ELECTRON TRANSPORT PROPERTIES OF

GaAs, Ga$_{1-x}$Al$_x$As AND InP

by

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Abstract

Measurements of low field Hall coefficient and electrical conductivity have been made as a function of temperature in the range from room to 500, 230 and 260°C for samples of GaAs, Ga$_{1-x}$Al$_x$As and InP respectively. For some InP samples, magnetoresistivity has been measured as a function of magnetic field at room temperature. All the samples used in this work are n-type and for the case of GaAs and Ga$_{1-x}$Al$_x$As, some of the samples chosen have been heavily doped to allow the study of the three conduction band structure, viz. the $\Gamma_1$, $L_1$ and $X_1$ bands, and the associated transport properties. In the theoretical analysis, polar and non-polar optical phonon, acoustic phonon, piezoelectric mode, interband, intervalley, ionized impurity, space charge and alloy scattering mechanisms have been taken into account. The scattering calculations have been carried out using the Fletcher and Butcher method (72F2) for solution of the Boltzmann equation to determine the effect of polar optical scattering and the relaxation time approximation for all other scattering mechanisms.

For GaAs, all transport measurements have been explained satisfactorily with a $\Gamma_1 - L_1 - X_1$ conduction band model and all three bands have had to be taken into account to obtain a fit to the high temperature data in this work. The values of acoustic deformation potentials determined in this study are $16.0 \pm 0.5$ and $12.5 \pm 0.5$ eV.
for the \( \Gamma_l \) and \( X_l \) bands respectively for GaAs. Interband scattering coupling coefficients giving the best fit to the experimental data have the values of \((8 \pm 1) \times 10^{10}\) and \((1.1 \pm 0.2) \times 10^{11}\) eV/m for the \( \Gamma_l - L_l \) and \( L_l - X_l \) band interactions respectively. Intervalley scattering is important in the \( L_l \) and \( X_l \) bands and the present work gives the coupling coefficients for the subsidiary bands to be \((5 \pm 2) \times 10^{10}\) eV/m. The assumptions that \( E_{DL} = E_{D\Gamma} \) and \( D_{TX} = D_{\Gamma L} \) have been found to be satisfactory here. The energy value of the \( L_l \) minima in GaAs has been determined from the analysis of three different sets of experimental data, high temperature and high pressure transport of GaAs and high temperature transport of the Ga\(_{1-x}\)Al\(_x\)As alloys, and the resulting values at 295 K are in the range 1.728 \(\sim\) 1.748 eV above the top of the valence band (\( \Gamma_{15} \)).

The analysis of the experimental data for the Ga\(_{1-x}\)Al\(_x\)As alloys indicates that a three-band model is required for \( x = 0 \sim 0.5 \), a two-band model (\( L_l \) and \( X_l \)) for \( x = 0.5 \sim 0.7 \) and a one-band model (\( X_l \)) for \( x = 0.7 \sim 1.0 \). The energy values of the \( L_l \) and \( X_l \) minima for this alloy system have been found to follow at 295 K the quadratic forms given by \( E_L = 1.734 + 0.574x + 0.055x^2 \) (in eV) and \( E_X = 1.911 + 0.005x + 0.245x^2 \) (in eV) where the energy is measured with respect to the valence band maximum. Band crossover points are close to each other in composition and energy at 295 K occurring at \( x = 0.405, 0.432 \) and 0.35 for the \( \Gamma_l - X_l, \Gamma_l - L_l \) and \( L_l - X_l \) crossovers respectively. Scattering parameters such as the acoustic deformation potentials \( (E_{DL}, E_{DX}) \) and
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In the case of InP, a one-band model is satisfactory and the values of low-frequency dielectric constant and acoustic deformation potential determined in this work are $12.5 \pm 0.1$ and $14.2 \pm 0.7$ eV respectively.

For pure samples of all three material considered, polar optical mode scattering predominates over the whole experimental temperature range. Interband scattering plays a significant role in restricting the carrier mobility when multiband effects occur.

The variation with temperature of the effective mass band gap which needed to be used here to explain the variation of effective mass in the $\Gamma_1$ band has found to be about two-thirds of the total band gap (optical gap) variation.
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CHAPTER I INTRODUCTION

GaAs and InP are binary III-V semiconductors possessing the zincblende structure and have their fundamental band gaps at the centre of the Brillouin zone. The direct gap semiconductors are of special importance in device applications such as microwave sources. However, the applications of binary semiconductor compounds are limited to some extent because their band structure cannot be varied to suit the application. This limitation has led to the recent development of III-V ternary alloys, for which the band structure and other semiconducting properties vary continuously between those of the two binary compounds. One of these alloys is the Ga$_{1-x}$Al$_x$As system which also has the zincblende structure and a direct-indirect band crossover at a certain composition.

Ehrenreich (60El) analyzed various existing experimental data on GaAs and suggested that the lowest subsidiary band minima have $\Delta_1$ symmetry and the next minima are far above the $\Delta_1$ minima. However, James et al. (68J1) showed from photoemission measurements that the second subsidiary band, the $L_1$ minima, is close in energy to the first subsidiary band minima, the $X_1$. Hence most of the transport experiments performed at high temperature, high pressure and high field have been explained in terms of the $\Gamma_1 - \Delta_1$ (or $X_1$) or $\Gamma_1 - \Delta_1$ (or $X_1$) - $L_1$ conduction bands in that order of increasing energy (72B1, 70P1, 70F1). However, Schottky-barrier electroreflectance experiments made
recently by Aspnes et al. (76A1) showed that the $L_1$ minima lie approximately $170 \pm 30$ meV below the $X_1$ minima in GaAs. To be consistent with this observation, the physical properties of GaAs must be described with a $\Gamma_1 - L_1 - X_1$ band model. Such a model is also supported theoretically by nonlocal pseudopotential calculations (74P1, 76C1).

In the case of the $Ga_{1-x}Al_x$ system, the fundamental band gap has been measured extensively using various methods (66B2, 69C1, 71B1, 76M2), but the results show a scatter in the measured values. Electrical transport properties have been analyzed in terms of the $\Gamma_1$ and/or $\Delta_1$ bands (74N1, 76M1) in this alloy system. According to the revised band structure for GaAs, however, the $L_1$ band minima can be expected to be near in energy to the $\Gamma_1$ minimum for some compositions in the direct gap region of the $Ga_{1-x}Al_x$ system and thus a three-band model is required in analyzing high temperature transport properties in this region.

Despite the long history of study of InP, the transport properties (75R2) and the subsidiary band structure (73P2) have not as yet been explained satisfactorily.

In this work, we are mainly concerned with d.c. low field electrical transport properties at high temperatures. The Hall coefficient and conductivity have been measured as a function of temperature
from room to 500, 230 and 260°C for all the samples of GaAs, Ga$_{1-x}$Al$_x$As and InP respectively. Higher temperatures than those limits were avoided because of the possible evaporation of the elements. All the samples used in this work exhibit n-type characteristics and some of the samples were heavily doped to allow, in the cases of GaAs and the Ga$_{1-x}$Al$_x$As alloys, observation of multi-conduction-band characteristics by exciting appreciable numbers of carriers into the higher lying conduction bands at the higher temperatures. Thus the first purpose of this work is to determine parameters characterizing the conduction band structure and the electron scattering process in the semiconductors concerned by analyzing the measured transport data.

In the electron transport calculations, most of the previous work has relied on the relaxation time approximation (R.T.A.). As indicated by Herring and Vogt (56H1) however, a relaxation time is not valid for the case of nonrandomizing inelastic scattering and thus the polar optical mode scattering is very poorly represented by the R.T.A. In most of the III-V direct gap semiconductors, polar optical scattering predominates in the case of the $\Gamma_1$ band and thus the transport properties can be described only qualitatively when the R.T.A. is used for the calculation of polar optical scattering at temperatures lower than the characteristic temperature defined by $\omega_o/k_B$, where $\omega_o$ is the longitudinal polar optical phonon energy and $k_B$ Boltzmann's constant. Recently Rode(75R2) wrote, "recent improvements in transport calculations allow quantitative comparisons with experiments which are
helpful in elucidating electron scattering mechanisms and in refining our knowledge of basic material constants". The improvements mentioned are the use of the iterative methods developed for the solution of the Boltzmann equation (70R1, 72F2, 74N1). For the present study we have chosen the iterative method of Fletcher and Butcher (72F2), which gives transport parameters as a function of magnetic field.

For the $\Gamma_1$ band calculations, we have assumed a non-parabolic band (57K1) and spherically symmetrical energy surfaces, while parabolic and spherical conditions have been assumed for the $L_1$ and $X_1$ bands. Admixture of s- and p-type electron wave functions has been included in the scattering calculations in the $\Gamma_1$ band to be consistent with the Kane type band structure (57K1). Fermi-Dirac statistics have been used for all bands concerned. Longitudinal polar optical phonon, longitudinal acoustic deformation potential, ionized impurity, space charge, interband and intervalley, piezoelectric and alloy scattering mechanisms have been taken into account depending upon material in this work.

Rather than explain the experiments qualitatively with existing parameter values, we have determined uncertain parameter values by adjusting them for precise fit to the measured quantities.

In the case of GaAs, the $\Gamma_1 - L_1 - X_1$ band ordering has been assumed and the parameters determined were the temperature coefficients
of the subsidiary band minima variation, acoustic deformation potential and interband and intervalley scattering coupling coefficients. Even at the highest temperature in our experiment, the carrier density in the X₁ band was too low to determine accurately the parameter values related to this band. For this case, previously published high pressure experimental data (70P1) has been analyzed to allow the relevant parameter values to be determined more accurately.

The L₁ and X₁ bands play a similar important role in the transport properties of those alloys of the Ga₁₋ₓAlₓAs system which show direct gap behaviour, as in the case of GaAs, and the energy values for the band minima have been determined in this work as a function of Al-concentration. Scattering parameters such as acoustic deformation potential and interband and intervalley coupling coefficients have also been treated as adjustable in this alloy system.

To explain the experimental data on the Hall coefficient and conductivity in InP we have adjusted the values of the low-frequency dielectric constant and acoustic deformation potential. In this material, previous work (73P2) on the band structure indicates that only the Γ₁ band has to be considered in the present experimental range. However, subsidiary band effects have been tried in the analysis to check a suggestion by Glicksman(59Gl), who observed <100> type anisotropic effects in his magnetoresistivity measurements. The resulting analysis has been compared with other experimental data on the magnetoresistivity
thermoelectric power, magnetoresistance mobility and Nernst-Ettingshausen coefficients for InP.

The theory necessary for the understanding of the present work will be reviewed in Chapter II, and some experimental aspects such as equipment, measuring techniques, sample preparations, etc. will be given in Chapter III. The following three chapters are devoted to a consideration of the three types of material, which are treated in this thesis. In each case, a review of published work is given first followed by a presentation of the present data and its analysis and finally a summary of the parameter values deduced.
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CHAPTER II THEORY

This chapter is devoted to a review of theory necessary for the understanding of the present work.

II-1 Band Structure

The III-V semiconducting compounds in the present work crystallize in the zincblende structure, which is composed of two interpenetrating face-centered cubic lattices with one sub-lattice containing group III atoms and the other group V atoms. The two sub-lattices are displaced by one quarter of a body diagonal. All of the samples used in this work show n-type electrical characteristics and this review will thus be restricted to conduction bands.

The energy $E$ of an electron in a semiconductor is a function of the wave vector $\mathbf{k}$ and the form of this dependence constitutes the energy band structure. If $E$ is plotted as a function of $\mathbf{k}$ for different directions in $\mathbf{k}$-space, for the case of a face centered cubic material, the band extrema are usually found to occur in special directions of high symmetry, such as the $<100>$ and $<111>$, as well as at the $\Gamma$ point. These extrema are shown in Fig. (II-1) where the band structure of GaAs is given as an example. If the $<100>$ minima occur at the Brillouin zone boundary in a cubic lattice, there will be three equivalent minima, and if the minima fall inside the zone, the number of equivalent minima is
six. The number of the equivalent <111> minima is four when they are at the zone edge, and eight if they occur within the zone. Each of these minima is characterized by equal energy surfaces which have cylindrical symmetry and are ellipsoidal in shape. The band at the Γ-point has a spherical energy surface to a good approximation and the structure is properly described by the Kane model (57K1).

A. Γ Band, Kane Model

All materials in this work, except some Ga_{1-x} Al_x As alloys with x > 0.4, have the lowest conduction band minimum at the Γ point and the valence band maximum at or near the Γ point and thus the Kane model is appropriate in this case.

With spin-orbit coupling included, the Schroedinger equation for an electron in a periodic potential V(r) is given by (55D1)

$$\left[ \frac{\hbar^2}{2m} + V(r) + \frac{\hbar}{4m^2 c^2} \left( \nabla \times \mathbf{P} \right) \cdot \mathbf{a} \right] \psi_k = E_k \psi_k$$  \hspace{1cm} (II-1)

where m is the free electron mass, \( \mathbf{P} \) and \( \mathbf{a} \) are momentum and spin operators respectively, \( \hbar \) is Planck’s constant divided by 2π, and \( E_k \) is the energy of a state with wave vector \( k \). The translational symmetry of the lattice requires that the wave functions be of the Bloch form,

$$\psi_k = U_k(r) e^{i k \cdot r}$$  \hspace{1cm} (II-2)
where $U_k(r)$, the cell-periodic function, satisfies the following equation

$$\left\{ \frac{p^2}{2m} + V(r) + \frac{k \cdot p}{m} + \frac{\hbar^2}{4m c^2} [\nabla V x p] \cdot \sigma + \frac{\hbar^2}{4m c^2} \right\} \cdot \sigma \cdot U_k(r) = E_k' U_k(r) \quad (I-3)$$

where $E_k' = E_k - \frac{\hbar^2 k^2}{2m}$.

A simplified Kane model neglects the fifth term in the above equation which represents the $k$-dependent spin-orbit interaction and turns out to be very small ($57k1$, $66k1$). The "small gap approximation" includes spin-orbit splitting and accounts for the interactions between the $\Gamma_1$ conduction band and $\Gamma_5$ valence bands. In this model the conduction band is doubly degenerate due to spin, a Kramers doublet, and the valence band consists of three Kramers doublets, the heavy-hole, light hole and spin-orbit split-off bands. In this analysis, Kane neglected the $k \cdot p$ interaction with more remote bands. The inclusion of the higher conduction and lower valence bands splits the Kramers doublet at points off the principal axes of symmetry and warps the constant energy surfaces so that they are no longer spherical. However, the splitting of the Kramers doublet is small for the $\Gamma_1$ band and the warped constant energy surface gives rise to a negligible amount of anisotropy in transport properties ($75r2$).
Kolodziejczak et al. (66K3) showed that the inclusion of higher and lower bands increases the non-parabolicity in the conduction band and thus the effective mass at high energies. This increase of nonparabolicity will be further discussed in the chapter treating GaAs but the result is negligible in the present study.

Kane restricted himself to the case of eight wave functions, two for the conduction band and six for the valence band. First order k-p perturbation theory leads to an 8 x 8 secular determinant whose solution near \( k = 0 \) is:

\[
E'[E'(E'_0-E_0)E'_1-E'_0A_0-k^2P^2(E'-2/3A_0)] = 0 \tag{II-4}
\]

where \( P \) is the momentum matrix element, \( E_0 \) is the principal gap and \( A_0 \) is the spin-orbit splitting of the valence band.

Assuming \( kP \ll E_0 \), Aubin (69A2) showed that a general solution for the conduction band, the \( \Gamma_1 \) band, with an arbitrary value of \( A_0 \), is

\[
E = \alpha k^2 + \frac{E_0}{2} \left[ (1 + \frac{\beta k^2 P^2}{E_0^2})^{1/2} - 1 \right] \tag{II-5}
\]

where \( \beta = \frac{4 + 8n/3}{1 + n} \), \( \alpha = \frac{\hbar^2}{2m} \), \( n = \frac{A_0}{E_0} \).

Eq. (II-5) gives the energy dependence of the cyclotron
effective mass in a non-parabolic band,

\[
\frac{1}{m^*} = \frac{1}{m} + (E_o^2 + \beta k^2 F^2)^{-\frac{1}{2}} \frac{p^2}{2\hbar^2} \tag{II-6}
\]

Thus at the bottom of the \( \Gamma_1 \) band, the effective mass is

\[
\frac{1}{m^*_0} = \frac{1}{m} + \frac{\beta p^2}{2\hbar^2 E_o} \tag{II-7}
\]

Combining this relation with that for \( \beta \), we obtain for the square matrix element \( F^2 \):

\[
F^2 = \frac{3\hbar^2 E_o (E_o + \Delta_o) \left( \frac{m}{m^*_0} - 1 \right)}{2m(3E_o + 2\Delta_o)} \tag{II-8}
\]

Eliminating \( F^2 \) and \( \beta \) from Eq. (II-5) we obtain

\[
E = \frac{\hbar^2 k^2}{2m} + \frac{E_o}{2} \left[ 1 + \frac{4\hbar^2 k^2}{2m E_o} \left( \frac{m}{m^*_0} - 1 \right) \right]^{\frac{1}{2}} - 1 \tag{II-9}
\]

For large \( E_o \) and \( m^* \ll m \), this equation reduces to the standard parabolic band, in which the effective mass is independent of energy,

\[
E = \frac{\hbar^2 k^2}{2m^*} \tag{II-10}
\]

Eq. (II-9) can be inverted to give \( k \) as follows

\[
k = \left( \frac{\hbar^2}{m^*_0} \right)^{\frac{1}{2}} \left[ 1 + \frac{2Em^*}{E_o m} - (1 + \frac{4Em^*}{E_o m} (1 + \frac{m^*}{m})^2) \right]^{\frac{1}{2}} \tag{II-11}
\]
Rewriting Eq. (II-4) and neglecting the first $E'$, we obtain

$$(E - a^2)(E + E_o + a^2)(E + E_o + a^2 + \Delta_o) - k^2 p^2 (E + E_o - a^2 + \frac{2}{3} \Delta_o)$$

$$= 0$$

For the case $E \gg a^2$, this relation becomes

$$E(E + E_o)(E + E_o + \Delta_o) - k^2 p^2(E + E_o + \frac{2}{3} \Delta_o) = 0$$

from which one obtains

$$k = \left[ \frac{E(E + E_o)(E + E_o + \Delta_o)}{(E + E_o + \frac{2}{3} \Delta_o)p^2} \right]^{\frac{1}{2}}$$

Strictly speaking the Kane model is calculated for absolute zero temperature. In this context, $E_0$ in the Kane equations should be replaced by $E_0(0)$, the band gap energy at 0 K.

It is known that the optical energy gap $E_o$ decreases with increasing temperature due to lattice dilation and electron-phonon coupling (51F1). Ehrenreich argued that the band curvature depends only on the lattice dilation and that at temperatures above zero, $E_0$ in the Kane model should be replaced by the "effective mass band gap" $E_0^*$ (57E1). The effective mass band gap $E_0^*$ will lie between $E_0(0)$ and $E_0$, and a convenient form of expression is (69C2)

$$E_0^* = E_0(0) - \frac{E_0(0) - E_0}{a}$$

(II-13)
where "a" is a parameter which determines the relative effect of lattice dilation and electron-phonon interaction on the band gap.

Varshni (67VL) has shown that for the most of diamond and zincblende type semiconductors, $E_o$ may be expressed as

$$E_o = E_o(0) + \frac{\alpha \hbar^2}{(\theta + T)}$$

(II-14)

where $\alpha$ and $\theta$ are constants which determine the band gap variation with temperature for a given material.

B. $L_1$ and $X_1$ Bands

The $L_1$ and $X_1$ bands play an important role in the electrical transport calculations for GaAs and Ga$_{1-x}$Al$_x$As in this work.

These bands have ellipsoidal constant energy surfaces characterized by effective masses $m_t$ and $m_l$ and for a single valley the energy near the band edge is given by (68S1)

$$E = \frac{\hbar^2}{2m_t} \left( \frac{2k_t^2}{m_t} + \frac{k_l^2}{m_l} \right)$$

(II-15)

where subscripts $t$ and $l$ stand for transverse and longitudinal and are defined with respect to the principal axes of the ellipsoidal energy surface. These bands can be, to a good approximation, treated as
parabolic and thus the effective mass value is independent of energy.

The density of states effective mass and conductivity
effective mass for a single ellipsoidal valley are given respectively
by (68S1)

\[
m^* = \left(\frac{m_L m_T}{m_T}\right)^{1/3}
\]
(II-16)

and

\[
\frac{1}{m_c} = \frac{1}{3} \left(\frac{2}{m_t} + \frac{1}{m_L}\right)
\]
(II-17)

Cardona and Greenaway showed that the k.p perturbation theory
by Kane can be applied to the L₁ point (62C1) and the resulting transverse
effective mass at the bottom of the band is given by (76A2)

\[
\frac{m}{m_{tL}} = 1 + E_{PL}\left(\frac{1}{E_1} + \frac{1}{E_1 + \Lambda_1}\right)
\]
(II-18)

where \(E_{PL}\) is an energy related to the momentum matrix element, and \(E_1\)
and \(\Lambda_1\) are the direct band gap and spin-orbit splitting respectively
at the \(L₁\) point.

Similarly Cardona showed that the transverse effective mass at
the \(X_1\) minima is given by the semi-empirical relation (67C2)

\[
\frac{m}{m_{tX}} = 1 + \frac{19}{E_2}
\]
(II-19)
where \( E_2 \) gap is given in eV.

The band minima variation with temperature may be estimated using a similar form to that of Eq. (II-14).

C. Alloy Semiconductors

There is a growing amount of experimental data on the energy gap \( E_o \), spin-orbit splitting \( \Lambda_0 \) and effective mass of electrons in semiconducting alloys. Thompson et al. (66T1) showed that the analysis of the experimental results for various alloy systems gives an \( E_o \) variation with composition \( x \) of the form,

\[
E_o(x) = E_A + bx + cx^2
\]  

(II-19)

where

\[ b = E_B - E_A - c \]

\( E_A \) and \( E_B \) are the \( E_o \) values of compounds \( AC \) and \( BC \) respectively in the alloy \( A_{1-x}B_x \), and \( c \) is the "band bowing parameter". Spin-orbit splitting also shows a similar variation with \( x \).

Van Vechten and Bergstresser (70V1) employed the dielectric model to explain this non-linear behavior. They argued that the disorder effect is of major importance and must be included in the calculation. They used the dielectric model in a virtual
Crystal approximation to give a gap $E_{ov}$ which shows "bowing" but always to a lesser degree than that found experimentally. The difference
\[ \delta E(x) = E_{ov} - E_o \]
has been attributed to the effects of the aperiodic potential due to disorder and to a good approximation it can be expressed by the semi-empirical form (70VI)
\[ \delta E(x) = x(1-x) - \frac{C_{FG}^2}{A_F} \] (II-20)
where $C_{FG}$ is the Phillips electronegativity difference between the mixed elements and $A_F$ is a constant bandwidth parameter.

Hill(74HI) maintained that short-range order cannot play any significant role in producing energy gap bowing and that the bowing is due to the non-linear dependence of the crystal potentials on the properties of the component ions.

Song(73Sl) has explained the bowing effect by calculating the energy gap slope at the limiting compositions. His calculation was made within the framework of the virtual crystal approximation and he took account of the configurationally averaged fluctuation as a perturbation.

Schulze et al.(76Sl) have calculated the band structure of Ga$_{1-x}$In$_x$As in the virtual crystal approximation using the empirical pseudopotential model. They concluded that disorder is not negligible in the band structure calculations for these alloys.
To explain the $\Delta_o$ variation with $x$, it has been suggested that, because of the breaking of the crystal symmetry by the aperiodic terms of the crystal potential, mixing of valence and conduction band states occurs at the $\Gamma$ point (72V1). If $y(x)$ denotes the fraction of conduction band $s$ character mixed into the valence band at $\Gamma$, $y(x)$ is assumed to have the form

$$y(x) = \frac{x(1 - x) C^2_{FG}}{A F E_{ov}}$$

where

$$\frac{3}{E_{ov}} = \frac{2}{E_{ov}} + \frac{1}{E_{ov} + \Delta_{ov}}$$

This $s$-like component makes zero contribution to $\Delta_o$ and so $\Delta_o$ is given by

$$\Delta_o (x) = [1 - y(x)] \Delta_{ov} (x) \quad (II-21)$$

Chadi (77Cl) has calculated the spin-orbit splitting using a tight-binding approach which includes spin-orbit interaction and his results indicate that the non-linear variation of $\Delta_o$ is a compositional disorder effect. With the assumption that the matrix element $p^2$ has no bowing effect (73B 77H1), when the measured values of $E_o$ and $\Delta_o$ are substituted into the Kane expression for the effective mass at $k = 0$, the resulting values are always lower than the measured ones. Berolo et al. (73B1) attributed the difference to the conduction-valence-band mixing.
In this case the effective mass is given by

\[
\frac{1}{m'^*_o} = \frac{1}{m'^*_{co}} + \frac{x(1-x)C^2_{FG}}{3A_h} \left[ \frac{1}{m'^*_{hh}} \frac{1}{E_{ov}} + \frac{1}{m'^*_{lh}} \frac{1}{E_{ov}} \right]
\]

\[
+ \frac{1}{m'^*_{so}} \left( \frac{E_{ov} + \Delta_{ov}}{E_{ov} + \Delta_{ov}} \right) - \frac{1}{m'^*_{co}} \left( \frac{2}{E_{ov}} + \frac{1}{E_{ov} + \Delta_{ov}} \right)
\]

(II-22)

where \( m'^*_{co}, m'^*_{hh}, m'^*_{lh} \) and \( m'^*_{so} \) are the effective masses of conduction band, heavy hole, light hole and spin-orbit split-off bands respectively in the absence of conduction-valence-band mixing.
One of the important quantum mechanical results is that in a perfectly periodic lattice, there would be no scattering of electrons. There are, however, always deviations from periodicity due to lattice vibrations, impurities, dislocations, etc., which limit the mobility of a carrier through scattering.

To determine the behaviour of any semiconductor it is necessary to know the distribution function $f(k, r, t)$ under the appropriate conditions which are determined by the scattering mechanisms for a given material. The distribution function is obtained by solving the Boltzmann equation which describes the classical transport phenomena that we are concerned with in this work. Most of the n-type GaAs and $Ga_{1-x}Al_xAs$ samples in the present analysis show multiband transport behaviour having contributions from the $\Gamma_1$-band and also the subsidiary bands. In the case of the $\Gamma_1$-band transport calculation we have used the exact solution of the Boltzmann equation, employing the Fletcher and Butcher method (72F2).

A. Boltzmann Equation

According to Liouville's theorem, electrons which at time $t$ are in the element $drd\mathbf{k}$ centred about $\mathbf{r}$ and $\mathbf{k}$ will at time $t + dt$ be located in an equal volume centred about $\mathbf{r} + \mathbf{r}dt$ and $\mathbf{k} + \mathbf{k}dt$. 
Scattering must account for the difference between the two states, and thus the Boltzmann transport equation is (68B1)

\[
\frac{df}{dt} = -k \cdot \nabla f - v \cdot \nabla f + \frac{3f}{\partial t} + \left[ \frac{3f}{\partial t} \right]_c \tag{II-23}
\]

The last term denotes the rate of accretion of electrons in d\(r\)d\(k\) due to scattering. Assuming steady-state conditions and uniform spatial distribution, Eq. (II-23) becomes

\[
\dot{k} \cdot \nabla f = \left[ \frac{3f}{\partial t} \right]_c \tag{II-24}
\]

In the presence of a vanishingly small electric field \(F\) and an arbitrary magnetic field \(B\), the distribution function may be written as (72F2)

\[
f(B, k) = f_0(E) \cdot \frac{df(E)}{dE} + \phi(B, k) \cdot F \tag{II-25}
\]

where \(f_0(E)\) is the undisturbed distribution function. Eq. (II-24) then becomes the linearized Boltzmann equation (68B2)

\[
F \cdot \left\{ -e \nabla(v) \frac{df_0(E)}{dE} - \frac{e}{n} \frac{df_0(E)}{dE} \left[ B \cdot \nabla(v) \times \nabla \right] \phi(B, k) \right\} = \left[ \frac{df}{dt} \right]_c \tag{II-26}
\]

The scattering term in Eq. (II-26) is given by
\[
\left[\frac{df}{dt}\right]_c = \mathbf{F} \cdot \left[ \frac{1}{k_B T} V(k,k') \{\phi(k') - \phi(k)\} \, d^3 k' \right] \quad (II-27)
\]

where

\[
V(k,k') = W(k, k') f_o(k) \{1 - f_o(k')\} = V(k', k) \quad (II-28)
\]

\(k_B\) is the Boltzmann constant and \(W(k, k')\) is the probability that an electron in the state \(k\) will be scattered into the state \(k'\).

\(W(k, k')\) depends upon the scattering mechanisms.

For a spherically symmetrical valley, \(\phi(B, k)\) will have cylindrical symmetry about \(B\). Taking the z-axis along \(B\), \(\phi(B, k)\) is given in the form \((72F2)\)

\[
\phi(B, k) = P_1 k_x + P_2 (\hat{z}, k_z) + P_3 k_z \hat{z} \quad (II-29)
\]

where \(k = (k_x, k_y, z)\), \(\hat{z} = (0, 0, 1)\) and \(P_i\) are scalar functions of \(k\) alone. Hence solution of Eq. (II-26) gives \(P_i\) which in turn provides the elements of the conductivity tensor and thus various transport parameters.

A simple and useful method of solution relies on the use of a relaxation time \(\tau\) defined by

\[
\left[\frac{df}{dt}\right]_c = -\frac{f - f_o}{\tau} \quad (II-30)
\]
However the relaxation time approximation is valid only if the scattering is elastic and randomizing. This is a good approximation for most of the scattering mechanisms but not for polar optical scattering when the thermal energy is lower than the phonon energy responsible for the scattering.

A more general solution of Eq. (II-26) can be obtained using the variational principle (53H1). This method is, however, much more involved. Recently Rode (70R1) and Fletcher and Butcher (72F2) developed elaborate methods of solution for the case of inelastic scattering. We have followed the latter (F-B) method in the present work when dealing with polar optical scattering.

B. Scattering Mechanisms in the Central Valley (Γ₁-Band)

Both Rode (75R2) and Zawadzki and Szymanska (71Z1) in considerations of scattering effects for the non-parabolic band case, indicated that it was inconsistent to use pure s-type wave functions since some admixture of p character must occur. Ehrenreich(59E2) calculated the effects of admixture of the conduction (s-type) and valence (p-type) basis functions on the scattering rates through an overlap integral between the initial and final states. Fawcett and Ruch (75R2) showed that wave function admixture has an effect on electron scattering which is comparable in magnitude with non-parabolicity.

The results of the F-B method (72F2) for intra-valley polar
optical scattering, modified to allow for the non-parabolicity of conduction band and admixed wave functions, will be briefly described. Also various other scattering mechanisms will be reviewed in this section. These latter mechanisms are elastic and relaxation time approximations are valid in these cases.

(a) **Intravalley Polar Optical Scattering**

Longitudinal phonons have an associated electric polarization wave in polar materials. The interaction of an electron with the associated electric field provides the dominant scattering mechanism in III-V compounds with temperatures near room and above except in the case of extremely heavily doped samples.

The scattering probabilities due to the polar phonon emission and absorption are given respectively by

\[
W_E(k, k') = \frac{\frac{e^2 \omega_o (N + 1)}{8 \pi^2 \epsilon_o}}{\left( \frac{1}{\kappa_\infty} - \frac{1}{\kappa_o} \right)} \frac{1}{|k - k'|^2} \delta(E(k') - E(k) + \hbar \omega_o)
\]

\[
W_A(k, k') = \frac{\frac{e^2 \omega_o N}{8 \pi^2 \epsilon_o}}{\left( \frac{1}{\kappa_\infty} - \frac{1}{\kappa_o} \right)} \frac{1}{|k - k'|^2} \delta(E(k') - E(k) - \hbar \omega_o)
\]

(II-31)
where $\omega_0$ is the phonon frequency, $\kappa_\infty$ and $\kappa_0$ are the high and low frequency dielectric constants of the lattice, $N$ is the thermal average number of phonons per mode and $\varepsilon_0$ is the permittivity of free space.

From Eqns. (II-26), (II-27), (II-29) and (II-31), we obtain the following set of difference equation for $P_i$ (75B1)

\[
\begin{align*}
L(P_1) &= Y\alpha(E) - \left[ \frac{Y\alpha(E)}{\hbar} \right] BP_2 \\
L(P_2) &= \left[ \frac{Y\alpha(E)}{\hbar} \right] BP_1 \\
L(P_3) &= Y\alpha(E)
\end{align*}
\]

where

\[
Y = \frac{4\pi\varepsilon_0}{e(\hbar\omega_0)[(1/\kappa_\infty) - (1/\kappa_0)]}
\]

\[
\alpha(E) = \frac{E}{k} \frac{\delta E}{\delta k}
\]

\[
L(P_i) = (N + 1) \frac{f_{0}^{(E + \hbar\omega_0)}}{f_{0}^{(E)}} P_{i}^{(E + \hbar\omega_0)} \left[ (2E + \hbar\omega_0) \right. \\
&\times \sin^{-1} \left( \frac{E}{\hbar\omega_0} \right)^{1/2} - \left\{ E(E + \hbar\omega_0) \right\}^{1/2} \bigg] - 2EP_{i}^{(E)} \\
&\times \sin^{-1} \left( \frac{E}{\hbar\omega_0} \right)^{1/2} + \theta(E - \hbar\omega_0) N \frac{f_{0}^{(E - \hbar\omega_0)}}{f_{0}^{(E)}} \\
&\times \left( P_{i}^{(E - \hbar\omega_0)} \right. \left[ (2E - \hbar\omega_0) \right. \times \cos^{-1} \left( \frac{E}{\hbar\omega_0} \right)^{1/2} \\
&\left. - \left\{ E(E - \hbar\omega_0) \right. \right\}^{1/2} \bigg] - 2EP_{i}^{(E)} \cos^{-1} \left( \frac{E}{\hbar\omega_0} \right)^{1/2}
\]
\[ \theta(x) = 0 \quad x < 0 \]
\[ \theta(x) = 1 \quad x > 0 \]

Eq. (II-32) includes the Kane model form of band structure (75B1) but neglects the wave function overlap. Inclusion of p-like terms in the wave functions reduces the polar optical scattering rates. The results of Rode's method (70R1) for the scattering calculation using admixed wave functions give a correction term for the third equation of Eq. (II-32), which is then given in the following form and the solution of which gives the longitudinal conductivity.

\[ L(P_3) = A(E)P_3(E + \eta_\omega) + \theta(E - \eta_\omega) B(E)P_3(E - \eta_\omega) + C(E)P_3(E) \]

(II-33)

where

\[ A(E) = (N+1) \frac{f_0(E + \eta_\omega)}{f_0(E)} \{ E(E + \eta_\omega) \}^{1/2} \left[ (A^+)^2 \right. \]

\[ \times \left( \frac{2E + \eta_\omega}{E(E + \eta_\omega)} \right)^{1/2} \sin^{-1} \left( \frac{E(E + \eta_\omega)^{1/2}}{1} - 1 - \frac{1}{3} c^2(c^+)^2 \right) \]

\[ B(E) = \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ E(E - \eta_\omega) \}^{1/2} \left[ (A^-)^2 \right. \]

\[ \times \left( \frac{2E - \eta_\omega}{E(E - \eta_\omega)} \right)^{1/2} \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 - \frac{1}{3} c^2(c^-)^2 \right) \]

\[ C(E) = -[E(N+1) \frac{f_0(E + \eta_\omega)}{f_0(E)} \{ 2 \sin^{-1} \left( \frac{E(E + \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^+)^2 \}

\[ - \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^+)^4 \]

\[ + \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^-)^4 \}

\[ + \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^+)^4 \}

\[ + \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^-)^4 \}

\[ + \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^+)^4 \}

\[ + \theta(E - \eta_\omega) N \frac{f_0(E - \eta_\omega)}{f_0(E)} \{ 2 \cos^{-1} \left( \frac{E(E - \eta_\omega)^{1/2}}{1} - 1 \right) - \frac{1}{3} c^2(c^-)^2 \}

\[ - (A^-)^4 \}]}
\[ A^\pm = a a^\pm + (k^\pm)^2 + k^2 + c c^\pm / 2k k \]

where the superscripts + and - correspond to scattering out of the differential element \( dk \) by phonon absorption and by phonon emission respectively. The corresponding energy values are given by the energy associated with \( k \) plus or minus the longitudinal polar optical phonon energy at the \( \Gamma \) point.

"a" and "c" provide normalization and wave function admixture consistent with non-parabolicity (75R2)

\[ a^2 + c^2 = 1 \]  \hspace{1cm} (II-34)

where

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

\[
\alpha = \left( 1 + \frac{2\hbar^2 k^2}{m^*_o} \left( \frac{m^*_o}{m^*_o} - 1 \right) \right)^{1/2}
\]

For the solution of the difference equation (II-32), Fletcher and Butcher adopted an iteration method (72F2) and the solution provides values of \( P_i \) from which we may calculate transport parameters for the polar optical scattering. \( L(P_3) \) in Eq. (II-32) is now replaced by Eq. (II-33).

The scattering probability \( W(k, k') \) in Eq. (II-28) comprises both inelastic and elastic scattering mechanisms. Eq. (II-26) has two integration terms, which correspond to scattering out of and scattering
into respectively the differential volume element $\text{d}k$ in momentum space (71R1). In the case of inelastic scattering, the two integration terms involve different energies $E(k)$ and $E(k) \pm \hbar \omega_0$ and cannot be combined into one value. The "scattering into" term involving $E \pm \hbar \omega_0$ constitutes the $A(E)$ and $B(E)$ terms in Eq. (II-33), and the "scattering out" term is included in $C(E)$ in that equation. For elastic scattering, there is no energy change in the interactions and both "scattering out" and "into" terms involve the electron energy $E(k)$ and are combined into a relaxation rate. This relaxation is then added to $C(E)$ in Eq. (II-33).

The elastic scattering mechanisms are thus included in the foregoing calculation simply by replacing $C(E)$ in Eq. (II-33) by (72P2)

$$C(E) \rightarrow C(E) + Y_s(E) \left( \frac{\hbar k}{e(\partial E/\partial k)} \right) \frac{\tau_s(E)}{s} \frac{1}{\tau_s(E)} , \quad (II-35)$$

where the $\tau_s(E)$ terms are the relaxation times for the various different mechanisms. The expressions for the various relaxation times are given in the next sections.

(b) **Interband Scattering**

In semiconductors with band structure such that two bands have minima close in energy, the electron scattering between the two bands may be important in transport calculations for either one or both bands. This process of interband scattering may be more effective than
polar optical scattering (intraband) in restricting the carrier mobility at high energies, depending upon the values of the coupling constant and the energy separation between the bands concerned. Here we are concerned with electron scattering from the $\Gamma_1$ band to upper subsidiary valleys. Conservation of crystal momentum requires that in the process, for the moderately doped samples in this work, a phonon with wave vector at the edge of the Brillouin zone and directed along <100> or <111> be emitted or absorbed. Selection rules (66B1) indicate that the phonons involved must be longitudinal optical mode. Longitudinal acoustic phonons may be responsible for this transition, but this mode of scattering into the $X_1$ band is prohibited if $M_V > M_{III}$. The relaxation time for this scattering mechanism is given by (68C2)

$$\frac{1}{\tau_{1j}} = \frac{N_j D_{1j}^2 m_j^{*3/2}}{\sqrt{2 \hbar^2 \rho \omega_{1j}}} \frac{1}{e^{\frac{\hbar \omega_{1j}}{k_B T}} - 1} \left\{ (E + \hbar \omega_{1j} - E_{1j}) \right\}^1 + e^{\hbar \omega_{1j}} (E - \hbar \omega_{1j} - E_{1j})^1 \right\} \quad (II-36)$$

where the index $j$ indicates the upper valley. $D_{1j}$ is the coupling constant between the $\Gamma_1$ and the $j$th bands, $N_j$ is the number of equivalent valleys denoted by "j", $m_j^*$ is the density of states effective mass for each valley into which an electron is scattered, $\hbar \omega_{1j}$ is the longitudinal phonon energy responsible for the scattering, $E_{1j}$ is the energy separation between the bands which interact, $\rho$ is the density of crystal, and $\hbar \omega_{1j} = \frac{\hbar \omega_{1j}}{k_B T}$. 
Deformation Potential Acoustic Mode Scattering

Bardeen and Shockley proposed electron scattering by the deformation potential \( E_D \) which is defined as the energy the conduction band edge shifts per unit strain due to longitudinal acoustic mode vibration (50Bl). Herring and Vogt (56H1) showed that the transverse modes are also important for deformation potential scattering in multi-valley conduction.

However, only longitudinal modes contribute to the conduction for the single isotropic \( \Gamma \)-valley. The relaxation time in this case is given by (71R1)

\[
\frac{1}{\tau_{ac}} = \frac{e^2 k_B T E_D^2}{3 \hbar C_\ell (dE/dk)} \left( 3 - 9c^2 + 6c^4 \right) \quad (II-37)
\]

where \( C_\ell \) is the spherically averaged elastic constant for longitudinal mode and is given by (64Zl)

\[
C_\ell = \frac{3 C_{11} + 2C_{12} + 4C_{44}}{5} \quad (II-38)
\]

for the case of sphalerite-type semiconductor. \( c \) is the wave function coefficient defined in Eq. (II-34).
Conwell and Weisskopf (50C1) employed Rutherford scattering to explain electron scattering by ionized impurities in semiconductors. The divergence arising from the increasing contribution of small angle scattering was removed by cutting off the scattering cross sections at a distance $1/r = N^{1/3}/2$, where $N$ is the impurity density. This empirical inclusion of a cut off distance simulates in the first approximation the effects of space charge screening considered in later work. Thus, Brooks and Herring (51B1,67F1) and Dingle (55D1) used a screened Coulomb potential, which takes care of the divergence difficulty. This arises from the fact that electrons distribute themselves around the impurity and cancel its field at large distances. Dingle (55D1) assumed for relatively low impurity concentrations that all impurities are ionized and form a random background array of immobile charge. Only the concentrations of carrier charges provide screening.

Meanwhile the Brooks and Herring theory (67F1) includes the screening of impurities by nearby impurities in addition to free carriers, and thus the screening formula involves the concentration of neutral as well as ionized centers.

From Dingle's theory, Rode (75R2) calculated the relaxation time for impurity scattering considering the conduction band non-parabolicity and the admixed electron wave function. The calculated relaxation
time is appropriate to n-type material and is given by

$$\frac{1}{\tau_{cc}} = \frac{e^4 N_{cc}}{8\pi \hbar^2 (\kappa_o \varepsilon_o)^2} \frac{1}{(dE/dk)} \frac{1}{\pi I}$$

(II-39)

where

$$F_I = D \ln(1 + 4k^2 / \beta^2) - B$$

$$D = \frac{2\beta^2 c^2}{k^2} + \frac{3\beta^2 c^2}{4k^2} + 1$$

$$B = \frac{4k^2 / \beta^2}{1 + 4k^2 / \beta^2} + \frac{8}{\beta^2 + 2k^2} + \frac{3\beta^2 + 6\beta^2 k^2 - 8k^2}{(\beta^2 + 4k^2) k^2}$$

and \(N_{cc}\) is the ionized impurity concentration. The inverse screening length \(\beta\) is given by

$$\beta^2 = \left( \frac{e^2}{\kappa_o \varepsilon_o k_B T} \right) \int \left( \frac{k}{\pi} \right)^2 f(1-f) \, dk$$

(II-40)

In the case of multi-band conduction, the screening effect of the electrons of other bands also must be taken into account (72B1). When electrons freeze out at low temperatures where the charged impurity concentration greatly exceeds electron density, one must use Brooks-Herring's theory, in which the impurity potentials overlap one another and screening is correspondingly enhanced. When both the above effects exist, Eq. (II-40) should be replaced by (67B1,75R2)

$$\beta^2 = \frac{e^2}{\kappa_o \varepsilon_o k_B T} \left[ \frac{3n_i}{3} \frac{3n_i}{3} \frac{3n_t}{3} \frac{3n_A}{3} \frac{3n_t}{3} \frac{3n_A}{3} \right] + \frac{(N_D - N_A - n_t)(n_t + N_A)}{N_D}$$

(II-41)

where \(n_i\) runs over all bands concerned, \(n_t\) is the total carrier density, \(N_A\) compensated acceptor concentration, \(N_D\) donor density and \(\eta = E_F / k_B T\).
In the above theory it is assumed that the impurities scatter electrons independently, that the transition probability may be evaluated in the first Born approximation and that the perturbing effects of the impurities on the electron energy levels and the wave functions may be neglected. Moore (67M1) has calculated the carrier mobility for ionized impurity scattering in degenerate material taking account of multiple scattering effects, a higher Born approximation for the incoherent scattering and the dressing effects of the impurities on the electron wave functions and energy levels. He treated the problem using quantum-transport theory and his result is given by (67M1)

$$\sigma_I = \sigma_{IO} \left[ 1 + \delta_B + \delta_M + \delta_D \right]$$  \hspace{1cm} (II-42)

where $\sigma_{IO}$ is the Brooks-Herring conductivity and $\delta_B$, $\delta_M$ and $\delta_D$ are correction parameters for the incoherent Born correction, multiple scattering and the impurity dressing effects respectively. In the case of low doped semiconductors, electron-electron interactions may not be neglected and this reduces the mobility (54D1, 65B1). Luong and Shaw (71L2) calculated the ionized-impurity mobility including electron-electron scattering effects for non-degenerate semiconductors and their result is

$$\mu_I = \left( 1 - \frac{1}{2!} \frac{n}{N_{cc}} + \frac{1}{3!} \frac{n^2}{N_{cc}^2} - \frac{1}{4!} \frac{n^3}{N_{cc}^3} + \ldots \right) \mu_{IO}$$  \hspace{1cm} (II-43)

where $\mu_{IO}$ is the Brooks-Herring mobility, $N_{cc}$ is the concentration of ionized impurities and $n$ is the carrier density.
(e) **Space Charge Scattering**

In some III-V compounds such as GaAs, InAs and InP, the curves of electron mobility vs. temperature for different low resistivity samples are observed to cross. Weisberg (62W1) proposed a process, termed by him "mobility killer", to explain these anomalous mobility effects. This process has a characteristic mobility proportional to $T^{-1/3}$ or $T^{-5/6}$ (62W1). The latter temperature dependence is due to the variation of the effective scattering area with temperature. It is generally considered that this effect is due to the occurrence of space charge regions which are formed by randomly distributed acceptor impurities which compensate the donors. To provide the appropriate potential difference with respect to the uncompensated material, a space charge region must be formed.

Conwell and Vassel (68C2) discussed the effects of the size of the space charge region, the carrier concentration and the potential barrier or step between the space charge region and the surrounding material and concluded that the maximum scattering rate is expected to occur in material with $10^{22} > n > 10^{20}/m^3$. Treating the space charge regions as impenetrable spheres of density $N_s$ and cross section $Q_s$, Conwell and Vassel calculated the relaxation time for this process (68C2). The relaxation time for a non-parabolic band is given by

$$\frac{1}{\tau_{sc}} = \frac{N Q_s}{n} \frac{dE}{dk} \quad (II-44)$$
(f) **Piezoelectric Acoustic Mode Scattering**

The piezoelectric stress tensor is nonvanishing in cubic crystal lacking inversion symmetry. Phillips and Van Vechten (69P2) investigated theoretically the piezoelectric constants and their results suggest that strain dependent ionicity may be the dominant source of piezoelectricity in III-V compounds. Piezocoupling occurs with acoustic modes of long wavelength and the perturbing potential is proportional to the strain gradient. Zook (64Z1) generalized piezoelectric scattering so as to take account of anisotropy in the effective mass. Rode (70R1) calculated the relaxation time for an isotropic band from Zook's treatment and his result is given by

\[
\frac{1}{\tau_{pe}} = \frac{e^2 k_B T P^2}{6 \pi \hbar K_0 \varepsilon (dE/dk)} (3 - 6c^2 + 4c^4) \tag{II-45}
\]

where \( P \) is a dimensionless piezoelectric coefficient which depends upon the crystal structure (64Z1), and is given for the sphalerite structure by

\[
P^2 = h_{14}^2 \kappa \varepsilon_0 \left[ \left( \frac{12}{C_L} \right) + \left( \frac{16}{C_T} \right) \right] / 35
\]

where

\[
C_T = \left( C_{11} - C_{12} + 3C_{44} \right) / 5
\]

and \( h_{14} \) is a piezoelectric stress tensor. This scattering mechanism is effective only for pure materials at lower temperature.
Neutral Impurity Scattering

Pearson and Bardeen (49P1) pointed out that the scattering due to neutral impurities must be considered in scattering calculations particularly at low temperatures and that the scattering may be calculated as for electrons scattered by neutral hydrogen atoms. A treatment of collisions of slow electrons with hydrogen atoms by Massey and Moiseiwitsch (50M1) was applied to this problem by Erginsoy (59E1) and by Sodha and Varshni (59S1). Erginsoy considered only the low energy range \( E < \frac{1}{4} E_d \), where \( E_d \) is the ionization energy of the impurity), while Sodha and Varshni (59S1) calculated the relaxation time for scattering in a wider range \( E = 0 \sim E_d \) and their result is given by

\[
\frac{1}{\tau_N} = \frac{YQ_0'}{C} \tag{II-46}
\]

where

\[
y = \frac{mv}{\hbar} \alpha_o
\]

\[
C = \frac{2^2 m}{N_n \hbar^3}
\]

\[
Q_0' = 10^5 / \left( 344 + 2440y + 7200y^3 \right)
\]

\( m \) and \( v \) are the mass and velocity of incident electron, \( \alpha_o \) is the first Bohr radius of bound electron, \( N_n \) is the concentration of scattering centres.
C. Transport Parameters for the $\Gamma_2$ Band.

With the scattering mechanisms discussed in the preceding section, we can calculate $P_1$ from Eq. (II-32). The elements of the conductivity tensor are given in terms of $P_1$.

$$\sigma_{ij} = \frac{e^3}{4\pi^2} \int v_i(k) \phi_j(B, k) \frac{d\phi_j}{dE} d^3k$$  \hspace{1cm} (II-47)

And the non-zero elements of the conductivity tensor are expressed as (75B1)

$$\sigma_{xx} = \sigma_{xy} = <P_1>$$

$$\sigma_{yx} = \sigma_{yy} = <P_2>$$  \hspace{1cm} (II-48)

$$\sigma_{zz} = <P_3>$$

where

$$<P_1> = \frac{e^2}{2\pi^2} \int_0^\infty P_i k^3 \left( - \frac{\partial f(E)}{\partial E} \right) dE$$

The transport parameters required in the analysis can now be calculated in terms of the elements given in Eq. (II-48).
(a) **Carrier Mobility**

When an electric field $F_x$ is applied to a semiconductor in the direction $x$, the average drift velocity of a carrier is given by

$$v_x = \mu F_x$$

where the proportionality constant $\mu$ is called the carrier mobility.

The mobility is expressed as

$$\mu = \frac{\sigma_{zz}}{ne}$$

where the carrier concentration $n$ is calculated using the form,

$$n = \frac{1}{3\pi^2} \int_0^\infty k^3 \frac{\partial f(E)}{\partial E} \, dk$$

or

$$n = \frac{1}{\pi^2} \int_0^\infty k^2 f(E) \, dk$$

(b) **Hall coefficient**

A Hall field $F_y$ in the $y$-direction is produced as a result of a current $i$ flowing in the $x$ direction and a magnetic field $B$ in the $z$-direction and given by

$$F_y = R_H iB$$
where $R_H$ is the Hall coefficient and is expressed in terms of the elements of the conductivity tensor as

$$R_H = \frac{\sigma_{xy}}{B(\sigma_{xx}^2 + \sigma_{xy}^2)} \quad (II-50)$$

(c) **Hall Scattering Coefficient**

The Hall scattering coefficient, sometimes called the "Hall number", may be expressed in terms of the Hall coefficient and the carrier concentration as

$$r = ne R_H$$

Hence, from Eq. (II-50)

$$r = \frac{ne \sigma_{xy}}{B(\sigma_{xx}^2 + \sigma_{xy}^2)} \quad (II-51)$$

(d) **Magnetoresistance (Transverse)**

In a magnetic field, the conductivity is (63Bl)

$$\sigma(B) = \frac{\sigma_{xx}^2 + \sigma_{xy}^2}{\sigma_{xx}}$$
Hence the magnetoresistivity can be measured by

\[
\frac{\Delta \rho}{\rho_0} = \frac{\rho(B) - \rho_0}{\rho_0} = \frac{\sigma_{xx} \sigma_{zz}}{\sigma_{xx}^2 + \sigma_{xy}^2} - 1
\]  

(II-52)

where \( \rho_0 \) is the resistivity at \( B = 0 \).

D. Scattering Mechanisms in the \( L_1 \) and \( X_1 \) Bands.

The \( L_1 \) and \( X_1 \) bands are subsidiary bands for GaAs, InP and the direct gap compositions of the \( \text{Ga}_{1-x}\text{Al}_x\text{As} \) system. In the scattering calculations, these bands are important only at high temperatures and pressures for the case of GaAs, but for all temperatures in the case of some of the \( \text{Ga}_{1-x}\text{Al}_x\text{As} \) alloys. These bands have ellipsoidal constant energy surfaces and for each band there are a number of equivalent minima and hence equivalent ellipsoids in \( k \)-space. The system may be referred to as a multivalley structure.

In addition to the intravalley and interband scattering mechanisms applicable to a single valley as reviewed in earlier sections, intervalley scattering between equivalent valleys must be taken into account to understand the electron behaviour in these bands. Also in the case of the interband scattering process, a transition from higher to lower bands must be included for the calculations.
For the present analysis we have employed Herring's method (55H1, 63B1). In this case the carrier mobility is calculated for a single valley and then a summation is carried out over the equivalent valleys for the conductivity calculation.

(a) **Optical Mode Intravalley Scattering**

Olechna and Ehrenreich (6201) showed that a good approximation to the correct intravalley polar optical mobility may be obtained by replacing the $m^{-3/2}$ that appears in the mobility expression for the polar optical scattering in spherical band by $\frac{1}{3}(m^*_{di})^{-\frac{1}{2}}(\frac{1}{m_{ki}} + \frac{2}{m_{ti}})$ and thus the relaxation time for the process is

$$\frac{1}{\tau_{op}} = \frac{e^2 m^*_{di} \hbar \omega}{4\hbar^2 \sqrt{2} \varepsilon_o \pi} \left( \frac{1}{\kappa_\omega} - \frac{1}{\kappa_o} \right) (2N + 1) \quad (II-53)$$

where

$$N_q = \frac{1}{\exp(\hbar \omega_i/k_B T) - 1}$$

$\omega_i$ is the longitudinal optical angular frequency responsible for the scattering and the subscript $i$ indicates the band for which the calculation is made. This relaxation time is valid only for carrier energies higher or comparable with the phonon energy. Therefore in the final analysis the iterative method of Fletcher and Butcher, quoted in the earlier section for the $\Gamma_1$ band calculation, was employed.
This is discussed in the chapter treating GaAs.

(b) **Intervalley scattering**

In intervalley scattering, electron transitions occur between states in different equivalent valleys. This transition is induced by emission or absorption of a phonon which may be of either acoustic or optical mode. Conwell and Vassel (68C2) showed that the relaxation time for this scattering due to polar optical phonons is

$$\frac{1}{\tau_{IV}} = \frac{N_i^2 \beta_{ii} m_i^* 3/2}{\sqrt{2\pi\hbar}} \frac{1}{\omega_{ii}} \left\{ \frac{1}{\exp(T\omega_{ii}/k_B T) - 1} \right\} + \exp(T\omega_{ii}/k_B T) \times (E - T\omega_{ii})^k \right\} \right\}$$

where $$N_i^1 = N_i - 1$$,

$$D_{ii}$$ is the coupling coefficient, $$\omega_{ii}$$ the angular frequency of the phonons for scattering and $$N_i$$ the number of equivalent valleys between which the transitions take place. The relaxation time for intervalley scattering due to acoustic phonons has the same form as Eq. (II-54), but with different values of coupling coefficient and phonon energy (55H1, 60L1). Conwell indicated the importance of non-polar optical scattering in ellipsoidal bands and the relaxation time in this case is formally identical with Eq. (II-54) but with a different coupling coefficient (67C3). Because of the equivalence of the equation for the relaxation
times of the three scattering mechanisms, Eq. (II-54) is used to cover all the three mechanisms permitted by the selection rules (66B1). Such an approach has previously been used by Rode (72R2) and by Basinski et al. (74B1), and the values of coupling coefficient will effectively be the root of the sum of the squares of the various coupling coefficients.

The electron-phonon interaction selection rule (66B1) shows that the phonon responsible for the intervalley optical scattering should be longitudinal for both of the \( L_1 \) and \( X_1 \) bands. In the case of acoustic mode scattering, the phonon involved is longitudinal when transition occurs between the \( L_1 \) valleys. A longitudinal acoustic phonon is responsible for scattering between the \( X_1 \) valleys, but scattering occurs only if \( M_V < M_{III} \), where \( M_V \) and \( M_{III} \) are the masses of the group V and III atoms respectively.

(c) Interband Scattering

In the case of interband scattering, possible transitions are: (a) \( L_1 \rightarrow X_1 \) and (b) \( L_1 \) (or \( X_1 \)) \( \rightarrow \) \( \Gamma_1 \). If in (a) the transition occurs from a lower to a higher band, the relaxation time is (68C2)

\[
\tau_{ij} = \frac{D_{ij}^{m^3/2}N_j}{\sqrt{2\pi\hbar^3}} \frac{1}{\exp(\frac{\hbar \omega_{ij}}{k_B T}) - 1} \{ (E + \hbar\omega_{ij} - E_{ij})^{1/2} + \exp(\frac{\hbar \omega_{ij}}{k_B T})(E - \hbar\omega_{ij} - E_{ij})^{1/2} \}
\]

(II-55)
where $D_{ij}$ is the coupling coefficient, $m^*_i$ and $N_j$ are the density of states effective mass and multiplicity respectively of the valleys into which the electron is scattered, $E_{ij}$, the energy difference between the two band minima which interact, $\omega_{ij}$ the angular frequency of the phonons responsible for the scattering. When the transition occurs from a higher to a lower band, a form similar to Eq. (II-55) is used for the relaxation time calculation by setting $E_{ij} = 0$ (67C3). The selection rules (66B1) show that longitudinal phonons, both optical and acoustic, are responsible for this interband scattering between the ellipsoidal bands. Non-polar optical interband scattering also may be expressed by Eq. (II-55). Hence Eq. (II-55) is used to calculate the above three mechanisms as in the case of intervalley scattering.

Conwell and Vassel (68C2) showed that the relaxation time for the process (b) is

\[
\frac{1}{\tau_{11}} = \frac{2}{D} \frac{m^*_3/2}{\rho \omega \Gamma_i} \frac{1}{\exp(\hbar \omega \Gamma_i/k_B T) - 1} \left\{ \gamma \frac{\hbar}{E + \hbar \omega \Gamma_i} \gamma' (E + \hbar \omega \Gamma_i) \ight. \\
\left. + \exp(\hbar \omega \Gamma_i/k_B T) \gamma \frac{\hbar}{E - \hbar \omega \Gamma_i} \gamma' (E - \hbar \omega \Gamma_i) \right\}
\]

(II-56)

where

\[
\gamma(E) = E(1 + \alpha E + \beta E^2 + \ldots)
\]

(II-57)

\[
\alpha = \frac{P^2}{E_o} \left( E_o^* + P \right)^2
\]

\[
\beta = -2 \frac{P^3}{E_o^*} \left( E_o^* + P \right)^4
\]

\[
\gamma' = \frac{d\gamma}{dE}
\]
Eq. (II-57) expresses the nonparabolicity of the $\Gamma_1$ band (57K1). This process, however, can be shown to be unimportant in the present analysis because the density of states effective mass of the $\Gamma_1$ band is small compared with those of the band for which scattering is calculated. Both longitudinal optical and acoustic phonons can give transitions between the $L_1$ and $\Gamma_1$ bands, while in the case of $X_1 \rightarrow \Gamma_1$ transitions, the phonon responsible for the scattering is longitudinal optical if $M_V > M_{III}$ and longitudinal acoustic if $M_V < M_{III}$.

(d) **Intravalley Acoustic Deformation Potential Mode Scattering**

The relaxation time for isotropic intravalley scattering is given by (50B1)

$$\frac{1}{\tau_{ac}} = \frac{\sqrt{2} E_D^2 m^*^{3/2} k_B T \sqrt{E}}{\pi \hbar^4 \rho U_L^2}$$

where $E_D$ is the pure dilatation deformation potential and $U_L$ is the longitudinal acoustic velocity. This expression is the same as that for the $\Gamma_1$ band except that the correction terms due to the admixture of $s$- and $p$-type wave functions and band nonparabolicity are negligible in the present case. Herring and Vogt (56H1) showed that intravalley acoustic scattering is not isotropic and that $\tau_{ac}$ should be represented by a tensor with principal components along the ellipsoidal axes for
a given valley. In view of the many unknown parameters for the present samples requiring $L_1$ and $X_1$ calculations, however, an anisotropic treatment may make the analysis untractable. Hence, for the present work, an isotropic treatment will be used as in the work of Basinski et al. (74B1) and Rode (72R2).

(e) **Ionized Impurity Scattering**

Herring and Vogt (56H1) showed that ionized impurity scattering is not randomizing and that an isotropic relaxation time which depends only on energy is not completely satisfactory. Since the $L_1$ and $X_1$ bands are important for GaAs only at higher temperatures where this scattering effect is almost negligible, however, an isotropic relaxation time is satisfactory in this case. Previous work on the $\text{Ga}_x\text{Al}_{1-x}\text{As}$ system showed that an isotropic treatment for ionized impurity scattering is reasonable there also (76M1). These points will be further discussed in the chapters treating the respective materials. The relaxation time for this scattering is (63B1)

$$\frac{1}{\tau_{cc}} = \frac{e^2 N_{cc} f(z)}{16\pi (\varepsilon_0^0)^2 \sqrt{2m^*}} E^{3/2}$$

where

$$f(z) = \ln(1 + z) - z/(z + 1)$$

$$z = (2ka)^2$$

$$\frac{1}{a} = \frac{e^2}{\varepsilon_0^0 k_B T} \frac{\partial}{\partial \eta}$$
This is the same form as that for the $\Gamma_1$ band except that we have ignored band non-parabolicity and admixture of electron wave functions in this case.

E. Transport Parameters in the $L_1$ and $X_1$ Bands

(a) Carrier Mobility

For an arrangement of ellipsoids possessing cubic symmetry, the zero-magnetic field mobility is the same in all directions and is given by (63B1)

$$\mu = e \frac{<\tau>}{m_c}$$

(II-60)

where

$$<A> = \frac{\int (-\frac{\partial f}{\partial E}) A E^{3/2} \, dE}{\int (-\frac{\partial f}{\partial E}) E^{3/2} \, dE}$$

$$\frac{1}{\tau} = \sum \frac{1}{\tau_i}$$

$\tau_i$ are the relaxation times associated with various scattering mechanisms considered above and $m_c$ the conductivity effective mass.
(b) Hall Scattering Coefficient

\[ r = \frac{\langle \tau \rangle^2}{\langle \tau \rangle^2} \]  

\[ \text{(II-61)} \]

(c) Hall Coefficient

When a summation is carried out over a set of equivalent valleys (55H1) we get

\[ \frac{\mu_H}{\mu} = r \cdot F \]  

\[ \text{(II-62)} \]

where \( \mu_H \) is the Hall mobility and \( F \) is an anisotropy factor given by

\[ F = \frac{3K(K + 2)}{(2K + 1)^2} \]  

\[ \text{(II-63)} \]

where \( K = \frac{m_e}{m_t} \). From Eq. (II-61) we obtain the Hall coefficient,

\[ R_H = \frac{\mu \cdot r \cdot F}{\sigma} = \frac{rF}{ne} \]  

\[ \text{(II-64)} \]

(d) Magnetoresistance

Abeles and Meiboom (54A1) showed that magnetoresistivity for semiconductors with constant energy surface in the form of ellipsoids is
\[ \frac{\Delta \rho}{\rho_0} = R^B \sigma_0^2 \frac{2}{H_0^2} \{ (1 + \xi) F(K) - 1 \} \]  \hspace{2cm} (II-65)

where

\[ F(K) = \frac{(K^2 + K + 1)(2K + 1)}{K(K + 2)^2} \]

and the magnetoresistance coefficient \( \xi \) is

\[ \xi = \frac{<T^3> - <T>}{<T^2>^2} - 1 \]

II-3 Charge Neutrality and Carrier Concentration

For the transport calculation it is necessary to consider in detail how electrons are distributed between the bands and the various sets of levels provided by impurities. The net charge within a semiconductor must be zero when the material is in an equilibrium state. This "charge neutrality" condition may be stated in the form

\[ n - p = N_d - N_A \]  \hspace{2cm} (II-66)

where \( n \) and \( p \) are the concentrations of electrons and holes respectively and \( N_d \) and \( N_A \) the densities of ionized donors and compensating acceptors respectively.
A single monovalent donor impurity is explained by analogy with the hydrogen atom. The ground state of hydrogen atom, the 1s state, has a spin degeneracy of 2. Possible states are the eight 2s and 2p states, the eighteen 3s, 3p and 3d states, and so on. Similarly a donor impurity may have excited states, and the concentration of unionized donors is given by (62B1)

\[
N_{DN} = \frac{N_D}{1 + \sum_r g_r \exp \left\{ (-E_r - E_d + E_\text{r})/kT \right\}}
\]  

(II-67)

where \(N_D\) is the total donor concentration, \(g_r\) a number to take account of degeneracy, \(E_d\) the ground state energy, \(r\) runs over the excited states and \(E_\text{r}\) is the energy difference between the ground (\(r = 1\)) and the \(r\)th excited states. It is necessary to consider only the first few excited states since the wave functions for the higher state will overlap strongly and these states will form part of the conduction band.

In calculation of carrier distribution between bands, we have assumed that all except the \(\Gamma_1\) band are parabolic, while for the \(\Gamma_1\) band a Kane band form (57K1) is assumed. Codere and Woolley (69C2) indicated that the carrier concentration of the \(\Gamma_1\) band is given by

\[
n_\Gamma = 4 \pi \left( \frac{2m_k^*}{\hbar^2} \right)^{3/2} \left[ F_{1/2}(\eta) + \left( \frac{5}{2} - 5\gamma \right) \beta F_{3/2}(\eta) + \left( \frac{7}{2} - \frac{21}{2}\gamma \right) \beta^2 F_{5/2}(\eta) \right]
\]

\[- \left( \frac{1}{4} + \frac{7}{2}\gamma \right) \beta^3 F_{7/2}(\eta) + \ldots \ldots \]

(II-68)
where \( n = \frac{E_p}{k_B T} \), \( \gamma = \frac{m^*}{m} \), \( \beta = \frac{k_B T}{E_o} \)

and

\[
F_n(\xi) = \int_0^\infty \frac{x^n dx}{\exp(x - \xi) + 1} \quad (II-69)
\]

For the L and X bands, the carrier density is

\[
n_i = 4\pi N_1 \left( \frac{2m^* k_B T}{h^2} \right)^{3/2} F_{\xi_i}(n - \xi_i) \quad (II-70)
\]

where

\[
\xi_i = \frac{E_i - E_o}{k_B T}
\]

\( E_i \) gives the energies of the L and X band minima relative to the top of the \( \Gamma_{15} \) state. Similarly the hole concentration is given by

\[
p = 4\pi \left( \frac{2m^* k_B T}{h^2} \right)^{3/2} F_{\Delta}(n - \Delta) \quad (II-71)
\]

where

\[
\Delta = \frac{E_o}{k_B T}
\]

\( m^* \) is the density of the states effective mass for the heavy hole valence band.
II-4. Multi-band Hall Effect and Conductivity

Most of the GaAs and Ga$_{1-x}$Al$_x$As samples used for this work show multi-band transport behaviour and in such a case each band contributes to the measured values. Hence the theoretical predicted values must be determined by including the effects of all relevant bands in terms of the theories reviewed in the preceding sections.

When we have many types of carriers, it is assumed that; i) the bands can be treated as isotropic and independent and ii) with low field conditions the variations of the Hall coefficient and conductivity of each separate band with magnetic field can be neglected, i.e. that single band effects are negligible. It is generally accepted that the constant energy surface at the $\Gamma$ point can be taken as spherical. The work of Gold and Roth (57G1) shows that in the cases of the L and X bands, the approximation to an isotropic form of energy surface is satisfactory provided that $\mu_B << 1$. The question of whether the bands may be considered independent when interband scattering can occur was discussed by Ehrenreich and Overhauser (56E1) and by Bear (63B1). They concluded that the bands are uncoupled mathematically and the above type of analysis is satisfactory. With regard to assumption (ii), it has been pointed out by Blatt (68B2) that in the majority of cases the assumption is valid. Basinski (72B1) discussed this point using the results of an analysis on GaSb and concluded that the assumption (ii) was valid in that case.
With the above assumptions, the equations for the longitudinal and transverse current densities in a magnetic field $B$ parallel to $z$-axis may be of the form (68S1)

\[ J_x = F \sum_{i=1}^{\Lambda} A_i - F \sum_{i=1}^{D_i} \]
\[ J_y = F \sum_{i=1}^{y} A_i + F \sum_{x=1}^{D_i} \]

(I1-72)

where

\[ A_i = \frac{\sigma_i}{1 + \frac{\sigma_i^2}{R_i} B^2} \]
\[ D_i = -\frac{\sigma_i R_i B}{1 + \frac{\sigma_i^2}{R_i} B^2} \]

$i$ runs over all bands occupied by carriers and $E_y$ is Hall field. From Eq. (II-72) we obtain the following expressions for $R_H$ and $\sigma$,

\[ R_H = -\frac{1}{B} \frac{\sum_i D_i}{\left( \sum_i A_i \right)^2 + \left( \sum_i D_i \right)^2} \]  

(II-73)

and

\[ \sigma = \frac{\left( \sum_i A_i \right)^2 + \left( \sum_i D_i \right)^2}{\sum_i A_i} \]

(II-74)

These equations have been used in the analysis for the multi-band case in terms of the single band values described in the preceding sections.
Fig. (II-1)  Band Structure of GaAs (66P1).

$k = \frac{2\pi}{a} (\text{III})$  \quad  $k = (000)$  \quad  $k = \frac{2\pi}{a} (100)$
CHAPTER III EXPERIMENTATION

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CHAPTER III  

EXPERIMENTATION

We have measured the Hall coefficient and electrical conductivity as a function of temperature for all material used in this work. For some of the samples, magnetoresistivity has been measured as a function of magnetic field at room temperature. Some pieces of equipment such as the temperature controlled furnace, the electromagnet, etc. and the measuring apparatus and techniques are described below. In the preparation of each sample, it was necessary to produce a sample which was exact in shape and which had mechanically stable electrodes and ohmic contacts. These points are discussed in this chapter.

III-1  
Temperature Controlled Furnace and Sample Holder.

The furnace originally designed by Dr. G. Dionne (71D1) for measurements between 77 and 800 K was reconstructed in part. A schematic drawing of the furnace is shown in Fig. (III-1). The principal features of this design are: (a) a small outside diameter in order that it could fit between the pole pieces of the Harvey-Wells 15 inch electromagnet with a gap of 1.25 inch and (b) low power consumption and good temperature stability. The two vacuum jackets can be separately evacuated to below $10^{-3}$ Pa. and give good insulation in the outer wall of the furnace. The maximum temperature of the outer stainless steel wall does not exceed 50°C for a specimen temperature of 430°C. A quartz tube is sealed at the bottom end forming the inner wall of the double jacket and the inner jacket
can be filled with nitrogen to facilitate measurements below room temperature. A sample holder fits inside a copper capsule around which a heater wire is wound. The inner-most region is evacuated and then filled with helium gas to prevent undue oxidation of the sample and to help in establishing temperature equilibrium. Because the copper capsule is a good conductor and well insulated, no temperature gradients within the capsule could be observed when a thermocouple probe was used. Temperatures are measured using a thermocouple (Pt vs. Pt + 13% Rh) which is attached to the sample holder. One of the junctions is placed within 1 mm of the sample.

Temperature control is achieved by use of the electro-optical system shown in Fig. (III-2). The signal from the thermocouple is fed into a Rubicon potentiometer set for a given temperature. When the galvanometer spot is in the off-balance position, no light falls on the photocell and maximum current is proportional to the photocell resistance. As the temperature rises and the light spot approaches the photocell the current falls, reaching equilibrium when the potentiometer is at balance. Temperature control to better than ±0.01°C was obtained over the whole temperature range (room to 430°C) when the applied magnetic field was zero. The thermocouple shows a Hall effect and a deviation of ±0.07°C has been observed when B = 3.0 Wb/m². The long term stability is ±0.05°C/hr. The drift problem arises mainly from the drift of the voltage supply to the potentiometer. The reference ice bath is stirred periodically to maintain its temperature constant.
The schematic of the sample holder designed by Dr. J. Basinski (72B1) is shown in Fig. (III-3). The sample holder was machined from pyrophylite and then fired at 1500°C in an inert atmosphere. The contacts to the sample are made with platinum or tungsten wires attached to the stainless steel screws (#304). The copper lead wires are then attached to the other end of the screws at the back of the holder and together with thermocouple wires, are cemented in place in grooves cut for the purpose. The narrow neck of the holder then fits inside a quartz tube which is attached to the upper flange of the furnace. The lead wires are passed through ceramic thermocouple feed-throughs placed inside the quartz tube and then passed through Kovar feed-throughs in the upper flange. In this way the lead and thermocouple wires are continuous from the sample holder to the outside of the furnace reducing possible thermal noise due to junctions.

III-2 Measuring Apparatus and Technique

The leads from the sample are soldered to a Leeds and Northrup selection switch which is connected to an Astrodata nanovolt amplifier, Model 120, the output of which is then connected to a five figure Dana digital voltmeter, Model 5330/360. The resolution of the voltmeter is 1 μV, but in conjunction with the nanovolt amplifier, which is used at gains of $10^3$ and $5 \times 10^3$, gives resolution of 5 nV, limited by the input noise of the instrument. The advantage of the nanovoltmeter amplifier is that it has a high input offset capability and hence the zero-field resistivity voltage and
the misalignment voltage on the Hall probes can be completely backed off.

The current to the sample is supplied by a 12V battery with suitable rheostats in the circuit. Currents below 10 mA have then been used depending on the sample resistance and the magnitude of the signals.

The electromagnet for this work is a Magnion-Harvey-Wells 15 inch model, with a pole gap of 1.25 inch and maximum field of $3.2 \text{ Wb/m}^2$. Proton resonance has been used to check the accuracy of the gaussmeter, but there was no observable difference in the field values measured by the proton resonance method and gaussmeter attached to the magnet. The accuracy with which any field can be determined is five parts in $10^5$ and the stability is one part in $10^6$. Uniformity over a 10 mm specimen placed in the centre of the pole pieces is one part in $10^5$ at maximum field. The field sensed by the power supply is that at the gaussmeter probe which must be removed from the centre of the pole gap to make way for the furnace. Therefore it has been necessary to calibrate the field setting to give the true magnetic field intensity at the sample position.

The calibration has been performed by a similar method to that used by Aubin (69A2). With the gaussmeter at the centre of the pole gap, and the operating mode on "Field Set", the dials were set for 1.0000 kG. The mode was then switched to "Sweep" but with a zero sweep velocity so that the current remained constant. The gaussmeter was moved to the "outside" position to make way for the furnace. The sensed field at this stage was
different from the dial field so that the signal caused the galvanometer needle to deviate from the balance position. The dial setting was then changed until the signal was zero. The results of the calibration for both field directions are shown in Table (III-1).

A schematic drawing of the measuring circuit is shown in Fig. (III-4). For the resistivity measurements, any unwanted signal was backed off before applying the electric field to the sample, the resistivity was measured with the electric field applied and then the resistivity signal backed off before the magnetic field was turned on for the magnetoresistivity measurements. The Hall voltage was measured by a similar method except that in this case only the misalignment voltage was backed off before the magnetic field was applied to the sample. The above measurements were repeated with reversed magnetic field and current for a given combination of probes. For a parallelopiped type sample, two different probe combinations are available for resistivity and Hall voltage measurements respectively. Hence measurements were repeated four times for the resistivity measurement and eight times for the Hall voltage measurement at a given temperature. In the case of a Van der Pauw type sample (58V1), there are four and two different probe combinations for the resistivity and Hall voltage measurements respectively, and thus the number of repetitions of the measurement increases correspondingly.
Material and Sample Preparation

A. Material

The semiconductors used for this work were GaAs, InP and Ga$_{1-x}$Al$_x$As. In all cases the samples were single crystal and showed n-type behaviours.

The GaAs samples were obtained from Monsanto Chemical Co., Bell Northern Research Lab. and Electrical Material Co. All the InP samples were cut from material obtained from Monsanto Chemical Co. The Ga$_{1-x}$Al$_x$As alloys were in the form of epitaxial layers grown on Cr-doped semi-insulating GaAs substrates by SpringThorpe et al. (75SI) at Bell Northern Research Lab. They examined the uniformity of their epitaxial layers using a step-growing technique and the results showed no measurable variation in Al-content in the direction of crystal growth, [100]. Alloy compositions were determined by using photoluminescence and electron-probe microanalysis. Springthorpe et al. also showed that the measured values of Hall coefficient and conductivity for the layers did not change when the substrate was removed.

B. Sample Preparation and Ohmic Contact

Two geometrical forms have been used for the samples in present measurements; one is the conventional parallelopiped and the
other the Van der Pauw type. For all five samples of GaAs and three of the five InP samples, the parallelopiped shape has been used. The Van der Pauw type has been employed for all alloy samples and two of the five InP samples.

The GaAs and InP samples were cut from the respective slices using a carborundum disc or a wire saw, and then the six sides were lapped using #3200 alumina lapping powder. Frequently too much lapping bowed the specimen surfaces, resulting in a sample thicker in the central part than at the edges because lapping usually begins from the edges of the sample. The surface bowing was appreciable particularly when the sample holder for lapping fitted loosely in the lapping block. Samples exact in shape could be obtained simply by cutting them using the wire saw with the proper low tension and velocity, so that lapping was not necessary. In the case of Ga$_{1-x}$Al$_x$As alloys, the layers were cleaved into squares. All the samples were boiled in trichloroethylene to get rid of grease and rinsed in boiling alcohol just before evaporating contacts.

In and Au (or Au-Ge alloy) were evaporated onto the contact points for InP and GaAs samples respectively. In the case of parallelopiped samples, the distances between the evaporated strips for the resistivity and Hall voltage measurement probes were 4 or 6 mm depending on the sample size. Both ends of the specimen were completely covered with the respective evaporants for current contacts. The sample dimensions were
between 12 x 1.5 x 0.55 mm and 10 x 1.2 x 0.3 mm, and thus it was not necessary to make corrections to the measured Hall voltages as discussed by Voger (50V1). In the case of Ga_{1-x}Al_{x}As, Au-Ge alloy was evaporated onto four corners of the square samples. The sample shapes used are shown in Fig. (III-5).

To obtain ohmic contacts, the evaporated In films at the contact points were alloyed into the InP crystals for three minutes at 300°C, while in the case of the GaAs samples the alloyings were performed for 2 minutes at 530°C and 4 minutes at 450°C for Au and Au-Ge films respectively in N₂ atmosphere. The bulk samples were then placed on the sample holder and 0.005 inch Pt wires were spark-welded to the contact points by discharging a condensor (~ 10 μF) charged to less than 10 V. This welding method has proved to give contacts which ensure ohmic behaviour up to the maximum temperature employed for the bulk samples.

Yokoyama et al. (75Y1) studied the alloying effects of Au-Ge alloy into n-type GaAs. The results showed that a rapid heating up to the alloying temperature alloys more uniformly the evaporated Au-Ge film with GaAs than does slow heating. Ge is distributed homogeneously over the uniformly alloyed GaAs-(Au-Ge) interface and helps reduce the contact resistance. In alloying Ga_{1-x}Al_{x}As samples with Au-Ge films evaporated onto the four contact points, we used a furnace preheated up to ~ 200°C in nitrogen atmosphere. In this way the annealing temperature of 410°C was obtained within 4 minutes, and the samples were annealed for 3 ~ 4 minutes.
In connecting the alloy sample to the probe screw on the sample holder, we have used a different method from that for the case of parallelopiped sample. This was because the samples were small and hence the distance between the contact points and screws was rather large and with long electrode wires attached to the screws it was not possible to keep the connections at the contact points mechanically stable. This problem of the mechanical strength of contacts occurred also in the case of the parallelopiped samples as indicated by Basinski (72B1). To meet these difficulties, we used the separate sample holder shown in Fig. (III-5b). In this holder the electrodes are cemented onto a strip of glass slide using a fire proof and insulating adhesive obtained from Säureisen Cement Co., Pittsburgh, Penn. The electrodes are then precisely arranged with proper tension so as to keep the sample stable mechanically when it is placed under the electrodes. Spark-welding was avoided for these alloy samples because the contacts were already ohmic and mechanically stable even at high temperatures. This method has been tried for parallelopiped sample and the results were satisfactory. The ohmic behaviour of the contacts was checked by measuring the I-V characteristics of the formed specimen.

Special care had to be taken with the size of the contact area and the geometrical symmetry of samples when we used the Van der Pauw method. The equations deduced by Van der Pauw for the calculation of the Hall coefficient and electrical resistivity from the measured values using this method are based on the assumptions that the electrodes are
on the circumference of the sample and that the contact area is very small. The equation for the resistivity includes a correction term which allows for asymmetric effects in the measured values with different combinations of probes. Wieder (76W1) discussed the errors in the measured values due to electrode size and asymmetry, spatial inhomogeneities, inhomogeneities in the sample thickness, etc, when the Van der Pauw method is employed in experiments. Chwang et al. (74C1), calculated the correction factor due to the finite size of contacts by considering the effects of voltage shorting due to the current electrodes and of current shorting due to the Hall voltage electrodes for square samples with electrodes of triangular and square shapes. The present measured values were corrected using the factors calculated by Chwang et al. Correction is obtained by multiplying the measured values by the appropriate correction factor. Other errors in the measured values may arise due to poor quality of the samples but effects of this type were neglected in this work. The sample dimensions and correction factors for the measured Hall coefficient with the square electrodes used on the Ga\textsubscript{1-x}Al\textsubscript{x} As alloy samples are given in Table (III-2). The correction factor for the measured Hall voltage is given as a function of Δl/l (Δl and l are the size of contact and sample respectively) and Hall angle. In the present case, the Hall angle θ was very small for all samples and the correction was made using the values calculated by Chwang et al. (74C1) for tan θ = 0.1. Correction factor values for resistivity range from 1.005 to 1.016 in the present case.
<table>
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<tr>
<th>Sample Site</th>
<th>Magnetic Field at kG</th>
<th>Gaussmeter Reading</th>
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<tbody>
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### Table III-2

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</tbody>
</table>

Table III-2  Sample dimensions and correction factor for measured Hall coefficient for square samples in Ga$_{1-x}$Al$_x$As. Millimeter was used as unit of length and contact size is average value.
To Vacuum Pump

Quartz Tube

Stainless Steel Tube
Sample Holder
Sample Chamber
Heater
Vacuum Jackets

Feed-throughs for Lead Wires and Thermocouple

A - Exchange Gas Inlet

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CHAPTER IV

IV-1 Introduction

Previous theoretical and experimental work in the field with which we are concerned will be reviewed in this section.

When no intentional dopant is added to the bulk, GaAs samples always grow n-type. This n-type nature is thought to be due to Si impurities, which enter into solid solution from the surrounding growth apparatus (62C2). Hicks and Green (70H1) found that in the growth of layers by the liquid-phase epitaxial method at temperatures between about 700 and 850°C, p-type layers were obtained, because at these temperatures Si shows a preference for the As sites. At higher growth temperatures n-type material is obtained, since Si then prefers the Ga sites.

Te, Se and Sn are well-known donor type impurities. The latter two elements are found to give more than one donor level (67H1). Te is known to exhibit an impurity level associated with the \( \lambda_1 \) band (70P1).

Callaway’s theoretical calculation (57C1) predicted that the lowest conduction band minimum in GaAs is at the centre of the Brillouin zone and that the subsidiary band minima are in the \(<111>\) directions a
few tenths of a volt above the $\Gamma_1$ minimum.

Ehrenreich (60E1) analyzed various experimental data on GaAs and concluded that the direct gap has a value of 1.53 eV at 0 K and that the effective mass for the central conduction band minimum is 0.072 m. From an overall fit to the experimental data he showed that the lowest subsidiary band is in the <100> directions. Wave-length derivative reflectance measurement by Sell (72S1) gave the band gap to be 1.5192 eV at 2 K. Aspnes and Studna (73A1) performed Schottky-barrier electroreflectance measurements, which give various band parameters at the $\Gamma$ and $X$ points. The analysis of the experiment gave a value for the direct band gap of 1.5177 eV at 4.2 K which is consistent with the value obtained by Sell (72S1).

Diverse data on the subsidiary bands are shown in previous work. Photoemission studies of James et al. (68J1) showed transitions to subsidiary minima at about 0.35, 0.45 and 0.95 eV above the $\Gamma_1$ minimum and were interpreted as being transitions to the minima at the $X_1$, $L_1$ and $X_3$ points in the Brillouin zone. From high pressure work, Pitt and Lees (70P1) showed that the $X_1$ minima are at 0.38 eV above the $\Gamma_1$ minimum and that the density of states effective mass of the minima is 0.85 m. Balslev (68B1) measured the indirect absorption from the $\Gamma_1$ minimum to the subsidiary minima as a function of uniaxial compression along various directions. The results reveal the subsidiary minima in the <100> directions at 0.43 eV at liquid nitrogen temperature.
Intraconduction band absorption measurements of Onton et al. (7201) gave a value of 0.483 eV at 2 K for the $X - \Gamma$ separation.

Band structure calculations also have not consistently predicted the relative position of the $X$ and $L$ minima (66C1, 69J1, 70C3, 68H1). Pseudopotential calculations of Cohen and Bergstresser (66C1) gave the $L$ minima to be 0.1 eV below the $X$ minima, whereas Jones and Lettington (69J2), using the same method but a different form of pseudopotential, calculated the $L$ minima to be 0.4 eV above the $X$ minima. The $k \cdot p$ calculation of Pollak et al. (66P1) placed the $L$ and $X$ minima at about the same energy. Collins et al. (70C3) calculated the electronic structure of GaAs using self-consistent orthogonalized-plane-wave method and showed that the $L$ minima are 0.38 eV above the $\Gamma$ minimum and that the next minima, occurring along <100> direction, are at 0.82 eV above the $\Gamma$ minimum. Herman et al. (68H1) showed that it is possible to adjust the Fourier coefficients of the potential used in the OPW calculation to obtain close agreement with the observed transition energies between the various minima throughout the band structure. They found that if the $L$ and $X$ minima were taken to lie 0.43 and 0.35 eV respectively above the $\Gamma$ minimum, then a good overall fit to the experimental data was obtained.

Recently Aspnes et al. (76A1) measured Schottky-barrier electroreflectance spectra and the results showed that the $L$ minima are located 170 ± 30 meV in energy below the $X$ minima, resulting in the subsidiary
band ordering opposite to that proposed from most of the previous experiments. In the light of this new conduction band ordering, $\Gamma_{1} - L_{1} - X_{1}$, Aspnes (76A2) re-examined comprehensively the existing experimental data and obtained a set of consistent band parameters. These band parameters obtained by Aspnes are in excellent agreement with the predictions of nonlocal-pseudopotential calculations (74P1, 76C1). Pandey and Phillips (74P1) predicted the existence of the $L_{1}$ and $X_{1}$ at 0.33 and 0.48 eV respectively above the $\Gamma_{1}$ minimum. The band structure of GaAs calculated by Chelikowsky and Cohen (76C1) using a nonlocal-pseudopotential method showed that the band gap is 1.51 eV and that the $L_{1}$ and $X_{1}$ minima are 0.31 and 0.52 eV respectively above the $\Gamma_{1}$ minimum.

Because of its theoretical and technological importance, GaAs is one of the III-V compounds whose transport properties have been intensively investigated. However uncertainty in the values of the material parameters and practical difficulties in the calculation have prevented a satisfactory explanation of the electrical transport phenomena.

Ehrenreich (60E1) calculated values of mobility by using polar optical, acoustic deformation potential and ionized impurity scattering to compare with experimental data measured in the temperature range from \( \sim 50 \) to 800 K and gave higher calculated values than the measured ones. He attributed the discrepancy to impurity scattering (space charge) as suggested by Weisberg (62W1).
Fortini et al. (70F2) calculated the carrier mobility due to polar optical scattering using an iterative procedure. The results were in reasonable agreement with experimental data at room temperature, but considerably larger than the measured values at higher temperatures. They concluded that the discrepancy at higher temperatures could be due to the fact that they neglected multiphonon effects and the temperature dependence of the dielectric constant in their calculation. However, Ikoma (70I1) showed that the two phonon process becomes important only at still higher temperatures, $T > 2\Theta$, where $\Theta$ is the characteristic temperature defined by $\Theta = \hbar \omega_0 / k_B$.

To explain the measured Hall mobility data between 20 and 600 K, Rode and Knight (71R1) employed various scattering mechanisms such as polar optical and acoustic modes, piezoelectric and ionized impurity scattering in their calculation. Their calculated electron drift mobility for the $\Gamma_1$ band was $0.79 \text{ m}^2/\text{V-sec}$ at 300 K and the corresponding Hall mobility $0.84 \text{ m}^2/\text{V-sec}$.

Akita et al. (71A1) considered a low frequency dielectric constant variation with temperature in the polar optical scattering calculation and explained their Hall mobility data for pure samples in the temperature range from room to 800 K by including two further scattering mechanisms, i.e., acoustic deformation potential and piezoelectric scattering in the calculation. The samples with $n = 1.6 \times 10^{20} \text{ m}^{-3}$ showed intrinsic behaviour above about 650 K.
Blood (72B2) measured transport characteristics for pure samples of vapor-phase epitaxial GaAs in the temperature range 300 \(^\circ\) 800 K. He compared his Hall mobility data with theoretically predicted values by Fortini et al. (70F2) and Rode (70R1). However, both theoretical values are about 20 \(^\circ\) 35\% higher than the measured values at all temperatures concerned.

All the theoretical work reviewed above has been carried out using a one-band model, the \(\Gamma_1\) band.

There is a large amount of experimental data on the \(X_1\) band transport properties. Measurements are usually carried out on GaAs under high pressure. Low field mobility values of 0.0155 and 0.011 \(m^2/V\cdot\text{sec}\) in the \(X_1\) band were obtained by King et al. (66K1) and Hutson et al. (67H1) respectively. Pitt and Lees (70P1) obtained Hall mobilities in the range 0.011 \(^\circ\) 0.041 \(m^2/V\cdot\text{sec}\) from high pressure work.

Vyas et al. (73V1) measured Hall mobility values for electrons in the \(X_1\) valleys from 300 down to 120 K at 40 Kbar. They calculated the Hall mobility using polar optical, intervalley, acoustic deformation potential and space-charge scattering mechanisms. They adjusted the deformation potential \(E_{DX}^{\text{polar}}\), intervalley scattering coupling coefficient \(D_{XX}\) and effective space-charge cross section \(N_{\text{eff}}Q_s\) to fit the measured values. The resulting parameter values are in good agreement with those which Fletcher and Butcher (73F1) used to reproduce theoretically...
the same experimental data. Both analyses (73V1, 73F1) agreed on the importance of intervalley and space charge scattering in the calculation. The importance of space charge scattering increases with carrier density, which is consistent with the results of the analysis of the low temperature GaP data of Toyama et al. (69T1).

To the author's best knowledge, there is no published experimental data on the transport properties of the $I_\perp$ valley in GaAs. Even at high temperatures, most previous authors explained transport effects in terms of the $I_\perp$ only or the $I_\perp$ and $X_\perp$ bands (70I1).

The two-band analysis developed by Kwan et al. (71K1) proved to be very successful in analyzing the data for GaSb (72B1). Basinski (72B1) measured the resistivity of GaAs as a function of magnetic field intensity at 400°C. This high temperature was chosen in order that sufficient carriers would be excited into the lowest subsidiary band to give a measurable two-band effect. However, when $\rho_0/\Delta\rho$ was plotted against $B^{-2}$, a systematic deviation from a straight line behaviour was observed and the intercept at $B^{-2} = 0$ was negative. Neither of these results are predicted by the two-band model (71K1). Thus it seems that the two-band model cannot be applied in this case, probably because of the effects of the third band.

In the analysis of the high temperature transport properties, Basinski (72B1) employed three different models of conduction band
IV-2  Experimental Results.

Four of the five GaAs samples for this work were doped with Te to a concentration between $4 \times 10^{23}$ and $5 \times 10^{24}$ m$^{-3}$ and the measurements of conductivity and Hall coefficient at a field of 0.80 Wb/m$^2$ were made by Dr. Basinski in the temperature range from 20 to 600°C. Here we have considered the data up to 500°C only because of possible loss of As in the higher temperature range. The Hall coefficient $R_H$ and conductivity $\sigma$ for these four samples measured by Basinski as a function of temperature are shown in Figs. (IV-2 to IV-5). No appreciable change in the measured Hall coefficient value is observed up to $\sim 200^\circ$C and the value increases with temperature above $\sim 200^\circ$C. The large increase in the $R_H$ value at high temperatures is expected to allow a meaningful multiband analysis in these samples.

In the case of one pure sample, the Hall coefficient at 0.4 Wb/m$^2$ and conductivity were measured in the temperature range from 20 to 400°C and the results are shown in Fig. (IV-1). The variations of the $R_H$ and $\sigma$ values in the lower temperature range imply a carrier density increase through the ionization of donors. Because of low
carrier density in this sample, significant numbers of carriers are not expected to be excited into the subsidiary bands in this temperature range. The room temperature data for the five samples are given in Table (IV-1).

IV-3 Assignment of Parameters

Following Ehrenreich's suggestion on the GaAs band structure, most previous experimental results have been explained in terms of the conduction band ordering \( \Gamma_1 - \Delta_1 \) (or \( X_1 \)) - \( L_1 \). There had been no conclusive experimental evidence on the \( L_1 \) minima until Aspnes et al. (76A1) observed the \( L_1 \) minima at 170 ± 30 meV below the \( X_1 \) minima in GaAs. With the band ordering, \( \Gamma_1 - L_1 - X_1 \), Aspnes (76A2) reinterpreted the various experimental data comprehensively and found a set of consistent band parameters by reanalyzing and combining the existing experimental and theoretical results. This band ordering will be employed in our analysis of GaAs transport properties. Some of the parameters such as the temperature coefficient of the subsidiary band gap variation with temperature, regarded as uncertain in Aspnes' analysis, will be treated as adjustable.
A. \( \Gamma_1 \) band

According to Eq. (II-14) the band gap variation is given by

\[
E_0 = 1.519 - \frac{5.405 \times 10^{-4} T^2}{204 + T}
\]

The parameter values in the above Varshni equation are those determined by Thurmond (75T1). The effective mass variation with temperature is one of the more important parameters in the transport calculation. Once the effective masses at two temperatures are given, we can find the value of "a" in Eq. (II-13) using Eqs. (II-13, 14). To determine the value of "a" some average values of the existing data on the effective masses at 0 and 300 K were chosen and the results are given in Table (IV-3) for three different cases. Now we can predict the bottom of the band effective mass variation with temperature using Eqs. (II-7, 13 and IV-1).

The acoustic deformation potential is usually estimated from the relationship, \( E_{DP} = -\left(\frac{\partial E}{\partial P}\right)_{T}/K \), where \( K \) is the compressibility and \( \left(\frac{\partial E}{\partial P}\right)_{T} \) is the band gap variation with pressure. Ehrenreich (61E1) indicated that the deformation potential calculated from the above approximation would be too low by no more than 30 \(^\circ\) 40\%, but not by a factor 3. However it is considered to be a controversial parameter in fact. For example, Zawadski and Szymanska (71Z1) have quoted a wide range of values of \( E_{DP} \), 7.2 \(^\circ\) 32 eV, for InSb from various different experimental
analyses. With $E_{DT} = 14.6 \text{ eV}$ they (7121) obtained the best fit to the experimental transport values in InSb. The same is true in the case of GaAs; values of 7.0 eV (60E1), 11.6 eV (71R1) and 14 eV (68I1) have been used. Hence $E_{DT}$ value is determined by adjusting it to fit the experimental results in the present work.

As the temperature increases, the number of electrons excited into the subsidiary bands increases and interband scattering between the bands becomes important. Conwell and Vassell (68C2) and Fawcett et al. (70F1) have calculated the high field transport characteristics and the results indicated values of coupling coefficient for interband scattering in the range $5 \times 10^9 \sim 2 \times 10^{11} \text{ eV/m}$. The calculations were made for interaction between the $\Gamma_1$ and $X_1$ bands. With the present band ordering, however, the high field properties need to be calculated in terms of the $\Gamma_1$, $L_1$ and $X_1$ minima. Work on this problem has only recently done (77A1, 78C1) after the present analysis had been completed. Hence both $D_{\Gamma L}$ and $D_{\Gamma X}$ are treated as adjustable in the present analysis. The other material parameters used in this analysis are given in Table (IV-2).

B. $L_1$ Valley

The $L_1 - \Gamma_1$ separation varies with temperature. This energy variation influences the interaction between non-equivalent valleys and affects the carrier distribution between the bands. Aspnes (76A2) obtained $\alpha_L = -6.5 \times 10^{-4} \text{ eV/K}$ and $\theta_L = 204 \text{ K}$ for the $L_1 - \Gamma_{15}$ energy gap
variation from the measured $L^C_6 - L^V_6$ variation between 4 and 295 K assuming a rigid valence band. He also analyzed the high-temperature transport measurements of Blood (72B2) and the results showed that the above value of $\alpha_L$ is too high. He choose $\alpha_L = -6.05 \times 10^{-4}$ eV/K as a compromise value between the two types of experiment and regarded this value as uncertain. Previous work (74A1) has shown that the assumption of a rigid valence band may introduce an error of $\sim 10\%$. In the present work, therefore, $\alpha_L$ and $\theta_L$ will be assumed adjustable.

For conduction band minima away from the centre of the Brillouin zone, the extremum energy of a particular valley depends on the magnitude of the stress and its direction with respect to the $k$-vector specifying the valley position. This energy shift is described by the deformation potentials of Herring and Vogt (56H1), $\Xi_d$ and $\Xi_\mu$ being the dilational and shear deformation potentials respectively. The effective deformation potential in the $L_1$ band is given by (73V1)

$$E^{DL} = \Xi_d + \frac{1}{3} \Xi_\mu - a$$

(IV-2)

where $a$ is the deformation potential constant of the valence band. These deformation potential components are not known. Hence acoustic deformation potential mode scattering (intra-valley) has been calculated using trial values of $E^{DL}$. 


As mentioned in Chapter II, both longitudinal polar optical and acoustic phonons contribute to the intervalley scattering in the L valleys. Each mode scattering is given in terms of its own coupling coefficient and phonon energy and thus the analysis becomes very involved because of the increase in the number of unknown parameters. Therefore an effective value of coupling coefficients covering both mode scattering mechanisms has been used in the present work and the value treated as adjustable. The intervalley scattering in the L valleys is just on the boundary between being an Umklapp and a normal process and requires a phonon very near the X point (75R2).

The other important scattering mechanisms are interband processes in which carriers are scattered into the \( \Gamma \) and \( X \) bands.

As a starting point, the coupling coefficient for the interband scattering between the \( L \) and \( X \) bands is assumed to be equal to \( D_{\Gamma L} \).

C. \( X \) valley

The \( X \) minima are at 1.98 eV above the top of the valence band at 0 K (76A2). Aspnes assumed \( \alpha_X \) to be \( 4.6 \times 10^{-4} \text{ eV/K} \), 85% of \( \alpha_\Gamma \), with \( \theta_X = \theta_\Gamma \). We take these temperature coefficient values as starting points, and then adjust them to give a good fit to the experimental data at the high temperatures for the cases of the heavily doped samples. The present band parameters give carrier density in the \( X \) valley of below 5% of the total carrier density at the highest temperature.
considered in this work, but the $X_1$ valley is expected to play a significant role in restricting the mobilities of the lower lying band carriers through interband scattering. Because the carrier mobility in this band is very low compared with those of the other two bands, the $X_1$ band would act as a "carrier sink" and hence reduce the total conductivity.

As a starting point, $E_{DX}$ and $D_{XX}$ are assumed to have the same values as $E_{DL}$ and $D_{LL}$ respectively. The final values of $E_{DX}$ and $D_{LX}$ are determined from the analysis of the high pressure data of Pitt and Lees (70P1).

IV-4 Method of Analysis

All the analysis is carried out using a method of fitting the theoretical values of conductivity and Hall coefficient to the experimental results by varying chosen appropriate parameters.

At about $120^\circ C$, carriers start to be excited into the subsidiary bands in doped samples and a multiband analysis is required above this temperature. Below this temperature, the transport properties are dominated completely by the $\Gamma_1$ carriers. Thus for all doped samples, in this temperature range we are dealing only with the $\Gamma_1$ electrons and only four scattering mechanisms need be considered, i.e., (1) longitudinal polar optical mode, (2) acoustic deformation potential
mode, (3) piezoelectric mode and (4) ionized impurity scattering mechanisms. Space charge scattering may need to be considered only for pure samples. Hence we have chosen the doped samples for the determination of $E_{D_T}$ and $N_A$, which are the only unknown parameters in these scattering calculations. The ionized impurity concentration is assumed to be

$$N_{cc} = n_t + 2N_A$$  \hspace{1cm} (IV-3)

where the compensated acceptors are assumed to be singly ionized. As the temperature increases, the interaction between the $\Gamma_1$ and subsidiary bands increases through interband scattering and thus the values of two different interband scattering coupling coefficients $D_{TL}$ and $D_{TX}$ should be known for the calculation of the $\Gamma_1$ band transport properties at the higher temperatures. Considering the large value of the $\Gamma_1 - X_1$ energy separation, the interband scattering between the two bands is negligible and thus we have set $D_{TX}$ equal to $D_{TL}$ for convenience, leaving one unknown parameter $D_{TL}$ in this case.

In the case of the $L$ valley we have five different unknown parameters, $\alpha_L$, $\theta_L$, $E_{DL}$, $D_{LL}$ and $D_{LX}$. Here $D_{LX}$ is assumed to be equal to $D_{TL}$ for the same reason as in the case of $D_{TX}$. As a starting point we have taken $E_{DL}$ for $E_{DL}$ because there is no good guide to the exact value in this case. $5 \times 10^{-10}$ eV/m has been employed as a starting value for $D_{LL}$, which is a similar value to that for GaSb (74B1). The analysis
has been repeated with various values of $E_{DL}$ and $D_{LL}$ in an effort to determine their acceptable ranges.

Because of the very low carrier mobility and density in the $X_\perp$ band compared to those in the other two bands, an exact calculation is not required in this band and thus the band parameters of Aspnes and scattering parameter values of the $L_\perp$ band have been assumed for the analysis of the $X_\perp$ band. However, for a good fit to the experimental results for doped samples above $450^\circ$C it was necessary to adjust the $X_\perp$ minima variation with temperature.

Pitt and Lees (70P1) showed that Te-doped GaAs has donor levels associated with the $X_\perp$ minima, which are far above the $\Gamma_\perp$ minimum. Hence we have assumed that all donors are ionized at room temperature and the carrier density is constant with temperature in doped samples. In fact the present analysis shows about 2 ~ 3\% carrier increase when temperature is increased from room to about $150^\circ$C in the doped samples. In the case of the pure sample EM 23/11, the experimental data in the temperature range 18 \~ 190\C could be reproduced simply by adjusting $N_{Ss}$ and $N_A$ using a one-band (the $\Gamma_\perp$) calculation with parameter values determined from the analyses of doped samples. The results showed an increase of carrier density with temperature. With this data on the variation of $n$ with temperature, we can estimate the donor level and concentration using a relation given by

\[
    n = N_{DS} - N_A + N_{DD} - N_{DU} \tag{IV-4}
\]
where \( N_{\text{DS}} \) is the concentration of shallow donors, which are assumed to be completely ionized at room temperature, and \( N_{\text{DD}} \) and \( N_{\text{DU}} \) are total and unionized deep impurity density respectively. The impurities have been assumed to be associated with the \( \Gamma_1 \) minimum and \( N_{\text{DD}} \) calculated using \( g_1 = 2 \) in Eq. (II-67) and neglecting excited states. Then the three-band analysis above \( 190^\circ \text{C} \) has been made with the carrier density calculated from Eq. (IV-4).

Fletcher and Butcher (F-B) (73F1) extended their iteration method which we are using in the present work for the calculation for the \( \Gamma_1 \) band to that for the calculation for an ellipsoidal valley. Unfortunately this extended method is very involved and we found it impossible to employ this method to the present work using the present computing facilities in this University. A large discrepancy has been shown in the polar optical mobility calculations between the relaxation time method and the F-B ellipsoidal method, i.e., the mobility value calculated using relaxation time approximation is about 60% of that given by the F-B method in the \( X_1 \) valley at room temperature. Rode (72R2) used his iterative method for a spherical valley to calculate the transport properties in an indirect gap material and obtained satisfactory results in the analysis. We have tried the same method, that is we have applied the iterative method used for the calculation for the \( \Gamma_1 \) band to the calculations for the subsidiary bands. We can define an effective relaxation time as (72F2)
\[ \tau_{\text{eff}} = -\frac{m^*}{e\hbar} P \] (IV-5)

where \( m^* \) is replaced by \( m_d^* \) for the calculation for an ellipsoidal valley and the value of relaxation time so determined is then used for the calculation of transport parameters as defined in Chapter II-2-E. When a calculation is made using this method with the same parameter values as F-B (73F1) used in the calculation for the \( X_1 \) band in GaAs, no appreciable difference is observed in the mobility values calculated using the present method and the F-B ellipsoidal method. Only the Hall scattering coefficient values calculated from the present method is about 2% lower than that of F-B above 300 K. Hence the effective relaxation time method is justified in this analysis.

Even at the highest temperature considered in the present work the \( X_1 \) band contribution is too small to allow a meaningful calculation in this band to be made. Under high pressure the \( X_1 \) band is dominant and thus we can get the parameter values concerning the \( X_1 \) band from an analysis of the transport data at high pressure. In this work we have assumed the following variations of the conduction band minima with pressure (\( P \)). For the \( \Gamma_1 \) minimum (75W1).

\[ E_\text{o}^*(P) = E^*_\text{o}(0) + a'P + b'P^2 \] (IV-6)

and for the \( L_1 \) and \( X_1 \) minima,

\[ E_\text{i}(P) = E_i(0) + a_i'P \] (IV-7)
where \( a' \) and \( b' \) are pressure coefficients of the band gap variation and \( i \) runs over the subsidiary bands, \( X_1 \) and \( L_1 \). To be consistent with these band gap variations, Eqs.(II-7, 18) have been used to estimate the effective mass variations in the \( \Gamma_1 \) and \( L_1 \) bands. The longitudinal phonon frequency has been shown by Buchenauer et al. (73P3) to vary linearly with pressure and such a variation is employed in the present analysis. All impurities are assumed to be ionized into the \( \Gamma_1 \) band at atmospheric pressure and a single impurity level is assumed to be associated with the \( X_1 \) minima (70P1). Hence the neutrality condition is expressed by

\[
{n}_t = {N}_d - {N}_A = {n}_r + {n}_L + {n}_X + n_d
\]

where \( n_d \) is the number of electrons in the impurity level. Considering the multiplicity of the \( X_1 \) minima, the degeneracy factor \( g_1 \) in Eq. (II-67) is 6 (private communication, Dr. K. S. Song). For reasons to be discussed in the next chapter, we have neglected excited states of the impurity level. To fit the experimental data, \( E_{DX}, D_{LX} \) and the \( L_1 \) minima energy have been found to be important and thus assumed adjustable in this analysis. The effects of intervalley scattering in the \( X_1 \) valleys have also been investigated here.
II-5 Results and Discussion

A. Analysis of High Temperature Transport Data

Most of the samples for this work are fairly heavily doped. In the case of doped samples, however, Ehrenreich (60E1) indicated that the Brooks-Herring theory for treating the ionized impurity scattering is questionable. But Rode (75R2) discussed this problem and concluded that good agreement between theory and experiment extending to carrier concentration of $10^{25} \text{ m}^{-3}$ justifies the use of the Dingle's formula.

Ehrenreich (57E1) suggested that the change in the effective mass due to the electron-phonon interaction is negligible and that the lattice dilatation would produce a much greater change in the band curvature. In this case the effective mass band gap $E^*_0$ is estimated by the lattice dilatation only and the variation of $E^*_0$ with temperature is given by

$$\frac{\delta E^*_0}{\delta T} = -\frac{3\alpha}{K} \frac{\delta E^*_0}{\delta P}$$

where $\alpha$ is the coefficient of linear expansion. Camassel and Auvergne (75C1) have shown that the above expression gives a temperature coefficient for the band gap of $-1.3 \times 10^{-4} \text{ eV/K}$ in GaAs, which corresponds
to about one third of the actual coefficient at room temperature. A value of \(-1.2 \times 10^{-4}\) eV/K was used in the calculation of the effective mass band gap variation by Rode (70R1). To be consistent with the above value, 'a' in Eq. (II-13) should be \(\sim 3\). The above values of the temperature coefficient are too low to explain the effective mass variation shown by Stradling and Wood (70S2). In view of this discrepancy, the value of 'a' has been determined by using available values of effective mass and band gap, and the results are shown in Table (IV-3). For the case of 'a' = 1, which corresponds to the case where the optical band gap is equal to the effective mass band gap, the room temperature effective mass value will be 0.0629 m when \(m_o(0) = 0.0665\) m; and this is the case which Aspnes (76A2) used to estimate effective mass variation with temperature. However, there is no experimental data showing so low a value at room temperature and so the case of 'a' = 1 has not been considered further in this work. The three different combinations of effective mass values give 1.36, 1.64, and 1.84 respectively for 'a' and the corresponding acoustic deformation potentials have the values of 16.4, 16.1, and 15.2 eV respectively. Because the mobility due to the acoustic deformation potential depends on effective mass, i.e.,

\[ \mu_{ac} \propto m^* \frac{5}{2}, \]

the fitted values of \(E_{D\Gamma} \) show an increase with decreased 'a'. Hence a lower value of \(E_{D\Gamma} \) is to be expected when only the lattice dilatation component of band gap variation is considered, but the value of 7.0 eV (60E1) estimated using the relationship \(E_D = \left(\frac{\partial E_o}{\partial P}\right)_T / k \) would be too low in the present case.
The $N_A$ values obtained from the present analysis are negligible for the three samples M0572/8, NE22/1 and M0807/8. Rode and Knight (71R1) also obtained the lowest compensation ratio for samples of the similar carrier density range. The most heavily doped sample, MO241/44/2, needs $N_A = 4 \times 10^{23} \text{m}^{-3}$ for the best fit to the experimental data. This higher compensation ratio in heavily doped samples has been shown in previous work (71R1). In this case of MO241/44/2, the scattering by acceptors corresponds to about 15% of the total ionized impurity scattering. The incoherent Born correction and multiple scattering correction calculated by Moore (67M1) for uncompensated GaAs give about 30% decrease of the conductivity calculated from the Brooks-Herring expression, which is too large to explain the present case in terms of such corrections.

The analysis has been performed with various trial values of $D_{LL}$ in the range $1 \sim 10 \times 10^{10} \text{eV/m}$, in an effort to find an acceptable range of parameter values. With high $D_{LL}$ values, the predicted conductivity is higher than the measured one when the other parameters are adjusted to fit the measured Hall coefficient. When the lower $D_{LL}$ value is employed, the opposite effect is observed in the fitting. The resulting values of $D_{LL}$ are in the range $3 \sim 7 \times 10^{10} \text{eV/m}$ as given in Table (IV-3). The value of $D_{TL}$ decreases with decreasing 'a' and increasing $D_{LL}$, but is found to lie in the narrow range of $7 \sim 10 \times 10^{10} \text{eV/m}$.
Up to this point, $E_{DL}^*$ has been assumed for convenience to have the same value as that of $E_{DL}$. Here the same question arises in the determination of $E_{DL}^*$ as for the $E_{DL}$. Pickering and Adams (77P1) found $\Xi_d - a = -11 \pm 3$ eV and $\Xi_{\mu} = 22 \pm 7$ eV in their stress experiments, while Aspnes and Cardona (78A1) determined $\Xi_{\mu} = 25 \sim 30$ eV from a piezoresistance experiment. When these data are applied to Eq. (IV-2), $E_{DL}^*$ have a value of approximately zero. In the case of the $X_1$ band, Pickering and Adams (77P1) obtained values of $\Xi_{\mu}$ and $\Xi_d - a$ from stress experiments, which give in turn a value of $E_{DX}$ of approximately zero. However Vyas et al. (73V1) showed that $E_{DX} = 6$ eV gives the best fit to the Hall mobility data obtained from high pressure experiment. As will be shown later, the high pressure data require a still higher $E_{DX}$ value. In view of this controversy, we have repeated our analysis with several trial values of $E_{DL}^*$ from 6 to 18 eV. For these trial analyses we have used $\alpha = 1.64$ and $E_{DL}^* = 16.1$ eV. 6 eV is the lowest value for the deformation potential which has ever been tried for the transport calculation in GaAs (73V1). With this lowest value, a reasonable fit has been obtained using the $D_{LL}$ values in the range $7 \sim 10 \times 10^{10}$ eV/m and $D_{\Gamma L}$ values in the range $7 \sim 11 \times 10^{10}$ eV/m. When 18 eV was used for $E_{DL}$, a reasonable fit could not be obtained with the $D_{LL}$ values higher than $3 \times 10^{10}$ eV/m. These trial analyses show that a lower $E_{DL}$ requires a high $D_{LL}$, which may be understood from the similar energy dependences for the two different scattering mechanisms related to the above two parameters. Thus we failed to confine the $E_{DL}$ and $D_{LL}$ values to a narrow acceptable range. However considering the experimental data on $D_{LL}$, viz.
1.8 \times 10^{10} \text{eV/m (77A1)} and 1 \times 10^{11} \text{eV/m (77L1)} for GaAs, 5.8 \times 10^{10} \text{eV/m (74B1)} for GaSb and 3 \times 10^{10} \text{eV/m (72R2)} for Ge, the values of 7 \sim 10 \\
\times 10^{10} \text{eV/m appear to be high and thus 6 eV is considered low for E}_{DL}. Also, the assumption that E}_{DL} = E}_{DL} does not seem to be unreasonable, since recent work (77A1, 77L1) has reported the same or similar values for E}_{DL} and E}_{DL} even though they used considerably lower values than those given here. Therefore the results given in Table (VI-3) provide acceptable ranges for the various parameter values except for some parameters related to the X band. Recent three-band analysis of high field transport properties in GaAs gave D}_{IL} = D}_{IX} = 1 \times 10^{11} \text{eV/m (77L1, 78K1)} which is in good agreement with the present results. The E}_{DL} value determined in the present work is to be compared with 14 eV of Ikoma (68I1).

For the pure sample EM23/11, a one-band calculation has been carried out from room to 190°C, where carrier excitation into the subsidiary bands is negligible. In addition to the scattering mechanisms considered for the calculation in the doped samples, space charge scattering has been included in the calculation for this pure sample. At the lower temperatures we obtained a good fit to the experimental data with N_A = 9 \times 10^{21} \text{m}^{-3} and N_Q = 1.05 \times 10^{6} \text{m}^{-1}. From the resulting variation of carrier density with temperature we obtained
\[ E_d = 0.09 \pm 0.002 \text{ eV}, \quad N_{DD} = 1.1 \times 10^{22} \text{m}^{-3} \quad \text{and} \quad N_{DS} - N_A = 3.07 \times 10^{21} \text{m}^{-3} \]
from Eqs. (II-67, IV-4). Using these values of E_d, N_{DD} and N_{DS} - N_A, the carrier density can be estimated above 190°C where a multiband calculation is required with parameter values already obtained from the
analysis for the doped samples. In this way we could reproduce the experimental values in the higher temperature range without adjusting any parameter. With the various sets of parameters determined in this work (Table IV-3) we can obtain fits to the experimental data within an error of 4%. Over the large majority of the range considered, the fit is very much better than this limit, but the largest discrepancy is observed at the highest temperature for the most heavily doped sample when a value of $7 \times 10^{-10}$ eV/m is used for $D_{\text{LL}}$ in Table (IV-3). In general the predicted conductivity is slightly higher than the measured one at the highest temperatures, which may be due partly to the fact that we have disregarded the effects of the subsidiary band carriers in the calculation of ionized impurity scattering for the $T_1$ band.

Thus the true value for $N_{cc}$ would be between $n_t + 2N_A$ and $n_t + 2N_A + \Sigma n_i$, where $n_i$ is the carrier concentration in the subsidiary bands (74B1). A possible change of dielectric constant with temperature (71A1) neglected in this study also may be the cause of such a discrepancy.

B. Analysis of High Pressure Experiments.

As in the case of transport properties at atmospheric pressure, the high pressure transport properties have previously been analyzed in terms of a two-band model (60E1, 70P1, 73V1). Now that we have explained satisfactorily the high temperature transport data in terms of a three-band model, it is of interest to re-examine the high pressure data in terms of such a model. We have chosen three sets of
data obtained by Pitt and Lees at room temperature (70P1), LEll, CL17/8, and
and G62A for this re-examination. In this work we assumed 'a' = 1.64,
\[ E_{DL} = E_{DR} = 16.1 \text{ eV}, \quad D_{\Gamma L} = D_{\Gamma X} = 8 \times 10^4 \text{ eV/m}, \quad a_L = -7.82 \times 10^{-4} \text{ eV/K} \]
\[ \theta_L = 490 \text{ K}, \quad a_X = -6.88 \times 10^{-4} \text{ eV/K} \quad \text{and} \quad \theta_X = 550 \text{ K}, \] which belong to the case No. 5 in Table (IV-3). In fact this set of parameter values is considered to be the most reasonable one because this set was obtained from the average value of effective mass data at zero and 294 K and \( D_{LL} \) value is an average of the three acceptable values. The pressure coefficients for the band minima variations are given in Table (IV-4).

By adjusting only \( N_A \), fits have been made to the Hall mobility data at 0 Kbar using the data on \( N_A - N_A \) given in the literature (70P1). Because of considerable scatter in the \( L_1 \) minima energy value \( (E_L) \) at room temperature (76A2, 78A1), we have treated this energy value as adjustable. This analysis shows that the \( E_L \) value is very important in determining the pressure value which gives the maximum normalized Hall coefficient \( R_H(P)/R_H(O) \) and thus \( E_L \) has been adjusted to fit the pressure value, 33 Kbar, showing maximum \( R_H(P)/R_H(O) \). To make a fit to the maximum \( R_H(P)/R_H(O) \) data, we have tried varying \( D_{\Gamma X}, D_{\Gamma X} \) and \( E_{\Gamma X} \) values and the latter two parameters have proved to have negligible effects on this fit. The experimental maximum values of \( R_H(P)/R_H(O) \) have been reproduced by adjusting only \( D_{\Gamma X} \). \( E_{\Gamma X} \) has been found to be important to make a fit to the reduced resistivity data \( \rho(P)/\rho(O) \) above 40 Kbar. The activation energy of the impurity level has been determined simply by adjusting it to fit the \( R_H(P)/R_H(O) \) data at highest pressures.
Because of the same intercompensating effects between the parameters which have been assumed to be adjustable in the analysis, the analysis has been repeated until a consistent fit was obtained to the three different data, \( \frac{R_H(P)}{R_H(0)} \), \( \frac{\mu_H(P)}{\mu_H(0)} \) and \( \frac{\rho(P)}{\rho(0)} \), throughout the range of pressure considered. The resulting parameter values which give the best fit to the experimental data are compiled in Table (IV-5). The fitted curves to the data for sample G62A are shown in Fig. (IV-6).

The value of \( E_L \) obtained in this analysis is 1.748 ± 0.005 eV at 296 K, which is to be compared with 1.708 eV (76A2), 1.728 eV (obtained from the present analysis of high temperature transport data) and 1.754 ± 0.040 eV (78A1). A value of 1.734 eV is obtained from the extrapolation of the \( L_\perp \) minima data of the \( \text{Ga}_{1-x}\text{Al}_x\text{As} \) alloys to be treated in the next Chapter.

The \( D_{LX} \) values show considerable scatter and are very high compared with recently reported data, \( 5.5 \times 10^{10} \) eV/m (77A1) and \( 5 \times 10^{10} \) eV/m (77L1). The measured normalized resistivity has a maximum value at about 40 Kbar and then decreases with increasing pressure, while the normalized Hall mobility exhibits a minimum value at about 45 Kbar and then increases with pressure. These results may be understood mainly in terms of an increase of the carrier mobility with pressure in the \( X_\perp \) band at high pressures. The present analysis indicates that the interband scattering between the \( L_\perp \) and \( X_\perp \) bands
shows decreasing effects as the pressure increases at high pressures because the energy difference between the $L_1$ and $X_1$ minima increases with pressure in this case. Therefore an increased mobility value is obtained at the highest pressures. The effective mass in the $\Gamma_1$ band is too small to affect the $X_1$ carrier mobility through interband scattering. However, with $D_{LX} = 5 \times 10^{10}$ eV/m it is impossible to make a fit to the maximum $R_H(p)/R_H(0)$ data and to explain the mobility behaviour in the high pressure range. We have already found that a higher $D_{LX}$ value is needed in the fit to the high temperature transport data. It is to be noted that Littlejohn et al. (77L1) used $5 \times 10^{10}$ eV/m for $D_{LX}$ and very high effective mass value of 0.58 m for the $X_1$ band to make a fit to the high field experimental data. The present $D_{LX}$ values are in good agreement with that of GaSb, $1.14 \times 10^{11}$ eV/m (74B1). The $E_{DX}$ values obtained are in the range $12 \sim 13$ eV, which are also very high compared to the frequently quoted value $6$ eV (73V1, 73F1), but consistent with those of GaP, $12.7$ eV (66E1) and $13$ eV (72R2). In this analysis $D_{XX}$ has been assumed to have the same value as $D_{LL} (= 5 \times 10^{10}$ eV/m) which is in good agreement with the theoretical value $5.5 \times 10^{10}$ eV/m of Herbert (73H1). However previous work (68C2, 73V1, 73F1) used $1 \times 10^{11}$ eV/m for $D_{XX}$ and $\sim 6$ eV for $E_{DX}$. We could obtain a fit to the $\rho(p)/\rho(0)$ data with the above $D_{XX}$ and $E_{DX}$ values, but the calculated values of $R_H(p)/R_H(0)$ and $\mu_H(p)/\mu_H(0)$ were then considerably higher than the measured ones. This discrepancy is due to the high value obtained for the Hall scattering coefficient $r_x$. 
when a high $D_{XX}$ value ($1 \times 10^{11}$ eV/m) is used in the calculation. Values of 1.195 and 1.305 are obtained for $r_x$ with $D_{XX} = 5 \times 10^{10}$ and $1 \times 10^{11}$ eV/m respectively.

Two samples CL17/8 (Te-doped) and G62A (undoped) show carrier freeze-out in the impurity level at high pressure, and the activation energy values are shown in Table (W-5). The $E_d$ values are lower than those obtained by Pitt and Lees for the same samples. This disagreement may be due to the different values of spin degeneracy factor used in the two different analyses. In the present analysis the effective mass at the bottom of the $T_1$ band changes from 0.0638 to 0.0871 m when the pressure increases from zero to 60 Kbar, while if the experimental values of $dm^*/dP = 0.007 m^*(O)/kbar$ (73P1) is employed, the effective mass is 0.0906m at 60 kbar. With the same pressure change, the density of states effective mass in a single valley shows a change from 0.2173 to 0.2264 m for the $L_1$ minima. The variation of $m_{dx}$ has been neglected in the present analysis.

We have chosen 12.5 eV and $1 \times 10^{11}$ eV/m as compromise values for $E_{DX}$ and $D_{LX}$ respectively and repeated the analysis on the high temperature transport data using these values. Fits have been recovered simply by reducing the $\alpha_X$ values by $\sim 1.5\%$ from those given in Table (IV-3). This reduction in the $\alpha_X$ value is required because interband scattering between the $L_1$ and $X_1$ bands is increased because of the new high $D_{LX}$ value.
C. Scattering Mechanisms in the Various Conduction Bands.

In this section the scattering mechanisms used in the present work are discussed for the three separate conduction bands. For convenience, the discussion will mainly be limited to the results of the analysis of the data for the medium doped sample MO807/8. The parameter values of case No. 5 of Table (IV-3) with $E_{DX}$, $D_L$ and $\alpha_x$ replaced by $12.5 \text{ eV}$, $1.1 \times 10^{11} \text{ eV/m}$ and $-6.77 \times 10^{-4} \text{ eV/K}$ respectively have been used for calculations of the relaxation times and the corresponding mobilities as shown in Figs. (IV-8 to 13).

Figs. (IV-8, 11) show the relaxation times and mobilities calculated for the $\Gamma_1$ band. In this band, the ionized impurity and polar optical scattering mechanisms are dominant at low energies. Because of the low effective mass value in the $\Gamma_1$ band, acoustic mode scattering is less important compared with the above two mechanisms at low energies, but its contribution increases with increasing energy. Near the sub-band gap energy, interband scattering commences to occur and it dominates all other mechanisms at high energies. However, no electron has such a high energy at low temperature, so that this interband scattering has negligible effect at low temperatures. Piezoelectric mode scattering is negligible over the entire energy range. The carrier mobility values as a function of temperature calculated from the relaxation times given in Fig. (IV-8) are shown in Fig. (IV-11). Polar optical mode scattering is the dominant mechanism over the whole
temperature range except near room temperature. Acoustic deformation potential mode scattering has previously been treated as being negligible or less important (60E1, 70F1, 70R1), but the present analysis shows that the mobility value due to this mechanism is only about twice that due to polar optical mode scattering. Interband scattering between the $\Gamma_1$ and $L_1$ bands is negligible at lower temperatures, but increases in importance with increasing temperature. Thus neglect of this mechanism increases the combined $\Gamma_1$ carrier mobility by about 12 and 16% at 450 and 520°C respectively and reduces the Hall scattering factor to about 95 and 93% of the values obtained by including interband scattering at the two temperatures. Interband scattering between the $\Gamma_1$ and $X_1$ bands and piezoelectric mode scattering are of no importance over the entire temperature range considered.

In the case of the $L_1$ valleys, the high effective mass value increases acoustic mode intravalley scattering and reduces ionized impurity scattering compared with the others as shown in Figs. (IV-9, 12), and acoustic mode scattering plays a dominant role in this band. The relaxation time due to polar optical scattering has been calculated using the R.T.A. method and the effective relaxation time method (E.R.T.). and the resulting values are denoted by dotted and full lines respectively in Fig. (IV-9). A significant difference is observed between the two values at low energies but they are in good agreement above 0.075 eV. The mobility value due to this mechanism shown in Fig. (IV-11) was calculated using the E.R.T. method and is a little higher than that due to
acoustic mode scattering at all temperatures. The intervalley and acoustic intravalley scattering mechanisms have similar dependences on energy and temperature as is shown in the two figures and thus the weightings of the two mechanisms are interchangeable in the fitting to the experimental data as we have indicated already. Interband scattering into the $X_1$ band is important at high temperatures but scattering into the $\Gamma_1$ band is completely negligible because the effective mass in the $\Gamma_1$ band is very small compared with that for the $L_1$ band.

Relaxation times and carrier mobilities calculated for each scattering mechanism in the $X_1$ band are shown in Figs. (IV-10, 13). Intervalley scattering has previously been regarded as the dominant mechanism in the $X_1$ band (73V1, 73F1, 68C2, 77A1). However, we have found that increased intervalley scattering due to a higher $D_{XX}$ value gives a rather poor fit to the high pressure transport data. In this band interband scattering into the $L_1$ band and intravalley acoustic mode scattering are more important than intravalley polar optical and intervalley scattering as is shown in Figs. (IV-10, 13). Again, interband scattering into the $\Gamma_1$ band is negligible for this band for the same reasons as in the case of the $L_1$ band. The resulting combined mobility values are 0.2966, 0.0818 and 0.0139 m$^2$/V/sec for the $\Gamma_1$, $L_1$ and $X_1$ bands respectively at room temperature.
The band minima variation with temperature has been calculated using both the temperature coefficients obtained in the present analysis and also those of Aspnes (76A2) and the two sets of results are compared in Fig. (IV-7). The $L_1$ minima energies calculated from the two different sets of temperature coefficients have almost the same values at the highest temperature considered and show the largest difference between them at around room temperature, where the $L_1$ minima energy obtained here is 20 meV higher than that of Aspnes (76A2). The $X_1$ minima energy calculated from the present temperature coefficients is also higher than that of Aspnes at room temperature but shows a steeper variation with temperature than the latter in the higher temperature range. The carrier distribution among the three different bands is shown as a function of temperature in Fig. (IV-14).

D. Comparison with the High Temperature Transport Data for Pure Samples.

Good transport data obtained for pure samples at high temperatures are now available for comparison with theory (71A1, 72B2). For these samples, the substrates were removed from epitaxially grown samples to eliminate some unwanted effects such as substrate conduction and deep impurities which are believed to occur at the interface between the epilayer and the substrate (71A1). These three different sets of data are given in Fig. (IV-15). The curves indicated by "R" and
"P" exhibit theoretical Hall mobility values quoted by Blood from the literature (70R1, 70F2) for comparison with his data. At room temperature the $\mu_H$ values for these samples are $0.7 \sim 0.76 \text{ m}^2/\text{V}-\text{sec}$, which are in good agreement with those of Stillman et al. (70S1) and Ikoma (70I1) for the samples of similar carrier concentrations.

In epitaxialy grown samples, space charge scattering would be negligible (70I1, 68C2). Thus the values of $\mu_H$ can be calculated using only the scattering mechanisms used in the analysis for the doped samples in the present work. Calculations have been carried out for the two samples of Blood only, since Akita et al. did not report the magnetic field intensity for their measurements and the $N_A$ value. The present parameter values give predicted $\mu_H$ values which are in good agreement with the experimental data as shown in Fig. (IV-15). In these predictions of $\mu_H$, we have neglected valence bands effects, but an estimate from the Fermi level determined in the above calculations shows the onset of appreciable intrinsic effect at about 670 K for the sample with $n_t = 1.1 \times 10^{21} \text{ m}^{-3}$. Therefore our three conduction band calculation is justified for the pure sample only below that temperature. The values of $\mu$, $r$ and $n$ obtained for the above pure sample are given in Table (IV-8). As Fortini et al. (70F2) and Rode (70R1) considered only the $\Gamma_1$ band in their calculations, comparison can be made only below about 500 K because the carrier density in the subsidiary $L_1$ band is significant above that temperature as shown in Table (IV-8). Some authors (60E1, 70F2) have tried to explain the $\Gamma_1$ band properties at or
near room temperature by employing only polar optical scattering. However, the mobility values due to this mechanism are calculated to be 1.002, 0.894 and 0.875 m²/V-sec at 300 K for samples with \( n_t = 1.1 \times 10^{21} \), \( 4.4 \times 10^{23} \) and \( 1.27 \times 10^{24} \) m⁻³ respectively, which are very high compared with the experimental data. The combined carrier mobility at 300 K including all the scattering mechanisms considered here is 0.642 m³/V-sec and the corresponding Hall mobility is 0.721 m²/V-sec for \( n_t = 1.1 \times 10^{21} \) m⁻³. Rode and Knight (71RI) considered all the scattering mechanisms used in the present work for their calculation on a pure GaAs sample and the results gave \( \mu = 0.79 \) m²/V-sec and \( \mu_H = 0.84 \) m²/V-sec, which are considerably higher than the present values. This discrepancy is appreciable and the main difference between the two different calculations is in the use of the values of acoustic deformation potential. Rode and Knight quoted 11.5 eV for \( E_{DT} \), that of ZnSe.

E. Carrier Mobility and Hall Scattering Coefficient.

In the \( \Gamma_1 \) band the carrier mobility at room temperature is in the range 0.22 \( \sim \) 0.67 m²/V-sec for the samples considered in this work, while the values for the \( L_1 \) and \( X_1 \) bands are 0.053 \( \sim \) 0.14 m²/V-sec and 0.01 \( \sim \) 0.02 m²/V-sec respectively. In estimating multiband transport properties it has previously been assumed that the mobility ratio \( \mu_{\Gamma}/\mu_X \) (or \( \mu_{\Gamma}/\mu_L \)) is constant with temperature or pressure (60AI, 70II, 72B2, 76A2). An estimate is usually made by considering the effective
mass ratio between the bands concerned and by assuming only the dominant scattering mechanisms in the bands. However the dominant scattering mechanism may depend upon the sample characteristics such as carrier density and compensating acceptor concentration and the dominant role may vary with temperature and pressure. Hence the above estimate may be seriously in error in these cases. In Fig. (IV-16) the variations of $\mu_\Gamma/\mu_L$ and $\mu_\Gamma/\mu_x$ with temperature are shown for four samples of different carrier concentrations. The curves indicated by BL in the figure are for the samples of Blood (72B2), with $n = 1.1 \times 10^{21} \text{m}^{-3}$. For comparison with the other samples in Fig. (IV-16), we have calculated the mobility with a constant carrier concentration $0.78 \times 10^{22} \text{m}^{-3}$ (room temperature value) at all temperatures and neglected space charge scattering for EM23/11. At room temperature, the $\mu_\Gamma/\mu_L$ values are in the range 3.5 - 4.9 and $\mu_\Gamma/\mu_x$ in the range 21 - 33 for these four samples. The ratios increase with decreasing carrier concentration and with increasing temperature. The carrier density dependence of the ratio can be understood in terms of ionized impurity scattering because this scattering has the largest effect in the $\Gamma_1$ band. The temperature dependence is partly related to the effective mass variation with temperature; when the temperature increases from room to $500^\circ\text{C}$, $m_0^*$ changes from 0.0638 to 0.0582 m, $m_{DL}^*$ from 0.2174 to 0.2046 m and $m_{dx}^*$ was assumed to be constant. The values of $E_F$, $\mu$, $r$ and $n$ calculated for the three different conduction bands as a function of temperature for the three different samples are given in Table (IV-6, 7, 8).
Fig. (IV-17) shows the variations of mobility and carrier density in the three different bands as a function of pressure calculated for sample LEll of Pitt and Lees (70P1). The mobility values show significant changes at pressures around which a band crossover occurs, and $\mu_\Gamma/\mu_L$ and $\mu_\Gamma/\mu_X$ are 4.9 and 32 respectively at atmospheric pressure, while the values are 2.1 and 3.7 respectively at 50 kbar. These changes are due mainly to interband scattering. For example, the $\Gamma_1$ minimum is the highest in energy at the high pressure and thus interband scattering into the $L_1$ and $X_1$ bands is enhanced, and the $X_1$ minima show the opposite interband effects, resulting in a higher $X_1$ mobility at the high pressure than that at atmospheric pressure. When we neglect the interband scattering between the $L_1$ and $X_1$ bands, the $\mu_H$ value in the $X_1$ band is 0.0312 m$^2$/V-sec and $\mu_{H\Gamma}/\mu_{HX}$ is 22.5 at atmospheric pressure which are in reasonable agreement with the values estimated from the extrapolation of the $\mu_H$ variation at high pressures by Pitt and Lees. However, when this interband scattering is included in the calculation, $\mu_{HX} = 0.025$ m$^2$/V-sec and $\mu_{H\Gamma}/\mu_{HX} = 28$. The values of $\mu_X$ derived from experimental data cover a wide range of values, 0.011 (67H1) $\sim 0.04$ m$^2$/V-sec (70P1). Theoretical calculations (69J1, 73V1, 73F1) give values much closer to the higher end of this range. These estimated values of $\mu_X$ are high because the $L_1$ band effects were neglected in the calculations. The results of the present calculations for sample ELll are given in Table (IV-9).
The values of Hall scattering coefficient obtained from the present analysis are shown in Figs. (IV-18, 19). The coefficient increases with decreasing carrier density, which is due to the degree of degeneracy and to impurity scattering (50J1, 50J2). The increase of $r_I$ with temperature in the higher temperature range indicates the increasing effect of interband scattering with increasing temperature. In Fig. (IV-18), $r_I$ values have been calculated for sample MO807/8 with and without interband scattering and the resulting values are 1.1 and 1.03 respectively at 500°C.

**F. Effects of Higher Conduction and Lower Valence Bands on the $\Gamma_1$ Band Structure.**

In this work, we have used a Kane form (57K1) which takes account only of spin-orbit splitting and the interaction between the $\Gamma_1$ conduction band and $\Gamma_{15}$ valence band. Kolodziejczak et al. (66K3) have shown that the inclusion of higher and lower bands in the Kane model results in an increased non-parabolicity in the conduction band and gives an expression for the $\Gamma_1$ band,

$$E = \frac{\hbar^2 k^2}{2m} - \frac{X - E_0}{2} + \frac{X + E_0}{2\chi} \frac{\hbar^2 k^2}{2m} + \frac{X - E_0 \hbar^2 k^2}{2m} \left(\frac{b + c}{5}\right)$$

(IV-10)

where $\chi$, $b$ and $c$ are functions of the various energy separations. Values of electron energy and cyclotron effective mass have been cal-
culated as a function of wave vector $k$ near the $\Gamma$ point at 500°C using Eqs. (II-9, IV-10) and the results are shown in Fig. (IV-20). At the high energy values the two different calculations give appreciable differences in the two parameter values, but in the present temperature range these discrepancies do not cause serious differences in the results of the transport calculations. When Eq. (IV-10) is employed in the calculation for the most heavily doped sample M0241/44/2 at 500°C, the predicted conductivity decreases by about 1% from that calculated using Eq. (II-9) and the Hall coefficient increases by the same ratio.

IV-6 Summary.

High temperature transport data on GaAs samples with a wide range of carrier concentration have been satisfactorily analyzed using a $\Gamma - L - X$ conduction band model. The temperature dependences of the subsidiary band minima and the effective masses in the $\Gamma$ and $L$ bands reported by Aspnes (76A2) have been modified by a small amount to explain the experimental data in the present study. The experimental data on the optical band gap and effective mass variations with temperature in the $\Gamma$ band indicate that the effective mass band gap variation corresponds to $\sim 1/1.6$ of the optical band gap variation, which is very high compared with the theoretical value $\sim 1/4$ calculated from lattice dilatation (75C1). The results of analysis on the high temperature transport data places the $L$ minima 304 meV above the $\Gamma$ minimum at room temperature, while a value of 324 meV has been obtained for the
same energy separation from the present analysis of high pressure data.
According to the present band parameters the effects of the $L_1$ and $X_1$
bands are negligible below $\sim 200$ and $\sim 400^\circ C$ respectively for a pure
sample. Below $\sim 400^\circ C$ intrinsic effects can be neglected for a pure
sample with $n \sim 1 \times 10^{21} m^{-3}$.

The values of acoustic deformation potential are $16.0 \pm 0.5$ eV
and $12.5 \pm 0.5$ eV for the $\Gamma_1$ and $X_1$ bands respectively. When the acoustic
deformation potential for the $L_1$ band is assumed to have the same value
as that for the $\Gamma_1$, the interband and intervalley scattering coefficients
$D_{\Gamma L}$ and $D_{LL}$ are in the ranges $7 \sim 9 \times 10^{10}$ eV/m and $3 \sim 7 \times 10^{10}$ eV/m
respectively. The interband scattering coefficient $D_{\Gamma X}$ obtained from
the high pressure experimental data has a value of $(1.1 \pm 0.2) \times 10^{11}$ eV/m.
The assumption that $D_{XX} = D_{LL}$ and $D_{TX} = D_{TL}$ has been found to be satis-
factory in the present analysis.

In the $\Gamma_1$ band for pure GaAs samples, polar optical scattering
is dominant at all temperatures and for a fit to the experimental data
acoustic deformation potential scattering is very important. Ionized
impurity scattering may be more important than the above two mechanisms
for a doped sample at the lower temperatures considered. Interband
scattering into the $L_1$ band plays a significant role in restricting the
carrier mobility in the $\Gamma_1$ band at high temperatures. In the $L_1$ band
acoustic intravalley scattering is dominant, while interband scattering
into the $L_1$ band is the most important mechanism in the $X_1$ band.
Table IV-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>T</th>
<th>$R_H$</th>
<th>$\sigma$</th>
<th>$n_t$</th>
<th>$N_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>10⁻⁵ m³/Coul</td>
<td>$10^4$ Ohm⁻¹ m⁻¹</td>
<td>10⁻²³ m⁻³</td>
<td>10⁻²² m⁻³</td>
</tr>
<tr>
<td>EM23/11</td>
<td>18.4</td>
<td>84.2</td>
<td>0.0599</td>
<td>0.0795</td>
<td>0.88</td>
</tr>
<tr>
<td>MO572/8</td>
<td>20.1</td>
<td>1.49</td>
<td>2.42</td>
<td>4.24</td>
<td>0.025</td>
</tr>
<tr>
<td>NE22/1</td>
<td>21.5</td>
<td>0.985</td>
<td>3.20</td>
<td>6.35</td>
<td>1.70</td>
</tr>
<tr>
<td>MO807/8</td>
<td>20.0</td>
<td>0.515</td>
<td>5.80</td>
<td>12.30</td>
<td>-</td>
</tr>
<tr>
<td>MO241/44</td>
<td>23.0</td>
<td>0.142</td>
<td>15.00</td>
<td>44.50</td>
<td>43.0</td>
</tr>
</tbody>
</table>

Table IV-1 Room temperature values of the Hall coefficient, conductivity and carrier density for the five samples of GaAs. The Hall coefficients were measured at a field of 0.4 Wb/m² for EM23/11 and at 0.8 Wb/m² for the other four samples. The value of $N_A$ was obtained from the analysis of the experiments under the assumption that $N_{CC} = n_t + 2N_A$. 
Table IV-2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_o(0)$</td>
<td>1.519 eV</td>
<td>75T1</td>
</tr>
<tr>
<td>$m_o(0)$</td>
<td>0.066 m</td>
<td>70S2,71S1,75P1,75R2</td>
</tr>
<tr>
<td>$m_o^*(295)$</td>
<td>0.0638 m</td>
<td>70S2,65M1</td>
</tr>
<tr>
<td>$\Lambda_o$</td>
<td>0.341 eV</td>
<td>75A1</td>
</tr>
<tr>
<td>$\alpha_o$</td>
<td>$-5.405 \times 10^{-4}$ eV/K</td>
<td>75T1</td>
</tr>
<tr>
<td>$\theta_o$</td>
<td>204 K</td>
<td>75T1</td>
</tr>
<tr>
<td>$m_{1L}$</td>
<td>1.9 m</td>
<td>76A2</td>
</tr>
<tr>
<td>$m_{tL}$</td>
<td>0.0754 m</td>
<td>76A2</td>
</tr>
<tr>
<td>$E_{L}(0)$</td>
<td>1.815 eV</td>
<td>76A1</td>
</tr>
<tr>
<td>$\Delta L$</td>
<td>0.22 eV</td>
<td>73A1</td>
</tr>
<tr>
<td>$E_1$</td>
<td>3.041 eV</td>
<td>73A1</td>
</tr>
<tr>
<td>$E_{X}(0)$</td>
<td>1.981 eV</td>
<td>76A2</td>
</tr>
<tr>
<td>$m_{1X}$</td>
<td>1.3 m</td>
<td>68C2</td>
</tr>
<tr>
<td>$m_{tX}$</td>
<td>0.23 m</td>
<td>66P2</td>
</tr>
<tr>
<td>$K_o$</td>
<td>10.91</td>
<td>75R2</td>
</tr>
<tr>
<td>$K_o$</td>
<td>12.91</td>
<td>75R2</td>
</tr>
<tr>
<td>$\tilde{\omega}_o$</td>
<td>0.0362 eV</td>
<td>70I2</td>
</tr>
<tr>
<td>$\tilde{\omega}_{ij}$</td>
<td>0.8 $\tilde{\omega}_o$</td>
<td>68C2</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$1.397 \times 10^{11}$ N/m$^2$</td>
<td>71C1</td>
</tr>
<tr>
<td>$\rho$</td>
<td>5307 Kg/m$^3$</td>
<td>71N1</td>
</tr>
<tr>
<td>$P_e$</td>
<td>0.052</td>
<td>75R2</td>
</tr>
</tbody>
</table>

Table IV-2 Material parameters of GaAs.
Table IV-3 Parameter values determined as a function of effective mass of the $\Gamma$ band. These results were obtained under the assumption that $E_{DL} = E_{DX} = E_{DF}$, $D_{TX} = D_{LX} = D_{TL}$, and $D_{XX} = D_{LL}$. However, the present analysis of the high pressure data gave $E_{DX} = 12.5 \pm 0.5$ eV and $D_{LX} = (1.1 \pm 0.2) \times 10^{11}$ eV/m, with which fits to the high temperature transport data were recovered by reducing $\alpha_x$ by $\sim 1.5\%$ of those given here.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>$m_0(0)$</th>
<th>$m^*(\text{room})$</th>
<th>$a$</th>
<th>$E_{DF}$ (eV)</th>
<th>$D_{TL}$ ($10^{10}$ eV/m)</th>
<th>$D_{LL}$ ($10^{10}$ eV/m)</th>
<th>$\alpha_L$ ($10^{-4}$ eV/K)</th>
<th>$\theta_L$</th>
<th>$\alpha_X$ ($10^{-4}$ eV/K)</th>
<th>$\theta_X$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.066</td>
<td>0.064</td>
<td>1.84</td>
<td>15.2</td>
<td>10.0</td>
<td>3.0</td>
<td>-7.72</td>
<td>485</td>
<td>-6.90</td>
<td>550</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>8.0</td>
<td>7.0</td>
<td>-7.75</td>
<td>490</td>
<td>-6.85</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>0.0638</td>
<td>1.64</td>
<td>16.1</td>
<td>3.0</td>
<td>-7.87</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5.0</td>
<td>-7.82</td>
<td>&quot;</td>
<td>-6.88</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7.0</td>
<td>7.0</td>
<td>-7.80</td>
<td>&quot;</td>
<td>-6.87</td>
</tr>
<tr>
<td>7</td>
<td>0.0665</td>
<td>1.36</td>
<td>16.4</td>
<td>8.0</td>
<td>3.0</td>
<td>-7.89</td>
<td>&quot;</td>
<td>-6.97</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7.0</td>
<td>5.0</td>
<td>495</td>
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<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7.0</td>
<td>6.0</td>
<td>-7.84</td>
<td>490</td>
<td>-6.85</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>0.0629</td>
<td>1.00</td>
<td>18.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table IV-4

<table>
<thead>
<tr>
<th>Pressure Coefficient</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$ (eV/Kbar)</td>
<td>$1.26 \times 10^{-2}$ (75W1)</td>
<td>$3.55 \times 10^{-3}$ (71C1, 76A2)</td>
<td>$-1.75 \times 10^{-3}$ (71C1, 76A2)</td>
</tr>
<tr>
<td>$b$ (eV/Kbar$^2$)</td>
<td>$-3.77 \times 10^{-5}$ (75W1)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\frac{\partial^2 \omega}{\partial P^2}$</td>
<td>0.16 (73P3)</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table IV-4 Pressure coefficients of the band gap and polar optical phonon frequency for GaAs.
Table IV-5

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_A$ ($10^{21} \text{ m}^{-3}$)</th>
<th>$E_{DX}$ (eV)</th>
<th>$D_{LX}$ ($10^{-10} \text{ eV/m}$)</th>
<th>$E_d$ (eV)</th>
<th>$\mu_X$ ($10^{-2} \text{ m}^2 /\text{V-sec}$)</th>
<th>$0 \text{ Kbar}$</th>
<th>$50 \text{ Kbar}$</th>
<th>$\mu_T/\mu_L$</th>
<th>$0 \text{ Kbar}$</th>
<th>$50 \text{ Kbar}$</th>
<th>$\mu_T/\mu_X$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EL11</td>
<td>0</td>
<td>12.2</td>
<td>9.5</td>
<td>0</td>
<td>2.20</td>
<td>3.35</td>
<td>4.91</td>
<td>1.78</td>
<td>29.0</td>
<td>3.53</td>
<td></td>
</tr>
<tr>
<td>G62A</td>
<td>1.6</td>
<td>13.0</td>
<td>13.0</td>
<td>0.148</td>
<td>1.74</td>
<td>3.23</td>
<td>5.05</td>
<td>2.49</td>
<td>37.8</td>
<td>3.75</td>
<td></td>
</tr>
<tr>
<td>CL17/8</td>
<td>35.0</td>
<td>12.0</td>
<td>9.5</td>
<td>0.018</td>
<td>1.48</td>
<td>2.45</td>
<td>3.71</td>
<td>1.51</td>
<td>18.9</td>
<td>3.25</td>
<td></td>
</tr>
</tbody>
</table>

Table IV-5 Some resulting parameter values obtained from the analysis of the high pressure transport data of GaAs.
Table IV-6

<table>
<thead>
<tr>
<th>T °C</th>
<th>E_F eV</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\mu$</td>
<td>$r$</td>
<td>$n \times 10^{23}$</td>
</tr>
<tr>
<td>20</td>
<td>0.0105</td>
<td>0.3510</td>
<td>1.010</td>
<td>4.240</td>
</tr>
<tr>
<td>100</td>
<td>-0.0017</td>
<td>0.3103</td>
<td>1.010</td>
<td>4.318</td>
</tr>
<tr>
<td>150</td>
<td>-0.0105</td>
<td>0.2908</td>
<td>1.010</td>
<td>4.343</td>
</tr>
<tr>
<td>200</td>
<td>-0.0203</td>
<td>0.2728</td>
<td>1.012</td>
<td>4.288</td>
</tr>
<tr>
<td>250</td>
<td>-0.0313</td>
<td>0.2559</td>
<td>1.017</td>
<td>4.188</td>
</tr>
<tr>
<td>300</td>
<td>-0.0440</td>
<td>0.2399</td>
<td>1.026</td>
<td>4.028</td>
</tr>
<tr>
<td>350</td>
<td>-0.0585</td>
<td>0.2249</td>
<td>1.040</td>
<td>3.803</td>
</tr>
<tr>
<td>400</td>
<td>-0.0752</td>
<td>0.2108</td>
<td>1.058</td>
<td>3.518</td>
</tr>
<tr>
<td>450</td>
<td>-0.0942</td>
<td>0.1967</td>
<td>1.081</td>
<td>3.192</td>
</tr>
<tr>
<td>500</td>
<td>-0.1157</td>
<td>0.1841</td>
<td>1.110</td>
<td>2.846</td>
</tr>
</tbody>
</table>

Table IV-6 Results of the analysis of the experimental data for sample M0572/8 ($N_A = 2.5 \times 10^{20} m^{-3}$). Unit of $\mu$ used in the table is $m^2/V$-sec and carrier density is given per $m^3$. 
Table IV-7  

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>E_F (eV)</th>
<th>$\Gamma_1$</th>
<th>L_1</th>
<th>X_1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\nu_{\Gamma}$</td>
<td>$r_{\Gamma}$</td>
<td>$n_{\Gamma} \times 10^{24}$</td>
</tr>
<tr>
<td>20</td>
<td>0.1394</td>
<td>0.2156</td>
<td>1.009</td>
<td>4.435</td>
</tr>
<tr>
<td>100</td>
<td>0.1363</td>
<td>0.1990</td>
<td>1.012</td>
<td>4.455</td>
</tr>
<tr>
<td>150</td>
<td>0.1327</td>
<td>0.1888</td>
<td>1.017</td>
<td>4.374</td>
</tr>
<tr>
<td>200</td>
<td>0.1274</td>
<td>0.1799</td>
<td>1.024</td>
<td>4.219</td>
</tr>
<tr>
<td>250</td>
<td>0.1203</td>
<td>0.1700</td>
<td>1.035</td>
<td>4.009</td>
</tr>
<tr>
<td>300</td>
<td>0.1112</td>
<td>0.1615</td>
<td>1.049</td>
<td>3.752</td>
</tr>
<tr>
<td>350</td>
<td>0.1003</td>
<td>0.1527</td>
<td>1.067</td>
<td>3.462</td>
</tr>
<tr>
<td>400</td>
<td>0.0876</td>
<td>0.1439</td>
<td>1.087</td>
<td>3.153</td>
</tr>
<tr>
<td>450</td>
<td>0.0732</td>
<td>0.1353</td>
<td>1.111</td>
<td>2.840</td>
</tr>
<tr>
<td>500</td>
<td>0.0572</td>
<td>0.1278</td>
<td>1.138</td>
<td>2.535</td>
</tr>
</tbody>
</table>

Table IV-7  Results of the analysis of the experimental data for sample MO241/44/12 (N_A = 4.3 x 10^{23} \text{m}^{-3}). Unit of $\nu$ used in the table is $\text{m}^2/\text{V-sec}$ and carrier density is given per $\text{m}^3$. 
<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μ</td>
<td>r</td>
<td>n $10^{21}$</td>
<td>μ</td>
</tr>
<tr>
<td>20</td>
<td>-0.1497</td>
<td>0.6675</td>
<td>1.133</td>
<td>1.100</td>
</tr>
<tr>
<td>100</td>
<td>-0.2021</td>
<td>0.4973</td>
<td>1.093</td>
<td>1.098</td>
</tr>
<tr>
<td>150</td>
<td>-0.2362</td>
<td>0.4323</td>
<td>1.076</td>
<td>1.092</td>
</tr>
<tr>
<td>200</td>
<td>-0.2712</td>
<td>0.3835</td>
<td>1.067</td>
<td>1.081</td>
</tr>
<tr>
<td>250</td>
<td>-0.3074</td>
<td>0.3451</td>
<td>1.063</td>
<td>1.058</td>
</tr>
<tr>
<td>300</td>
<td>-0.3451</td>
<td>0.3136</td>
<td>1.066</td>
<td>1.021</td>
</tr>
<tr>
<td>350</td>
<td>-0.3847</td>
<td>0.2867</td>
<td>1.077</td>
<td>0.967</td>
</tr>
<tr>
<td>400</td>
<td>-0.4264</td>
<td>0.2632</td>
<td>1.094</td>
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</tr>
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<td>450</td>
<td>-0.4704</td>
<td>0.2423</td>
<td>1.117</td>
<td>0.816</td>
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<tr>
<td>500</td>
<td>-0.5169</td>
<td>0.2234</td>
<td>1.147</td>
<td>0.728</td>
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</table>

Table IV-8 Results of the analysis of the experimental data for sample TG368 of Blood (72B2) 
(N = $1.7 \times 10^{21}$ m$^{-3}$ and B = 0.1 Wb/m$^2$). Unit of $\mu$ used in the table is m$^2$/V-sec and 
carrier density is given per m$^3$. 
Table IV-9

<table>
<thead>
<tr>
<th>P (kbar)</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$ (r)</th>
<th>$L_1$ (10$^{-21}$)</th>
<th>$X_1$ (10$^{-21}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-0.0971</td>
<td>0.6372</td>
<td>1.104 9.248</td>
<td>0.1295 1.166 -</td>
</tr>
<tr>
<td>10.0</td>
<td>-0.0997</td>
<td>0.5815</td>
<td>1.110 9.228</td>
<td>0.1240 1.212 0.019</td>
</tr>
<tr>
<td>20.0</td>
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Table IV-9 Results of the analysis of the high pressure data of Pitt and Lees (70P1) for sample EL11 ($N_A = 0.0$, $B = 0.625$ Wb/m$^2$).
Fig. (IV-1) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample EM23/11 of GaAs.
Fig. (IV-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO572/8 of GaAs.
Fig. (IV-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample NE22/1 of GaAs.
Fig. (IV-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO807/8 of GaAs.
Fig. (IV-5) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO241/44/2 of GaAs.
Fig. (IV-6) Normalized Hall mobility, Hall coefficient and resistivity measured as a function of pressure for sample G62A of Pitt and Lees (70P1) and curves fitted to the data.

--- experimental data
--------- fitted curves.
Fig. (IV-7) Band gap variation with temperature for GaAs.

--- Aspnes (76A2),

--- present results ($\alpha_L = -7.82 \times 10^{-4}$ eV/K and $\theta_L = 490$ K for the L\textsubscript{1} minima, and $\alpha_X = -6.77 \times 10^{-4}$ eV/K and $\theta_X = 550$ K for the X\textsubscript{1} minima.
Fig. (IV-8) Relaxation times as a function of energy in the $\Gamma_1$ band with $E_D^\Gamma = 16.1$ eV, $D_{\Gamma L} = 8 \times 10^{10}$ eV/m, $a = 1.64$ and the band minima variation with temperature as given in Fig. (IV-7).
Fig. (IV-9) Relaxation times as a function of energy in the $L_1$ band with $E_{DL} = 16.1$ eV, $D_{LL} = 5 \times 10^{10}$ eV/m, $D_{LX} = 1.1 \times 10^{10}$ eV/m and the other parameters as used for the calculation of $\tau_F$ in Fig. (IV-8). The values of $\tau_{op}$ given by the full and dotted lines were calculated using the Fletcher and Butcher method (72F2) and the relaxation time approximation respectively.
Fig. (IV-10) Relaxation times as a function of energy in the $X_1$ band with $E_{DX} = 12.5$ eV, $D_{XX} = 5 \times 10^{10}$ eV/m and the other parameter values as used for the calculation of $\tau_L$ in Fig. (IV-8).
Fig. (IV-11) Carrier mobility as a function of temperature in the $\Gamma_1$ band. Calculation was made using the data given in Fig. (IV-8).
Fig. (IV-12) Carrier Mobility as a function of temperature in the $L_1$ band. Calculation was made using the data given in Fig. (IV-9).
Fig. (IV-13) Carrier mobility as a function of temperature in the $X_\perp$ band. Calculation was made using the data given in Fig. (IV-10).
Carrier distribution in the three conduction bands of GaAs. Calculations carried out for sample MO807/8 using the following temperature variation of band minima: $\Gamma_1$ minimum, Thurmond (75T1) $L_1$ and $X_1$ minima, present analysis as shown in Fig. (IV-7).
Fig. (IV-15) Comparison of theoretical curves with experimental Hall mobility data of Blood (72B2) and Akita et al. (71A1) for pure GaAs samples.

F and R theoretical curves quoted by Blood from (70F2) and (70R1) and ------- Present theoretical curves for samples TG 368 \((n = 1.1 \times 10^{21} \text{m}^{-3})\) and TG 366 \((n = 1.8 \times 10^{21} \text{m}^{-3})\) respectively.
Fig. (IV-16) Mobility ratios $\mu_\Gamma/\mu_L$ and $\mu_\Gamma/\mu_X$ vs temperature for GaAs.
Fig. (IV-17) Mobility and carrier density variations with pressure in the three conduction bands for GaAs.
Fig. (IV-18) Hall scattering coefficient $r_T$ vs. temperature for GaAs.
Fig. (IV-19) Hall scattering coefficients $r_L$ and $r_X$ vs. temperature for GaAs.
Fig. (IV-20) Energy and cyclotron effective mass as a function of wave vector near the $\Gamma_1$ point for GaAs;

- --- present model (small gap approximation)
- --- model with higher and lower bands included (66K1).
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CHAPTER V  Ga\textsubscript{1-x}Al\textsubscript{x} As

V-1  Introduction

Ga\textsubscript{1-x}Al\textsubscript{x} As alloys are promising material for optoelectronic applications (71S2, 74R1). Thus the band structure and the electrical and optical properties have been extensively investigated. Measurements of diode emission (69K4), optical absorption (69P1, 76M2), photoresponse (69C1) and electroreflectance (71B1) have been used to determine the fundamental band gap values and the composition at which the direct-indirect gap transition occurs.

From photoresponse measurements, Casey and Panish (69C1) showed that the direct-indirect crossover composition (x) and energy gap are 0.37 and 1.92 eV respectively at room temperature. They employed a quadratic formula (67T1) for the direct-gap-composition relation in these alloys using 1.435 eV and 2.9 eV for GaAs and AlAs respectively. Values of 1.855 eV and 2.13 eV were used for the indirect gap of GaAs and AlAs respectively to set up a similar expression for the X\textsubscript{1} minima.

Onton et al. (7101) measured the alloy composition dependence of the direct band gap in Ga\textsubscript{1-x}Al\textsubscript{x} As at 300 K for 0 < x < 0.5 by means of electron microprobe cathode luminescence. They obtained $E_o = 1.439 + 1.042x + 0.468x^2$ from the experimental data. Assuming a linear composition dependence of the X\textsubscript{1} minima they determined the direct-indirect
band crossover to be at $x = 0.44$ and $E_o = 1.99$ eV. Values of 2.16 and 1.87 eV for AlAs and GaAs respectively were used for the linear interpolation of the indirect gap.

Berolo and Woolley (71B1) measured the electroreflectance spectra of the present alloys and determined various transition energies as a function of composition. The resultant direct-indirect band gap transition energy was 1.9 eV at $x = 0.35$. The measured transition energies could be expressed in the form of Eq. (II-19) and the bowing parameter was shown to be 0.26 eV in the case of the $\Gamma_1$ minima.

Neumann and Junge (76N1) measured the indirect band gap variation with composition and temperature for four different compositions with $x > 0.45$ and obtained $rac{dE}{dT} = -(4.2 \pm 0.3) \times 10^{-4}$ eV/K. These measured values for the $X_1$ minima lie between the two sets of data on these minima obtained by Black and Ku (66B2) and Casey and Panish (69C1).

The direct band gap was measured by Klug and Neumann (75K1) using Schottky barrier photovoltage measurements and the results could be expressed by $E_o = 1.433 + 1.281x + 0.194x^2$. The temperature dependence of $E_o$ measured between 77 and 300 K shows $\frac{dE}{dT} = -(4.3 \pm 0.3) \times 10^{-4}$ eV/K.
Monemar et al. (76M2) attributed the scatter in the experimental data described above to the use of variety of experimental method and to the probable inadequate control over sample preparation. Their optical transmission and photo luminescence data show an appreciable deviation from the previous data of the \( \Gamma_1 \) minimum for compositions with \( x < 0.5 \). They concluded that the usual quadratic expression for the band gap bowing does not hold in these alloys. Simply connecting linearly the \( X_1 \) minima of the compounds (2.00 ± 0.015 eV at 4 K in GaAs and 2.229 and 2.153 eV in AlAs at 4 and 300 K respectively), the band crossover points were obtained at \( x = 0.35 \pm 0.01 \) and \( 0.37 \pm 0.01 \) at 4 and 293 K respectively. The effective mass variation of the \( \Gamma_1 \) minimum estimated from their absorption coefficient values shows appreciable deviation from a linear variation and the extrapolated effective mass value for AlAs was 0.113 m.

The various experimental data on the band gap have been collected and are shown in Fig. (V-1). The experimental points show scatter of the order of 100 meV over the complete composition range. However the data for the direct band gap may be considered by dividing them into two groups. One group consists of the data reported by Monemar et al. (76M2), which does not show a bowing effect of the band gap in the direct gap region. The data in the other group is well described by the expression \( E_0 = 1.424 + 1.266x + 0.26x^2 \) (74R1), which is based upon the band gap values of Berolo and Woolley (71B1) and Casey and Panish (69C1).
Baldereschi et al. (77B1) calculated the band structure of Ga$_{1-x}$Al$_x$As using the empirical pseudopotential method and an extended virtual crystal approximation. For the lowest direct gap, the theoretical calculation predicted a linear variation with composition. An absence of bowing in Ga$_{1-x}$Al$_x$As also was predicted theoretically by van Vechten and Bergstresser (70V1). Van Vechten and Bergstresser proposed that the bowing parameter $c$ should be the sum of the intrinsic bowing $c_i$ found in the virtual crystal approximation and an extrinsic bowing $c_e$ due to the effects of aperiodicity, and the result of the calculations using a dielectric model gives $c_i = 0$ and $c_e = 0.03$ eV for Ga$_{1-x}$Al$_x$As. Baldereschi et al. also predicted a linear variation of the indirect band gap with composition. They discussed the disorder effects in their calculation and concluded that the effect is small. In the above theoretical calculation, the direct-indirect band crossover was found to be at $x = 0.3$.

Neumann et al. (73N1) investigated the electrical transport properties of n-type Ga$_{1-x}$Al$_x$As bulk single crystals of two compositions of $x = 0.83$ and 0.84 without special doping. The main residual impurity was found to be Si with concentration of the order of $10^{23} \sim 10^{25}$ m$^{-3}$. Analysis of the measured Hall coefficient shows that donor levels are located at 36 $\sim$ 60 meV below $\Delta_1$ minima and that the density of states effective mass ranges between 1.45 and 1.84 m. The measured mobilities were 0.007 $\sim$ 0.015 m$^2$/V-sec at 300 K. Acoustic, nonpolar and polar optical phonon scattering and the scattering due to ionized impurities
and space charge were taken into account to explain the mobility variation with temperature from 77 to 300 K.

Neumann and Flohrer (74N1) measured the composition dependence of the electron mobility in liquid phase epitaxial crystals over the composition range $x = 0$ to 0.8. In addition to the above mechanisms, disorder scattering was employed in the transport calculation for the indirect gap region. The scattering mechanisms of polar optical, ionized impurity and disorder were used for the mobility calculation in the direct gap region. Interband scattering was considered only in the direct-indirect gap transition region.

Kravchenko et al. (75K2) analyzed the Hall coefficient variation with composition and temperature from 77 to 800 K in Te-doped $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys. The carrier concentration was estimated from the relation $n = 1/eR_H$ for all compositions. The resultant analysis gives the impurity activation energy to be $0.052 \sim 0.08$ eV. From the transport analysis, they obtained a sub-band gap energy, and the effective mass and the mobility ratios between the two non-equivalent bands. The results for the sub-band gap energy locate the band crossover at $x = 0.3$. The effective mass ratio has values in the range $18.6 \sim 14.2$, and the mobility ratio $0.06 \sim 0.26$. The density of states effective mass was found to have the values 1.18 to 1.46 m for compositions in the indirect band gap region. In the above analysis they assumed the degeneracy factor of the donor levels to be 2 and 12 for
the direct and indirect band gap regions respectively.

Maronchuk and Yakushowa (76M1) analyzed the data from transport experiments on Ga$_{1-x}$Al$_x$As performed in the temperature range 77 to 400 K and obtained similar results to those above for the donor levels. When alloy scattering was included according to Eq. (1) of Ref. (73M1), the predicted carrier mobility was approximately half the experimental value in the indirect gap region. Neumann and Flohrer (74N1) also suggested the importance of alloy scattering over all compositions and showed that the scattering due to ionized impurity and to alloy disorder both have effects similar in magnitude to those of the other mechanisms. Maronchuk and Yakusheva assumed that the high electron density has a screening influence on the aperiodic potential caused by the alloy disorder and this reduces the alloy scattering. In the same study, the influence of the anisotropy was found to be unimportant in the calculation of ionized impurity scattering; the inclusion of the anisotropy effect increased the total mobility by $\sim 13\%$ at 100 K and by $\sim 1.8\%$ at 300 K.

SpringThorpe et al. (75S1) measured the Hall coefficient and resistivity in the temperature range 77 $\sim$ 400 K on similar samples to the ones we have used in this work. The activation energy of impurity levels was found to have a maximum value at about the direct-indirect band crossover point. The Te-donor level was shown to give a straight line variation with composition for $x \geq 0.37$, and the line is parallel
to the $L_1$ minima variation obtained by linearly connecting the $L_1$ minima values of GaAs and AlAs.

Various material parameters of Ga$_{1-x}$Al$_x$As may be estimated from the values for compounds GaAs and AlAs. We have discussed GaAs in the previous chapters and thus the band parameters of AlAs only will be reviewed briefly here. Very little information on AlAs has been published, partially because of some difficulties in its preparation. Optical absorption measurements by Yim (71Y1) show that the direct and indirect gaps are 3.14 and 2.14 eV respectively at 300 K. Onton (70O1) has shown from electroreflectance work that the direct gap energy is 2.95 ± 0.02 eV and the spin-orbit splitting 0.275 eV. Optical transmission measured by Lorenz et al. (70L1) locates the fundamental gap at 2.16 eV at 300 K, which is consistent with that obtained by Wolff et al. (55W1).

Stukel and Euwema (69S1) calculated the band structure of AlAs and the resultant indirect band gap was 2.38 eV. The same calculation locates the $\Gamma_1$ and $L_1$ minima at 2.5 and 2.57 eV respectively above the $\Gamma_{15}$ state. Hess et al. (73H2) also calculated the band structure using a combination of the pseudopotential method with the $k.p$ method. The $\Gamma'_1$, $L'_1$, and $X'_1$ minima were shown to be at 3.21, 2.76 and 2.25 eV above the $\Gamma_{15}$ in the calculation. The theoretical band structure locates the subsidiary band minima along $\Delta$ and $\Lambda$. The calculated
effective masses are $m_o = 0.15 \, m$, $m_t(\Lambda) = 0.15 \, m$, $m_x(\Lambda) = 1.32$, $m_t(\Delta) = 0.24 \, m$ and $m_x(\Delta) = 1.48 \, m$. Rheinlander et al. (72R1) measured the effective mass at the $X_\perp$ point in $k$-space in AlAs using the Faraday rotation experiment and the values obtained are $m_t = 0.19 \, m$ and $m_x = 1.1 \, m$.

V-2. Experimental Data

The measured Hall coefficients and conductivities (together with theoretical lines) for twelve samples of different compositions are shown in Figs. (V-2 - 13) and the room temperature characteristics are compiled in Table (V-1). Fig. (V-2) shows the experimental data for a sample of composition $x = 0.08$ without intentional doping. $R_H$ decreases with the initial temperature increase and then increases with temperature, and $\sigma$ decreases as temperature increases over the whole temperature range. This $R_H$ behaviour implies a transition from one-band to multiband characteristics, that is, carrier excitation from the $T_1$ band to subsidiary bands.

Three subsequent samples with $x = 0.106, 0.13$ and $0.232$ show similar temperature dependence of $R_H$ and $\sigma$ as is shown in Figs. (V-3, 4, 5); $R_H$ increases and $\sigma$ decreases with temperature. These are the same effects as were found in GaAs, i.e. all donors are fully ionized at room temperature and the subsidiary band contribution increases with temperature.
Two samples with $x = 0.27$ and $0.3$ show an initial increase of $\sigma$ and a decrease of $R_H$ with increasing temperature, which can be understood in terms of an increase in carrier concentration. The behaviour of $R_H$ and $\sigma$ at higher temperatures is similar to that for the lower Al-concentration samples, and thus the donors are all ionized at this temperature. However, this is not always true, because the same behaviour could be expected if the number of carrier excited into the subsidiary bands exceeds the increase in total carrier concentration.

All samples with $x$ greater than $0.35$ show $R_H$ decreasing with temperature over the range used in this work, while the $\sigma$ values show maxima at different temperatures depending on composition. The general form of the two curves for these samples shows that deep donors are having an effect on the total carrier concentration.

V-3 Assignment of Parameters

It has been assumed in previous work that the electrical transport properties of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys may be calculated in terms of a one- or two-band model comprising the $\Gamma_1$ and $X_1$ (or $\Delta_1$) bands as in the case of previous work on GaAs. Several reports on transport studies on $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys have been published as we have seen in the introduction, but no detailed parameter values are to be found in the literature. We have explained the transport properties of GaAs by including the $L_1$ valley and thus it seems inevitable that the subsidiary valley in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy must be considered especially as theoretical
analysis indicates that the <111> minima are not far above the <100> minima in AlAs (69S1, 73H2). In addition to the three conduction bands, we have found it necessary to consider the effect of impurity levels in the case of some alloys.

Monemar et al. (76M2) showed experimentally that for the Γ₁ and X₁ minima, the energy variation with temperature in the respective minima is the same for all compositions and thus as a starting point the temperature coefficients of the band gaps for GaAs have been assumed for the three band minima throughout this alloy system.

Rode estimated the room temperature effective mass of 
\[ m_{\text{Ga}_{1-x}\text{Al}_{x}\text{As}} = 0.0636 + 0.0552x + 0.0092x^2 \]  
(74R1). This expression has been used as a starting point here but with the first term replaced by 0.066 m for the value of the effective mass at 0 K. The value of "a" in Eq. (II-13) has been assumed to have the same value as for GaAs. No data are available on the effective masses in the \( L_1 \) and \( X_1 \) bands of this alloy system and so we have assumed a linear interpolation between those of GaAs and AlAs to estimate the effective mass values of the alloys. Considering the low bowing in the \( m^* \) values for the various ternary alloys (73B1), the above assumption should be quite satisfactory. In this interpolation, for AlAs we have used the values of \( m_\perp = 0.15 \, m \) and \( m_\parallel = 1.32 \, m \) in the \( L_1 \) band (73H2) and \( m_\perp = 0.19 \, m \) and \( m_\parallel = 1.1 \, m \) in the \( X_1 \) band (72R1). The experimental data for \( E_1 \) of Berolo and Woolley (71B1) have been used
for the calculation of the temperature variation of the $m_t^*$ values using Eq. (II-18). Considering the high value of $E_2$ (71B1) and the low temperature coefficient of the band minima variation, we have neglected any effective mass variation with temperature in the $X_1$ band.

No data on the energy values for the $L_1$ minima have been reported for any alloy composition nor for the $X_1$ minima in the composition range with direct gap behaviour. At intermediate compositions, the energy values of the $L_1$ and $X_1$ minima with respect to the $\Gamma_1$ minima are of critical importance in the transport calculation, and so the minima energy values have been treated as adjustable with the $\Gamma_1$ minimum value estimated from the available experimental data in this range.

Ilegems and Pearson (70I2) observed two longitudinal phonon branches of different energies in $Ga_{1-x}Al_x As$, which correspond to those of the two compounds. For samples near to a compound the phonon intensity corresponding to the other compound is negligible and thus for the three samples with $x = 0.08$ to $0.13$, the phonon energy of GaAs has been used in the calculation, while for the sample with $x = 0.95$ the phonon energy of AlAs has been employed. Two phonon effects are to be expected for the other compositions but the present transport theory cannot deal with such effects. Therefore we have used a linear interpolation approximation for the value of polar phonon energy in these materials. For transport calculations in $InAs_{x}P_{1-x}$, Ehrenreich (69E1)
used a linear interpolation to estimate the material parameter values including the polar phonon energy and concluded that a linear interpolation is reasonable. The phonon energy responsible for interband and intervalley scattering has been assumed to have $0.8 \hbar \omega_0$ as in the case of GaAs. Some material parameters of AlAs used here for a linear interpolation are shown in Table (V-2).

No direct evidence of the multiplicity of the $L_1$ and $X_1$ band minima is available and thus the values have been assumed to be the same as those for GaAs, i.e., four and three for the $L_1$ and $X_1$ valleys respectively. Higher values of multiplicity have been tried also and the effects will be discussed in a later section.

V-4 Method of Analysis

The general method of analysis for $\text{Ga}_1-x\text{Al}_x\text{As}$ is the same as in the case of GaAs in Chapter IV.

Alloy scattering has been included in the calculations in addition to all the scattering mechanisms except piezoelectric mode scattering used in analyzing the transport properties of GaAs. Piezoelectric mode scattering was excluded in the present analysis because this mechanism was found to be completely negligible for GaAs in the temperature range with which we are concerned here.
Acoustic deformation potential and interband and intervalley scattering coupling coefficients are important scattering parameters in the calculation and their values are determined by adjusting them to fit the measured Hall coefficient and conductivity data. These parameters are $E^{\text{DL}}$, $E^{\text{DL}}$, $E^{\text{DX}}$, $D^{\text{TX}}$, $D^{\text{TX}}$, $D^{\text{LL}}$, and $D^{\text{XX}}$. To simplify the analysis, we have assumed that $E^{\text{DL}} = E^{\text{DL}}$ and $D^{\text{LL}} = D^{\text{XX}}$, since this assumption was found to be satisfactory for GaAs. Although there are a large number of parameters unknown for the alloys, one useful fact in the analysis is that the various parameters must vary uniformly with $x$ and in many cases different parameters are important in different ranges of the analysis. Initially we have assumed the parameters to vary linearly with $x$ for this alloy system as Ehrenreich (59E2) did for the analysis on InAs$_x$P$_{1-x}$.

$E^{\text{DX}}$ and $D^{\text{XX}}$ are related only to the $X_1$ band and their values are determined from the analysis for compositions with an indirect gap where the behaviour is dominated by the $X_1$ band. Because of the effective mass dependence of alloy scattering, this mechanism can be expected to show greater effects in the indirect gap compositions and thus the parameter necessary for the calculations of this effect has been obtained by analyzing alloys in that composition range. Makowski and Glicksman (73M1) discussed alloy scattering in III-V alloy systems and proposed the Brook's expression for the mobility due to this effect

$$
\mu_{\text{ALL}} = \frac{\sqrt{2}\pi e^{4} N}{3m^{5/2} \sqrt{k_{B} T}} \frac{x(x - 1)(E_{A} - E_{B})^2}{\sigma(x - 1)}
$$

(V-1)
where \( N_0 \) is the number of atoms per unit volume and \( E_A \) and \( E_B \) are the band gap energies for the two element compounds \( A \) and \( B \) respectively. Considering the approximate nature of the theory, the following expression for the relaxation time due to the scattering has been used in this work.

\[
\frac{1}{\tau_{\text{A\&B}}} = m^*^{3/2} x(x - 1) \frac{E_h^4}{A_p}
\]

where \( A_p \) is assumed independent of \( x \) and determined from analysis of the data for the indirect gap compositions. Polar optical scattering predominates in the indirect gap region in the present alloys and so the dielectric constant is one of the most important parameters in these calculations. However, no data on the constant are available for these alloys and the published experimental values of the constant show considerable scatter for AlAs, that is, the values range from 8.16 (71F2) to 15.2 (71M1) in the case of \( \kappa_\infty \). The value of \( \kappa_\infty \) for AlAs has been adjusted to give a fit to experiment for the alloys with an indirect gap, using a straight line interpolation expression, \( \kappa_\infty(x) = 10.91 - (10.91 - \kappa_\infty(\text{AlAs}))x \), to give \( \kappa_\infty \) value for the alloys while the low-frequency dielectric constant \( \kappa_0 \) has been taken as 10.0 in AlAs (70M1) and a similar linear interpolation used for the alloys. The parameter values thus determined in the indirect gap region have then been used to give estimates of the values of the corresponding parameters for the direct gap compositions where some other unknown parameters needed to be determined in this analysis.
In a one-band model using the $X_1$ band only, as in the case for the indirect gap region in this alloy system, the exact value of the band minima energy is not necessary for the calculation of transport properties because the effective mass variation with temperature is neglected in this analysis. However in the direct gap region, which requires three-band analysis, the energy values of the subsidiary band minima with respect to the $\Gamma_1$ minimum are more important than the values of $\Gamma_1$ minimum energy in the calculation. This is because the interband interaction and the carrier distribution among the bands are more important than the effective mass variation with temperature in the $\Gamma_1$ band in this case. However, for the determination of the absolute energy values of the subsidiary band minimum, the energy value of the $\Gamma_1$ minimum needs to be known, but the experimental data on the $\Gamma_1$ minimum show considerable scatter as is shown in Fig. (V-1). The data on the $\Gamma_1$ minimum may be divided into two parts for convenience, one consisting of the results reported by Monemar et al. (76M2) and showing no bowing behaviour in the direct gap compositions, and the other showing bowing and with values which are 30 to 100 meV lower than those of Monemar et al. (76M2). The latter set of data consists mainly of the results obtained by Casey and Panish (69C1), Berolo and Woolley (70B1) and Onton et al. (73P1). In order to choose between the two sets of data for use in the transport calculation for the compositions requiring three-band analysis, we checked with the three samples with $x = 0.08, 0.106$ and 0.13 respectively. For the analysis of these three samples, which are close to GaAs in composition, except for the parameters
mentioned in the previous section and shown in Table (V-2), parameter values for GaAs were used for the $\Gamma_1$ and $L_1$ bands in this preliminary analysis. For the calculation of the $X_1$ band properties, the necessary parameters values were estimated by linear interpolation between those for GaAs and those for the indirect gap compositions. But as will be shown later, the effect of the $X_1$ band is negligible at these compositions. Hence only the three parameter values of $N_A$ and the energies of the $\Gamma_1$ and $L_1$ minima required adjustment to give a fit to the experimental $R_H$ and $\sigma$ data. The results place the $\Gamma_1$ minimum at 1.601, 1.635 and 1.662 eV above the $\Gamma_{15}$ maximum at 0 K for $x = 0.08$, 0.106 and 0.13 respectively. These values correspond to values of 1.507, 1.541 and 1.568 respectively at 295 K, and these values are lower by up to $\approx$ 20 meV than those given by Rode's approximation introduced in Section 1, and by about 30 to 50 meV than the data given by Monemar et al. (76M2) for the composition range near GaAs. In the same analysis the $L_1$ minima were found to be at 1.885, 1.888 and 1.903 eV at 0 K in the three samples respectively. In the sample with $x = 0.13$ which shows the lowest energy difference between the $\Gamma_1$ and $X_1$ minima of the three samples, we assumed the energy value of the $X_1$ minima at 0 K to be 1.9815 estimated by linearly connecting the experimental value of 1.981 for GaAs (76A2) and those for the indirect gap alloys obtained by Casey and Panish (69C1) as shown in Fig. (V-1). In this case, the value of $n_x$ is only 1.5% of the $n_{01}$ value at the highest temperature in our measurements and thus the contribution of the $X_1$ band is of no importance for these samples. This analysis for these three samples is not
final but gives a good indication of the set of data on the $\Gamma_1$ minimum to be used for the five samples with $x$ in the range 0.232 - 0.40. The data set showing a bowing effect given by the three different papers indicated above have been considered preferable and used in this work. Extrapolation of the results of the analysis for the five samples with $x$ in the range 0.232 - 0.40 gives parameter values a little different from those of GaAs for the three samples near GaAs and a consequent repeat of the analysis for these samples shows small changes in the values for the band minima. These final results will be further discussed later.

For the five samples with $x$ in the range 0.232 - 0.40, $E_{D1}'$, $D_{L1}'$, $D_{LX}$ and the energy values of the $L_1$ and $X_1$ minima are important and determined by treating them as adjustable.

One of the major problems is to determine carrier density values for these alloys. In a one-band model the value of carrier density is calculated using the measured value of $R_H$ and the value of the Hall scattering coefficient $r$ calculated from the scattering mechanisms. This method was used for GaAs at room temperature and can be justified for the four samples near GaAs and two samples near AlAs. But in the case of multiband calculations, no proper method for the estimation of the value of $r$ is available. Furthermore the present samples show impurity effects and the carrier density varies with temperature. In this case, four more unknown parameters, i.e., $N_D$, $E_d'$
and the number of excited states of the donor level, should be included in the analysis even in the case where only one impurity state is considered. To avoid the difficulties caused by so many unknowns, we have used a single adjustable parameter in the form of an "effective scattering coefficient, $r_{\text{eff}}$" to determine $n$ from $n = r_{\text{eff}}/R_H$ at each temperature of observation. "$r_{\text{eff}}$" was adjusted to give fit to the measured $R_H$ value.

The above analysis was repeated for all compositions until we obtained that uniform variation of parameters with composition which gave the best fit to all the experiments.

V-5 Results and Discussion

A. General results

The results of the analysis for the twelve samples indicate that the eight samples with $x$ in the range $0.08 \sim 0.4$ are direct gap material, and the other four samples have an indirect gap and are dominated by the $X_1$ band. One-band analysis for the four samples with $x = 0.52, 0.6, 0.71$ and $0.95$ gave the variation of parameter values with composition as $\kappa_\infty = 10.91 - 2.31x$, $D_{XX} = (5 - x) \times 10^{10}$ and $E_{DX} = 12.5 - 10.75x$ and $A_p = 4.6 \times 10^{68}$. The expression for $\kappa_\infty$ gives a value of $8.6 \pm 0.1$ for AlAs, which is in good agreement with the experimental value $8.5$ obtained by Monemar et al. (70M1). Values of
$E_{DX} = 1.80 \pm 0.30$ eV and $D_{XX} = (4.0 \pm 0.2) \times 10^{10}$ eV/m are obtained for AlAs from the corresponding expressions above. While the value of $D_{XX}$ shows little difference from that of GaAs, the $E_{DX}$ value is far lower than that of GaAs. Maronchuk and Yakusheva(76M1) showed that the calculated mobility is approximately half the measured one in the indirect gap compositions of Ga$_{1-x}$Al$_x$As when Eq. (V-1) is used to represent alloy scattering. They suggested that high electron density gives a screening effect on the potential for alloy scattering and thus reduces the scattering. In the case of multiband model, a problem arises as to what should be used for $E_A - E_B$ in Eq. (V-1) as discussed by Makowski and Glicksman (73M1). In view of this, we have used a simple form of Eq. (V-2) for the scattering calculation with a single value of $A_p$ for all bands concerned, independent of $x$. The value of $A_p = 4.6 \times 10^{68}$ obtained here corresponds to $|E_A - E_B| = 0.23$ eV in Eq. (V-1), which is far lower than the energy difference between the fundamental band gaps of the two compounds which form this alloy system, i.e., about 0.7 eV.

In the present calculations with the inclusion of alloy scattering the $X_1$ mobility decreased by $\sim 12\%$ from that without the scattering in the case of the alloy with $x = 0.52$. When 0.7 eV is used for this calculation the mobility decrease in the $X_1$ band is estimated to be nine times the above decrease, 12\%, and the results are consistent with that of Maronchuk and Yakusheva(76M1).

Despite having similar carrier density to samples nearby in composition, the sample with $x = 0.71$ shows a much lower value of
conductivity. This phenomenon is often found in boat-grown samples with low carrier density and has been attributed to space charge scattering (62W1, 68C2). Such scattering has been considered by Neumann et al. (73N1) for some Ga_{1-x}Al_{x}As alloys. In the present work, a good fit to the data for the sample with x = 0.71 using parameter values consistent with those for other values of x could be obtained only if space charge scattering was included in that particular case. The best fit was then obtained with a value of N_{s}Q_{s} = 9.6 \times 10^{6} m^{-1}.

The results of a one-band calculation using the X_{1} band give conductivity values a little lower than the measured ones at the higher temperatures for the two indirect gap samples with x = 0.52 and 0.6. Considering the low energy value of the L_{1} minima for GaAs (see Chapter IV) and AlAs (69S1, 73H2), it is not unreasonable to expect some contribution from the L_{1} band under these conditions and the small discrepancy between theory and experiments can be explained in terms of carrier excitation from the X_{1} band into the L_{1} band where the carrier mobility is higher than that of the X_{1} band. Thus a two-band analysis was made using parameters consistent with those for the lower Al-concentration samples and the resulting values of E_{DL}, D_{LX} and the L_{1} and X_{1} minima for these two samples are given in Table (V-3, 4). The values of E_{DL}, D_{LX} and the X_{1} minima energy for these samples were determined from an extrapolation using their variations with x obtained for the samples with lower x discussed below.
All three conduction bands play important roles in determining the overall carrier mobility for the five samples with \( x \) in the range 0.232 - 0.40. From a three-band analysis for these alloys we obtained linear expressions for \( E_{\text{DL}} \) and \( D_{\text{LX}} \) values given approximately by

\[
E_{\text{DL}} = 16.1 - 13.5 x \quad \text{and} \quad D_{\text{LX}} = (11.0 - 10.5x) \times 10^{10}
\]

using the values of the corresponding parameters for GaAs determined in Chapter IV. When these values were readjusted from the linear variation with \( x \) for better fit to each sample, the readjusted values showed some scatter within the limits of ±3% from the above linear variation and the values are shown in Table (V-3). In the case of \( D_{\text{TL}} \), the values do not follow a linear variation with \( x \), showing a steeper decrease with increasing \( x \) than the above two parameters up to \( x = 0.3 \) but then remaining almost constant for \( x = 0.3, 0.335 \) and 0.4, as shown in Table (V-3). The values of \( D_{\text{TL}} \) for these last three compositions; \( 2.2 \sim 2.7 \times 10^{10} \text{eV/m} \), are far lower than that for GaAs, but a similar low value, \( D_{\text{TX}} = 3 \times 10^{10} \text{eV/m} \), has been quoted by Neumann and Flohrer (74N1) for Hall mobility calculations in the direct-indirect transition region of Ga\(_{1-x}\)Al\(_x\)As. The parameter values thus determined were then used to estimate the corresponding values for the other samples for which the values are hard to determine from the analysis of the corresponding samples because the parameters have negligible effects in the calculation or because some other unknowns need to be adjusted in the analysis.
The $X_1$ band minima energy can be determined from the analysis only for the above five samples. This is because the $X_1$ band is of no importance in the calculation for the samples nearby GaAs as is discussed earlier, and this band is dominant in the indirect gap region but the minima energy has no effects on a one-band calculation since the effective mass variation with temperature is negligible in this band for the present analysis. A least square fit to the $X_1$ minima values for GaAs (see Chapter IV) and AlAs (70L1) together with the five samples with $x$ in the range $0.232 \sim 0.40$ gives $E_X(295 \text{ K}) = 1.9106 + 0.0048x + 0.245x^2$. This expression was then used to estimate the band minima energy for the three direct gap samples with $x = 0.08$, 0.106 and 0.13 and also for the four indirect gap samples with $x$ in the range $0.52 \sim 0.95$. The energy values for the $L_1$ minima were determined for the ten samples with $x$ in the range $0.08 - 0.60$ and the results will be further discussed later.

During the analysis for the five intermediate compositions, it was found that a small increase in the contribution of the $\Gamma_1$ band improved the fit which could be obtained, and thus the effective mass values were adjusted by using the expression $m_0(x) = 0.066 + (m_0(\text{AlAs}) - 0.066)x$ for the values at 0 K. A linear form of $m_0$ variation was assumed, neglecting any possible small bowing, to avoid the problems discussed in Chapter II. The resulting effective mass of AlAs is $0.154 \pm 0.005 \text{ m}$ which is in good agreement with the theoretical value of 0.15 m of Stukel and Euwema (69S1) and Hess et al. (73H2).
The six samples with \( x \) in the range 0.27 - 0.60 required a smaller variation of the \( X_\perp \) minima with temperature than that for GaAs which we assumed for the present analysis, and thus only \( a_x \) was adjusted and a value of \(- (6.15 \pm 0.15) \times 10^{-4} \text{eV/K} \) gave the best fit for the two samples with \( x = 0.40 \) and 0.60. This value of \( a_x \) gives a 64.7 ± 1.6 meV change in the \( X_\perp \) minima when the temperature is raised from 0 to 300 K. For comparison, we have shown that GaAs exhibits a 71 meV change and Monemar et al. (76M2) estimated from experimental results that for the same temperature variation alloys in the indirect gap region showed a change of 70 meV. The value of \( a_x \) given above was assumed here for all compositions in the indirect gap range. For the four direct gap samples with \( x \) in the range 0.27 - 0.335, the values of \( a_x \) for the best fit were a little different from that above, while the \( X_\perp \) band contribution was not sufficient to determine \( a_x \) for lower Al-\( 1-x \) concentration samples and a simple interpolation between the values for GaAs and the alloy with \( x = 0.27 \) was assumed to estimate the value in this range. The resulting values of \( a_x \) are shown in Table (V-3).

The repeated analysis on the three samples with \( x = 0.08 \), 0.106 and 0.13 using the re-determined parameter values places the \( \Gamma_1 \) minimum about 10 meV higher than the values from the preliminary analysis, while the \( L_1 \) minima are now 5 to 8 meV lower than the values from the first analysis. These results for the \( \Gamma_1 \) minimum still indicate the experimental data on the \( \Gamma_1 \) minima which show bowing are more consistent with the present work.
The values of "effective scattering factor $r_{\text{eff}}$" employed to calculate the carrier density for the samples showing deep donor and multiband characteristics were found to be very different from that of unity which is usually assumed. For example, for the sample with $x = 0.3$, $r_{\text{eff}}$ varies from 1.265 to 1.695 when the temperature is increased from 18.5 to $225^\circ$C. Similarly the sample with $x = 0.335$ shows an $r_{\text{eff}}$ variation from 1.46 to 1.865 over a similar temperature range, but $r_{\text{eff}}$ decreases with increasing temperature for the sample with $x = 0.4$, varying from 1.665 to 1.475 in the experimental temperature range.

Values of $N_A$ were determined under the assumption $N_{cc} = n_t + 2N_A$ and the results are shown in Table (V-1). Except for the sample with $x = 0.71$, the values of $N_A$ are effectively zero for the samples where the $X_1$ band dominates. Since $N_A \neq 0$ for most of the direct gap samples, this suggests a possibility that the ionized impurity scattering is not accurately calculated for the $X_1$ (and $L_1$) bands. These bands have ellipsoidal constant energy surfaces and so an anisotropic calculation should be made. However, Maronchuk and Yakasheva (76M1) showed that an anisotropic treatment of the scattering increased the calculated total mobility by 1.8% for samples in the indirect gap region at 300 K. Thus the use of an isotropic form should not seriously change the results of calculations made here. Full calculations by the Fletcher and Butcher technique for anisotropic conditions (73F1) are being considered by Dr. Juravel of this Department but the computation is
very lengthy and it appears impossible that a fitting analysis using anisotropic conditions for the \( L_1 \) and \( X_1 \) bands could be carried out with the present computing facilities.

Some authors have considered neutral impurity scattering in the analysis of data for \( \text{Ga}_{1-x} \text{Al}_x \text{As} \) (74N1, 76M1, 73N1). The theory for the scattering mechanism discussed in Chapter II is for slow electrons scattered by hydrogen-like impurities and thus will be suitable in explaining the carrier transport of semiconductors which have shallow impurities which are unionized only at low temperatures. Hence this theory cannot be employed in the calculations for the present materials which show deep donor effects at some compositions. Sclar (56S1) suggested a theory for neutral impurity scattering which is valid only at high temperature. This theory would seem to be appropriate for the present analysis but was found to have negligible effect in the present case. Hence neutral impurity scattering could safely be neglected in this work.

The final curves fitted to the experimental data using the parameter values determined in the present analysis are shown in Figs. (V-2 to 13). The experimental data were fitted at all points to an accuracy better than \( \pm 1.5\% \) for the samples near the two compounds. Some discrepancies are observed for the samples of intermediate compositions and the worst fits, \( \pm 3\% \) are exhibited by the two samples with \( x = 0.335 \) and 0.52 as can be seen in Figs. (V-8, 10). Considering
the many unknown parameters and assumptions we used for this calculation, these small disagreements are not unreasonable for the intermediate range. The results of analysis for six different samples are given in Tables (V-6 to 11).

B. Impurity Level

As indicated in the section treating experimental results, the six samples with \( x \) in the range \( 0.335 \sim 0.95 \) show deep donor effects. Using the temperature dependences of \( n_t \) and \( E_F \) resulting from the above analysis, the impurity level characteristics were estimated using the neutrality condition given by Eq. (II-66). The spin degeneracy factor \( g_\perp \) in Eq. (II-67) has been assumed to be 2 in one analysis as in the case of GaAs (70P1) and GaAs\(_{1-x}\)P\(_x\) (68C3). In this analysis, the excited states of the donor level have been neglected and a single donor level has been assumed to be associated with the \( X_1 \) minima as in the case of Te-doped GaAs (70P1). The sample with \( x = 0.3 \) has been excluded from this analysis because of the small temperature range in which carrier excitation is observed. The resultant \( N_D \) and \( E_d \) are compiled for the six samples as shown in Table (V-5). The activation energies range from 0.07 to 0.133 eV, the maximum value being shown by the sample with \( x = 0.4 \), in the vicinity of which composition the band crossover points are observed as will be discussed in a later section. The \( E_d \) value decreases with
increasing x and the rate of decrease is too large to be attributed to
the effects of the dielectric constant and effective mass variations
using a simple hydrogenic model. The \( N_D \) value calculated here has
then been used in correcting ionized impurity scattering calculation
because the unionized impurity plays a role in screening the scattering
centre. However since ionized impurity scattering has a small effect
in the resulting calculation for the indirect gap region, the effect of
an increase in \( N_D \) was negligible. However in the direct gap region, a
small increase in \( N_A \) was required to recover the fit to the experimental
data.

\( g_1 \) should involve the multiplicity of the band minima with
which the impurity level is associated, and thus \( g_1 = 6 \) would be
reasonable in the present case. \( E_d \) decreased by about 20% and \( N_D \)
increased by the same ratio when this increased degeneracy factor was
used and these results also are shown in Table (V-5). However, the
\( E_d \) variation with x does not show any change in form. These \( E_d \) values
for \( g_1 = 6 \) are in reasonable agreement with those determined previously
for samples with \( x > 0.6 \) (73N1, 75K2, 76M1). In those cases, however,
the authors assumed \( g_1 \) to be 12 and the results of their Hall coefficient
analysis showed the activation energy to be almost independent of x in
the indirect gap region, showing no particular increase in \( E_d \) around
the band crossover point (75K2, 76M1).
With \( g_1 = 6 \) we obtained \( N_D = 8.0 \times 10^{23} \text{ m}^{-3} \) and \( E_d = 0.116 \text{ eV} \) for the sample with \( x = 0.4 \) when the first excited state was included in the impurity levels concerned. \( N_D = 8.7 \times 10^{23} \text{ m}^{-3} \) and \( E_d = 0.11 \text{ eV} \), and \( N_D = 1.05 \times 10^{24} \text{ m}^{-3} \) and \( E_d = 0.105 \text{ eV} \) were obtained when the second and third excited states respectively were included. However, as the number of the excited states is increased, the fit to the \( n_t \) variation with temperature deteriorates in this case. In the case of samples showing donor levels of low activation energy, the inclusion of excited states has significant effect on the results. For instance, we find \( N_D = 1.65 \times 10^{24} \text{ m}^{-3} \) and \( E_d = 0.05 \text{ eV} \) when the two lowest excited states are included in the analysis for the sample with \( x = 0.71 \), and a poor fit is obtained. The calculated \( N_D \) and \( E_d \) values therefore depend upon the spin degeneracy factor and the number of excited states of the donor levels employed in the calculation. Since higher excited states can be overlapped with the conduction band any way, the number of excited states to be included in the calculation is related to the activation energy of the ground state. A single impurity band assumption may not be valid, as indicated by Pitt and Lees (70P1), but a multiband calculation requires too many unknown parameters to be included. These problems discussed above prevent an accurate calculation of the impurity characteristics in this type of analysis and other methods such as electroluminescence measurements would be required to solve the problem. The \( E_d \) vs. \( N_D^{1/3} \) relationship (49P1, 70P1) was not observed in the above analysis.

Because any impurity band will interact with nearby conduction bands, we may use the two-band \( (L_1 \text{ and } X_1) \) model of Aspnes (76A2) for the
impurity level calculation and compare the results with those from the present experimental work. In this model, the $\Gamma_1$ band was neglected because of its low effective mass value compared with those of the $L_1$ and $X_1$ bands. The two-band model gives the energy of the impurity level as

$$E_I = \frac{1}{2} (E_X + E_L) - \frac{1}{2} \left\{ (E_X - E_L)^2 + 4V^2 \right\}^{\frac{1}{2}}$$

where $E_X$ and $E_L$ are the energy values of the $X_1$ and $L_1$ minima as defined previously, and $V$ is an adjustable parameter. In the present work, $V$ has been determined by fitting the experimental values of $E_X - E_d (\equiv E_I)$ to Eq. (V-4). A good fit to the data could be obtained with $V = 0.12$ eV for $g_1 = 6$ or with $V = 0.14$ eV for $g_1 = 2$. The experimental impurity levels and the theoretical values for $g_1 = 6$ are shown in Fig. (V-14).

For comparison it should be noted that Aspnes determined a value of $V = 0.18$ eV for the nitrogen level in GaAs$_{1-x}$P$_x$ (76A2).

C. Band Structure.

For no other III-V alloy system has the band structure been investigated so thoroughly as for Ga$_{1-x}$Al$_x$As. Most of the experimental data on the $\Gamma_1$ minimum show downward bowing as shown in Fig. (V-1). However this bowing has not been predicted theoretically (70V1, 72S1, 77B1), and the theoretical values of the bowing parameter $c$ in Eq. (II-19) are very low, e.g., $c = 0.03$ eV (70V1 0.05 eV (72S1) and zero (77B1).
Experimental data on the \( \Gamma_1 \) minimum by Monemar et al. (76M2) show no bowing in the direct gap region, and they attributed the band bowing in the indirect gap region to the effects of disorder. We have shown that these data by Monemar et al. for the direct gap region do not fit well the experimental data in the present work.

The energy values for the \( \Gamma_1 \) minimum have been determined in this work only for the three samples with \( x = 0.08, 0.106 \) and \( 0.13 \), while for the six samples with \( x \) in the range of \( 0.232 \sim 0.52 \) we have estimated the \( \Gamma_1 \) minimum positions from the experimental data of Onton et al. (73P1), Casey and Panish (69C1) and Berolo and Woolley (71B1). These values for the \( \Gamma_1 \) minimum used in the calculation for the alloys are shown for 0 and 295 K in Table (V-4). The value of the \( \Gamma_1 \) minimum energy at 295 K for AlAs is quoted from Onton's experimental data (7001). The value for the \( \Gamma_1 \) minimum for GaAs is the one used in Chapter IV. A least squares fit to these data gives an expression for the \( \Gamma_1 \) minimum variation with \( x \) at 295 K as

\[
E_\circ (295 \text{ K}) = 1.425 + 1.155x + 0.37x^2
\]  

(V-5)

This bowing parameter is effectively an average value of those of two previous works (7101, 71B1). Eq. (V-5) gives the energies of the \( \Gamma_1 \) minimum considerably lower than the values obtained by Monemar et al. in the direct gap region. However the latest report quoted by Casey (78C1) gives \( E_\circ (297 \text{ K}) = 1.424 + 1.247x \) in the direct gap region,
which gives the $\Gamma_1$ minimum at about 20 meV lower than the values given by Eq. (V-5) for compositions around the band crossover value, $x = 0.4$. The bowing parameter value calculated for the $\Gamma_1$ minimum is very sensitive to the value of the $\Gamma_1$ minimum energy for AlAs. Mead and Spitzer (63M1) measured the $\Gamma_1$ minimum energy for AlAs to be 2.9 eV at room temperature and when this value together with the data for the alloys and GaAs shown in Table (V-4) are used in a least squares fit, we obtain an expression, $E_o (295 K) = 1.425 + 1.192x + 0.285x^2$. In this case, the bowing parameter value is in good agreement with that of Berolo and Woolley (71B1).

Except for the two samples with $x = 0.71$ and 0.95, the $L_1$ band is of importance in calculating transport properties and the minima energy values determined in the present work for the remaining alloys are given in Table (V-4). A least squares fit to the $L_1$ minima values at 295 K for the ten alloys provides the form

$$E_L (295 K) = 1.734 + 0.574x + 0.055x^2 \quad (V-6)$$

Here the bowing parameter value is very low compared with that for the $\Gamma_1$ minimum given above. This expression for the $L_1$ minima energy places the $L_1$ minima at 1.734 eV above the top of the $\Gamma_{15}$ state for GaAs, which is in good agreement with values obtained from the analyses on GaAs in Chapter IV, where $L_1$ minima energies of 1.728 and 1.748 eV were found to give best fit to the high temperature and high pressure
transport measurements respectively. Eq. (V-6) gives $E_L = 2.363 \text{ eV}$ for AlAs which is a little higher than the estimated value by Dingle et al., $E_L = 2.25 \sim 2.35 \text{ eV}$ at 297 K (78C1), while theoretical calculations gave $E_L = 2.57 \text{ eV}$ (69S1) and 2.76 eV (73H2).

The energy value of the $X_1$ minima has been treated as adjustable for only five samples with $x$ in the range 0.232 $\sim$ 0.4. We have made a least squares fit to the $X_1$ minima data for the five alloys above (present analysis), GaAs (see Chapter IV) and AlAs (70L1) as shown in Table (V-4) and the result is given by

$$E_X(295 \text{ K}) = 1.911 + 0.005x + 0.245x^2$$

(V-7)

which gives values in good agreement with the experimental data of Neumann and Junge (76N1) for the indirect gap region of this alloy system and also those by Casey and Panish (69C1) when a correction is made to their data according to their discussion. But the minima values given by Eq. (V-7) are lower by about 20 meV at around the band crossover point than those of Dingle et al., quoted by Casey (78C1), which are expressed by the form $E_X(297 \text{ K}) = 1.9 + 0.125x + 0.143x^2$.

From Eqs. (V-5, 6, 7) we have band crossover points at 295 K as follows:

- $\Gamma_1 - L_1$ crossover: $x = 0.432$, $E_O = 1.992 \text{ eV}$
- $\Gamma_1 - X_1$ crossover: $x = 0.405$, $E_O = 1.953 \text{ eV}$
- $L_1 - X_1$ crossover: $x = 0.35$, $E_L = 1.942 \text{ eV}$
These points are very close to each other both in composition and in energy. Previous data indicated the $\Gamma_1 - X_1$ crossover to be in the range $x = 0.31$ (77B1) to 0.5 (66B2). Casey's estimate from quoted data (78C1) locates the $\Gamma_1 - X_1$ crossover at $x = 0.45$, and the other two crossover points also at slightly higher $x$ values than those shown in the present work. No other data on the latter two band crossover points is known. The band crossovers at 0 K are found to be,

\[
\begin{align*}
\Gamma_1 - L_1 & \text{ crossover; } x = 0.424, \quad E_o = 2.075 \text{ eV} \\
\Gamma_1 - X_1 & \text{ crossover; } x = 0.38, \quad E_o = 2.011 \text{ eV} \\
L_1 - X_1 & \text{ crossover; } x = 0.30, \quad E_L = 1.998 \text{ eV}
\end{align*}
\]

The resulting conduction band minima behaviour with composition is shown in Fig. (V-14), which is very much similar to that of GaAs with pressure.

Under the assumption that the measured $E_1$ and $E_2$ values apply to the $L$ and $X$ points respectively, the room temperature energy values of points in the valence band relative to the valence band maximum can be approximated from the electroreflectance data of Berolo and Woolley (71B1) and the present conduction band data to be

\[
\begin{align*}
E^V_L (L_3 - \Gamma_{15} \text{ energy difference}) &= -1.236 + 0.034x - 0.395x^2 \\
E^V_X (X_5 - \Gamma_{15} \text{ energy difference}) &= -3.089 + 0.135x + 0.225x^2
\end{align*}
\]

(V-8)
The two valence band points show opposite band bowing.

As has been indicated, Rode's estimated value of the effective mass for the $\Gamma_1$ minimum (74R1) was found to be lower than that for the best fit to the experimental data. The effective mass values determined by analyzing the five samples with $x$ in the range $0.232 \sim 0.4$ are expressed by

$$m^*(0) = 0.066 + 0.088x$$

which gives $0.154m \pm 0.005$ for AlAs in reasonable agreement with the theoretical value, $0.15m$ (69S1, 73H2). Meanwhile Rode's estimate gives $m^* = 0.128m$ for AlAs at room temperature.

D. Multiplicity of Equivalent Valleys in the <111> and <100> Directions.

Theoretical prediction (73H2) and experimental analysis (73H3) of the optical data for AlAs suggest that the band minima to be found in the <100> and <111> directions are not at the Brillouin zone boundary. Because of these possible differences in band form, the present analysis has been repeated for some samples using multiplicities of $N_L = 8$ and $N_X = 6$. It has been found for the sample with $x = 0.95$ that a fit to the experimental data could be made simply by reducing the value of $D_{XX}$ from $4.05 \times 10^{10}$ to $2.4 \times 10^{10}$ eV/m. This reduction in the value of $D_{XX}$ is due to the enhanced intervalley scattering
because of the increase in band multiplicity. For the sample with 
\( x = 0.52 \), \( D_{XX} = 3.5 \times 10^{10} \text{ eV/m} \) was now required for the best fit, 
which is a little lower than the estimated value from straight line 
interpolation using the values for GaAs and the alloy with \( x = 0.95 \). 
And the value of the \( \Lambda \) minima energy is 6 meV higher than that for 
the \( L \) minima obtained for the case of \( N_L = 4 \) and \( N_X = 3 \). In the 
analysis with higher multiplicity values, alloy scattering was neglected 
because this mechanism has no significant effect on the resulting 
calculations and because the conductivity value calculated by using 
the same method as that in the case of low multiplicity was lower than 
the measured one even if we neglected this mechanism. To make a reason­
able fit to the data for the sample with \( x = 0.4 \), \( 3.8 \times 10^{10} \text{ eV/m} \) was 
required for the value of \( D_{LX} \). When the smaller multiplicity values 
were used, \( D_{LX} \) was shown to have the value of \( 6.8 \times 10^{10} \text{ eV/m} \) for the 
same sample. The energy values for the \( \Lambda \) and \( \Lambda \) minima were now 113 
and 15 meV higher respectively than the corresponding minima values 
obtained with the lower multiplicity values. These higher energy values 
for the \( \Lambda \) and \( \Lambda \) band minima were required for a fit because the \( \Gamma \) band 
plays an important role at this composition and when the energy 
values determined for the lower multiplicity case are used in the cal­
culation with high multiplicity, the values of carrier density and 
 mobility in the \( \Gamma \) band are much reduced as compared with the values deter­
mined for the lower multiplicity case. With this resulting band structure, 
the carrier density in the \( \Lambda \) band is only \( \approx 7\% \) of the total density at 
the highest experimental temperature and thus a two-band model comprising
the $\Gamma_1$ and $\Delta_1$ bands would give a reasonable approximation when the increased band multiplicity is used as was shown to be the case in previous work (74N1, 75K1, 76N1).

Similar effects were observed in the case of the sample with $x = 0.27$, that is, the resulting energy values of the $\Lambda_1$ and $\Delta_1$ minima are 2.01 and 2.008 eV respectively above the top of the $\Gamma_{15}$ state at 0 K, which are higher than those obtained using lower band multiplicity.

As a result of using the higher multiplicity values, the energy value of the $\Lambda_1$ minima increases with $x$ at approximately the same rate as the $\Gamma_1$ minimum variation in the direct gap range and then decreases abruptly at around the onset of the indirect gap composition. Even if the abrupt decrease at the band transition region were attributed to possible error in the $\Lambda_1$ band calculation, the high values of the $\Lambda_1$ minima energy in the direct gap samples are not reasonable when the previous work on the two compounds, GaAs (76A2) and AlAs (69S1, 73H2) is considered. Casey (78C1) reported the band structure of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ using a set of quoted data on the $\Gamma_1$, $L_1$, and $X_1$ bands for these alloys. This recent report supports the lower multiplicity of the bands in the $<111>$ and $<100>$ directions and was published after the present analysis on the alloy system had been completed. While the present results are not conclusive, the lower multiplicity values, i.e., the assumption of band minima at the $L_1$ and $X_1$ points is more in line with recent results.
obtained for Ga$_{1-x}$Al$_x$As alloys and GaAs.

E. Some Scattering Parameter Values and Carrier Mobility

Some of the more important scattering parameters are the deformation potential $E_D$, the interband scattering coupling coefficient $D_{ij}$ and the intervalley scattering coupling coefficient $D_{ii}$. No work has been reported on these parameters for Ga$_{1-x}$Al$_x$As and AlAs. Hence, in the present analysis, a trial and error method was the only available way of analysis using a fitting procedure to the experimental data.

With many unknown parameter values to be adjusted, we have assumed that $E_D = E_D$, $D_{LL} = D_{XX}$ and $D_{IX} = D_{IL}$, which was found to be satisfactory for GaAs. Also the parameters have been assumed to vary linearly with composition. Fortunately, no appreciable intercompensation effect between the above parameters was observed, which can be easily understood from the form of the mobility variation of each scattering mechanism with temperature as shown in Figs. (V-15, 16, 17). The resulting parameter values are summarized as follows

\[
\begin{align*}
E_D &= 16.1 - 13.5x \quad \text{(eV)} \\
E_{DX} &= 12.5 - 10.75x \quad \text{(eV)} \\
D_{LL} &= 5.0 - 1.0x \quad \text{($10^{10}$ eV/m)} \\
D_{LX} &= 11.0 - 10.5x \quad \text{($10^{10}$ eV/m)}
\end{align*}
\]

(V-10)

The values for $E_D$ and $D_{LX}$ have not been checked for the samples with
x > 0.6 because the scattering effects corresponding to these two parameters are negligible and the validity of the values is in doubt for this range. In the case of $D_{\Gamma L}$, we found it impossible to fit the experimental data with a variation linear in $x$ and the resulting values are shown in Table (V-3). It is to be noted that except for $D_{LL}(=D_{XX})$ the values of all the scattering parameters determined above decrease rapidly with increasing $x$. However, a theoretical treatment of the parameter variation with composition seems to be lacking at present.

In Figs. (V-15, 16, 17), we present the carrier mobility values for all the scattering mechanisms in each conduction band for the sample with $x = 0.4$, a composition close to which the band crossovers occur. In the $\Gamma_1$ and $X_1$ bands, polar optical scattering is the dominant mechanism. Though the value of $D_{\Gamma L}$ is very low compared with that of GaAs, interband scattering plays a more important role in the $\Gamma_1$ band for this alloy than for GaAs because the band minima which interact are much closer in energy in this case. The four mechanisms of ionized impurity, acoustic deformation potential and interband $(\Gamma_1 - L_1$ and $\Gamma_1 - X_1$) scattering have similar mobility values at about $200^\circ$C in the $\Gamma_1$ band. Alloy scattering is not important in this band as shown in Fig. (V-15). In GaAs, the two scattering mechanisms of acoustic deformation potential and interband between the $X_1$ and $L_1$ valleys are more important than the polar optical mode for the $X_1$ band, but their importance is decreased for this alloy because of the low values of $E_{DX}$ and $D_{LX}$ in this case.
In the $L_1$ band, interband scattering between the $L_1$ and $X_1$ valleys is dominant over all other mechanisms for the same reasons as in the case of the $\Gamma_1$ band. For the $X_1$ and $L_1$ bands, interband scattering into the $\Gamma_1$ band is negligible as is the case of GaAs. Because of the high effective mass for the $X_1$ band, alloy scattering plays a substantial role in this valley.

In Fig. (V-18), the carrier mobility values obtained from the analysis for all alloys at room temperature are shown for all bands considered. The mobility data for GaAs were quoted from the results for the sample MO807/8 in Chapter IV. The high values of $\mu_1$ obtained for the two samples of $x = 0.08$ and 0.4 are due to their low carrier density. To avoid some difficulties in understanding the mobility behaviour with $x$ because of different $n_t$ and $N_A$ values for different samples, using the parameter values determined here we have calculated the mobility behaviour as a function of $x$ at 20°C assuming $n_t = 10^{22} \text{m}^{-3}$ and $N_A = n_t'$, and the results for the mobility, carrier density and "effective scattering coefficient" are illustrated by curves in Fig. (V-18).

For the calculation of $\mu_1$ for $x > 0.4$, the alloys in this range have been assumed to have the same $D_{TL}$ value as that for $x = 0.4$. Even though the band gap variation with $x$ for this alloy system is similar to that with pressure for GaAs, detailed comparison is not possible for the resulting values, mainly because the scattering parameter values depend upon composition and the effective mass variation with $x$ is greater for this alloy system than that with pressure for GaAs. Because
of very low interband coupling coefficients in the alloys compared with those for GaAs, the rapid change in mobility value with pressure close to the band crossover in GaAs is not seen in the alloys.

As discussed above, polar optical scattering is dominant in the $\Gamma_1$ band for all compositions which required the $\Gamma_1$ band in the calculation and thus the decrease in mobility with $x$ is mainly due to the increase in the effective mass with $x$. The predicted $\mu_{\Gamma}$ value for AlAs is very low as shown in Fig. (V-18), which may be due to the assumption that $D_{\Gamma L}$ for $x > 0.4$ is equal to that for $x = 0.4$. In the $L_1$ band, the calculated mobility shows a minimum value close to the band crossover ($L_1$ - $X$) point, which can be understood in terms of an increase of the interband scattering around the crossover point as discussed above. It is noteworthy that the mobility in the $X_1$ band increases with $x$ and the value for AlAs is about five times that for GaAs. In GaAs, the dominant scattering mechanisms were found to be interband and acoustic deformation potential modes in the $X_1$ band, but these two mechanisms show decreasing contribution with increasing $x$ because of the rapid decrease of the $E_{DX}$ and $D_{LX}$ values with $x$. Furthermore, the effective mass in the $X_1$ band decreases with increasing $x$; $m^*$ values are 0.4097 and 0.341 m for GaAs and AlAs respectively. Thus the rapid increase in the $\mu_X$ value with $x$ is understandable.

The carrier distribution between the bands in these alloys varies with $x$ in quite a similar way to that with pressure in GaAs.
because the distribution is determined by the band minima separations in energy and effective mass value only, as shown in Figs. (V-18, IV-17). The "effective scattering coefficient" calculated from \( r_{\text{eff}} = n e t R_{H}^2 \) has a maximum value, 2.4, at \( x \approx 0.36 \) for \( n_t = 10^{22} \text{ m}^{-3} \). The corresponding maximum value for GaAs under pressure can be approximated from the maximum value of the measured normalized Hall coefficient \( R_H(P)/R_H(0) \) to be \( 3 \approx 4.5 \) for the samples (70P1) treated in Chapter IV. The low maximum value of \( r_{\text{eff}} \) in this alloy system is due to the lower scattering coefficient in all bands considered for the alloys as compared with those for GaAs. The high values of scattering coefficient in the case of GaAs are mainly due to interband scattering.

We have tried various values of polar phonon energy and effective mass in the \( L_1 \) band using the sample with \( x = 0.4 \) to see their effects on the resulting parameter values determined in this work. We have shown the importance of the \( L_1 \) band in Ga\(_{1-x}\)Al\(_x\)As system and thus the effective mass in this band is one of the more important parameters in the analysis. In order to estimate the effective mass values of the \( L_1 \) minima for the alloys we have used a linear interpolation using the data for the compounds. Since no experimental value is available for AlAs, we quoted theoretical values of Hess et al., \( m_t = 0.15 \text{ m} \) and \( m_L = 1.32 \text{ m} \), which give \( m_d^* = 0.306 \text{ m} \). But Aspnes (78C1) estimated recently the effective mass in the \( L_1 \) minima for AlAs to be \( m_d^* = 0.266 \text{ m} \) which is lower by 13% than the above theoretical value we have employed for the present work. Only \( m_t \) was adjusted to give \( m_d^* = 0.266 \text{ m} \), and
\( m_t = 0.12 \text{ m} \) was obtained. With this trial value \((m_t = 0.12 \text{ m for AlAs})\), the density of states effective mass for \( x = 0.4 \) is \( 0.24 \text{ m} \), which is lower by 7.7\% than that given by \( m_t = 0.15 \text{ m} \) for AlAs. With this lower value of \( m^* \) for \( x = 0.4 \), a fit was recovered by replacing \( 2.8 \times 10^{10} \) with \( 3.0 \times 10^{10} \text{ eV/m} \) for \( D_{\text{TL}} \), \( 6.8 \times 10^{10} \) with \( 7.4 \times 10^{10} \text{ eV/m} \) for \( D_{\text{LX}} \), 2.057 with 2.06 eV for \( E_L^x(0) \) and 2.015 with 2.013 eV for \( E_X^x(0) \). A considerable change (9\%) is seen only for the value of \( D_{\text{LX}} \).

\( \text{Ga}_{1-x}\text{Al}_x\text{As} \) alloys have two longitudinal phonon branches of different energy values as shown by Ilegems and Pearson (70I2). However, theory is lacking at present for treating this problem in transport calculation. Thus a linear interpolation has been used to give a single phonon energy for the intermediate compositions where experiment indicates two phonon branches (70I2). With this linear interpolation, a phonon energy of 0.0407 eV is determined for \( x = 0.4 \) which is about 12\% higher than that for GaAs. Since a lower phonon energy is more effective in restricting carrier mobility, a value of 0.0386 eV also has been tried in the analysis to see the effects, assuming an error in the phonon energy estimate of 5\%. With this lower phonon energy, only two parameters have to be readjusted for a fit to the experimental data, i.e., from \( 6.8 \times 10^{10} \) to \( 6.5 \times 10^{10} \text{ eV/m} \) for \( D_{\text{LX}} \), from 2.015 to 2.017 eV for \( E_X^x(0) \). Again the changes in the resulting analysis are not serious. Thus we have considered two parameters for which the values are considered to be less certain and the changes in the final values obtained are not serious.
Some experimental errors are expected when the Van der Pauw method is used as discussed by Wieder (76W1). The most serious error may be made in the measurement of Hall voltage due to the finite size of the electrodes (74Cl). The correction factors used in this work were between 1.10 and 1.27 as shown in Table (II-2). Considering these difficulties in the measurement of Hall coefficient, for the sample with \( x = 0.4 \) we made the assumption of a 10% error in the measured \( R_H \) values and a fit was made to the 10% reduced \( R_H \) values by readjusting three of the most sensitive parameters. In this case, the resulting parameter values were \( E_{L}(0) = 2.045 \) eV, \( E_{D_{LX}} = 12.4 \) eV and \( D_{LX} = 7.6 \times 10^{10} \) eV/m. Despite the considerable change in \( R_H \) values used for the analysis, the resulting parameter values are not seriously changed.

Other possible sources of error which may arise in the calculations have already been indicated, such as the approximations made in the transport calculations for the \( L \) and \( X \) bands, the assumption of linear variation of some parameters with \( x \), etc. It is difficult to give any numerical value to such errors but it may be argued, as above, that these effects will be small. In light of the above discussions, estimates of the error in the various parameters can be attempted. The analysis is most sensitive to the energy values of the \( L \) and \( X \) minima and here it is considered that the error will not exceed 20 meV. Variation in the values of the scattering parameters such as deformation potential and interband and intervalley coupling coefficients has less effect on the fit to the experimental
data but even in these cases the error should not exceed a maximum of about 25%.

V-6 Summary

We have used a three-conduction-band model in the calculations of transport properties for eight samples with $x$ in the range $0.08 \sim 0.4$. For two samples with $x = 0.52$ and 0.6, only the $L_1$ and $X_1$ band have to be considered, and the experimental data for the other two samples with $x = 0.71$ and 0.95 were explained in terms of one-band model, the $X_1$ band.

All the conduction band minima values follow a quadratic relation with composition, i.e., $E_o(x) = 1.425 + 1.155x + 0.37x^2$, $E_L(x) = 1.734 + 0.574x + 0.055x^2$ and $E_X(x) = 1.911 + 0.005x + 0.245x^2$ at 295 K. The $\Gamma_1 - X_1$ band crossover occurs at $x = 0.405$ at 295 K which is a little higher than the previous estimate of $x = 0.37$ (69C1) but lower than the recent calculation of $x = 0.45$ (78C1). At the same temperature, the $\Gamma_1 - L_1$ and $L_1 - X_1$ band crossovers are found to be $x = 0.432$ and 0.35 respectively.

The $L_1$ valley was found to be important for the samples with $x \leq 0.6$ in the present work and the extrapolation of the band minima values obtained in this analysis to GaAs gives 1.734 eV at 295 K which is in good agreement with those obtained from the analyses of high
temperature and high pressure work in Chapter IV. A similar extrapolation to AlAs places the $L_\perp$ minima at 2.363 eV above the top of the $\Gamma_{15}$ state at 295 K.

The assumption of the band minima at general points in the $A_\perp$ and $A_\perp$ directions gives results which are less satisfactory than those obtained assuming minima at the $L_\perp$ and $X_\perp$ points.

Scattering parameter values of $E_{DL} (= E_{DL})$, $E_{Dx}$ and $D_{DX}$ determined using the assumption that they vary linearly with $x$ show a rapid decrease with increasing $x$. Similar behaviour is observed in the value of $D_{TL} (= D_{TX})$ for the samples with $x < 0.3$, but the best fits to the experimental data require almost constant value of $D_{TL}$ for the three samples with $x = 0.3$, $0.335$ and $0.4$. The variation of $D_{LL} (= D_{XX})$ with $x$ is much smaller than that of the other parameters above.

Polar optical scattering is dominant in the $\Gamma_\perp$ band at all compositions considered and also in the $X_\perp$ band for the alloys of $x \geq 0.4$. For the samples near GaAs, acoustic deformation potential and interband scattering between the $L_\perp$ and $X_\perp$ bands are more important in the calculations for the $X_\perp$ band than is polar optical. In the $L_\perp$ bands, acoustic deformation potential scattering predominates over all other mechanisms for samples near GaAs and the effect decreases with increasing $x$. As $x$ increases interband scattering between the $L_\perp$ and
$X_1$ bands becomes important in the $L_1$ band and the maximum effect is shown at the composition of $x \sim 0.35$. 
Table V-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>$R_H \times 10^{-5}$ m$^3$/Coul</th>
<th>$\sigma \times 10^3$ Ohm$^{-1}$m$^{-1}$</th>
<th>$n_t \times 10^{23}$ m$^{-3}$</th>
<th>$N_A \times 10^{23}$ m$^{-3}$</th>
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<tbody>
<tr>
<td>BL080</td>
<td>18.0</td>
<td>126.2</td>
<td>0.329</td>
<td>0.052</td>
<td>0.22</td>
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<td>51.50</td>
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<td>3.574</td>
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<td>1.406</td>
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<tr>
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<td>1.80</td>
<td>3.003</td>
<td>3.414</td>
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</table>

Table V-1  Room temperature values of the Hall coefficient, conductivity and carrier density for the twelve samples of the Ga$_{1-x}$Al$_x$As system. The sample number indicates Al-concentration of the sample, i.e., BL335 is the sample with $x$=0.335. The Hall coefficients were measured at 0.3 Wb/m$^2$, and the values of $N_A$ were obtained under the assumption that $N_{cc} = N_t + 2N_A$. 
Table V-2

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
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<tr>
<td>$m_o(0)$</td>
<td>0.154 m</td>
<td>*</td>
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<tr>
<td>$m_{tL}$</td>
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<td>(73H2)</td>
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<tr>
<td>$m_{XL}$</td>
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<td>(73H2)</td>
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<td>$\Delta o$</td>
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<td>(7001)</td>
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<td>(7012)</td>
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<td>$\kappa_\infty$</td>
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<tr>
<td>$D_{XX}$</td>
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<tr>
<td>$\rho$</td>
<td>3598 kgm/m$^3$</td>
<td>(75W2)</td>
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Table V-2 Material parameters of AlAs. *-determined in the present analysis.
Table V-3

<table>
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<tr>
<th>Sample</th>
<th>$E_{D\Gamma}$</th>
<th>$D_{\Gamma L}$</th>
<th>$D_{LX}$</th>
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<td>-6.15</td>
</tr>
<tr>
<td>BL600</td>
<td>7.8</td>
<td>-</td>
<td>4.8</td>
<td>-6.15</td>
</tr>
</tbody>
</table>

Table V-3 Composition dependences of the values of $E_{D\Gamma}$, $D_{\Gamma L}$, $D_{LX}$ and $\alpha_X$ for the Ga$_{1-x}$Al$_x$As system. We assumed that $E_{DL} = E_{D\Gamma}$ and $D_{LX} = D_{\Gamma L}$. 
Table V-4

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_o$ eV</th>
<th>295 K</th>
<th>$E_L$ eV</th>
<th>295 K</th>
<th>$E_X$ eV</th>
<th>295 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.519</td>
<td>1.425</td>
<td>1.821</td>
<td>1.734</td>
<td>1.981</td>
<td>1.911</td>
</tr>
<tr>
<td>0.081</td>
<td>1.608</td>
<td>1.514</td>
<td>1.873</td>
<td>1.786</td>
<td>1.981</td>
<td>1.913</td>
</tr>
<tr>
<td>0.106</td>
<td>1.639</td>
<td>1.545</td>
<td>1.882</td>
<td>1.795</td>
<td>1.981</td>
<td>1.914</td>
</tr>
<tr>
<td>0.130</td>
<td>1.674</td>
<td>1.580</td>
<td>1.898</td>
<td>1.811</td>
<td>1.982</td>
<td>1.915</td>
</tr>
<tr>
<td>0.232</td>
<td>1.802</td>
<td>1.708</td>
<td>1.951</td>
<td>1.864</td>
<td>1.994</td>
<td>1.929</td>
</tr>
<tr>
<td>0.270</td>
<td>1.855</td>
<td>1.764</td>
<td>1.976</td>
<td>1.889</td>
<td>1.994</td>
<td>1.929</td>
</tr>
<tr>
<td>0.300</td>
<td>1.899</td>
<td>1.805</td>
<td>1.994</td>
<td>1.907</td>
<td>1.998</td>
<td>1.934</td>
</tr>
<tr>
<td>0.335</td>
<td>1.938</td>
<td>1.844</td>
<td>2.033</td>
<td>1.946</td>
<td>2.003</td>
<td>1.940</td>
</tr>
<tr>
<td>0.400</td>
<td>2.040</td>
<td>1.946</td>
<td>2.057</td>
<td>1.970</td>
<td>2.015</td>
<td>1.952</td>
</tr>
<tr>
<td>0.520</td>
<td>2.220</td>
<td>2.126</td>
<td>2.157</td>
<td>2.070</td>
<td>2.043</td>
<td>1.979</td>
</tr>
<tr>
<td>0.600</td>
<td>-</td>
<td></td>
<td>2.177</td>
<td>2.090</td>
<td>2.066</td>
<td>2.002</td>
</tr>
<tr>
<td>0.710</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td>2.102</td>
<td>2.038</td>
</tr>
<tr>
<td>0.950</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-</td>
<td>2.200</td>
<td>2.136</td>
</tr>
<tr>
<td>1.000</td>
<td>3.044</td>
<td>2.950</td>
<td>2.450</td>
<td>2.363</td>
<td>2.224</td>
<td>2.160</td>
</tr>
</tbody>
</table>

Table V-4 Conduction band minima energy values vs. composition for Ga$_{1-x}$Al$_x$As at 0 and 295 K. The energy values are measured with respect to the maximum of the valence band.
Table V-5

<table>
<thead>
<tr>
<th>X</th>
<th>( g_1 = 2 )</th>
<th>( g_1 = 6 )</th>
<th>( N_A )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( N_D \ 10^{23} \text{ m}^{-3} )</td>
<td>( E_d \text{ eV} )</td>
<td>( N_D \ 10^{23} \text{ m}^{-3} )</td>
</tr>
<tr>
<td>0.335</td>
<td>17.7</td>
<td>0.102</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>11.6</td>
<td>0.126</td>
<td>13.8</td>
</tr>
<tr>
<td>0.40</td>
<td>5.3</td>
<td>0.133</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>6.9</td>
<td>0.118</td>
<td>9.7</td>
</tr>
<tr>
<td>0.60</td>
<td>7.5</td>
<td>0.102</td>
<td>10.4</td>
</tr>
<tr>
<td>0.71</td>
<td>7.4</td>
<td>0.070</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>6.8</td>
<td>0.075</td>
<td>8.4</td>
</tr>
<tr>
<td>0.95</td>
<td>7.3</td>
<td>0.086</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Table V-5  Impurity level characteristics for Ga\(_{1-x}\)Al\(_x\)As.

\( E_d \) was calculated with respect to the \( X_{1} \) minima. For two samples BL335 and BL710, we have made calculation by (a) including and (b) excluding \( N_A \), because the assumption of singly ionized acceptors made in the present analysis may not be true and hence the value of \( N_A \) may be incorrect.
Table V-6

<table>
<thead>
<tr>
<th>T °C</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\mu$</td>
<td>$r_n 10^{24}$</td>
<td>$\mu$</td>
</tr>
<tr>
<td>18</td>
<td>0.0546</td>
<td>0.2045</td>
<td>1.021</td>
<td>1.58</td>
</tr>
<tr>
<td>60</td>
<td>0.0512</td>
<td>0.1958</td>
<td>1.022</td>
<td>1.57</td>
</tr>
<tr>
<td>100</td>
<td>0.0472</td>
<td>0.1881</td>
<td>1.022</td>
<td>1.55</td>
</tr>
<tr>
<td>140</td>
<td>0.0424</td>
<td>0.1804</td>
<td>1.022</td>
<td>1.52</td>
</tr>
<tr>
<td>180</td>
<td>0.0364</td>
<td>0.1735</td>
<td>1.023</td>
<td>1.47</td>
</tr>
<tr>
<td>225</td>
<td>0.0280</td>
<td>0.1648</td>
<td>1.025</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table V-6 Results of the analysis for sample BL106. Unit of $\mu$ is $m^2/V$-sec and carrier density is given per m$^3$. $E_F$ was calculated with respect to the $\Gamma_1$ minimum.
Table V-7

<table>
<thead>
<tr>
<th>T °C</th>
<th>E_F (eV)</th>
<th>( l_\mu )</th>
<th>r</th>
<th>( n \times 10^{24} )</th>
<th>L_1</th>
<th>( l_{\mu} )</th>
<th>r</th>
<th>( n \times 10^{23} )</th>
<th>X_1</th>
<th>( l_{\mu} )</th>
<th>r</th>
<th>( n \times 10^{22} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5</td>
<td>0.0335</td>
<td>0.1512</td>
<td>1.025</td>
<td>1.216</td>
<td>0.0489</td>
<td>1.034</td>
<td>0.921</td>
<td>0.0149</td>
<td>1.029</td>
<td>1.189</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>0.0267</td>
<td>0.1458</td>
<td>1.024</td>
<td>1.137</td>
<td>0.0451</td>
<td>1.042</td>
<td>1.590</td>
<td>0.0136</td>
<td>1.028</td>
<td>2.385</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.0177</td>
<td>0.1390</td>
<td>1.023</td>
<td>1.035</td>
<td>0.0413</td>
<td>1.051</td>
<td>2.436</td>
<td>0.0123</td>
<td>1.028</td>
<td>4.121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>0.0069</td>
<td>0.1327</td>
<td>1.022</td>
<td>0.921</td>
<td>0.0381</td>
<td>1.059</td>
<td>3.361</td>
<td>0.0112</td>
<td>1.029</td>
<td>6.243</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>-0.0057</td>
<td>0.1268</td>
<td>1.022</td>
<td>0.806</td>
<td>0.0352</td>
<td>1.068</td>
<td>4.281</td>
<td>0.0103</td>
<td>1.031</td>
<td>8.574</td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>-0.0201</td>
<td>0.1211</td>
<td>1.021</td>
<td>0.696</td>
<td>0.0328</td>
<td>1.077</td>
<td>5.144</td>
<td>0.0094</td>
<td>1.033</td>
<td>10.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table V-7 Results of the analysis for sample BL232. Unit of \( \mu \) is \( m^2/V\text{-sec} \) and carrier density is given per \( m^3 \). \( E_F \) was calculated with respect to the \( \Gamma_1 \) minimum.
<table>
<thead>
<tr>
<th>T °C</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu \times 10^{23}$</td>
<td>$r$</td>
<td>$n \times 10^{23}$</td>
<td>$\mu \times 10^{23}$</td>
</tr>
<tr>
<td>18.5</td>
<td>-0.0213</td>
<td>0.1111</td>
<td>1.060</td>
<td>2.553</td>
</tr>
<tr>
<td>60</td>
<td>-0.0314</td>
<td>0.1076</td>
<td>1.055</td>
<td>2.494</td>
</tr>
<tr>
<td>100</td>
<td>-0.0449</td>
<td>0.1038</td>
<td>1.052</td>
<td>2.232</td>
</tr>
<tr>
<td>140</td>
<td>-0.0615</td>
<td>0.0999</td>
<td>1.050</td>
<td>1.903</td>
</tr>
<tr>
<td>180</td>
<td>-0.0810</td>
<td>0.0978</td>
<td>1.043</td>
<td>1.568</td>
</tr>
<tr>
<td>225</td>
<td>-0.1049</td>
<td>0.0943</td>
<td>1.039</td>
<td>1.260</td>
</tr>
</tbody>
</table>

Table V-8 Results of the analysis for sample BL300. Unit of $\mu$ is m$^2$/V-sec and carrier density is given per m$^3$. $E_F$ was calculated with respect to the $\Gamma_1$ minimum.
Table V-9

<table>
<thead>
<tr>
<th>T ( ^\circ C )</th>
<th>( E_F ) ev</th>
<th>( \Gamma_1 )</th>
<th>( L_1 )</th>
<th>( X_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu )</td>
<td>( r )</td>
<td>( n \times 10^{22} )</td>
<td>( \mu )</td>
</tr>
<tr>
<td>18.5</td>
<td>-0.1236</td>
<td>0.2167</td>
<td>1.094 0.567</td>
<td>0.0632</td>
</tr>
<tr>
<td>60.5</td>
<td>-0.1332</td>
<td>0.1742</td>
<td>1.066 0.919</td>
<td>0.0503</td>
</tr>
<tr>
<td>104.0</td>
<td>-0.1468</td>
<td>0.1463</td>
<td>1.046 1.236</td>
<td>0.0416</td>
</tr>
<tr>
<td>125.0</td>
<td>-0.1555</td>
<td>0.1373</td>
<td>1.042 1.318</td>
<td>0.0385</td>
</tr>
<tr>
<td>127.0</td>
<td>-0.1768</td>
<td>0.1213</td>
<td>1.034 1.437</td>
<td>0.0334</td>
</tr>
<tr>
<td>222.0</td>
<td>-0.2041</td>
<td>0.1093</td>
<td>1.032 1.414</td>
<td>0.0301</td>
</tr>
</tbody>
</table>

Table V-9 Results of the analysis for the sample BL400. Unit of \( \mu \) is \( m^2/V \text{-sec} \) and carrier density is given per \( m^3 \). \( E_F \) was calculated with respect to the \( \Gamma_1 \) minimum.
Table V-10 Results of the analysis for sample BL600. Unit of $\mu$ is m$^2$/V-sec and carrier density is given per m$^3$. $E_F$ was calculated with respect to the $X_1$ minima.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$X_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\mu$</td>
<td>$r$</td>
</tr>
<tr>
<td>21</td>
<td>-0.1057</td>
<td></td>
<td>0.0676</td>
<td>1.123</td>
</tr>
<tr>
<td>60</td>
<td>-0.1160</td>
<td></td>
<td>0.0552</td>
<td>1.098</td>
</tr>
<tr>
<td>100</td>
<td>-0.1297</td>
<td></td>
<td>0.0470</td>
<td>1.081</td>
</tr>
<tr>
<td>140</td>
<td>-0.1464</td>
<td></td>
<td>0.0413</td>
<td>1.069</td>
</tr>
<tr>
<td>180</td>
<td>-0.1654</td>
<td></td>
<td>0.0370</td>
<td>1.062</td>
</tr>
<tr>
<td>225</td>
<td>-0.1894</td>
<td></td>
<td>0.0336</td>
<td>1.057</td>
</tr>
</tbody>
</table>
Table V-11 Results of the analysis for sample BL950. Unit of $\mu$ is $m^2/V$-sec and carrier density is given per $m^3$. $E_F$ was calculated with respect to the $\Gamma_1$ minimum.

<table>
<thead>
<tr>
<th>$T^\circ_C$</th>
<th>$E_F$ (eV)</th>
<th>$\Gamma_1$</th>
<th>$L_1$</th>
<th>$\chi_1$</th>
<th>$\mu$</th>
<th>$r$</th>
<th>$n \times 10^{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>-0.0957</td>
<td></td>
<td></td>
<td></td>
<td>0.061</td>
<td>1.112</td>
<td>3.40</td>
</tr>
<tr>
<td>60</td>
<td>-0.1084</td>
<td></td>
<td></td>
<td></td>
<td>0.051</td>
<td>1.085</td>
<td>4.12</td>
</tr>
<tr>
<td>100</td>
<td>-0.1223</td>
<td></td>
<td></td>
<td></td>
<td>0.044</td>
<td>1.063</td>
<td>4.43</td>
</tr>
<tr>
<td>140</td>
<td>-0.1380</td>
<td></td>
<td></td>
<td></td>
<td>0.040</td>
<td>1.049</td>
<td>5.16</td>
</tr>
<tr>
<td>180</td>
<td>-0.1540</td>
<td></td>
<td></td>
<td></td>
<td>0.036</td>
<td>1.038</td>
<td>5.37</td>
</tr>
<tr>
<td>225</td>
<td>-0.1734</td>
<td></td>
<td></td>
<td></td>
<td>0.033</td>
<td>1.030</td>
<td>5.61</td>
</tr>
</tbody>
</table>
Fig. (V-1) Experimental data on the band gap in the Ga$_{1-x}$Al$_x$As system; 0 (73P1), @ and △ (69C1), • (71B1), + (75K1), X and V (6682), ← (76M2), Δ (76N2), ◊ (76C1), • and △ (63M1), △ (70L1), ✡ (71Y1) and ◆, ■ and ▴ (see chapter IV).
Fig. (V-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL080 of Ga$_{1-x}$Al$_x$As.
Fig. (V-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL106 of Ga$_{1-x}$Al$_x$As.
Fig. (V-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL130 of Ga$_{1-x}$Al$_x$As.
Fig. (V-5)  Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL232 of Ga$_{1-x}$Al$_x$As.
Fig. (V-6) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL270 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$. 
Fig. (V-7) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL300 of Ga$_{1-x}$Al$_x$As.
Fig. (V-8) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL335 of Ga$_{1-x}$Al$_x$As.
Fig. (V-9) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL400 of Ga$_{1-x}$Al$_x$As.
Fig. (V-10) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL520 of Ga$_{1-x}$Al$_x$As.
Fig. (V-11) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL600 of Ga$_{1-x}$Al$_x$As.
Fig. (V-12) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL710 of Ga$_{1-x}$Al$_x$As.
Fig. (V-13) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL950 of Ga$_{1-x}$Al$_x$As.
Fig. (V-14) Band gap and impurity level energy as a function of x in the Ga$_{1-x}$Al$_x$As system. The curves are given by Eqs. (V-5, 6, 7, and 4).
Fig. (V-15) Carrier mobility and carrier density variations with temperature in the \( \Gamma_1 \) band for sample BL400 of Ga\(_{1-x}\)Al\(_x\)As.
Carrier mobility and carrier density variations with temperature in the $L_1$ band for sample BL400 of Ga$_{1-x}$Al$_x$As.
Fig. (V-17) Carrier mobility and carrier density variations with temperature in the $X_1$ band for sample BL400 of Ga$_{1-x}$Al$_x$As.
Fig. (V-18) Carrier mobility, carrier density and "effective Hall scattering coefficient" vs. temperature for the Ga\textsubscript{1-x}Al\textsubscript{x}As alloys at 295 K. 0, + and x show values of $\mu_p$, $\mu_L$ and $\mu_x$ respectively obtained for the alloys considered here. Theoretical curves for the three different mobility values were calculated for the case of $n_t = 10^{21}$ m$^{-3}$ and $N_A = n_t$. 
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CHAPTER VI  

VI-1  Introduction

InP exhibits the Gunn effect and thus this crystal is one of the suitable semiconductors for microwave oscillatory devices (70H2). However, the band structure and electrical properties necessary for designing the devices are not fully understood as discussed elsewhere (73P2, 75R2, 76H1).

Electroreflectance measurements by Cardona et al. (67C1) indicate that the direct band gap energy is 1.34 eV at room temperature. Rochon and Fortin (75R1) showed from photovoltaic effect and interband magneto-optical transition measurements that the band gap energy is 1.423 ± 0.0005 eV at 4.2 K which is in good agreement with the theoretical value 1.42 eV of Lawaetz (71L1) and with other experimental ones, 1.4206 eV (64T1) and 1.424 eV (72F1). Turner et al. (64T1) measured the band gap variation with temperature from 6 to 298 K using the optical absorption technique, from which Varshni (67V1) deduced an expression for the band gap variation given as

$$E_0 = 1.4206 - 4.906 \times 10^{-4} \times T^2/(T + 327).$$

The experimental values obtained by various authors for the effective mass at the bottom of the $\Gamma_1$ band differ considerably as shown by Kesamanly et al. (69K1), that is, the values range from 0.03 to 0.1 m...
for the samples of lower carrier density. Far infrared cyclotron resonance for the \( \Gamma_1 \) band minimum investigated by Chamberlain et al. (70C1) gave 0.081 m for the effective mass value at 10 K. Eaves et al. (70E1) measured the effective mass variation with temperature by means of the magnetophonon effect and the resulting values are (0.082 \pm 0.001)m and (0.0781 \pm 0.0010)m at 77 and 300 K respectively. The data obtained from the above two different experiments are in reasonable agreement with the latest experimental value (0.079 \pm 0.001)m obtained by Rochon and Fortin (75R1).

As shown in a review on the band structure data for InP by Pitt (73P2), the energy values of the subsidiary band minima show significant scatter, i.e. the \( E_{o1} \) values range from 0.4 to 0.8 eV and the \( E_{o2} \) values from 0.66 to 1.5 eV.

Most of the previous studies (58R1, 67K1, 70C2) on electrical transport for InP have been made at temperatures below room. However, Galavanov and Siukaev (70G1) measured the Hall coefficient and conductivity in the temperature range from 77 to 1000 K. They explained their high temperature data by using polar optical and acoustic mode scattering, but inclusion of ionized and neutral impurity scattering was necessary to explain the experimental results below 150 K. Their measured Hall mobility values were from 0.234 to 0.48 \( m^2/V\text{-sec} \) at room temperature for samples with \( n \) in the range \( 2.6 \sim 3.0 \times 10^{21} \text{ m}^{-3} \).
Blood and Orton (74B2) recently measured the magnetoresistance mobility of liquid-phase epitaxial n-type samples from 300 to 700 K using the geometrical magnetoresistance effect and the resulting values for samples with \( n = 1.9 \times 8 \times 10^{21} m^{-3} \) were between 0.427 and 0.528 \( m^2 / V \cdot \text{sec} \) at 300 K. Rode (75R2) calculated theoretically the drift mobility using polar optical, acoustic deformation potential, ionized impurity and piezoelectric mode scattering and obtained 0.515 \( m^2 / V \cdot \text{sec} \) at room temperature for pure samples. Rode compared the calculated drift mobility values with existing experimental Hall mobility data and found that his theoretical values lie 15% above the measured data at temperatures from 150 to 600 K.

### VI-2 Experimental Results

The Hall coefficient and conductivity were measured as a function of temperature for five n-type samples with different carrier concentrations and the results are shown in Figs. (VI-1 to 4). Two of the samples were undoped and the others Sn-doped single crystals. Room temperature characteristics for the samples are compiled in Table (VI-1). Higher temperatures than 260°C were not used in this work because of possible evaporation of P. Transverse magnetoresistivity was measured as a function of magnetic field at room temperature for the three samples RRE1, RRE2 and RRE4 and the results are illustrated in Fig. (VI-5). Nernst-Ettingshausen coefficients and thermoelectric power have been measured by Demars in this laboratory for some samples.
to be discussed latter.

The measured Hall coefficient values decrease with increasing temperature resulting in $2\sim 8\%$ change in the values in the present temperature range, indicating the Hall scattering coefficient or carrier density change with temperature.

VI-3 Method of Analysis

Previous work on the band structure places the subsidiary band minima far above the $\Gamma_1$ minimum in InP (73P2) and thus a one-band model is justified for the transport calculation in the temperature range used here. However, an analysis including the subsidiary band effects have been tried in this work to check some previous experimental results, which show an anisotropic effect in the measurements of magneto-resistance (59G1) and an abrupt increase of the effective mass in optical absorption and thermoelectric power experiments (58N1) for high carrier density samples.

Polar optical, acoustic deformation potential, ionized impurity and space charge scattering mechanisms are taken into account in the analysis of the experimental data. Polar optical scattering is expected to be dominant in this case as indicated by Ehrenreich (69E1). Hence the dielectric constant is one of the most important parameters in the
scattering calculation and will be treated as adjustable. Only the low-frequency dielectric constant $\kappa_0$ is varied while $\kappa_\infty$ constant at 9.55 (75R2). The values of $E_D$, $N_A$ and $N_{S^-S}$ will also be determined by adjusting them for fit to the experimental data.

InP exhibits two interesting problems with regard to effective mass; one is its magnitude and the other its variation with temperature. The experimental effective mass value at the bottom of the $\Gamma_1$ band (70E1, 75R1) is very high compared with the theoretical estimate from $k\cdot p$ method (66P1). That is, this material does not follow the rough rule that the effective mass value is proportional to the band gap value. In this case, Rochon and Fortin have shown that the energy equivalent to the momentum matrix elements $p^2$ is 17 eV, which is lower than those for the other III-V semiconductors, $\sim 21$ eV (73H4). The experimental effective mass vs. temperature measured by Eaves et al (70E1) and Chamberlain (70C1) are replotted in Fig. (VI-6). In this figure, we have made three different theoretical predictions for the temperature variation of the effective mass for a comparison with this experimental data. For the curve (A), we have used Ehrenreich's expression (57E1) for the effective mass energy gap variation,

$$E^*_O = E_0(0) - \frac{3\alpha T}{K} (\frac{\partial E_0}{\partial P})_T$$

(VI-1)

and a Kane form (67K1) for the effective mass variation at the bottom of the band,
\[ \frac{1}{\frac{m^*}{m_0}} = 1 + \frac{2}{3} \left( \frac{2}{E_0^*} + \frac{1}{E_0^* + \Delta o} \right) \]  

(VI-2)

where the parameters are the same as defined earlier. The second term in Eq. (VI-1) can be calculated from the experimental values of the respective parameters and Rode showed for InP that \( \frac{3a}{K} (\frac{\alpha}{3p})_T = 5 \times 10^{-5} \text{eV/K} \) (70R1). The spin-orbit splitting \( \Delta o \) is 0.108 eV (75R1). \( P^2 \) has been assumed constant with temperature and calculated using experimental data for the band gap \( E_o^*(0) = 1.423 \text{eV} \) (75R1) and the effective mass \( m^*(0) = 0.082 m \). According to the above coefficient value, as estimated by Rode, 0.015 eV change is obtained in the value of \( E_o^* \) as a result of 300 K change in temperature. For the predictions (B) and (C), Eqs. (11-13, 14, and VI-2) were employed. To calculate the optical band gap variation, the temperature coefficient determined by Varshni for InP was used (57V1). In this case a 0.069 eV change is estimated in for \( E_o^* \) value when the temperature is raised from 0 to 300 K. The curves (B) and (C) correspond to "a" = 1.5 and 1.0 respectively in Eq. (II-13). Curve (A) calculated under the assumption that the band curvature is related to lattice dilatation only is much higher than the experimental variation, a similar result to that for the case of GaAs in Chapter IV. The best agreement between the theory and experiment is shown with "a" = 1, but unity for the value of "a" seems unreasonable according to the discussion of Ehrenreich (67E1) and low considering the values for similar materials, "a" = 1.64 for GaAs (see Chapter IV) and "a" = 2 for GaSb (72B1). Furthermore, a reasonable fit to the experi
mental data could not be made with "a" = 1 for the pure samples in this work. This was because a low value of "a" provides a rapid variation of the effective mass value with temperature, giving low effective mass values and thus a higher calculated conductivity than the measured value at high temperatures. But the sample RREl, the most heavily doped sample in this work, requires a low "a" value. In this case we chose "a" = 1.5 ± 0.2 as a compromise value for both low and high carrier density samples.

The recent experimental value of 0.079 m (75R1) was employed for the effective mass value at 0 K in the present analysis. The various material parameters of InP used in this analysis are given in Table (VI-2). This analysis gives $P_i$ values as defined in Chapter II, from which the longitudinal and transverse Nernst-Ettingshausen coefficients $Q_\parallel$ and $Q_\perp$ can be calculated. $Q_\parallel$ as a function of magnetic field is given by (73D1)

$$Q_\parallel (B) = |\alpha(B)| - |\alpha(0)|$$  \hfill (VI-3)

where

$$\alpha(B) = \frac{\sigma_{xx} \theta_{xx} + \sigma_{xy} \theta_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} - \frac{E_F}{eT}$$

and thermoelectric power is defined as

$$\alpha(0) = \frac{\theta_{zz}}{\sigma_{zz}} - \frac{E_F}{eT}$$  \hfill (VI-4)
The transverse coefficient $Q_\perp$ is expressed by

$$Q_\perp(B) = \frac{1}{B} \frac{\sigma_{xy} \theta_{xx} - \sigma_{xx} \theta_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2}$$  \hspace{1cm} (VI-5)$$

The conductivity tensor elements are defined in terms of $P_\perp$ in Eq. (II-48) and the components of thermoelectric tensor

$$\theta_{xx} = \langle \frac{E}{P_{\perp}} \rangle$$
$$\theta_{xy} = \langle \frac{E}{P_{\perp}^2} \rangle$$
$$\theta_{zz} = \langle \frac{E}{P_{\perp}^3} \rangle$$

where $\langle A \rangle$ is also defined by Eq. (II-48).

VI-4 Results and Discussion

As with the "a" parameter, the sample REB1 requires also a lower $\kappa_\circ$ value for the best fit than those for the samples of low carrier density. Here again we determined a compromise value of $\kappa_\circ = 12.5 \pm 0.1$, which is to be compared with published values of $12.9$ ($\kappa_\circ = 10.9$) (71N1), $12.38$ ($\kappa_\circ = 9.55$) (72R2) and $15.0$ ($\kappa_\circ = 10.6$) (58N1).
As in the case of other III-V semiconductors, the acoustic deformation potential $E_D$ for InP shows a scatter in the quoted values, i.e., 6.8 eV by Rode (75R2), 21 eV by Galavanov and Siukaev (70G1) and 18 eV by Nag (private communication). Therefore we have treated $E_D$ as adjustable and the value for the best fit was found to be $14.2 \pm 0.7$ eV, which compares well with those of GaAs ($16.1 \pm 0.5$ eV) (see Chapter IV) and of InSb ($14.6$ eV) (71zl).

Zawadzki and Szymanska (71zl) suggested that the transverse acoustic phonons give rise to scattering due to the p-like components of the total electronic wave functions. The present analysis, however, shows that the transverse term in the acoustic mode scattering is completely negligible even at the highest temperature in this work.

Weisberg (62W1) indicated that some III-V semiconductors show different mobility values even if their carrier concentrations are the same and suggested that this effect is due to scattering caused by space charge variation. InP is one of the materials exhibiting this space charge behaviour. Space charge scattering was found to be important only in four samples in this work, and the values obtained for the effective scattering cross-section $N_0s^*$ from the present analysis decrease with increasing carrier concentration and could be neglected in fitting the data for the sample RRE1. This phenomenon is consistent with the discussion of Conwell and Vassel that space charge scattering
is more probable in boat-grown samples with low carrier density (68C2). The values of $N_Q$ are shown in Table (VI-1).

The $N_A$ values determined in the ionized impurity scattering calculation were negligible for the four lower $n$ samples and 
$3.5 \times 10^{22} \text{ m}^{-3}$ for RR1. This lower compensation ratio can be observed in previous transport work (70G1, 74B2, 71B2). Resulting theoretical curves for $R_H$ and $\sigma$ calculated using the parameter values shown in Table (VI-2) and determined here are compared with the measured variations of $R_H$ and $\sigma$ with temperature in Figs. (VI-1 to 4). The calculated conductivity value was about 4% higher than the measured value at the highest experimental temperatures. This phenomenon may be expected to occur if the subsidiary bands make a contribution to the transport properties. To obtain a better fit to the high temperature data and to check the anisotropic effect suggested by Glicksman (59G1) we have tried a two-band analysis by adjusting some parameters related to the $L_1$ band, but failed to obtain any consistent fit to both the $R_H$ and $\sigma$ data, i.e., the calculated $R_H$ increased with temperature at high temperature range when calculations were made to fit the $\sigma$ data. The discrepancies at high temperatures can be attributed to the possible variation of dielectric constant with temperature which we have neglected in the present analysis. Also inaccuracies in the data of the effective mass and temperature coefficient of the band gap variation may cause such a discrepancy. At room temperature the calculated
total mobility values are 0.378, 0.323, 0.291, -0.254 and 0.182 m²/V-sec for RRE4, RRE2, ISM2, ISM3 and RRE1 respectively.

Fig. (VI-7) shows the carrier mobility variation with temperature calculated for each scattering mechanism for the case of the sample RRE2. As indicated earlier in this Chapter, polar optical scattering predominates in this material as shown in Fig. (VI-7). The room temperature mobility value \( \mu_{op} \) due to polar optical scattering is 0.56 m²/V-sec, which is low compared with that of GaAs (\( \mu_{op} = 0.95 \) m²/V-sec). Two scattering mechanisms, viz. acoustic deformation potential and space charge, give similar mobility values throughout the experimental temperature range. The mobility value \( \mu_{ac} \) due to acoustic deformation potential mode scattering is calculated to be 2.15 m²/V-sec at room temperature. Because of the negligible effect of ionized impurity scattering, as shown in Fig. (VI-7) the carrier mobility for a pure InP sample can safely be attributed to two scattering mechanisms only, viz. polar optical and acoustic deformation potential modes, and estimated to be \( \sim 0.44 \) m²/V-sec, which is lower by 15% than the theoretical value 0.515 m²/V-sec calculated by Rode (75R2). The disagreement between the two values is mainly due to the difference in the \( E_D \) values used for the two different calculations. Rode found that his theoretical drift mobility values are generally 15% higher than the measured Hall mobility, however when the Hall scattering coefficient is taken into account in the drift mobility value for approximating the theoretical Hall mobility, the disagreement between the calculated and
measured values will be over $\sim 30\%$. Rode attributed the discrepancy to impurity scattering, which seems to indicate space charge. This is consistent with the results obtained in the present analysis, since he neglected space charge scattering in his calculation.

Measured $R_H$ values decrease by $2 \sim 8\%$ in our experimental temperature range. These variations in $R_H$ values with temperature can be shown to be mainly due to variation of the Hall scattering coefficient with temperature. The Hall scattering coefficient $r$ was calculated as a function of magnetic field and temperature for all samples in the present work and the results are given in Fig. (VI-8). The $r$ vs. magnetic field relation was calculated only at room temperature. The calculated $r$ value decreases with both temperature and magnetic field, and the rate of decrease slows down as the carrier density increases. In the degenerate sample RRE1, $r$ shows almost constant value with temperature, 1.003, in the present ranges of temperature and magnetic field. Some disagreement has occurred previously in the estimates of $r$ (70Gl, 73H4, 75R2). Hilsum et al. (73H4) measured the Hall coefficient as a function of magnetic field and obtained $r = 1.17$ at low field for two pure samples ($n = 2.2 \times 10^{20}$ and $5.4 \times 10^{19} \text{ m}^{-3}$) at room temperature. The present analysis indicates this experimental value to be a little low, and the low $r$ value may be due to the fact that Hilsum et al. did not use a field intensity large enough to satisfy the condition $\mu B \gg 1$.

Rode's calculation for a pure sample gave $\mu_H = 0.637 \text{ m}^2/\text{V-sec}$ and
\[ \mu = 0.515 \text{ m}^2/\text{V-sec}, \text{ giving } r = 1.237, \text{ which is consistent with our estimate of 1.22. Except for the case of RRE1, no appreciable carrier increase is observed in the present analysis in this experimental temperature range, indicating that the measured } R_H \text{ variation measured in the other four samples is due to the } r \text{ variation with temperature. The most heavily doped sample RRE1 shows } \sim 3\% \text{ carrier increase at the highest temperature, which may be related to the ionization of deep donors. The published ionization energy values of deep donors in InP are 0.13, 0.33 and 0.72 eV (70G).} \]

\[ \frac{\Delta \rho}{\rho_0} \text{ was calculated as a function of magnetic field intensity and of temperature using the magnetic field intensity value used for the measurements of } R_H. \text{ The resulting values are compared with the experimental data as shown in Fig. (VI-5). Good agreement between the calculated and measured values is shown only for the sample RRE4. However considering the practical difficulties such as contact problems discussed by Glicksman (59G), the discrepancies shown by the two other samples are not unreasonable.} \]

\[ \text{Fig. (VI-9) shows the thermoelectric power variation with temperature calculated for all the present samples and the experimental points quoted for comparison. Demars determined } \alpha(0) \text{ for a sample cut from the same crystal slice as RRE1 to be } -183.52 \text{ } \mu\text{V/K at room temperature (denoted by } \text{ in the figure) which is in good agreement} \]
with the calculated value $-177 \mu V/K$. The data points denoted by X and 0 are those for samples with $n = 7.1 \times 10^{21}$ and $2.1 \times 10^{23}$ m$^{-3}$ respectively, measured by Kudman and Steigmeier (64K1). The other experimental points were obtained by Kesamanly et al. (69K1) and are shown by *, o and + in Fig. (VI-9) for three different samples with $n = 2.2 \times 10^{23}$, $9 \times 10^{23}$ and $7.3 \times 10^{24}$ m$^{-3}$ respectively. Precise comparison of the present theoretical values with the quoted experimental data may not be valid because of the different characteristics of the samples used for the theoretical calculations and the experiments. Previous analysis of experimental data shows that the thermoelectric power value depends mainly upon carrier density (69K1) and polar optical scattering (64K1) in InP. Thus this comparison is considered appropriate and the agreement between the calculated and measured values is reasonable as shown in Fig. (VI-9) when the differences in the carrier densities of the samples used for the theoretical calculation and experimental measurements are taken into account. The present analysis indicates that the scattering term's contribution to $\alpha(0)$ increases with carrier density, i.e., in the case of RRE2, the calculated $\alpha(0)$ value is $-612 \mu V/K$, the Fermi energy term giving $-436 \mu V/K$, while in the case of RRE1, the calculated $\alpha(0)$ is $-177 \mu V/K$ and the Fermi energy term is $121 \mu V/K$. Therefore the method of estimating effective mass values from the measured thermoelectric power without using detailed scattering calculations is suspect, the errors could be serious especially for the calculation of the effective mass variation.
with carrier density. For example, Newman (58N1) measured thermoelectric power for two samples with \( n = 5 \times 10^{21} \) and \( 5 \times 10^{24} \, \text{m}^{-3} \) and obtained values of -400 and -100 \( \mu \text{V/K} \) respectively. This leads to effective mass values of 0.07 and 0.2 \( \text{m} \) respectively for the two samples. This unreasonable result may be due partially to the effects discussed above. Also this experimental \( a(0) \) value for the sample of lower carrier density is considerably lower than the other experimental data considered here.

The longitudinal and transverse Nernst-Ettingshausen coefficients calculated as a function of magnetic field intensity at room temperature are shown in Fig. (VI-10). Both values decrease with carrier density and the full and dotted lines in Fig. (VI-10) represent the calculated \( Q_{\parallel} \) and \( Q_{\perp} \) values respectively. The data denoted by o and • in the figure are \( Q_{\parallel} \) values measured by Demars for the two samples cut from the same crystal slices as RRE1 and RRE2 respectively. \( Q_{\parallel} \) data measured by Kesamanly et al. (69K1) for two samples with \( n = 9 \times 10^{23} \) and \( 7.7 \times 10^{22} \, \text{m}^{-3} \) are denoted by X and + respectively in Fig. (VI-10). The disagreement between the theoretical and experimental values in \( Q_{\parallel} \) is quite large. However the experimental results are not consistent in themselves and hence more data would be needed to give a conclusive comparison with theory. Considering the good agreement between theory and experiment for the other transport behaviour discussed above, it is concluded that the
discrepancy here is more likely to be due to errors in the experimental data than in the computational analysis. The experimental points denoted by © are the $Q_\perp$ values measured by Demars at room temperature for a sample cut from the same crystal slice as RRE1 and the experimental curve with magnetic field is parallel to the theoretical one for RRE1, but large differences in the theoretical and experimental values are observed. Such disagreement is frequently observed with $Q_\perp$ values and has been attributed to the effect of microinhomogeneities in the sample, the $Q_\perp$ value corresponding to these inhomogeneities being independent of magnetic field (73D1). Here again a quantitative comparison with experiment is not possible because of lack of knowledge about the inhomogeneity in the measured $Q_\perp$ values in this case.

Blood and Orton (74B2) measured the magnetoresistance mobility defined by $\mu_m = (\Delta \rho/\rho_0)^{\frac{1}{2}}/B$ where the fractional change in resistivity is measured on specimens having electrodes of diameter much greater than the specimen length and the magnetic field $B$ is applied perpendicular to the direction of current flow. They chose the geometrical magnetoresistance method because Van der Pauw measurements on the InP layers grown on a semi-insulating substrate are suspect at room temperature, because of the possibility of conduction in the substrate material (74B2). The measurements were made from 300 to 700 K for six different epitaxial samples with $n$ in the range of 2 to $8 \times 10^{21} \text{m}^{-3}$. For these pure samples the transport properties can be explained in terms of three scattering mechanisms only, viz. polar optical and acoustic phonons and
ionized impurity, neglecting space charge scattering in accordance with
the discussion of Conwell and Vassel (68C2). \( N_A \) can be neglected in
the present calculation because the values of \( N_A \) given in the work (74B2)
are low and were obtained by adjusting them to give a fit to the
\( \mu_H \) data using the rather high theoretical \( \mu_H \) values of Rode (71R2).
Hence the difference in mobility values between the samples should be
due to the different carrier concentrations and our estimate indicates
that with the narrow range of carrier concentrations used, the distribu­
tion of mobility values should not exceed ± 3% at room temperature.
The measured \( \mu_m \) values at 300 K for five of the samples lie within a
range of ± 5.5% around the average value of 0.44 m\(^2\)/V-sec, while the
corresponding \( \mu_H \) values are spread through a wide range of 0.45 — 0.53
m\(^2\)/V-sec. For the single sixth sample, the measured values of \( \mu_m \) and
\( \mu_H \) are 0.528 and 0.53 m\(^2\)/V-sec respectively. The larger scatter in
the \( \mu_H \) data may be due to substrate effects indicated by Blood and Orton
(74B2). Thus from our above estimate, it would appear that the \( \mu_m \)
values of the five samples are the more reliable data.

Measurements on GaAs (71B2,7301) gave experimental values
of \( \mu_m \) in the range 0.9 — 1.0 \( \mu_H \) and thus Blood and Orton suggested
that in their work on InP the measured value of \( \mu_m \) should be equal
to \( \mu_H \), although, as indicated above, for five samples \( \mu_m \) was lower
than \( \mu_H \) by up to 15% and only in a single sample were the values
of \( \mu_m \) and \( \mu_H \) close. They attributed the low \( \mu_m \) values for the five
to the presence of parasitic resistance associated with the metal contacts.

Here we have calculated $\mu_H$ and $\mu$ (drift mobility) for a sample with $n = 1.9 \times 10^{21} \text{ m}^{-3}$ using no adjustable parameters and the results are compared with the experimental data of Blood and Orton in Fig. (VI-11). The experimental $\mu_m$ data for the five samples show good agreement with the theoretical $\mu$ curve, while for the single sixth sample the measured $\mu_m$ value agrees with $\mu_H$ curve. If, as indicated above, the $\mu_m$ data on the five samples are the more reliable data, this would indicate that $\mu_m$ is more likely to be equal to $\mu$ and hence less than $\mu_H$. However, this is to be contrasted with the theoretical calculations (63B1) showing that $\mu_m$ is greater than both $\mu_H$ and $\mu$. The values determined in the above calculations are $\mu_H = 0.5285 \text{ m}^2/\text{V-sec}$, $\mu = 0.435 \text{ m}^2/\text{V-sec}$ and $r = 1.215$ at room temperature. The $r$ value is to be compared with the value of 1.237 given by Rode (75R2).

The results of the analysis for the three samples RRE4, ISM2 and RRE1 are given in Tables (VI-3, 4, 5).

VI-5 Summary

A one-band model, the $\Gamma_1$ band, was found in this work to be satisfactory to explain various transport properties of InP in the temperature range from room to 260°C. With inclusion of subsidiary
band effects in the analysis, it was impossible to fit the measured values of $R_H$ and $\sigma$ simultaneously.

To fit the experimental data of effective mass variation with temperature (70E1, 70Cl), the value of "a" in Eq. (II-13) is 1. However, this value was found to be too low to explain the transport properties and the best fit to the experimental $R_H$ and $\sigma$ data was obtained when 'a' = 1.5 which is to be compared with the value of 1.64 for GaAs. The values of the low-frequency dielectric constant and acoustic deformation potential determined in this work are $12.5 \pm 0.1$ and $14.2 \pm 0.7$ eV respectively.

Polar optical scattering predominates over the whole temperature range. Space charge scattering plays an important role in restricting the carrier mobility in the case of boat-grown bulk samples of low carrier density, but this scattering can be neglected for pure epitaxial samples. The compensation ratio is very low and the $N_A$ values can be neglected for pure InP samples.

In contrast to the theoretical calculations, the geometrical magnetoresistace mobility has a value nearer to the drift mobility rather than to the Hall mobility. More experimental data on the magnetoresistance effects are required before a conclusion on this problem can be reached.
Table VI-1

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ ($^\circ$C)</th>
<th>$R_H$ $10^{-4}$ m$^3$/Coul</th>
<th>$\sigma$ $10^3$ Ohm$^{-1}$m$^{-1}$</th>
<th>$n_t$</th>
<th>$N_A$</th>
<th>$N_Q/s_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RRE1</td>
<td>18.0</td>
<td>0.055</td>
<td>32.30</td>
<td>113.0</td>
<td>3.80</td>
<td>-</td>
</tr>
<tr>
<td>RRE2</td>
<td>22.4</td>
<td>20.74</td>
<td>0.1624</td>
<td>0.3514</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>RRE4</td>
<td>18.3</td>
<td>21.51</td>
<td>0.2149</td>
<td>0.347</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>ISM2</td>
<td>18.0</td>
<td>1.333</td>
<td>2.467</td>
<td>5.20</td>
<td>-</td>
<td>1.65</td>
</tr>
<tr>
<td>ISM3</td>
<td>22.0</td>
<td>0.4793</td>
<td>5.59</td>
<td>13.90</td>
<td>-</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table VI-1  Room temperature values of the Hall coefficient, conductivity and carrier concentration for the five samples of InP. The Hall coefficient was measured at a field of 0.3 Wb/m$^2$ for RRE4 and at 1.09 Wb/m$^2$ for the other four samples. The values of $N_Q/s_s$ and $N_A$ were obtained from the analysis of the experimental data.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_o (O)$</td>
<td>1.423 eV</td>
<td>(75R1)</td>
</tr>
<tr>
<td>$m_o (O)$</td>
<td>0.079 m</td>
<td>(75R1)</td>
</tr>
<tr>
<td>$\Delta_o$</td>
<td>0.108 eV</td>
<td>(75R1)</td>
</tr>
<tr>
<td>$\alpha_T$</td>
<td>$-4.91 \times 10^{-4}$ eV/K</td>
<td>(67V1)</td>
</tr>
<tr>
<td>$\theta_T$</td>
<td>327 K</td>
<td>(67V1)</td>
</tr>
<tr>
<td>$\hbar\omega_o$</td>
<td>0.0429 eV</td>
<td>(66M1, 72A1)</td>
</tr>
<tr>
<td>$\kappa_\infty$</td>
<td>9.55</td>
<td>(70R1)</td>
</tr>
<tr>
<td>$\kappa_o$</td>
<td>$12.5 \pm 0.1$</td>
<td>*</td>
</tr>
<tr>
<td>$C_e$</td>
<td>$12.1 \times 10^{10}$ N/m^3</td>
<td>(75R2)</td>
</tr>
<tr>
<td>$E_D$</td>
<td>$14.2 \pm 0.7$ eV</td>
<td>*</td>
</tr>
</tbody>
</table>

Table VI-2 Material parameters of InP

*-determined in the present work.
Table VI-3

| T     | E_F  | μ     | r     | Δρ/ρ_0 | 10^{-4} | α(0) | Q_|| | μV/K | Q_⊥  | 10^{-6} m^2/K.S. |
|-------|------|-------|-------|--------|---------|------|------|------|------|-----------------|
| °C    | eV   | m^2/V-sec | 1.09 T | 1.09 T | 2.8 T   | μV/K | 1.09 T | 2.8 T | 1.09 T | 2.8 T            |
| 18.0  | -0.1266 | 0.3777    | 1.196  | 0.1743 | 9.671   | 610.5 | 0.2617 | 14.47 | 0.1102 | 0.074            |
| 60.0  | -0.1504 | 0.3062    | 1.177  | 0.1176 | 6.950   | 631.6 | 0.2128 | 12.44 | 0.0963 | 0.0668           |
| 100.0 | -0.1737 | 0.2604    | 1.156  | 0.0834 | 5.101   | 650.0 | 0.1583 | 10.49 | 0.0827 | 0.0592           |
| 140.0 | -0.1975 | 0.2277    | 1.135  | 0.0590 | 3.767   | 666.5 | 0.1246 | 8.700 | 0.0701 | 0.0517           |
| 180.0 | -0.2216 | 0.2033    | 1.116  | 0.0424 | 2.809   | 680.6 | 0.0962 | 7.131 | 0.0590 | 0.0446           |
| 200.0 | -0.2339 | 0.1933    | 1.108  | 0.0363 | 2.439   | 687.2 | 0.0864 | 6.451 | 0.0541 | 0.0414           |

Table VI-3 Results of analysis for sample RRE4. Δρ/ρ_0, Q_||, and Q_⊥ were calculated using B = 0.3 and 2.8 Wb/m^2 respectively.
Table VI-4

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$E_F$ (eV)</th>
<th>$\mu$ (m²/V·sec)</th>
<th>$r$</th>
<th>$\Delta\rho/\rho_0$ x $10^{-2}$</th>
<th>$\alpha(0)$ (μV/K)</th>
<th>$Q_\parallel$ (μV/K)</th>
<th>$Q_\perp$ ($10^{-5}$ m²/K·s)</th>
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<tr>
<td>18.0</td>
<td>-0.0580</td>
<td>0.2909</td>
<td>1.112</td>
<td>0.9618</td>
<td>393.0</td>
<td>1.582</td>
<td>0.6115</td>
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<tr>
<td>60.0</td>
<td>-0.0724</td>
<td>0.2500</td>
<td>1.099</td>
<td>0.6733</td>
<td>413.6</td>
<td>1.376</td>
<td>0.5529</td>
</tr>
<tr>
<td>100.0</td>
<td>-0.0869</td>
<td>0.2211</td>
<td>1.088</td>
<td>0.4845</td>
<td>431.6</td>
<td>1.157</td>
<td>0.4883</td>
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<tr>
<td>140.0</td>
<td>-0.1020</td>
<td>0.1989</td>
<td>1.076</td>
<td>0.3539</td>
<td>448.0</td>
<td>0.956</td>
<td>0.4247</td>
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<tr>
<td>180.0</td>
<td>-0.1173</td>
<td>0.1814</td>
<td>1.066</td>
<td>0.2622</td>
<td>462.5</td>
<td>0.786</td>
<td>0.3666</td>
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<td>220.0</td>
<td>-0.1330</td>
<td>0.1673</td>
<td>1.057</td>
<td>0.1975</td>
<td>475.2</td>
<td>0.644</td>
<td>0.3163</td>
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<tr>
<td>260.0</td>
<td>-0.1493</td>
<td>0.1558</td>
<td>1.050</td>
<td>0.1513</td>
<td>486.9</td>
<td>0.534</td>
<td>0.2741</td>
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</table>

Table VI-4 Results of analysis for sample ISM2. $r$, $\Delta\rho/\rho$, $Q_\parallel$ and $Q_\perp$ were calculated using $B = 1.09$ Wb/m³.
### Table VI-5

Results of analysis for sample RREl, $\Delta\rho/\rho_o$, $Q_\parallel$, $Q_\perp$ were calculated using $B = 1.09$ and $2.8$ Wb/m$^2$ respectively.

<table>
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<tr>
<th>$T$ (°C)</th>
<th>$E_F$ (eV)</th>
<th>$\mu$ (m$^2$/V-sec)</th>
<th>$r$</th>
<th>$\Delta\rho/\rho_o$</th>
<th>$10^{-4}$</th>
<th>$\alpha(0)$</th>
<th>$Q_\parallel$ (µV/K)</th>
<th>$Q_\perp$ (10$^{-6}$ m$^2$/K.S.)</th>
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<td>18.0</td>
<td>0.0358</td>
<td>0.1815</td>
<td>1.0032</td>
<td>0.706</td>
<td>4.234</td>
<td>177.1</td>
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<td>-0.3865</td>
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<tr>
<td>60.0</td>
<td>0.0329</td>
<td>0.1674</td>
<td>1.0029</td>
<td>0.601</td>
<td>3.500</td>
<td>191.8</td>
<td>-0.1013</td>
<td>-0.5604</td>
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<tr>
<td>100.0</td>
<td>0.0292</td>
<td>0.1569</td>
<td>1.0029</td>
<td>0.563</td>
<td>3.319</td>
<td>205.0</td>
<td>-0.1120</td>
<td>-0.6561</td>
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<tr>
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<td>1.0031</td>
<td>0.563</td>
<td>3.371</td>
<td>223.6</td>
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<td>-0.7295</td>
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<tr>
<td>220.0</td>
<td>0.0138</td>
<td>0.1345</td>
<td>1.0032</td>
<td>0.505</td>
<td>3.090</td>
<td>239.6</td>
<td>-0.1129</td>
<td>-0.6997</td>
</tr>
<tr>
<td>250.0</td>
<td>0.0095</td>
<td>0.1302</td>
<td>1.0032</td>
<td>0.4864</td>
<td>2.829</td>
<td>246.5</td>
<td>-0.1073</td>
<td>-0.665</td>
</tr>
</tbody>
</table>
Fig. (VI-1) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for samples RRE2 and RRE4 of InP.
Fig. (VI-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample ISM2 of InP.
Fig. (Vi-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample ISM3 of InP.
Fig. (VI-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample RRE1 of InP.
Fig. (VI-5) Magnetoresistivity measured as a function of magnetic field for the three samples, RRE1, RRE2 and RRE4 and theoretically predicted curves. Measurements have been made at room temperature.
Fig. (VI-6) Variation with temperature of experimental value of effective mass

- (70C1) ○ (70E1) Experimental values

--- Theoretical curves (see text)
Fig. (VI-7) Mobility calculated as a function of temperature for each scattering mechanism for InP.
Fig. (VI-B)  Hall scattering coefficient as a function of magnetic field at room temperature and of temperature at the magnetic field used for the measurements of Hall coefficient. Full line denotes r vs. T relation.
Theoretically predicted variation of thermoelectric power with temperature. Experimental points are: Δ measured by Demars for a sample cut from the same crystal slice as RRE1, X and Θ by Kudman and Steigmeier (64K1) for samples with \( n = 7.1 \times 10^{21} \) and \( 2.1 \times 10^{23} \text{ m}^{-3} \) respectively and 0, • and + by Kesamanly et al. (69K1) for three different samples with \( n = 2.2 \times 10^{23}, 9 \times 10^{23} \) and \( 3.2 \times 10^{24} \text{ m}^{-3} \) respectively.
Fig. (VI-10) Longitudinal and transverse Nernst-Ettingshausen coefficient curves predicted as a function of magnetic field for InP. Experimental data to be compared with theoretical curves are:

- $Q_{\perp}$ value by Demars for a sample cut from the same crystal slice as RRE1, 0 and $Q_{\parallel}$ dat by Demars for two different samples cut from the same slice as RRE1 and RRE2 respectively, X and + $Q_{\parallel}$

values by Kesamanly et al. (69K1) for samples with $n = 9 \times 10^{23}$ and $7.7 \times 10^{22} \text{m}^{-3}$ respectively.
Fig. (VI-11) Theoretical comparison with geometrical magnetoresistance mobility measured by Blood and Orton (74B2). The values of carrier density are: $1.9 \times 10^{21} \, \text{m}^{-3}$ (△ and ●), $4.9 \times 10^{21} \, \text{m}^{-3}$ (▲), $5 \times 10^{21} \, \text{m}^{-3}$ (+), $7 \times 10^{21} \, \text{m}^{-3}$ (○) and $8 \times 10^{21} \, \text{m}^{-3}$ (X). --- and ---- present theoretical curves of $\mu_H$ and $\mu$ for $n = 1.9 \times 10^{21} \, \text{m}^{-3}$. 
CHAPTER VII CONCLUSION

The analyses described in the previous chapters have provided values for a considerable number of band structure and scattering parameters for the materials investigated. The accuracy of the parameter values depends upon the assumptions made in the theoretical development and in the fitting process and also upon the uniqueness of the fit obtained. The assumptions have been carefully considered and appear to be justified and the question of uniqueness of fit has been considered in some detail and ranges of values given in those cases where more than one set of parameters will fit the experimental data.

One set of parameters which have considerable importance are the various band gaps and their temperature coefficients and these have been determined with reasonable accuracy in the analysis. For GaAs, the results agree well with the proposed band ordering of Aspnes, the parameter values differing by only small amounts. For the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys the positions of the important band minima have been determined across the whole composition range and the contributions of the $L_1$ band clarified.

One further band gap parameter investigated is the effective mass band gap $E^*$ for the $\Gamma_1$ band. This parameter, introduced in a semi-empirical way by Ehrenreich, has never been put on a firm theoretical
basis. Here $E^*_0$ has been used as a normalizing parameter to relate known values of $\Gamma_1$ band effective mass to the known $E^*_0$ values. The values so obtained differ considerably from the values calculated from compressibility values etc in the way suggested by Ehrenreich. More accurate values of effective mass over a considerable temperature range are needed to provide better experimental values of $E^*_0$ and more detailed theoretical investigation is clearly required.

Various scattering parameter values have been determined for the present materials, some with good accuracy but for others only a feasible range can be quoted. In most cases the values lie close to those previously obtained or expected. One parameter of interest however is the deformation potential. Taking the case of $E_{D\Gamma}$ for the $\Gamma_1$ band the value obtained by fitting to the transport results are considerably larger than the values determined from experimental elastic constants and pressure effect data. This is consistent with recent results of other workers and again it appears that further consideration needs to be given to the parameters involved in the scattering theory. The similar parameters for interband and intervalley scattering may show the same effect, but much less information is available in this case and in the present work the parameters determined are an effective average for two or three types of scattering and hence the values give less insight into their physical significance.
For the ellipsoidal $X_\perp$ and $L_\perp$ bands, an anisotropic analysis is strictly required but because of the complexity of the problem, the spherical approximation has been used here. Comparison with other available data seems to indicate that the resulting error is relatively small and will only be of any importance when the band concerned dominates the transport behaviour. The question is mainly of interest for the case of polar optical scattering where an iterative solution of the Boltzmann equation needs to be used. The presently available methods become so lengthy in this case and involve so much computer time that the method of fitting to the experimental data as used here is out of the question. Other methods of solution would be necessary before an anisotropic analysis could be used.

From the scattering parameters determined, mobility values appropriate to the various scattering mechanisms for the various bands have been calculated. As has been seen, the parameter values can be reasonably well determined only when the band concerned dominates the transport behaviour or makes an appreciable contribution in the presence of another band whose parameters are already known. Thus in the case of $\text{Ga}_{1-x}\text{Al}_x\text{As}$, for low $x$ values little could be determined about the $X_\perp$ band from the present transport results while at high $x$ values nothing could be determined concerning the $L_\perp$ and $\Gamma_\perp$ bands. However as was seen in the case of GaAs, data determined at high pressure gave useful results on the $X_\perp$ band parameters. Thus work on the alloys at high pressure or in an extended temperature range could give further useful
information on the behaviour of the subsidiary bands.

The method used here has been found to be very productive for determining various material parameters and it could be usefully extended to other materials showing multiband behaviour, such as $\text{Ga}_x\text{In}_{1-x}\text{P}$, $\text{GaAs}_{1-x}\text{P}_x$, $\text{GaAs}_{1-x}\text{Sb}_x$, and some quaternary III-V alloys.
REFERENCES


1950 (50B1) J. Bardeen and W. Shockley, Phys. Rev. 80, 72
(50C1) E. M. Conwell and V. F. Weisskopf, Phys. Rev. 77, 388
(50E1) C. Erginsoy, Phys. Rev. 79, 1013
(50J1) H. Jones, Phys. Rev. 81, 149
(50J2) V. A. Johnson and K. Lark-Horovitz, Phys. Rev. 79, 176
(50M1) H. S. W. Massey and B. L. Moiseiwitsch, Phys. Rev. 78, 180
(50V1) J. Voger, Phys. Rev. 79, 1023

1951 (51B1) H. Brooks and C. Herring, Phys. Rev. 83, 879
(51F1) H. Y. Fan, Phys. Rev. 82, 900.

A219, 53.

1954 (54A1) B. Abeles and S. Meiboom, Phys. Rev. 95, 31
(54D1) P. P. Debye and E. M. Conwell, Phys. Rev. 93, 693

1955 (55D1) R. B. Dingle, Phil. Mag. 46, 831
(55H1) C. Herring, Bell System Tech. J. 34, 237
(55W1) G. A. Wolff, R. A. Herbert and J. D. Broder,
Phys. Rev. 100, 1144
      (56H1) C. Herring and E. Vogt, Phys. Rev. 101, 944
      (56S1) N. Sclar, Phys. Rev. 104, 1559

1957 (57C1) J. Callaway, J. Electron. 2, 330
      (57G1) L. Gold and L. M. Roth, Phys. Rev. 107, 358
      (57K1) E. O. Kane, J. Phys. Chem. Solids 1, 249

      (58R1) F. J. Reid and R. K. Willardson, J. Electron. 5, 54
      (58V1) L. J. Van der Pauw, Phil. Res. Rep. 13, 1

      (59G1) M. Glicksman, J. Phys. Chem. Solids 8, 511
      (59S1) M. S. Sodha and Y. P. Varshni, Can. J. Phys. 37, 1552

      (60E1) H. Ehrenreich, Phys. Rev. 120, 1951
      (60L1) D. Long, Phys. Rev. 120, 2024

        (62C1)  M. Cardona and D. L. Greenaway. Phys. Rev. 125, 1291
                109, 149
                23, 1513
        (62S1)  A. G. Samoilovich, I. Ya. Korenblit and I. V. Dakhovskü,
                Soviet Phys. – Doklady, 6, 606
        (62W1)  L. R. Weisberg, J. Appl. Phys. 33, 1817

1963  (63B1)  A. C. Beer, Galvanomagnetic Effects in Semiconductors,
        (63M1)  C. A. Mead and W. G. Spitzer, Phys. Rev. Lett. 11, 358

1964  (64A1)  D. G. Andrianov, I. V. Dakhovskü, E. M. Omelýanovskü and
            V. I. Fistul, Sov. Phys. – Solid State 6, 2244
        (64K1)  I. Kudman and E. F. Steigmeier, Phys. Rev. 133, A1665
                136, A1467
        (64Z1)  D. J. Zook, Phys. Rev. 136, A869

1965  (65B1)  R. T. Bate, R. D. Baxter, F. J. Reid and A. C. Beer,
            J. Phys. Chem. Solids 26, 1205
                No. HP-15.
1966

3. P. N. Butcher and W. Fawcett, Phys. Lett. 21, 489
7. G. King, J. Lees and M. P. Wasse, quoted by P. N. Butcher and W. Fawcett, Phys. Lett. 21, 489
9. S. M. Ku and J. F. Black, J. Appl. Phys. 37, 3733

1967


(67F1) L. M. Falicov and M. Cuevas, Phys. Rev. 164, 1025

(67H1) A. R. Hutson, A. Jayaraman and A. S. Coriell, Phys. Rev. 155, 786


(67M1) E. J. Moore, Phys. Rev. 160, 607 and 618


(67V1) Y. P. Varshni, Physica 34, 149

1968 (68B1) I. Balslev, Phys. Rev. 173, 762


(68C1) W. M. Coderre and J. C. Woolley, Can. J. Phys. 46, 1207

(68C1) E. M. Conwell and M. O. Vassel, Phys. Rev., 166, 797


(68J1) L. W. James, R. C. Eden, J. L. Moll and W. E. Spicer, Phys. Rev. 174, 909

(68S1) R. A. Smith, Semiconductors, (Cambridge Univ. Press)
1969  (69A1)  M. J. Aubin, M. B. Thomas, E. H. van Tongerloo and
(69A2)  M. J. Aubin, Ph.D. Thesis, University of Ottawa
(69C1)  H. C. Casey, Jr. and M. B. Panish, J. Appl. Phys. 40, 4910
(69C2)  W. M. Coderre and J. C. Woolley, Can. J. Phys. 47, 2553
(69H1)  T. C. Harman and J. M. Honig, Thermoelectric and thermo-
magnetic effects and application (McGraw-Hill, N.Y.)
(69J1)  L. W. James and J. L. Moll, Phys. Rev. 183, 740
(69J2)  D. Jones and A. H. Lettington, Solid St. Commun. 7, 1319
(69K1)  F. P. Kesamanly, D. N. Nasledov, A. Ya. Nasheiskii and
         V. A. Skripkin, Sov. Phys. - Semicond. 2, 1221
         23, 1115
(69S1)  D. J. Stukel and R. N. Euwema, Phys. Rev. 188, 1193
         8, 358

1970  (70C1)  J. M. Chamberlain, P. E. Simmonds and R. A. Stradling,
(70C2)  R. C. Clarke, B. D. Joyce and W. H. E. Wilgoss, Solid
         St. Commun. 8, 1125
         B1, 724


A. Fortini, D. Diguet and J. Lugand, J. Appl. Phys. 41, 3121

V. V. Galavanov and N. V. Siukaev, Phys. Stat. Sol. 38, 523

H. G. B. Hicks and P. D. Green, Proc. of III Int. Symposium and GaAs and Related Compounds Achen, Germany, October.

C. Hilsum and H. D. Rees, Electron Lett. 6, 278


M. Ilegems and G. L. Pearson, Phys. Rev. B1, 1576

M. R. Lorenz, R. Chicotka, G. D. Pettit and P. J. Dean, Solid St. Commun. 8, 693

B. Monemar, Solid St. Commun. 8, 2121


G. D. Pitt, Solid St. Commun. 8, 1119


(70V1) J. A. Van Vechten and T. K. Bergstresser, Phys. Rev. B1, 3351

(71B1) O. Berolo and J. C. Woolley, Can. J. Phys. 49, 1335
(71F2) R. E. Fern and A. Onton, J. Appl. Phys. 42, 3499
(71L1) P. Lawaetz, Phys. Rev. B4, 3460
(71L2) M. Luong and A. W. Shaw, Phys. Rev. B4, 2436
(71M1) H. T. Minden, Appl. Phys. Lett. 17, 358
(71R1) D. L. Rode and S. Knight, Phys. Rev. B3, 2534
(71R2) D. L. Rode, Phys. Rev. B3, 3287
(71S2) K. Sugiyama and T. Kawakami, Japanese J. Appl. Phys. 10, 1007
(71Y1) W. M. Yim, J. Appl. Phys. 42, 2854

(72B1) J. Basinski, Ph.D. Thesis, University of Ottawa
(72B2) P. Blood, Phys. Rev. B6, 2257
(72F2) K. Fletcher, P. N. Butcher, J. Phys. C: Solid State Phys. 5, 212
(72R2) D. L. Rode, Phys. Stat. Sol. (b) 53, 245
(72S1) D. D. Sell, the same with (72O1), p. 800
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<td>(73B1) O. Berolo, J. C. Woolley and J. A. Van Vechten, Phys. Rev. B8, 3794</td>
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<td>(73D1) D. J. E. Demars and J. C. Woolley, Can. J. Phys. 51, 2369</td>
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<td>(73H1) D. C. Herbert, J. Phys. C: Solid State Phys. 6, 2788</td>
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<td>(73M1) L. Makowski and M. Glicksman, J. Phys. Chem. Solids 34, 487</td>
</tr>
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<td></td>
<td>(73M2) B. Monemar et al., Phys. Rev. B8, 5711</td>
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<td>(73O1) J. W. Orton, J. Phys. D: Appl Phys. 6, 851</td>
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<td>(73P1) M. B. Panish, J. Appl. Phys. 44, 2667</td>
</tr>
<tr>
<td></td>
<td>(73P2) G. D. Pitt, J. Phys. C: Solid State Phys. 6, 1586</td>
</tr>
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<td>(73S1) K. S. Song, Solid Stat. Commun. 13, 1397</td>
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P. Rochon and E. Fortin, Phys. Rev. B12, 5803

D. L. Rode, the same with (75P1), p. 1

A. J. SpringThorpe, F. D. King and A. Becke, J. Electron. Mat. 4, 101

C. D. Thurmond, J. Electrochem. Soc. 122, 1133


J. D. Wiley, the same with (75P1), p. 91

N. Yokoyama and S. Ohkawa, Japan J. Appl. Phys. 14, 1071


D. E. Aspnes, Phys. Rev. B14, 5331


Y. E. Maronchuk and N. A. Yakusheva, Sov. Phys. Semicond. 10, 800


(77C1) D. J. Chadi, Phys. Rev. B16, 790
(77H1) C. Hermann and C. Weisbuch, Phys. Rev. B15, 823
(77L1) M. A. Littlejohn, J. R. Hauser and T. H. Glisson, J. Appl. Phys. 48, 4587

(78C1) H. C. Casey, Jr. J. Appl. Phys. 49, 3684
(78K1) S. Kratzer and J. Frey, J. Appl. Phys. 49(7), 4064