length. The correlation of impurities is accounted for in terms of an additional ionic screening resulting from the plasma of ionized impurities in the melt during growth. This additional Debye screening is characterized by a temperature, \(T_c\), at which impurity diffusion effectively stops. Consequently we can regard the impurity distribution in the sample to be a "snap-shot" at that temperature. Yanchev et al.\(^{107}\) argue that \(T_c \approx 900K\) in uncompensated LPE GaAs as discussed in chapter 3. If we assume a similar temperature for InP, and calculate the pressure dependence of the electron mobility in the 1.2x10\(^{17}\)cm\(^{-3}\) sample with zero compensation using Matthiessen's rule we obtain the dot-dashed curve in Figure 5.3. Clearly the agreement is very good. In Figure 5.7 we show the calculated variation of the pressure dependence of the Hall mobility by the dot-dashed curve. The theory, as derived by Yanchev, only applies in the limit of high degeneracy: the characteristic energy, \(E_F\), used in equation 3.5-15 goes negative implying a negative mobility at lower electron concentrations! The characteristic electron energy under such circumstances is no longer well described by \(E_F\). Also, the theory is only appropriate if the magnitude of the potential fluctuations (83meV for 1.2x10\(^{17}\)cm\(^{-3}\) sample) are small compared to the characteristic electron energy (~190meV), i.e. perturbation theory is valid. Clearly for the
highly doped sample considered here both these criteria are well satisfied.

We have also calculated the temperature dependence of the mobility, and assuming a Matthiessen's rule analysis we obtained the dot-dashed curve shown in Figure 5.1. Again we see rather, good agreement, and it must be emphasized again that this was calculated assuming that the sample was uncompensated. Thus impurity correlation effects reduce the electron mobility. This can be understood qualitatively. The distorted conduction band arising due to potential fluctuations causes a lowering of the Fermi level and a decrease in the electron mobility as a result of the reduced electron kinetic energy. This effect is described in the Yanchav theory by including the corrections given by equations 3.5-10-3.5-12.

If the previous discussion is correct this clearly has important consequences for the determination of impurity concentrations. For example, in Figure 5.8 we show the variation of the Hall and drift mobility with free carrier concentration, at 300K, for a variety of compensation ratios as calculated by the ISBE using the Brooks-Herring model of ionized impurity scattering. Also shown is the curve of Walukiewicz et al for the drift mobility in uncompensated InP\(^{119}\), as well as the results of Anderson et al\(^{122}\) obtained on many samples with a variety of dopants. A comparison of the ISBE curves and the experimental data clearly supports the idea discussed elsewhere that autocompensation reduces the mobility in highly doped material\(^{123}\). Note that some of the experimental mobilities in the carrier concentration range ~7x10\(^{14}\)–10\(^{18}\)cm\(^{-3}\) exceed the ISBE calculations. This apparent discrepancy is removed when screening of polar-optic phonons is included as indicated by
Figure 5.8

Mobility (cm²/Vs)

Carrier Concentration (cm⁻³)

- Dotted curve - Isbell calculated Hall mobility with $\rho = 0$ and including a screened potential
- Dotted curve - Isbell calculated mobility with $\rho = 0$ and including a screened potential
- Solid line - Mobility from Anderson et al. (122) and the author, solid and dashed curve - mobility from Anderson et al. (122), dl Poisson-Boltzman et al. (124), and the author. Solid and dashed curves - Isbell calculated Hall and drift mobility respectively for various mobility vs. electron concentration in InP at 300K. Experimental results are of the Hall
the dot-dashed curve in Figure 5.8. Rode\cite{92} did not include screening of polar optic phonons, but it was incorporated in the calculations of Walukiewicz et al. It is also interesting to notice that, as discussed by Anderson et al\cite{122}, that there is no systematic difference between samples with different dopants. This casts doubt on the significance of central-cell scattering as different dopants are likely to have different central-cell corrections. Also the samples appear to depart from the $\theta=0$ ISBE curve including the screened polar phonon mechanism at similar mobilities to those where the difference between ISBE Brooks-Herring theory and the pressure dependence of the mobility of Figure 5.7 becomes significant. It seems unlikely that this is coincidental. By including at high impurity concentrations the Yanchav rather than the Brooks-Herring model for ionized impurity scattering and combining the mobility components assuming Matthiessen's rule, which is valid at such high carrier concentrations, we obtained the dot-dot-dashed curve shown in Figure 5.8. Clearly the agreement is very good and implies that most of the samples are relatively uncompensated.

We show in Figure 5.9 the variation of mobility with carrier concentration at 77K. Note that all the experimental results of Anderson et al\cite{122} lie below the $\theta=0$ curve. The curve of Walukiewicz et al\cite{88} for $\theta=0$ is also given and screening of the polar-phonon interaction is not significant at this temperature. It is interesting to note that a recent result by di Forte-Poisson et al\cite{124}, shown by the cross in Figure 5.9 lies slightly above both our curve and the curve of Walukiewicz et al, for $\theta=0.0$. At higher carrier concentrations a consistent compensation ratio, $\theta=0.3$ can be interpreted in terms of correlation effects\cite{104}. It remains to be shown whether correlation effects are responsible for the apparent
Figure 5.9 Mobility vs. electron concentration in InP at 77K. Experimental results are of the Hall mobility from Anderson et al (122), di Forte-Poisson et al (124), and the author. Solid and dashed curves— ISBE calculated Hall and drift mobility respectively for various compensations, θ. Dotted curve—drift mobility for θ=0 after Walukiewicz et al (86).
autocompensation down to carrier concentrations as low as 
7x10^{15} \text{cm}^{-3}, and whether these samples also exhibit an 
increased pressure dependent mobility compared to pure 
material at these temperatures.

In Figure 5.10 the calculated temperature dependence of the 
low magnetic field limit Hall scattering factor is shown 
calculated using the ISBE and including the Brooks-Herring 
ionized impurity scattering. Figure 5.10 (a) shows the 
temperature dependence of \( r_m \) for a range of fixed carrier 
concentrations in uncompensated InP, while Figure 5.10 (b) 
shows the temperature dependence of \( r_m \) for a fixed carrier 
concentration of 10^{12} \text{cm}^{-2} with a variety of compensation 
ratios. The accurate calculation of these curves should now 
allow the theory to be tested further. Preliminary analysis of 
the results of Anderson et al.\cite{12} indicate that this is 
possible although their results are difficult to analyse 
because of magneto-resistance effects that were not eliminated 
in their experiments.

Finally, with respect to the Hall scattering factor in InP, 
it is interesting to note that Walukiewicz et al indicate that 
\( r_m \) is within 10\% of unity at 77K so that no correction is 
necessary to convert Hall to drift mobilities. This is 
apparently based on Rode’s analysis\cite{13} which, however, only 
refers to ideally pure material. The results of theoretical 
calculations shown in Figure 5.10 indicate that for a wide 
variety of carrier concentrations and compensation ratios \( r_m \) 
is significantly greater than unity at 77K; i.e., for 
n=1x10^{15} \text{cm}^{-3}, \mu=7x10^4 \text{cm}^2/\text{Vs}, \ r_m=1.2 \) even for magnetic fields of 
0.4 Tesla, a field of ~1.4 Tesla being required to reduce \( r_m \) 
to within 5\% of unity. This of course presumes that the \( r_m \) 
values calculated are correct, which in turn requires the 
Brooks-Herring theory to be valid at these carrier
Figure 5.10 Temperature dependence of the Hall scattering factor in InP calculated from an ISBE with $E_{AC} = 11.5 \text{eV}$ and including Brooks-Herring ionized impurity scattering. (a) For uncompensated InP with various fixed carrier concentrations ($\text{cm}^{-3}$), and (b) for various compensations $\theta$ with $n=10^{15} \text{ cm}^{-3}$. Experimental results after Potter (115).
concentrations and temperatures. Any discrepancies observed may be explainable by including the Yanchev model of impurity scattering. This remains just speculation at present but high-pressure low-temperature high magnetic field transport measurements are planned to confirm or negate this idea.

5.5 Conclusions.

We have shown that accurate analysis of Hall effect and resistivity measurements requires that the effect of the Hall scattering factor be accurately included. Measurements of the electron Hall mobility as a function of pressure in pure InP support a value of $E^m = 11.5eV$. At high carrier concentrations the pressure dependence of the mobility indicates that the Brooks-Herring theory of scattering from ionized impurities is inadequate. Additional scattering from space-charge regions or scattering from the central-cell of impurities gives no better agreement. However, much improved agreement is obtained if potential fluctuations are included resulting from correlated impurity distributions as described by Yanchev et al. Further, such a model eliminates the requirement for autocompensation in highly doped samples.

It seems likely that if such a mechanism is important in InP then it should also be apparent in other materials and in the next chapter we look for similar effects in GaAs.
CHAPTER 6.
TEMPERATURE AND PRESSURE DEPENDENCE OF THE ELECTRON MOBILITY IN GaAs.

6.1 Introduction.

This chapter is conveniently divided into three sections. Initially we consider the temperature and pressure dependence of the electron Hall mobility in LPE grown GaAs over a wide range of carrier concentrations. In subsequent sections we look at similar experiments made on GaAs grown by MBE, and on bulk GaAs subjected to neutron transmutation doping.

6.2 LPE GaAs.

6.2.1 High purity LPE GaAs.

As in the previous chapter, measurements of the Hall effect and resistivity have been made as a function of temperature and pressure, but this time on a number of LPE grown GaAs samples, with carrier concentrations in the range \(3 \times 10^{13} - 1 \times 10^{19} \text{ cm}^{-3}\). The results obtained are shown in Figures 6.1-6.4.

As in InP we observe that the temperature dependence of the mobility shown in Figure 6.1 is limited in high purity material by intrinsic phonon scattering mechanisms for temperatures above \(\sim 100\text{K}\). The theoretical dependences of the Hall mobility calculated using a self-consistent ISBE are shown by the solid curves in Figure 6.1. These were obtained with a value of \(E_{\text{A}}=9.0\text{eV}\) and the compensation ratios indicated in the figure. The dashed curves in Figure 6.2 are
Figure 6.1  Temperature dependence of the Hall mobility in seven LPE GaAs samples. Solid curves—ISBE calculated Hall mobilities for samples with increasing carrier concentrations and compensation ratios of $\theta=0.24$, 0.62 and 0.33 respectively. Dashed curve—ISBE for sample with $n_H=1.7\times10^{17}$ cm$^{-3}$, $\theta=0.25$. Dot-dash curve—drift mobility including scattering from a correlated distribution of impurities ($n_H=9.7\times10^{18}$ cm$^{-3}$, $\theta=0.0$).
Figure 6.2 Dependence of carrier concentration on reciprocal temperature for seven LPE GaAs samples. Solid curve—Hall carrier concentration fits to data. Dashed curve—self-consistent ISBE calculated drift carrier concentration.
Figure 6.3 Pressure dependence of the Hall mobility for samples of LPE GaAs normalized to atmospheric pressure. Solid curve- ISBE for $n_H=1\times10^{14}\text{ cm}^{-3}$. Dashed curve- ISBE for sample with $n_H=1.7\times10^{17}\text{ cm}^{-3}$. Dotted curve- phase shift analysis for sample with $n_H=1.7\times10^{17}\text{ cm}^{-3}$. Dot-dashed curve- drift mobility limited by scattering from correlated distribution of impurities ($n_H=9.7\times10^{18}\text{ cm}^{-3}$, $e=0.0$).
Figure 6.4  Pressure dependence of the Hall carrier concentration concentration of five LPE GaAs samples normalized to atmospheric pressure.
the calculated "drift" carrier concentrations obtained by correcting the Hall carrier concentration for the effect of \( n_H \) calculated using the ISBE. We observe that this eliminates the anomalous dip in \( n_H \) observed in the three purest samples. Clearly good agreement with the results for the pure material shown in both Figures 6.1 and 6.2 is obtained.

In contrast to our conclusions regarding InP, the deformation potential in GaAs is in good agreement with other published data. Look and Colter analysed very high mobility low compensation VPE grown GaAs and obtained a value of \( E_{dc} = 10 \text{eV} \). Rode's value of \( 8.6 \text{eV} \) is in very close agreement, while the value of \( 7.0 \text{eV} \) used by Walukiewicz et al. appears just slightly low although the mobilities given agree well with the ones presented here and the material parameters quoted by Walukiewicz et al. accord well with our own in all other respects.

The good agreement obtained for the deformation potential in GaAs also supports the value of \( E_{dc} \) obtained in InP as a consistent discrepancy in both GaAs and InP might cast doubt on the accuracy of our theoretical calculations.

Additional evidence for this value of \( E_{dc} \) is shown by the solid line in Figure 6.3 which indicates the pressure dependence of the mobility for an uncompensated GaAs sample with a carrier concentration of \( 1 \times 10^{14} \text{cm}^{-3} \) calculated using the ISBE with the pressure coefficients of the GaAs material parameters described in chapter 2. Good agreement is observed between the theoretical curve and the experimental results obtained for samples with similar carrier concentrations. This is perhaps indicated more clearly by the good agreement over the high mobility region of Figure 6.5 which shows the relative change in the Hall mobility to pressures of 8kbar plotted as a function of the mobility at atmospheric pressure.
Figure 6.5

Relative change in the Hall mobility in 8kbars at 300K plotted as a function of the Hall mobility at atmospheric pressure. Curves- theoretically predicted dependence using the analysis technique and model of ionized impurity scattering indicated.
6.2.2 High Carrier Concentration LPE GaAs.

With increasing carrier concentration we observe experimentally an increase in the pressure dependence of the Hall mobility as shown in Figure 6.3 as well as a reduction in the low temperature mobility shown in Figure 6.1. As was the case in InP, the pressure dependence of the mobility is accurately described only for high purity GaAs. As the carrier concentration increases, and the mobility decreases, the difference between standard theory and experiment becomes increasingly large. For the sample with a carrier concentration of $9.7 \times 10^{16} \text{cm}^{-3}$ the pressure dependence of the mobility is $\%60$ larger than that predicted by the ISBE calculation. Note that this sample shows a small "trap-out" of free carriers (~2% in 8kbar), and is the only LPE GaAs sample that shows this effect. This can be attributed to loss of carriers to the L minima. This occurs as a result of the high position of the Fermi level (~180meV above the bottom of the undoped conduction band) and the decrease of the $\Gamma$-L separation with pressure, to an extent that the energy gap between the Fermi level and the minima has been reduced from ~110meV at 0kbar to ~100meV at 8kbar. Note that this rather small difference is due to the lowering of the Fermi level with applied pressure as a result of the increased electron effective mass. Such effects have been included in the ISBE analysis although small changes of the measured carrier concentration of this type are found to have no significant effect on the pressure dependence of the mobility.

At intermediate carrier concentrations and mobilities as indicated in Figure 6.5 the discrepancy is still present although not as large. We notice that for the sample with a
carrier concentration of $1.7 \times 10^{17}$ cm$^{-3}$, for which the Born approximation is just still valid, the temperature dependence of the mobility in Figure 6.1 is not well described by the dashed curve obtained from the ISBE. As argued in the previous chapter and as indicated in Figure 6.1 by the dashed curve, this sample cannot be described theoretically by including Brooks-Herring type ionized impurity scattering. If no other extrinsic mechanisms were important, only a deformation potential that decreased with increasing carrier concentration could explain the temperature dependence of the mobility. This however, would increase further the disagreement with the pressure dependence of the mobility shown in Figure 6.3, as $\mu_{Dp} \propto m^{-5/2}$ while $\mu_{Dp} \propto m^{-3/2}$. Consequently a deformation potential that increased with increasing carrier concentration would be required to achieve improvement agreement with the results obtained as a function of pressure. Clearly then neither agreement to the pressure dependence nor to the temperature dependence of the mobility can be achieved using the ISBE with the Brooks-Herring model of ionized impurity scattering.

This result is contrary to the conclusions of Walukiewicz et al. who indicate that good agreement to the temperature dependence of the mobility measured experimentally can be achieved provided a rigorous numerical analysis is undertaken. They concluded that the additional scattering mechanisms invoked by some workers to account for their measured temperature dependence of the mobility were artefacts of the Matthiessen's rule analysis used. Although our results indicate that such a rigorous analysis is not sufficient, the incorporation of additional extrinsic scattering mechanisms, such as space-charge or central-cell scattering is also unsatisfactory. Good agreement can be obtained with the
temperature dependence of the mobility by suitable choice of space-charge scattering cross-section and/or central-cell strength and concentration. Such mechanisms, however, completely fail to account for the enhanced pressure dependence of the mobility that is observed because of their dependence on the effective mass, just as was found to be the case for InP.

Alternatively we have also calculated the corrections of Moore\cite{100} for multiple scattering, dressing effects, and higher Born approximations and the mobility limited by scattering from a screened coulomb potential using the variational method of Meyer and Bartoli\cite{102}, which avoids the use of the Born approximation altogether. The calculated corrections for GaAs using Moore's theory are in good agreement with his published results on GaAs and are very similar to those calculated for InP and shown previously in Figure 3.2. This is not surprising as the parameters which enter the expressions for the correction terms are, to a good approximation the same for both GaAs and InP. Consequently as the pressure coefficients of the material parameters in the two materials are also similar we found that, as in InP, the pressure dependence of Moore's corrections were negligibly small. The phase shift analysis of Meyer and Bartoli does result in a slightly increased pressure dependence of the mobility as shown by the dotted curve in Figure 6.3 for a carrier concentration of 1.7x10^{17}cm^{-3}, and by the dashed curve in Figure 6.5. The difference between the higher Born corrections as calculated by Moore and the analysis of Meyer and Bartoli is not clear. However, Figure 6.5 indicates that the inclusion of the phase shift analysis is still not sufficient to explain the pressure dependence of the mobility in high carrier concentration, low mobility GaAs grown by LPE.
However, as shown by the dot-dashed curve in Figure 6.3, very good agreement is found for the pressure dependence of the mobility for the highest carrier concentration sample if one uses the model of Yanchev et al. for scattering from a correlated distribution of ionized impurities, characterized by a temperature $T_0$. This was obtained assuming the sample was uncompensated. Using the same model the temperature dependence, shown by the dot-dashed curve in Figure 6.1 was also obtained. We find that, as for InP, the need for high compensation ratios is removed if such a model is assumed. This very interesting result confirms the original results in InP, and indicates the clear inadequacy of the Brooks-Herring theory of ionized impurity scattering.

We show in Figure 6.6 the carrier concentration dependence of the mobility in a large number of samples published by a number of authors. Also shown in the figure are the predicted variations of the Hall mobility (solid curve) and drift mobility (dashed curve) for a number of compensation ratios calculated using the ISBE, as well as the drift mobility in uncompensated GaAs given by Walukiewicz et al. Although the experimental results are slightly more scattered than those shown for InP in the previous chapter the apparent effect of autocompensation is readily apparent at high carrier concentrations. The predicted carrier concentration dependence of the drift mobility including correlated impurity scattering effects is shown by the dot-dot-dash curve and clearly implies that autocompensation is not significant in many of the samples indicated.

A similar set of results is plotted in Figure 6.7 for a temperature of 77K. Again we show the predicted carrier concentration dependence of the Hall and drift mobility at a number of compensations by the solid and dashed curves.
Figure 6.6 Mobility vs. electron concentration in GaAs at 300K. Experimental results are of the Hall mobility from Vilms et al (127), Mehal et al (128), Parsons et al (129), Kuech et al (130), and the author. Solid and dashed curves - ISBE calculated Hall and drift mobility respectively for various compensations, $\theta$. Dotted curve - drift mobility for $\theta=0$ after Walukiewicz et al (84). Dot-dashed curve - ISBE calculated Hall mobility for $\theta=0$ with screened polar phonon interaction. Dot-dot-dashed curve - Matthiessen's rule analysis with scattering from correlated impurity distribution.
respectively. The dotted curve shows the predicted dependence for uncompensated GaAs given by Walukiewicz et al\(^{105}\). The autocompensation effect is apparent down to carrier concentrations as low as mid \(10^{19}\) cm\(^{-3}\). Our calculations of the carrier concentration dependence of the mobility at 77K agree well with those of Yanchev et al\(^{104}\) when correlation effects of impurities are taken into account. We show the calculated results of Yanchev et al\(^{107}\) in Figure 6.7 for uncompensated GaAs, with a \(T_0\) of 900K, by the dot-dashed curve. They find very good agreement with experiment provided \(\theta \leq 0.3\) and this is also apparent if we extrapolate the Yanchev et al \(\theta = 0.0\) line in Figure 6.7 to carrier concentrations down to mid \(10^{17}\) cm\(^{-3}\). Yanchev et al\(^{107}\) argue that \(T_0\) is dependent on the degree of compensation in the samples and indicate that for GaAs with increasing compensation \(T_0\) should rise, reaching \(\sim 1300\) K for a compensation ratio \(\sim 0.3\), resulting in a carrier concentration dependence of the mobility also shown by a dot-dashed curve in Figure 6.7. It is interesting to note that, in their paper, they indicate that they no longer obtain good agreement between theory and experiment for LPE GaAs deliberately compensated to \(\theta > 0.3\). This they attribute to the \(T_0\) for such samples being greater than the growth temperature. Consequently correlation in the melt is low and a more nearly random impurity distribution should thus be obtained. Consequently it might be argued that under these circumstances improved agreement with the Brooks-Herring theory should be observed for measurements undertaken both as a function of temperature and of pressure. Indeed as a function of temperature this appears to be the case. The results of Yanchev et al are in close agreement with the ISBE calculations for a compensation ratio of 0.4 compared to Yanchev's estimated compensation of 0.3. Notice that the
Mobility vs. electron concentration in GaAs at 77K. Experimental results are from Poth et al.\textsuperscript{(123)} and the author. Solid and dashed curves- ISBE calculated Hall and drift mobility respectively for various compensations, $\theta$. Dotted curve- drift mobility for $\theta=0$ after Walukiewicz et al.\textsuperscript{(85)} . Dotted-dashed curve- drift mobility limited by scattering from a correlated impurity distribution after Yanchev et al.\textsuperscript{(107)}. 

Figure 6.7
inclusion of phase shift calculations and Moore's corrections tend to give improved agreement between the two compensation ratios. No measurements, however, have been made on high carrier concentration, highly compensated LPE GaAs as a function of pressure as no samples are presently available.

Clearly the dependence of impurity correlation effects on the value of $T_o$ is very significant and this effect is investigated further in the next section.

6.3 GaAs grown by MBE.

6.3.1 Introduction.

The influence of $T_o$ on the effects of impurity correlation can be investigated further. A value of $T_o=900K$ has been associated with a number of commonly used dopants although other values may be attainable. However, Yanchev et al have observed that correlation effects are no longer significant when $T_o$ is greater than the growth temperature of the material. Consequently we look in this section at MBE grown GaAs for which the growth temperature was $\leq 850K$ and investigate both the temperature and pressure dependence of the mobility.

6.3.2 Temperature dependence of the Hall mobility.

The temperature dependence of the mobility and carrier concentration for the three samples measured is shown in Figures 6.8 and 6.9 respectively. Note from Figure 6.8 that the sample with a room temperature carrier concentration of $1.7\times10^{15}cm^{-3}$ has almost the same temperature dependence of the mobility as the sample with a carrier concentration of.
Figure 6.8  Temperature dependence of the Hall mobility in three samples of MBE GaAs. Solid curves- ISBE calculated Hall mobility with the compensation ratios indicated.
Figure 6.9  Dependence of the carrier concentration on reciprocal temperature for three samples of MBE GaAs. Solid curve—Hall carrier concentration fits to data. Dashed curve—self-consistent ISBE calculated drift carrier concentration.
1.2 \times 10^{16} \text{cm}^{-3}$, shown by the triangular data points. The third sample has the lowest mobility of the three, but has a similar carrier concentration to the sample with triangular data points. The solid curves shown in Figure 6.8 are the calculated temperature dependence of the mobility using the ISBE calculation with the indicated compensation ratios obtained by self-consistent calculations. The corresponding Hall and "drift" carrier concentrations calculated are shown by the solid and dashed curves respectively in Figure 6.9.

The agreement with the temperature dependence of the mobility is rather good although the temperature dependence of the carrier concentration for the sample with $n_c = 1.2 \times 10^{16} \text{cm}^{-3}$ has an anomalous dip at high temperatures which is not eliminated by the inclusion of the Hall scattering factor corrections. The good agreement with the temperature dependence of the mobility in these samples is in sharp contrast to the poor agreement observed in the LPE sample with a carrier concentration of $1.7 \times 10^{17} \text{cm}^{-3}$, shown in Figure 6.1, whose mobility at low temperatures appears anomalously low compared to its room temperature mobility. This may indicate that impurity correlation becomes more significant at low temperatures.

6.3.3 Pressure Dependence of the Hall Mobility

The pressure dependence of the Hall mobility and carrier concentration is shown in Figures 6.10 and 6.11. Notice that the MBE samples show a trap-out of carriers with pressure. This effect is not related to loss of carriers to subsidiary minima, as was the case for highly doped LPE GaAs, but may be associated with some unknown level which traps out carriers. It is interesting to note that this level is not observed in
Figure 6.10  Pressure dependence of the Hall mobility in three MBE GaAs samples normalized to atmospheric pressure. Solid and dashed curves—ISBE calculated dependence assuming constant $n_H$ and trap-out of $n_H$ with pressure respectively.
Figure 6.11  Pressure dependence of the Hall carrier concentration in three MBE GaAs samples normalized to atmospheric pressure.
temperature dependent measurements down to 77K and must therefore be within a few meV of the conduction band edge at atmospheric pressure. Even these changes of carrier concentration with pressure, however, are not found to significantly affect the pressure dependence of the mobility as is indicated in Figure 6.10 by the solid curves, which assume no change in carrier concentration with pressure and the dashed curves where the carrier concentration is allowed to "trap-out" with increasing pressure. In all cases we observe quite good agreement between theory and experiment.

The pressure dependence of the mobility to 8kbar for the MBE samples has also been plotted in Figure 6.5 as the open data points. It is very striking from this figure that good agreement is obtained between experiment and ISBE calculations for the MBE samples, whereas for similar mobility LPE samples a clear discrepancy is apparent. It is interesting to consider the reason for the difference observed between LPE and MBE samples. One possibility is that the large difference in growth temperature between the two techniques which allow impurity correlation effects in the former case but inhibit them in the latter. Alternatively the high compensation ratios of the MBE samples may increase the value of To in these samples, as argued by Yanchev et al\textsuperscript{107}, again leading to a loss of impurity correlation effects. In either case it seems that the MBE samples studied do not exhibit impurity correlation scattering effects. It would be interesting to observe if highly doped MBE GaAs grown at low temperatures, shows any apparent increase in mobility compared to LPE grown material, although the author is not aware of any such results.

There are obviously a number of further experiments we could undertake to test the effects of impurity correlation
effects. Firstly we could anneal MBE grown samples at temperatures >900K for differing periods and look for variations in electron mobility and carrier concentration and their pressure dependence. It would also be informative to look at alternative growth techniques such as MOCVD. All these ideas are to be actively investigated in the near future.

6.4 Neutron Transmutation Doped GaAs.

Another approach which we have already studied is neutron transmutation doping (NTD) of GaAs. Perhaps the most rigorous method for testing for the effects of correlated impurity distributions is to look at materials in which the impurities are known to be randomly distributed. Greene has investigated NTD GaAs for use as a high doping technique. In NTD GaAs, the neutron induced nuclear reactions convert Ga to Ge and As to Se (both of which are donors in GaAs) randomly throughout the crystal, resulting in highly doped material. The resulting radiation damage must then be annealed. This limits the applicability of NTD doped samples for the study of impurity correlation effects to low anneal temperatures. Fisher has made preliminary measurements on some NTD doped GaAs, annealed at 750°C for 10 hours, as a function of temperature and pressure and the results obtained are shown in Figures 6.12 and 6.13. Quite good agreement is obtained with the temperature dependence of the mobility and carrier concentration using a self-consistent IBBE and a compensation ratio of 0.65. However, it was found that although no freeze-out was observed as a function of temperature a large trap-out (~40%) was observed as a function of pressure in 8kbar. Such large changes in carrier concentration significantly affect the importance of impurity scattering in
Figure 6.12  Temperature dependence of the Hall mobility and carrier concentration in neutron transmutation doped GaAs. Solid curve—ISBE calculated Hall mobility and carrier concentration. Dashed curve—ISBE calculated drift mobility and carrier concentration.
Figure 6.13 Pressure dependence of the Hall mobility ■, and carrier concentration ●, in neutron transmutation doped GaAs normalized to atmospheric pressure. Solid and dashed curves—ISEE calculated dependence of the Hall mobility assuming carrier concentration trap-out onto ionized donors and neutral defects respectively.
such samples and lead to severe difficulties in interpretation which consequently cast doubt on the conclusions obtained. For instance, the pressure dependent trap-out of carriers may occur onto ionized impurity sites reducing the impurity concentration, or onto neutral defects, perhaps associated with unannealed radiation damage, which increases the number of ionized impurity sites. Alternatively any intermediate case may also prevail. Consequently a broad range of predicted changes in mobility with pressure, the limits of which are shown by the solid and dashed curves in Figure 6.13, can be obtained. It is interesting to see the close agreement between the solid curve, which assumes that all the electrons are trapped onto ionized donors, and the experimental pressure dependence of the mobility. Again such close agreement argues in favour of scattering from a random impurity distribution, which was certainly not the case for equivalent carrier concentration samples grown by LPE. Additional annealing at higher temperatures is being considered in an attempt to remove residual radiation damage, and reduce the observed carrier trap-out with pressure. Clearly, however, the random impurity distribution is no longer guaranteed if the anneal temperature greatly exceeds the \( T_o \) value of 900K.

6.5 Conclusions.

We have shown in this chapter that the pressure dependence of the Hall mobility in high carrier concentration LPE GaAs cannot be described using the usual Brooks-Herring model, just as was found to be the case for VPE InP. Analysis including electron scattering from space-charge regions and the central-cells of impurities was not found to improve the agreement. Neither did the inclusion of multiple scattering,
dressing, corrections and higher Born approximations as described by Moore. The breakdown of the Born approximation was also shown not to be responsible for the discrepancy by calculating the scattering from a screened coulomb potential as described by Meyer and Bartoli using a phase shift analysis. The only model found which did give improved agreement was that of Yanchev et al for scattering from a correlated impurity distribution. This is described in terms of a temperature, $T_0$, below which impurities are unable to correlate.

For GaAs grown by MBE and for bulk GaAs subjected to neutron transmutation doping good agreement between theory and experiment was obtained both as a function of temperature and pressure when the Brooks-Herring theory of ionized impurity scattering was used in the ISBE. This is in contrast to LPE samples with similar mobilities. For the MBE grown GaAs this was related to either the low growth temperature or the high compensation ratios. Both of these factors, as argued by Yanchev et al, inhibit the correlation of impurities during growth. For the neutron transmutation doped GaAs sample the distribution of impurities is random provided a low anneal temperature is used so that they are unable to move appreciable distances. Consequently we have shown that there is strong evidence to support the claim that impurity correlation effects have a very significant effect on the electron mobility in highly doped GaAs.

A number of approaches to further test the significance of impurity correlation effects can be suggested, of which perhaps the most interesting in the short term are the investigations of neutron transmutation doped GaAs and high carrier concentration MBE GaAs grown at varying substrate temperatures and with varying degrees of compensation.
In the next chapter we describe further high pressure transport measurements made on the narrow gap semiconductor InSb and the ternary alloy Ga$_{0.45}$In$_{0.55}$As/InP.
CHAPTER 7.
TEMPERATURE AND PRESSURE DEPENDENCE OF THE ELECTRON
MOBILITY IN Ga$_{0.47}$In$_{0.53}$As and InSb.

7.1 Introduction.

In this chapter we consider the pressure dependence of the mobility in two more direct band gap III-V semiconductors, namely Ga$_{0.47}$In$_{0.53}$As and InSb. Both semiconductors, because of their small band gap and its large pressure coefficient, have an electron effective mass which is more pressure sensitive than either GaAs or InP. Also in the former material there is additional scattering attributable to alloy disorder while in the latter intrinsic material electron-hole scattering can be important. InSb has been investigated previously. However, in the light of new experimental results further work seems appropriate.

7.2 Electron Mobility in Ga$_{0.47}$In$_{0.53}$As.

7.2.1 Introduction.

The quaternary alloy Ga$_x$In$_{1-x}$As$_y$P$_{1-y}$, lattice matched to InP ($X=Y/2.1$) has significant commercial applications in a number of opto-electronic devices. This alloy has been investigated previously by a number of authors. Hayes et al. were the first to use the pressure dependence of the mobility to distinguish between alloy and space-charge scattering. The alloy scattering limited mobility is proportional to $m^{*}_{a} - 3/2$ (cf. equation 3.4-12), while space-charge scattering is proportional to $m^{*}_{a} - 1/2$ (cf.
equation 3.4-11). Measurements of the temperature dependence of the mobility are unable to distinguish between the two as both are proportional to $T^{-1/2}$.

Hayes et al. used equation 2.2-3 to calculate the pressure dependence of the effective mass as a function of the alloy composition. They obtained values of 0.72%/kbar and 1.22%/kbar for compositions of $y=0.5$ and 0.91 respectively. With these values they showed, using a Matthiessen's rule analysis, that the component of the mobility proportional to $T^{-1/2}$ also had an effective mass dependence $m^* = 5/2$. Consequently the scattering mechanism was attributed to alloy disorder.

However, it has recently been shown by Shantharama et al. that the pressure dependence of the electron effective mass in the quaternary alloy $G_{x}I_{1-x}A_{y}S_{1-y}/I_{n}P$ is significantly larger than that predicted by k.p theory and used by Hayes et al. Also Sarkar and Nicholas have shown that the non-parabolicity in this material is approximately twice the value predicted by k.p theory. These factors cast doubt on the previous analysis of Hayes et al. In this section we investigate the temperature and pressure dependence of a number of $G_{0.47}I_{0.53}A_{0.53}$ samples (hereafter referred to as GaInAs) grown by LPE at $\sim 660^\circ$C.

7.2.2 Temperature Dependence of Electron Mobility in GaInAs.

The temperature dependence of the electron Hall mobility and carrier concentration of six samples, two from each of three wafers are shown in Figures 7.1 and 7.2.

Using an ISBE including alloy scattering as the $T^{-1/2}$ dependent component of the mobility, and assuming an electron interaction with only a single polar phonon with an energy of
34.1meV, the fits shown by the solid curves to the temperature dependence of the mobility of Figure 7.1 were obtained. The compensation ratios, θ, and alloy scattering potentials, ΔU, are given in the figure. We have neglected the compositional dependence of the ΔU, i.e. X(1-X)ΔU, preferring instead to quote an effective ΔU for the specific composition analysed. This can then be directly related to the ΔU's determined by Hayes (11), Marsh (133) and others (134, 135).

If we consider the results of Figure 7.1 we see that to obtain good agreement with experiment for all the carrier concentrations we are forced to allow the alloy scattering potential to depend on the sample carrier concentration. The alloy scattering potential decreases as the carrier concentration increases. For the sample with highest mobility and lowest carrier concentration we find that good agreement is obtained with ΔU=0.51eV. This result is midway between that of ΔU=0.6eV of Hayes et al (11) and the value of ΔU=0.42eV reported by Marsh et al (133) although the measured mobilities are comparable. We have, however, included a deformation potential of 5.9eV (30), whereas Marsh used a value of 18eV (133) while Hayes et al (11) and Greene et al (134) neglected deformation potential scattering altogether. It is interesting to note that the carrier concentration in all but the lowest carrier concentration sample is effectively constant in the temperature range 77-450K, while for the sample with carrier concentration of 3.6x10^15cm^-3 the increase in carrier concentration is apparently corrected by including self-consistent Hall scattering factor corrections. It can be noted that the Hall scattering factor corrections implicit in Figure 7.2 are in good agreement with other calculated values (30), but are larger than observed experimentally (136). However, such corrections in alloy semiconductors may be
Figure 7.1  Temperature dependence of the Hall mobility in six samples of LPE GaInAs. Solid curves—predicted dependence from ISBE with (a) $n_H = 3.6 \times 10^{15} \text{cm}^{-3}$, $\theta = 0.05$, $\Delta U = 0.51 \text{eV}$, (b) $n_H = 5.1 \times 10^{16} \text{cm}^{-3}$, $\theta = 0.15$, $\Delta U = 0.37 \text{eV}$, (c) $n_H = 1.5 \times 10^{17} \text{cm}^{-3}$, $\theta = 0.26$, $\Delta U = 0.30 \text{eV}$. 
Figure 7.2 Dependence of carrier concentration on reciprocal temperature for six LPE GaInAs samples. Solid curves—ISBE calculated Hall carrier concentration. Dashed curves—self-consistent ISBE calculated drift carrier concentration.
inaccurate. Also, the cause of the variation in $\Delta U$ with carrier concentration remains unclear. Both effects may be due to an inadequate theory for scattering due to alloy disorder. If this were the case Hall scattering factor corrections determined by including this model of alloy scattering may be incorrect. The variations of $\Delta U$ with carrier concentration will be discussed further in the next section. However, it should be noted that the original theory on which the present model is based, was associated with the effects of substitution in dilute alloys$^{80}$. It seems unlikely that an alloy in which "substitutional" atoms amount to ~50% is necessarily well described by such a theory. Further progress in this area awaits a new, more rigorous formulation of scattering due to alloy disorder.

7.2.3 Pressure Dependence of Electron Mobility in GaInAs.

Bearing the cautionary words of the last section in mind we measured the pressure dependence of the Hall mobility and carrier concentration and the results are shown in Figures 7.3 and 7.4 respectively. Only the two samples with highest 77K mobilities show any trap-out of carriers with pressure. However, just as for some GaAs and InP samples, such small changes in carrier concentration have a negligible affect on the pressure dependence of the Hall mobility shown in Figure 7.3. It can be seen that the pressure dependence of the mobility is larger for this material than for either GaAs or InP. We have calculated the pressure dependence of the Hall mobility for one sample from each of the three layers using an ISBE with alloy scattering, and these are shown by the solid curves in Figure 7.3. Similar calculations but assuming
space-charge rather than alloy scattering are shown by the dashed curves. Note that we have not incorporated the high non-parabolicity measured by Sarkar and Nicholas\(^{121}\) in these calculations, which is a good approximation for all but the highest carrier concentration sample considered here.

For the samples with carrier concentration \(\sim3.5\times10^{16}\text{cm}^{-3}\) it is interesting to note the large difference in the pressure dependence of the mobility, although there is no significant difference between the two as a function of temperature. This result gives a clear example of the care which must be taken in eliminating spurious data. We found that the high pressure dependence of the mobility in the \(3.6\times10^{15}\text{cm}^{-3}\) sample was due to a highly pressure sensitive asymmetry between adjacent pairs of contacts on the clover leaf sample. This was the only sample measured where such an effect was observed, although the cause remains unclear. Obviously the results obtained for the pressure dependence of the mobility in this sample cannot be relied upon.

For the two samples with carrier concentrations of \(\sim5.1\times10^{16}\text{cm}^{-3}\) the measured pressure dependence of the mobility is rather similar and lies close to the dashed curve, labelled (b), indicating that the predicted pressure dependence of the mobility assuming space-charge scattering is important gives the best agreement with our results. This is in contrast to the conclusions of Hayes et al\(^{11}\). Alternatively, if we assume that scattering associated with alloy disorder is significant the above results then indicate the inadequacy of the theoretical model presently used for alloy scattering.

For the sample with a carrier concentration of \(1.2\times10^{17}\text{cm}^{-3}\), the mobility decreases faster than predicted, even using the ISBE with alloy scattering included. Again this discrepancy may be due to an inadequate model of alloy
Figure 7.3 Pressure dependence of the Hall mobility in five LPE GaInAs samples normalized to atmospheric pressure. Solid curves- ISBE calculation with alloy scattering. Dashed curve- ISBE calculation with space-charge scattering. Curves are for samples with
(a) $n_H=3.6 \times 10^{15} \text{ cm}^{-3}$, $\theta=0.05$, $\Delta U=0.51\text{eV}$,
(b) $n_H=5.1 \times 10^{16} \text{ cm}^{-3}$, $\theta=0.15$, $\Delta U=0.37\text{eV}$,
(c) $n_H=1.2 \times 10^{17} \text{ cm}^{-3}$, $\theta=0.26$, $\Delta U=0.30\text{eV}$.
Figure 7.4  Pressure dependence of the Hall carrier concentration in five LPE GaInAs samples normalized to atmospheric pressure.
scattering. Note that the inclusion of the large non-parabolicity determined by Barkar and Nicholas enhances the disagreement between theory and experiment, as non-parabolicity reduces the pressure dependence of the mobility. Alternatively one can speculate that at such high carrier concentrations impurity correlation effects are becoming important, as was observed in GaAs and InP and which generally lead to an increased pressure dependence of the mobility. The occurrence of such an effect would also result in a modified alloy scattering potential as a function of carrier concentration if not taken into account. A combination of all these effects is most probable and the resulting analysis is likely to be complex. However, as an initial study it would be interesting to undertake high pressure transport measurements on very high carrier concentration GaInAs.

7.3 Pressure Dependence of the Hall Mobility in InSb.

7.3.1 Introduction.

The pressure dependence of the electron Hall mobility in InSb has been measured and analysed previously by Tatham. However, his analysis was limited to a Matthiessen's rule approach and recently it has been suggested by Zawadzki and Wlasak that the pressure dependence of the dielectric constants may be very large in this material. They had previously been assumed to be independent of pressure by Tatham. Consequently we discuss in the rest of this chapter a revised analysis of his results.
7.3.2 Pressure Dependence of the Carrier Concentration and Mobility.

The two samples of InSb measured by Tatham\(^{22}\) were bulk grown and had carrier concentrations and mobilities at 77K of \(5.3 \times 10^{13} \text{cm}^{-3}\) and \(5 \times 10^{5} \text{cm}^{2}/\text{Vs}\), respectively. This carrier concentration is \(\sim 10^2\) larger than the intrinsic carrier concentration at this temperature and consequently we assumed this value for the exhausted extrinsic carrier concentration. At 300K the carrier concentration and mobility were \(1.6 \times 10^{14} \text{cm}^{-3}\) and \(7.6 \times 10^4 \text{cm}^{2}/\text{Vs}\), respectively. This carrier concentration is due to intrinsic carriers, but also results in an equivalent number of holes being generated in the valence band. This would be expected to complicate the measurement because of the two carrier nature of the sample. Under these conditions the conductivity and Hall coefficient are given by\(^{44-51}\)

\[
\sigma = n\mu_e + p\mu_h, \tag{7.3-1}
\]

and

\[
R_h = \frac{p\mu_h^2 - n\mu_e^2}{e(n\mu_e + p\mu_h)^2}, \tag{7.3-2}
\]

respectively. However, the high effective mass of holes, and consequently their low mobilities mean that they can safely be neglected. The holes however, also act as ionized impurities and enable electron-hole scattering to become important at sufficiently high hole concentrations. For a hole concentration of \(1.6 \times 10^{14} \text{cm}^{-3}\) the electron-hole scattering limited mobility as determined by equation 3.4-5 gives a value of \(\sim 7.0 \times 10^5 \text{cm}^{2}/\text{Vs}\), and thus contributes \(\sim 10\%\) of the scattering rate at 300K. Although electron-hole scattering is important at room temperature the mobility measured indicates that the
mobility is not just limited by electron-hole and polar-phonon scattering. We found good agreement provided a deformation potential of 15.0 eV was used. This is somewhat larger than that used by Rode, but is in very good agreement with the value of 14.6 eV used by Zawadzki and Symanska. Even with this deformation potential, mobilities as low as 5x10^{15} \text{cm}^2/\text{Vs} at 77K indicate that the value of N_z was considerably higher than the measured extrinsic carrier concentration. We obtained good agreement assuming a value for N_z of 1.1x10^{15} \text{cm}^{-3} indicating that the samples were highly compensated.

The experimental results obtained by Tatham for the pressure dependence of the Hall carrier concentration and mobility in the two samples of InSb are plotted in Figures 7.5 and 7.6, respectively. The carrier concentration of Figure 7.5 is shown to decrease by almost two orders of magnitude in 16 kbars. This is directly related to the pressure dependence of the direct band gap. For an intrinsic semiconductor the carrier concentration is given by:

\[ n_s = (N_cN_v)^{1/2} \exp \left[ \frac{-E_g}{2k_B T} \right] \]

where \( N_c \) and \( N_v \) are the effective density of states in the conduction and valence bands respectively, and are given by an expression of the form:

\[ N_c = \frac{2\pi m^*k_BT}{\hbar^2} \]

By using the measured pressure dependence of the electron effective mass and assuming that the density of states effective mass for holes was independent of pressure, Tatham showed that the results of Figure 7.5 were well described.
Figure 7.5 Pressure dependence of the Hall carrier concentration in two samples of InSb normalized to atmospheric pressure. Solid curve—calculated dependence assuming the pressure coefficients of $E_0$ and $m^*$ discussed in the text.
assuming a band gap pressure coefficient of 14.6 meV/kbar as indicated by the solid curve in Figure 7.5.

Using this value for the band gap pressure coefficient and the measured value of the pressure dependence of the electron effective mass of 6.2%/kbar, we calculated the pressure dependence of the Hall mobility using the ISBE, shown by the solid curve in Figure 7.6. For reference the pressure dependence of the mobility \( \sim m^2 - 3/2 \) is shown by the dot-dashed curve in the figure. This corresponds to the predicted pressure dependence assuming that only phonon scattering processes are significant. The ISBE analysis included all the relevant electron scattering mechanisms but assumed that the high and low frequency dielectric constants were independent of pressure, as was initially considered by Tatham. However, unlike Tatham's analysis, the solid curve in Figure 7.6 does not describe the measured pressure dependence of the Hall mobility at all well. More importantly it underestimates the pressure dependence of the mobility.

Tatham found that including electron-hole scattering limited mobility at atmospheric pressure gave good agreement with the results of Figure 7.6. The importance of such a mechanism decreases quickly with increasing pressure due to fast decrease in the carrier concentration. This results in a decreased pressure dependence of the mobility compared with the dot-dashed curve of Figure 7.6. Indeed the \(-10\%\) contribution of electron-hole scattering when added to the dot-dashed curve does give quite good agreement with the experimental results as indicated by the dot-dot-dashed curve. This however, is still rather different to that calculated using the ISBE, which also includes electron-hole scattering. The difference between the two curves is due to the high non-parabolicity in InSb. This results in an effective mass
Figure 7.6  Pressure dependence of the Hall mobility in two samples of InSb normalized to atmospheric pressure. Solid curve- ISBE calculated pressure dependence with constant dielectric constants. Dot-dashed curve- predicted dependence of $\mu = n^{*-3/2}$. Dot-dot-dashed curve- Matthiessen's rule analysis. Dotted curve- ISBE calculation with pressure coefficients of $\varepsilon_s$ and $\varepsilon_\infty$ of Zawadzki and Wlasak (48). Dashed curve- ISBE calculated best fit with $\varepsilon_s$ and $\varepsilon_\infty$ decreasing by 12% in 9kbar.
which is quite strongly energy dependent. The changes in the electron distribution that occur as the carrier concentration decreases with applied pressure can be thought of as decreasing the effective pressure dependence of the electron effective mass. This was not included in Tatham's analysis. Clearly then it seems that the good agreement obtained previously by Tatham for InSb was in error. An ISBE analysis which takes into account accurately the energy dependence of the effective mass gives a pressure dependence of the Hall mobility which is less than that observed experimentally.

As has been mentioned previously Zawadzki and Wlasak have found that, to explain the magneto-optic results on shallow donors in InSb, a highly pressure dependent dielectric constant had to be included. They assumed that both the high and low frequency dielectric constants decreased by ~10% in 9kbar. Using similar values for the pressure dependence of the dielectric constants and extrapolating to 15kbars we obtained the dotted curve in Figure 7.6. Clearly the agreement is significantly improved. The dashed curve also shown was obtained by increasing the pressure dependence of the dielectric constants still further so that both decreased by ~12% in 9kbar. A note of caution should be observed here, as any difference in the pressure dependences of ε₁ and ε₁₁ can have a significant effect on this result. However, assuming that ε₁ and ε₁₁ vary by the same percentage as a function of pressure is a reasonable first approximation, and our analysis clearly supports a highly pressure dependent dielectric constant in InSb.

7.4 Conclusions.

We have shown that the interpretation of the temperature
dependent component of the mobility proportional to $T^{-1/2}$ as being due to either alloy or space-charge scattering in GaInAs has not been determined conclusively. The pressure dependence of the mobility in pure material is well described if space-charge scattering is included. Alternatively, one can use the discrepancy between the results and the theory assuming alloy scattering as evidence of the inadequacy of the theory of alloy scattering presently used. At high carrier concentrations an increased pressure dependence of the mobility is observed, as in GaAs and InP. Further measurements on highly doped GaInAs would be of interest and might reveal effects associated with correlated impurity distributions.

For InSb, Tatham's analysis, which ignored the effects of non-parabolicity was shown to be incorrect. However, the pressure dependence of the mobility in intrinsic InSb at room temperature is not well described by the ISBE, even with the inclusion of electron-hole scattering, if the dielectric constants are assumed independent of pressure. A large decrease in the high and low frequency dielectric constants, ~12% in 9kbars, is required to give good agreement between the predicted pressure dependence of the mobility calculated using an ISBE and the experimental results. This agrees quite well with the pressure coefficients of the dielectric constants determined by Zawadzki and Wlasak.
CHAPTER 8.

TEMPERATURE AND PRESSURE DEPENDENCE OF THE ELECTRON MOBILITY IN Ge, Si, and GaP.

8.1 Introduction.

In this last chapter of experimental results, we investigate briefly the pressure dependence of the electron mobility in three indirect gap semiconductors, namely Ge, Si, and GaP, using the convenient if less accurate Matthiessen's rule technique. As we have already indicated in chapter 2, the pressure dependence of the electron effective mass is generally smaller in indirect gap materials. Also, there are several degenerate minima at the L and X points and consequently, we might expect to see effects not observed previously, particularly those associated with intervalley scattering. Measurements as a function of pressure have been undertaken previously on Ge\textsuperscript{137} and Si\textsuperscript{138}. However, no measurements have been published to the authors' knowledge, on the pressure dependence of electron transport in GaP. The results obtained for the temperature dependence of the Hall mobility and carrier concentration of one sample of Ge, Si, and GaP are shown in Figures 8.1 and 8.2 respectively. The pressure dependence of the Hall mobility of the same samples is shown in Figure 8.3. The results obtained for each material are discussed in the following sections.

8.2 Electron Mobility in Ge.

The transport properties of n-type Ge at atmospheric pressure are well understood\textsuperscript{139}. Intravalley scattering
Figure 8.1 Temperature dependence of the Hall mobility for samples of Si, Ge and GaP. Curves— theoretical drift mobilities calculated using Matthiessen's rule.
Figure 8.2 Dependence of carrier concentration on reciprocal temperature for samples of Si, Ge and GaP. Dashed curve - temperature dependence of intrinsic carrier concentration in Ge. Solid curve - best fit to GaP data using equation 2.3-2 with $E_d=97\text{meV}$ and $\theta=0.1$. 
Figure 8.3 Pressure dependence of the Hall mobility in Ge, Si and GaP normalized to atmospheric pressure. Solid, dashed and dot-dashed curves—predicted pressure dependence of the drift mobility assuming $\nu_1/\nu_0$ is constant. Dotted curve—predicted pressure dependence of the drift mobility in GaP with $\nu_1/\nu_0$ increasing by 0.08%/kbar.
occurs via ionized impurities, and acoustic and non-polar optical modes. Intervalley scattering proceeds via LA and LO phonons of similar energy\(^{32}\). Consequently, following Rode\(^{32}\) we combined non-polar optical and intervalley scattering and assume that this can be described by a single phonon of 32.9meV. With this approximation and using the material parameters given in Tables 2.2 and 2.3 we obtained the curve for the Ge sample shown in Figure 8.1. Clearly rather good agreement is obtained for temperatures \(\leq 300K\). Above \(\sim 350K\), the agreement is not as good. However, it can be seen from Figure 8.2 that in this temperature range the sample is becoming intrinsic, as indicated by the dashed curve. Consequently it might be thought that, as for InSb discussed previously, electron-hole scattering might also be included. However, the situation is more complicated than this as the assumption that the hole mass is much greater than the electron mass, made for InSb, does not hold so well for Ge. Consequently, at temperatures above \(\sim 350K\) two carrier transport should be considered. For the present however, we are concerned with the pressure dependence of the mobility at 300K, where the contribution from intrinsic carriers is negligibly small as indicated by the fact that no decrease in the carrier concentration was observed as a function of pressure below \(\sim 5kbar\), after which it was seen to decrease by \(\sim 3\%\) to \(8kbar\). From Figure 8.1 it is apparent that acoustic phonon scattering is the most important mechanism at room temperature, with intervalley scattering somewhat less significant. Using the pressure coefficient of the direct gap at the L point of 7.5meV/kbar\(^{134}\) we have calculated the pressure dependence of the transverse effective mass in the L minima using equation 2.2-3. Assuming that the longitudinal effective mass is independent of pressure, results in a
pressure dependence of the density of states effective mass of 0.21%/kbar. Including also the pressure dependence of the longitudinal elastic constant given in chapter 2 results in the solid curve shown in Figure 8.3. At low pressures the agreement with experiment is not unreasonable, but at pressures above ~5kbar the experimental results decrease more swiftly than the theoretical curve. This may be due to the influence of additional non-equivalent intervalley scattering involving the high density of states A minima which approach the L minima quite swiftly with increasing pressure\(^{23}\). However, such effects have not been considered further. Instead we note that Ahmad\(^{23}\) has measured the mobility as function of pressure in the range 0-70kbar and observes that the mobility is almost constant above ~40kbar, when all the electrons are located in the A minima. He also performed Hall effect and resistivity measurements, as a function of temperature, at these high pressures and was able to show that intervalley scattering was the dominant scattering mechanism for electrons around room temperature. Clearly it would be interesting to measure in more detail the pressure dependence of the mobility of electrons confined to the A minima in Ge. However, electrons in Si at atmospheric pressure are confined to the A minima and consequently measurements made on one Si sample, by Saxena, are discussed in the next section. We can conclude however, that for the L minima in Ge both the temperature and pressure variation of the mobility indicate that it is dominated by acoustic deformation potential scattering.

8.3 Electron Mobility in Si.

The results obtained for the temperature dependence of the
Hall mobility and carrier concentration in one Si sample are shown in Figure 8.1 and 8.2 by the square data points. Harrison has shown that non-polar optical scattering is negligible. Intervalley g-type scattering occurs via LO phonons at approximately one third of the way to the Brillouin zone edge in the X direction while intervalley f-type scattering occurs via LA and TO phonons at a point on the Brillouin zone edge 0.6 of the way from the X point to the K point (see Figure 2.2). Following Long we assign energies to these phonons of 16.4meV and 54.3meV respectively. See Figure 2.3 for the phonon dispersion curve of Brockhouse for Si. Using these energies together with the ratio of the coupling strengths of electrons to acoustic and intervalley phonons, determined by Long and given in Table 2.4, together with the other material parameters given in chapter 2 we obtained the curve for Si shown in Figure 8.1. Clearly the agreement is quite good, and in this case, in contrast to the Ge sample studied previously we observe that intervalley scattering is the most significant scattering mechanism at room temperature. We show the pressure dependence of the mobility in the Si sample by the square data points in Figure 8.3 where the carrier concentration remained constant over the entire pressure range considered. We note that the mobility increases with increasing pressure, and that this is the first material considered in which such a dependence has been observed.

Using the pressure dependence of the direct gap at the X point of 3meV/kbar, and adjusting for the minima lying ~0.83 of the way to the zone boundary, by linearly interpolating between the pressure coefficients of the direct gaps at the Γ and X points we calculated the pressure dependence of the transverse effective mass. Assuming that the
longitudinal effective mass is independent of pressure we calculate the pressure dependence of the density of states effective mass to be 0.025%/kbar. Note that this is a factor of 8 smaller than that calculated for Ge and a factor of 20 times smaller than that observed in InP, which has the smallest pressure dependence of the effective mass of any of the direct band gap semiconductors considered. Consequently it is not surprising that the pressure dependence of the mobility is somewhat different to that measured previously as it is no longer the pressure dependence of the effective mass that is dominant but other parameters such as the phonon energies.

To calculate the theoretical pressure dependence of the mobility we followed the analysis of Rodé[30] and Long[31] including the effect of both the g-type and f-type scattering phonons. Their variation with pressure was determined from the data of Weinstein and Piermarini[32]. They found a non-linear pressure dependence of the phonon energies over the pressure range 0 to ~100kbar. However, for pressures in the range 0-8kbar their variation is to a good approximation linear. We determined from their data pressure coefficients for the f-type (16.4meV) and g-type (54.3meV) scattering phonons of -0.1%/kbar and 0.2%/kbar, respectively. The result obtained using a Matthiessen's rule analysis is shown by the dashed curve in Figure 8.3. We have included the pressure dependence of the longitudinal elastic constant, given in chapter 2 but assume that the ratio \( \frac{w_\perp}{w_\parallel} \) is independent of pressure. For Si this is a good approximation as the pressure coefficients of the longitudinal sound velocity and the intervalley phonon energy almost cancel. The agreement between theory and experiment determined is very good, and clearly supports the importance of intervalley scattering in the A minima in Si. Another material in which intervalley scattering is important
Electrons in GaP, as well as being scattered by acoustic and intervalley modes and ionized impurities are also scattered by the polar phonon interaction that is important in the other III-V semiconductors considered previously. As was described in chapter 3, polar phonon scattering is not well described in the relaxation time approximation, but unlike the other compound semiconductors considered in this thesis, it is not the dominant scattering mechanisms in GaP at room temperature. Consequently, we have continued to adopt the simple Matthiessen's rule analysis as used previously for Si and Ge. Following the work of Rode 39, we have assumed that the conduction band minima in GaP are located at the Brillouin zone edge at the X point and that intervalley scattering occurs via 30.9meV LA phonons. Using this information and the material parameters given in Tables 2.3 and 2.4 we have calculated the temperature dependence of the mobility shown by the curves for GaP shown in Figure 8.1. Note that to obtain good agreement with the experimental data, obtained by Saxena, over the whole temperature range although we had to include space-charge scattering as was found to be necessary by Tayama et al.41. The temperature dependence of the carrier concentration shown in Figure 8.2 is typical of GaP, and the values of $E_o$ and $\Theta$ determined from a least squares fit using equation 2.3-2 are given in the figure. It can be noted that the value of $E_o=97$meV is typical of values obtained by other authors.41.

The temperature dependence of the mobility shown in Figure
E3.1 indicates that the mobility at 300K is limited predominantly by intervalley, polar phonon, and space-charge scattering. However it is apparent that the increase in mobility in 8kbar is somewhat larger for GaP than for Si. To analyse these results we calculated the pressure dependence of the transverse effective mass using equation 2.2-3 and the pressure dependence of the direct band gap at the X point of 3meV/kbar determined by Zallen and Paul \(^{139}\). Assuming that the longitudinal effective mass is independent of pressure we found that the density of states effective mass increases by 0.04%/kbar. Assuming initially that \(w_A/w_m\) was independent of pressure, but including the pressure dependence of the longitudinal elastic constant, assumed to be intermediate between the value determined for Si and for GaAs we obtained the dashed curve in Figure 8.3. If the pressure dependence of the ratio of \(w_A/w_m\), calculated from equation 2.4-1, but assuming that the pressure dependence of \(E^a\) and \(D_m\), is negligible, we obtained the dotted curve shown. The agreement with the dashed curve is very good, but is still within the experimental error for the dotted curve. Clearly then we observe that for the GaP sample considered here we obtain consistently good agreement with both the temperature and the pressure dependence of the mobility, even though a number of assumptions have been made and space-charge scattering has to be incorporated. It might be noted that the high carrier concentration in this sample means that impurity correlation effects may be important, but because of the low pressure dependence of the electron effective mass, high pressure measurements are not so sensitive to its presence. Further work is necessary to check if it is important in this material.
7.5 Conclusions.

It is very interesting to observe the totally different pressure dependence of the mobility observed in Si and GaP, both of which increase with increasing pressure, while in Ge, the mobility decreases slowly. It is interesting to note also that in the latter material the change of the lowest minima from L to A at pressures of ~40 kbar, means that in this material we should be able to observe both an increasing and a decreasing pressure dependence of the mobility, depending upon which type of minima the electrons occupy. Such an experiment is planned for the near future. The use of Matthiessen's rule to analyse the data is clearly unsatisfactory, particularly for GaP, and consequently the inclusion of intervalley scattering into the ISBE code is being considered, so that a more rigorous analysis of the experimental results can be made.
In this thesis we have reported the systematic measurement of the pressure and temperature dependence of the Hall mobility in a variety of group IV and III-V semiconductors.

We have shown that for the indirect band gap semiconductors, Si, Ge and GaP, the pressure dependence of the mobility is small, and that it is in quantitative agreement with standard theory given the relevant pressure coefficients of the electron effective masses and phonon energies.

In InSb we have shown that the pressure dependence of the mobility is only well described theoretically if a highly pressure dependent dielectric constant is included. For the alloy GaInAs, the mobility component proportional to $T^{-1/2}$ is found to have a pressure dependence which is close to that predicted assuming space-charge rather than alloy scattering is significant. However, the status of alloy and space-charge scattering remains unclear as the disagreement with alloy scattering may also be interpreted as being associated with an inadequate model of electron scattering due to alloy disorder.

For relatively pure GaAs and InP, consistent agreement between theory and experiment both as a function of pressure and temperature can be obtained provided deformation potentials of 9.0eV and 11.5eV are included respectively. We have also shown that in so doing, a self-consistent analysis including Hall scattering factor corrections must be included.

At high carrier concentrations in GaAs, InP and GaInAs an increase in the pressure dependence of the Hall mobility is observed which is in excess of that predicted theoretically assuming the Brooks-Herring model of scattering from ionized
impurities. For GaAs and InP, analysis including extrinsic scattering mechanisms, higher Born approximations, multiple scattering corrections and phase shift calculations in which the Born approximation is not invoked have been described. All such effects were shown not to be responsible for the increased pressure dependence of the Hall mobility observed. However, by including the theory of Yanchev et al. for scattering from a correlated impurity distribution very good agreement was obtained. Further evidence for the importance of scattering from such impurity distributions was obtained by studying GaAs grown by MBE at temperatures below the correlation temperature, T₀, and GaAs subjected to neutron transmutation doping in which the dopant atoms are randomly distributed. Both techniques produced samples in which the pressure dependence of the mobility was very close to that predicted using the ISBE including scattering from ionized impurities in the Brooks-Herring model.

A number of areas of further work have been suggested throughout the text. However, the most interesting of these is likely to be the extension of the pressure dependent transport measurements made here to lower temperatures, to investigate further the pressure dependence of the mobility associated with scattering from ionized impurities.
APPENDIX A.

The band gaps indicated in Figure 2.3 were calculated using the prescriptions given by Van Vechten and Bergstresser\(^{(9)}\) while their pressure coefficients were determined by the expressions given by Camphausen et al\(^{(10)}\). The prescriptions are:

1. Homopolar energy gaps scale with nearest neighbour distance, and can be written as,

\[
E_{\text{h,n}} = E_{\text{h,n}}^0 \cdot \left[ \frac{d}{d_0} \right]^{-\delta},
\]

where \(E_{\text{h,n}}^0\) is the homopolar energy gap of silicon, \(d\) and \(d_0\) are the nearest neighbour distances of the material under consideration and silicon respectively and \(\delta\), the exponent, is given in Table A1.

2. The direct energy gaps \(E_i, i=0,1, 2\), in the absence of d-core electrons are given by,

\[
E_i = E_{\text{h,n}}^0 \left[ 1 + \left( \frac{C}{E_{\text{h,n}}^0} \right)^2 \right]^{1/2}.
\]

3. The direct energy gaps \(E_0, E_1, E_2\) are affected by d-core electrons and are given by,

\[
E_i = (E_{\text{h,n}}^0 - (D\Delta - 1) \Delta E_i) \left[ 1 + \left( \frac{C}{E_{\text{h,n}}^0} \right)^2 \right]^{1/2}.
\]

For energy gaps, \(E_i\), Lawaetz\(^{(140)}\) indicates that \(C' = 1.25C\) should be used instead of \(C\).

4. The ionisation potential, \(IP\), i.e. the difference
between the top of the valence band at the \( \Gamma \) point and the vacuum level is given by,

\[
IP = IP_n \left[ 1 + \left( \frac{C}{IP_n} \right)^2 \right]^{1/2},
\]

where \( IP_n \) is given by an analogous expression to (1).

(5) The effect of d-core electrons is described by two terms \( (D_{av-1}) \) and \( \Delta E_i \). The \( \Delta E_i \) are a function of the nearest neighbour distance only and scale as per (1). \( (D_{av-1}) \) gives a measure of the coupling between the d-core electrons and the valence band. Camphausen et al gives,

\[
(D_{av-1}) = R_a (1 - f_i) X, \quad \frac{d}{[d_{av}]} Y, \quad -A5
\]

\[
f_i = \frac{C^2}{E_{av}^2 + C^2}, \quad -A6
\]

and \( E_{av} \) scales as in (1). Camphausen et al give \( X \approx 2.4 \) and \( Y \approx 13.0 \).

(6) According to Van Vachten the energy of the top of the valence band at \( X \) relative to the vacuum level is independent of \( C \), but we have used the modified expression of Camphausen et al because of the improved pressure coefficients of the band gaps thus obtained. Camphausen et al use,

\[
E_{X,av} = E_{X,av,n} \left[ 1 + \left( \frac{C}{E_{X,av,n}} \right)^2 \right]^{1/2}, \quad -A7
\]

where again \( E_{X,av,n} \) scales as (1).

(7) Van Vachten describes the valence band edge at the \( L \) point as being midway between the values at \( \Gamma \) and \( X \).
Camphausen et al argue, however, that the expression below gives better agreement.

\[ E_{L_3} = IP + 0.4(E_{X_2} - IP). \]  

(8) The splitting of the conduction band \( X \) levels \( X_1 \) and \( X_3 \) is proportional to \( C \):

\[ E_{X_3} - E_{X_1} = 0.071C. \]

(9) To calculate the pressure coefficients of the band gaps we used the expression of Camphausen et al:

\[
\frac{dE_i}{dP} = \left[ \frac{dE_i}{dP} - \frac{\Delta E_i}{dP} \frac{d(D_{av}-1)}{dP} - (D_{av}-1) \right] \frac{d\Delta E_i}{dP} \times \\
\left[ 1 + \left( \frac{C}{E_i} \right)^2 \right]^{1/2} + \left[ 1 + \left( \frac{E_i - 1}{C} \right)^2 \right] \left[ \frac{1}{C} \frac{dC}{dP} - \frac{1}{E_i} \frac{dE_i}{dP} \right],
\]

and assumed that \( C \) was independent of pressure.

The pressure coefficients of the band gaps were calculated using the bulk compressibility,

\[ \kappa = -\frac{1}{V} \frac{dV}{dP}, \]

where as \( V \propto d^3 \), obviously,

\[ \frac{dd}{dP} = -k_d \frac{d}{3} \]

Thus by differentiating the previous expressions, A1-A9, with respect to 'd' as appropriate, all the pressure coefficients described before were easily obtained.
Table A1. Energies for Predicting Chemical Trends.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value for Si (eV)</th>
<th>Exponent $\delta$</th>
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<td>$I_{Pn}$</td>
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<tr>
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<td>1.67</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$E_n$</td>
<td>4.77$^b$</td>
<td>2.50$^b$</td>
</tr>
</tbody>
</table>

All values taken from Van Vechten and Bergstresser$^{(a)}$ except for $^a10$ and $^b141$. 
REFERENCES.


82. R.A. Faulkner, Phys. Rev. 175, 991 (1968).


