

ELECTRON TRANSPORT PROPERTIES OF

GaAs, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$, some of the samples chosen have been heavily doped to allow the study of the three conduction band structure, viz. the Γ_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 ± 0.5 and 12.5 ± 0.5 eV

for the Γ_1 and X_1 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 $\Gamma_1 - L_1$ and $L_1 - X_1$ band interactions respectively. Intervalley scattering is important in the L_1 and X_1 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 $D_{\Gamma X} = D_{\Gamma L}$ have been found to be satisfactory here. The energy value of the L_1 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 (Γ_{15}).

The analysis of the experimental data for the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys indicates that a three-band model is required for $x = 0 \sim 0.5$, a two-band model (L_1 and X_1) for $x = 0.5 \sim 0.7$ and a one-band model (X_1) for $x = 0.7 \sim 1.0$. The energy values of the L_1 and X_1 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 $\Gamma_1 - X_1$, $\Gamma_1 - L_1$ and $L_1 - X_1$ crossovers respectively. Scattering parameters such as the acoustic deformation potentials ($E_{D\Gamma}$, E_{DX}) and

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the interband and intervalley scattering coupling coefficients (D_{Γ_L} , D_{LX} , D_{LL}) show values decreasing with increasing x in these alloys. All the above parameter values except for D_{Γ_L} , the coupling coefficient between the Γ_1 and L_1 bands, can be expressed as linear functions of x , i.e., $E_{D\Gamma} = 16.1 - 13.5x$ (in eV), $E_{DX} = 12.5 - 10.75x$ (in eV), $D_{LX} = 11.0 - 10.5x$ (in 10^{10} eV/m) and $D_{LL} = 5.0 - 1.0x$ (in 10^{10} eV/m). The value of D_{Γ_L} shows a more rapid decrease than the above parameters with increasing x up to $x = 0.3$ but has a value of $(2.5 \pm 0.2) \times 10^{10}$ eV/m for $x = 0.3 \sim 0.4$.

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 ± 0.1 and 14.2 ± 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 Γ_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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ system which also has the zincblende structure and a direct-indirect band crossover at a certain composition.

Ehrenreich(60E1) analyzed various existing experimental data on GaAs and suggested that the lowest subsidiary band minima have Δ_1 symmetry and the next minima are far above the Δ_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 ± 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 Γ_1 and/or Δ_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 Γ_1 minimum for some compositions in the direct gap region of the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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, $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 Γ_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 $\hbar\omega_0/k_B$, where $\hbar\omega_0$ 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 Γ_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 Γ_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 X_1 band was too low to determine accurately the parameter values related to this band. For this case, previously published high pressure experimental data (70Pl) has been analyzed to allow the relevant parameter values to be determined more accurately.

The L_1 and X_1 bands play a similar important role in the transport properties of those alloys of the $Ga_{1-x}Al_xAs$ 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 Γ_1 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(59G1), who observed $\langle 100 \rangle$ 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 $\underline{k}$ and the form of this dependence constitutes the energy band structure. If E is plotted as a function of $\underline{k}$ for different directions in $\underline{k}$ -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 $\langle 100 \rangle$ and $\langle 111 \rangle$, as well as at the Γ point. These extrema are shown in Fig. (II-1) where the band structure of GaAs is given as an example. If the $\langle 100 \rangle$ 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 $\langle 111 \rangle$ 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_1 Band, Kane Model

All materials in this work, except some $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $V(\underline{r})$ is given by (55D1)

$$\left[\frac{\underline{p}^2}{2m} + V(\underline{r}) + \frac{\hbar}{4m c^2} (\underline{\nabla} V \times \underline{p}) \cdot \underline{\sigma} \right] \psi_{\underline{k}} = E_{\underline{k}} \psi_{\underline{k}} \quad (\text{II-1})$$

where m is the free electron mass, $\underline{p}$ and $\underline{\sigma}$ are momentum and spin operators respectively, $\hbar$ is Planck's constant divided by 2π , and $E_{\underline{k}}$ is the energy of a state with wave vector $\underline{k}$. The translational symmetry of the lattice requires that the wave functions be of the Bloch form,

$$\psi_{\underline{k}} = U_{\underline{k}}(\underline{r}) e^{i \underline{k} \cdot \underline{r}} \quad (\text{II-2})$$

where $U_{\underline{k}}(\underline{r})$, the cell-periodic function, satisfies the following equation

$$\left\{ \frac{\underline{p}^2}{2m} + V(\underline{r}) + \frac{\hbar}{m} \underline{k} \cdot \underline{p} + \frac{\hbar}{4m} \frac{\underline{p}^2 \underline{p}^2}{c^2} [\underline{V} \underline{V} \underline{x} \underline{p}] \cdot \underline{\sigma} + \frac{\hbar}{4m} \frac{\underline{p}^2 \underline{p}^2}{c^2} \right. \\ \left. \times [\underline{V} \underline{V} \underline{x} \underline{k}] \cdot \underline{\sigma} \right\} U_{\underline{k}}(\underline{r}) = E'_{\underline{k}} U_{\underline{k}}(\underline{r}) \quad (\text{II-3})$$

where $E'_{\underline{k}} = E_{\underline{k}} - \frac{\hbar^2 \underline{k}^2}{2m}$.

A simplified Kane model neglects the fifth term in the above equation which represents the $\underline{k}$ -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 Γ_1 conduction band and Γ_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 $\underline{k} \cdot \underline{p}$ 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 Γ_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:

$$E'[E'(E' - E_o)(E' + \Delta_o) - k^2 P^2(E' - 2/3\Delta_o)] = 0 \quad (\text{II-4})$$

where P is the momentum matrix element, E_o is the principal gap and Δ_o is the spin-orbit splitting of the valence band.

Assuming $kP \ll E_o$, Aubin (69A2) showed that a general solution for the conduction band, the Γ_1 band, with an arbitrary value of Δ_o , is

$$E = ak^2 + \frac{E_o}{2} \left[\left(1 + \frac{\beta k^2 P^2}{E_o^2} \right)^{1/2} - 1 \right] \quad (\text{II-5})$$

$$\text{where } \beta = \frac{4 + 8\eta/3}{1 + \eta}, \quad a = \frac{\hbar^2}{2m}, \quad \eta = \frac{\Delta_o}{E_o}.$$

Eq. (II-5) gives the energy dependence of the cyclotron

effective mass in a non-parabolic band,

$$\frac{1}{m^*} = \frac{1}{m} + (E_o^2 + \beta k^2 P^2)^{-\frac{1}{2}} \frac{P^2}{2\hbar^2} \quad (\text{II-6})$$

Thus at the bottom of the Γ_1 band, the effective mass is

$$\frac{1}{m_o^*} = \frac{1}{m} + \frac{\beta P^2}{2\hbar^2 E_o} \quad (\text{II-7})$$

Combining this relation with that for β , we obtain for the square matrix element P^2 :

$$P^2 = \frac{3\hbar^2 E_o (E_o + \Delta_o) \left(\frac{m}{m_o^*} - 1\right)}{2m(3E_o + 2\Delta_o)} \quad (\text{II-8})$$

Eliminating P^2 and β from Eq. (II-5) we obtain

$$E = \frac{\hbar^2 k^2}{2m} + \frac{E_o}{2} \left[\left\{ 1 + \frac{4\hbar^2 k^2}{2mE_o} \left(\frac{m}{m_o^*} - 1\right) \right\}^{\frac{1}{2}} - 1 \right] \quad (\text{II-9})$$

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

$$E = \frac{\hbar^2 k^2}{2m^*} \quad (\text{II-10})$$

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

$$k = \left(\frac{m_o^* E_o}{2\hbar^2} \right)^{\frac{1}{2}} \left[1 + \frac{2Em_o^*}{E_o m} - \left(1 + \frac{4Em_o^*}{E_o m} \left(1 + \frac{m_o^*}{m} \right) \right)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (\text{II-11})$$

Rewriting Eq. (II-4) and neglecting the first E' , we obtain

$$\begin{aligned} (E - ak^2)(E + E_o + ak^2)(E + E_o + ak^2 + \Delta_o) - k^2 P^2 (E + E_o - ak^2 + \frac{2}{3}\Delta_o) \\ = 0 \end{aligned}$$

For the case $E \gg ak^2$, 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

$$k = \left[\frac{E(E + E_o)(E + E_o + \Delta_o)}{(E + E_o + \frac{2}{3}\Delta_o)P^2} \right]^{\frac{1}{2}} \quad (\text{II-12})$$

Strictly speaking the Kane model is calculated for absolute zero temperature. In this context, E_o in the Kane equations should be replaced by $E_o(0)$, 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_o in the Kane model should be replaced by the "effective mass band gap" E_o^* (57E1). The effective mass band gap E_o^* will lie between $E_o(0)$ and E_o , and a convenient form of expression is (69C2)

$$E_o^* = E_o(0) - \frac{E_o(0) - E_o}{a} \quad (\text{II-13})$$

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

Varshni (67V1) has shown that for the most of diamond and zincblende type semiconductors, E_o may be expressed as

$$E_o = E_o(0) + \frac{\alpha T^2}{(\theta + T)} \quad (\text{II-14})$$

where α and θ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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)

$$E = \frac{\hbar^2}{2} \left(\frac{2k_t^2}{m_t} + \frac{k_l^2}{m_l} \right) \quad (\text{II-15})$$

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)

$$m_d^* = (m_\ell m_t^2)^{1/3} \quad (\text{II-16})$$

and

$$\frac{1}{m_c} = \frac{1}{3} \left(\frac{2}{m_t} + \frac{1}{m_\ell} \right) \quad (\text{II-17})$$

Cardona and Greenaway showed that the k.p perturbation theory by Kane can be applied to the L_1 point (62C1) and the resulting transverse effective mass at the bottom of the band is given by (76A2)

$$\frac{m}{m_{tL}} = 1 + E_{PL} \left(\frac{1}{E_1} + \frac{1}{E_1 + \Delta_1} \right) \quad (\text{II-18})$$

where E_{PL} is an energy related to the momentum matrix element, and E_1 and Δ_1 are the direct band gap and spin-orbit splitting respectively at the L_1 point.

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

$$\frac{m}{m_{tX}} = 1 + \frac{19}{E_2} \quad (\text{II-19})$$

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 Δ_O and effective mass of electrons in semi-conducting 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,

$$E_O(x) = E_A + bx + cx^2 \quad (\text{II-19})$$

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 $A_{1-x}B_xC$, 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 (70V1)

$$\delta E(x) = x(1 - x) \frac{C_{FG}^2}{A_F} \quad (II-20)$$

where C_{FG} is the Phillips electronegativity difference between the mixed elements and A_F is a constant bandwidth parameter.

Hill(74H1) 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(73S1) 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.(76S1) have calculated the band structure of $Ga_{1-x}In_xAs$ 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 Δ_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 Γ point (72V1). If $y(x)$ denotes the fraction of conduction band s character mixed into the valence band at Γ , $y(x)$ is assumed to have the form

$$y(x) = \frac{x(1-x)C_{FG}^2}{A_F E_{ov}}$$

where

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

This s -like component makes zero contribution to Δ_o and so Δ_o is given by

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

Chadi(77C1) 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 Δ_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 Δ_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

$$\begin{aligned} \frac{1}{m_o^*} = & \frac{1}{m_{co}^*} + \frac{x(1-x)C_{FG}^2}{3A_h} \left[\frac{1}{m_{hh} E_{ov}} + \frac{1}{m_{lh} E_{ov}} \right. \\ & \left. + \frac{1}{m_{so} (E_{ov} + \Delta_{ov})} - \frac{1}{m_{co}^*} \left(\frac{2}{E_{ov}} + \frac{1}{E_{ov} + \Delta_{ov}} \right) \right] \end{aligned}$$

(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.

II-2 Transport Theory in III-V Compounds

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 $f(\underline{k}, \underline{r}, t)$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ samples in the present analysis show multiband transport behaviour having contributions from the Γ_1 -band and also the subsidiary bands. In the case of the Γ_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 $d\underline{r}d\underline{k}$ centred about $\underline{r}$ and $\underline{k}$ will at time $t + dt$ be located in an equal volume centred about $\underline{r} + \dot{\underline{r}}dt$ and $\underline{k} + \dot{\underline{k}}dt$.

Scattering must account for the difference between the two states, and thus the Boltzmann transport equation is (68B1)

$$\frac{df}{dt} = -\dot{\underline{k}} \cdot \nabla_{\underline{k}} f - \underline{v} \cdot \nabla_{\underline{r}} f + \frac{\partial f}{\partial t} + \left[\frac{\partial f}{\partial t} \right]_c \quad (\text{II-23})$$

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

$$\dot{\underline{k}} \cdot \nabla_{\underline{k}} f = \left[\frac{\partial f}{\partial t} \right]_c \quad (\text{II-24})$$

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

$$f(\underline{B}, \underline{k}) = f_o(E) - \frac{df_o(E)}{dE} \phi(\underline{B}, \underline{k}) \cdot \underline{F} \quad (\text{II-25})$$

where $f_o(E)$ is the undisturbed distribution function. Eq. (II-24)

then becomes the linearized Boltzmann equation (68B2)

$$\begin{aligned} \underline{F} \cdot \left\{ -e \underline{v}(\underline{k}) \frac{df_o(E)}{dE} - \frac{e}{\hbar} \frac{df_o(E)}{dE} [\underline{B} \cdot \underline{v}(\underline{k}) \times \nabla_{\underline{k}}] \phi(\underline{B}, \underline{k}) \right\} \\ = \left[\frac{df}{dt} \right]_c \end{aligned} \quad (\text{II-26})$$

The scattering term in Eq. (II-26) is given by

$$\left[\frac{df}{dt}\right]_c = \underline{F} \cdot \left[\frac{1}{k_B T} V(\underline{k}, \underline{k}') \{ \phi(\underline{k}') - \phi(\underline{k}) \} d^3 \underline{k}' \right] \quad (\text{II-27})$$

where

$$V(\underline{k}, \underline{k}') = W(\underline{k}, \underline{k}') f_o(\underline{k}) \{1 - f_o(\underline{k}')\} = V(\underline{k}', \underline{k}) \quad (\text{II-28})$$

k_B is the Boltzmann constant and $W(\underline{k}, \underline{k}')$ is the probability that an electron in the state $\underline{k}$ will be scattered into the state $\underline{k}'$. $W(\underline{k}, \underline{k}')$ depends upon the scattering mechanisms.

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

$$\phi(\underline{B}, \underline{k}) = P_1 k_{\underline{t}} + P_2(\hat{\underline{z}}, \underline{k}_{\underline{t}}) + P_3 k_{\underline{z}} \hat{\underline{z}} \quad (\text{II-29})$$

where $\underline{k}_{\underline{t}} = (k_x, k_y, 0)$, $\hat{\underline{z}} = (0, 0, 1)$ 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 τ defined by

$$\left[\frac{df}{dt}\right]_c = - \frac{f - f_o}{\tau} \quad (\text{II-30})$$

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 (Γ_1 -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

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

$$\delta\{E(\underline{k}') - E(\underline{k}) + \hbar\omega_o\}$$

$$W_A(\underline{k}, \underline{k}') = \frac{e^2 \omega_o N}{8\pi^2 \epsilon_o} \left(\frac{1}{\kappa_\infty} - \frac{1}{\kappa_o} \right) \frac{1}{|\underline{k} - \underline{k}'|^2}$$

$$\delta\{E(\underline{k}') - E(\underline{k}) - \hbar\omega_o\}$$

(II-31)

where ω_0 is the phonon frequency, κ_∞ and κ_0 are the high and low frequency dielectric constants of the lattice, N is the thermal average number of phonons per mode and ϵ_0 is the permittivity of free space.

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

$$\begin{aligned} L(P_1) &= Y\alpha(E) - [Y\alpha(E)/\hbar] BP_2 \\ L(P_2) &= [Y\alpha(E)/\hbar] BP_1 \\ L(P_3) &= Y\alpha(E) \end{aligned} \quad (\text{II-32})$$

where

$$\begin{aligned} Y &= \frac{4\pi\epsilon_0}{e(\hbar\omega_0) \left[(1/\kappa_\infty) - (1/\kappa_0) \right]} \\ \alpha(E) &= \frac{E}{k} \left(\frac{dE}{dk} \right)^2 \\ L(P_i) &= (N+1) \frac{f_0(E + \hbar\omega_0)}{f_0(E)} P_i(E + \hbar\omega_0) \left[(2E + \hbar\omega_0) \right. \\ &\quad \times \sin h^{-1} (E/\hbar\omega_0)^{\frac{1}{2}} - \{E(E + \hbar\omega_0)\}^{\frac{1}{2}} \left. \right] - 2EP_i(E) \\ &\quad \times \sin h^{-1} (E/\hbar\omega_0)^{\frac{1}{2}} + \theta(E - \hbar\omega_0) N \frac{f_0(E - \hbar\omega_0)}{f_0(E)} \\ &\quad \times (P_i(E - \hbar\omega_0) \left[(2E - \hbar\omega_0) \times \cos h^{-1} (E/\hbar\omega_0)^{\frac{1}{2}} \right. \\ &\quad \left. \left. - \{E(E - \hbar\omega_0)\}^{\frac{1}{2}} \right] - 2EP_i(E) \cos h^{-1} (E/\hbar\omega_0)^{\frac{1}{2}} \right) \end{aligned}$$

$$\theta(x) = 0 \quad x < 0$$

$$\theta(x) = 1 \quad x > 0$$

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.

$$L(P_3) = A(E)P_3(E + \hbar\omega_0) + \theta(E - \hbar\omega_0) B(E)P_3(E - \hbar\omega_0) + C(E)P_3(E) \quad (\text{II-33})$$

where

$$\begin{aligned} A(E) &= (N+1) \frac{f_0(E + \hbar\omega_0)}{f(E)} \{ E(E + \hbar\omega_0) \}^{\frac{1}{2}} [(A^+)^2 \\ &\quad \times \left(\frac{2E + \hbar\omega_0}{\{E(E + \hbar\omega_0)\}^{\frac{1}{2}}} \sin^{-1}(E/\hbar\omega_0)^{\frac{1}{2}} - 1 - \frac{1}{3} c^2 (c^+)^2 \right] \\ B(E) &= \theta(E - \hbar\omega_0) N \frac{f_0(E - \hbar\omega_0)}{f_0(E)} \{E(E - \hbar\omega_0)\}^{\frac{1}{2}} [(A^-)^2 \\ &\quad \times \left(\frac{2E - \hbar\omega_0}{E(E - \hbar\omega_0)^{\frac{1}{2}}} \cos^{-1}(E/\hbar\omega_0)^{\frac{1}{2}} - 1 - \frac{1}{3} c^2 (c^-)^2 \right] \\ C(E) &= -[E(N + 1) \frac{f_0(E + \hbar\omega_0)}{f_0(E)} \{2 \sin^{-1}(E/\hbar\omega_0)^{\frac{1}{2}} (A^-)^2 - A^- c c^- \\ &\quad - a a^+ c c^+ \} + \theta(E - \hbar\omega_0) N \frac{f_0(E - \hbar\omega_0)}{f_0(E)} \{ 2 \cos^{-1}(E/\hbar\omega_0)^{\frac{1}{2}} (A^+)^2 \\ &\quad - A^+ c c^+ - a a^- c c^- \}] \end{aligned}$$

$$A^{\pm} = aa^{\pm} + (k^{\pm})^2 + k^2 + cc^{\pm}/2k^{\pm}k$$

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 Γ point.

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

$$a^2 + c^2 = 1 \quad (\text{II-34})$$

where

$$a = \left(\frac{1 + \alpha}{2\alpha} \right)^{1/2}$$

$$\alpha = \left\{ 1 + \frac{2\hbar^2 k^2}{mE_o^*} \left(\frac{m}{m_o^*} - 1 \right) \right\}^{1/2}$$

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 dk 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 (72F2)

$$C(E) \rightarrow C(E) + Y\alpha(E) \frac{\hbar k}{e(dE/dk)} \sum_S \frac{1}{\tau_S(E)} \quad (\text{II-35})$$

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 Γ_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 $\langle 100 \rangle$ or $\langle 111 \rangle$ 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)

$$\frac{1}{\tau_{1j}} = \frac{N_j D_{1j}^2 m_{dj}^{*3/2}}{\sqrt{2} \pi \hbar^3 \rho \omega_{1j}} \frac{1}{e^{x_{1j}-1}} \{ (E + \hbar \omega_{1j} - E_{1j})^{1/2} + e^{x_{1j}} (E - \hbar \omega_{1j} - E_{1j})^{1/2} \} \quad (\text{II-36})$$

where the index j indicates the upper valley. D_{1j} is the coupling constant between the Γ_1 and the j th bands, N_j is the number of equivalent valleys denoted by " j ", m_{dj}^* 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, ρ is the density of crystal, and $x_{1j} = \hbar \omega_{1j} / k_B T$.

(c) 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 (50B1). 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 Γ -valley. The relaxation time in this case is given by (71R1)

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

where C_ℓ is the spherically averaged elastic constant for longitudinal mode and is given by (64Z1)

$$C_\ell = (3 C_{11} + 2C_{12} + 4C_{44})/5 \quad (\text{II-38})$$

for the case of sphalerite-type semiconductor. c is the wave function coefficient defined in Eq. (II-34).

(d) Ionized Impurity Scattering

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 $1/r = N_{cc}^{1/3}/2$, where N_{cc} 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

$$\frac{1}{\tau_{cc}} = \frac{e^4 N_{cc}}{8\pi\hbar k^2 (\kappa_o \epsilon_o)^2} \frac{1}{(dE/dk)} F_I \quad (II-39)$$

where

$$\begin{aligned} F_I &= D \ln(1 + 4k^2/\beta^2) - B \\ D &= \frac{2\beta^2 c^2}{k^2} + \frac{3\beta^2 c^2}{4k^2} + 1 \\ B &= \frac{4k^2/\beta^2}{1 + 4k^2/\beta^2} + 8 \frac{\beta^2 + 2k^2}{\beta^2 + 4k^2} + \frac{3\beta^2 + 6\beta^2 k^2 - 8k^2}{(\beta^2 + 4k^2) k^2} \end{aligned}$$

and N_{cc} is the ionized impurity concentration. The inverse screening length β is given by

$$\beta^2 = \left(\frac{e^2}{\kappa_o \epsilon_o k_B T} \right) \int \left(\frac{k}{\pi} \right)^2 f(1-f) dk \quad (II-40)$$

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)

$$\beta^2 = \frac{e^2}{\kappa_o \epsilon_o k_B T} \sum_i \frac{\partial n_i}{\partial \eta} + \frac{(N_D - N_A - n_t)(n_t + N_A)}{N_D} \quad (II-41)$$

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)

$$\sigma_I = \sigma_{IO} / [1 + \delta_B + \delta_M + \delta_D] \quad (\text{II-42})$$

where σ_{IO} is the Brooks-Herring conductivity and δ_B , δ_M and δ_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

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

where μ_{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 $T^{-1/2}$ 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 $10^{22} > n > 10^{20}/\text{m}^3$. Treating the space charge regions as impenetratable 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

$$\frac{1}{\tau_{sc}} = \frac{N_s Q_s}{\hbar} \frac{dE}{dk} \quad (\text{II-44})$$

(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

$$\frac{1}{\tau_{pe}} = \frac{e^2 k_B^2 P^2}{6\pi\hbar\kappa_o \epsilon_o (dE/dk)} (3 - 6c^2 + 4c^4) \quad (\text{II-45})$$

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

$$P^2 = h_{14}^2 \kappa_o \epsilon_o \left[\left(\frac{12}{C_\ell} \right) + \left(\frac{16}{C_t} \right) \right] / 35$$

where

$$C_t = (C_{11} - C_{12} + 3C_{44})/5$$

and h_{14} is a piezoelectric stress tensor. This scattering mechanism is effective only for pure materials at lower temperature.

(g) Neutral Impurity Scattering

Pearson and Bardeen (49Pl) 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 (50Ml) was applied to this problem by Erginsoy (59E1) and by Sodha and Varshni (59S1). Erginsoy considered only the low energy range ($E < \frac{1}{2}E_d$, 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

$$\frac{1}{\tau_N} = \frac{yQ'_0}{C} \quad (\text{II-46})$$

where

$$y = \frac{mv}{\hbar} a_0$$

$$C = \frac{e^2 m^2}{N_n \hbar^3}$$

$$Q'_0 = 10^5 / (344 + 2440y + 7200y^3)$$

m and v are the mass and velocity of incident electron, a_0 is the first Bohr radius of bound electron, N_n is the concentration of scattering centres.

C. Transport Parameters for the Γ_1 Band.

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

$$\sigma_{ij} = \frac{e}{4\pi} \int v_i(k) \phi_j(B, k) \frac{df_o(E)}{dE} d^3k \quad (\text{II-47})$$

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

$$\sigma_{xx} = \sigma_{yy} = \langle P_1 \rangle$$

$$\sigma_{xy} = -\sigma_{yx} = \langle P_2 \rangle \quad (\text{II-48})$$

$$\sigma_{zz} = \langle P_3 \rangle$$

where

$$\langle P_i \rangle = \frac{e}{3\pi^2 \hbar} \int_{-\infty}^0 P_i k^3 \left(- \frac{\partial f_o(E)}{\partial E} \right) dE$$

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 μ is called the carrier mobility.

The mobility is expressed as

$$\mu = \frac{\sigma_{zz}}{ne} \quad (\text{II-49})$$

where the carrier concentration n is calculated using the form,

$$n = \frac{1}{3\pi^2} \int_0^\infty k^3 \frac{\partial f_o(E)}{\partial E} dE$$

or

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

(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

$$F_y = R_H i B$$

where R_H is the Hall coefficient and is expressed in terms of the elements of the conductivity tensor as

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

(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)

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

(d) Magnetoresistance (Transverse)

In a magnetic field, the conductivity is (63B1)

$$\sigma(B) = \frac{\sigma_{xx}^2 + \sigma_{xy}^2}{\sigma_{xx}}$$

Hence the magnetoresistivity can be measured by

$$\frac{\Delta\rho}{\rho_o} = \frac{\rho(B) - \rho_o}{\rho_o} = \frac{\sigma_{xx}\sigma_{zz}}{\sigma_{xx}^2 + \sigma_{xy}^2} - 1 \quad (\text{II-52})$$

where ρ_o 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 (62O1) 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 $\frac{1}{3}(m_{di}^*)^{-1/2}(\frac{1}{m_{li}} + \frac{2}{m_{ti}})$ and thus the relaxation time for the process is

$$\frac{1}{\tau_{op}} = \frac{e^2 m_{di}^{*1/2} \hbar \omega_i}{4\hbar^2 \sqrt{2} \epsilon_o \pi} \left(\frac{1}{\kappa_\infty} - \frac{1}{\kappa_o} \right) (2N_q + 1) \quad (\text{II-53})$$

where

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

ω_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 Γ_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

$$\frac{1}{\tau_{IV}} = \frac{N_i^1 D_{ii}^2 m_{di}^{*3/2}}{\sqrt{2} \pi \rho \hbar^3 \omega_{ii}} \frac{1}{\exp(\hbar \omega_{ii}/k_B T) - 1} \{ (E + \hbar \omega_{ii})^{1/2} + \exp(\hbar \omega_{ii}/k_B T) \times (E - \hbar \omega_{ii})^{1/2} \} \quad (II-54)$$

where $N_i^1 = N_i - 1$,

D_{ii} is the coupling coefficient, ω_{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)

$$\frac{1}{\tau_{ij}} = \frac{D_{ij}^2 m_j^{3/2} N_j}{\sqrt{2\pi} \rho \hbar^3 \omega_{ij}} \frac{1}{\exp(\hbar\omega_{ij}/k_B T) - 1} \{ (E + \hbar\omega_{ij} - E_{ij})^{1/2} + \exp(\hbar\omega_{ij}/k_B T) (E - \hbar\omega_{ij} - E_{ij})^{1/2} \} \quad (\text{II-55})$$

where D_{ij} is the coupling coefficient, m_{dj}^* 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, ω_{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

$$\begin{aligned} \frac{1}{\tau_{il}} = & \frac{D_{\Gamma i}^2 m_o^{*3/2}}{\sqrt{2} \pi \hbar^3 \rho \omega_{\Gamma i}} \frac{1}{\exp(\hbar \omega_{\Gamma i} / k_B T) - 1} \{ \gamma^{\frac{1}{2}}(E + \hbar \omega_{\Gamma i}) \gamma'(E + \hbar \omega_{\Gamma i}) \\ & + \exp(\hbar \omega_{\Gamma i} / k_B T) \gamma^{\frac{1}{2}}(E - \hbar \omega_{\Gamma i}) \gamma'(E - \hbar \omega_{\Gamma i}) \} \end{aligned} \quad (\text{II-56})$$

where

$$\begin{aligned} \gamma(E) &= E(1 + \alpha E + \beta E^2 + \dots) \\ \alpha &= P^2 / E_o^* (E_o^* + P)^2 \\ \beta &= -2P^3 / E_o^* (E_o^* + P)^4 \\ \gamma' &= d\gamma/dE \end{aligned} \quad (\text{II-57})$$

Eq. (II-57) expresses the nonparabolicity of the Γ_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 Γ_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 Γ_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)

$$\frac{1}{\tau_{ac}} = \frac{\sqrt{2} E_D^2 m_d^{*3/2} k_B T \sqrt{E}}{\pi \hbar^4 \rho U_\ell^2} \quad (\text{II-58})$$

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 Γ_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 τ_{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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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)

$$\frac{1}{\tau_{cc}} = \frac{e^2 N_{cc} f(z)}{16\pi (\epsilon_{\text{O}} \kappa_{\text{O}})^2 \sqrt{2m_{\text{d}}^*} E^{3/2}} \quad (\text{II-59})$$

where

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

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

$$\frac{1}{a^2} = \frac{e^2}{\epsilon_{\text{O}} \kappa_{\text{O}} k_{\text{B}} T} \sum_i \frac{\partial n_i}{\partial \eta}$$

This is the same form as that for the Γ_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)

$$\mu = e \frac{\langle \tau \rangle}{m_c} \quad (\text{II-60})$$

where

$$\langle A \rangle = \frac{\int \left(- \frac{\partial f_o}{\partial E} \right) A E^{3/2} dE}{\int \left(- \frac{\partial f_o}{\partial E} \right) E^{3/2} dE}$$

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

τ_i are the relaxation times associated with various scattering mechanisms considered above and m_c the conductivity effective mass.

(b) Hall Scattering Coefficient

$$r = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \quad (\text{II-61})$$

(c) Hall Coefficient

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

$$\frac{\mu_H}{\mu} = r.F \quad (\text{II-62})$$

where μ_H is the Hall mobility and F is an anisotropy factor given by

$$F = \frac{3K(K+2)}{(2K+1)^2} \quad (\text{II-63})$$

where $K = m_l/m_t$. From Eq. (II-61) we obtain the Hall coefficient,

$$R_H = \frac{\mu \cdot r \cdot F}{\sigma} = \frac{rF}{ne} \quad (\text{II-64})$$

(d) Magnetoresistance

Abeles and Meiboom (54A1) showed that magnetoresistivity for semiconductors with constant energy surface in the form of ellipsoids is

$$\frac{\Delta \rho}{\rho_0} = R_H^2 \sigma_B^2 \{ (1 + \xi) F(K) - 1 \} \quad (\text{II-65})$$

where

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

and the magnetoresistance coefficient ξ is

$$\xi = \frac{\langle \tau^3 \rangle \langle \tau \rangle}{\langle \tau^2 \rangle^2} - 1$$

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

$$n - p = N_d - N_A \quad (\text{II-66})$$

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)

$$N_{DN} = \frac{N_D}{1 + \sum_r g_r \exp \{(-E_F - E_d + E_r)/kT\}} \quad (\text{II-67})$$

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_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 Γ_1 band are parabolic, while for the Γ_1 band a Kane band form (57K1) is assumed. Coderre and Woolley (69C2) indicated that the carrier concentration of the Γ_1 band is given by

$$n_{\Gamma} = 4 \pi \left(\frac{2m_o k_B T}{h^2} \right)^{3/2} \{ F_{1/2}(\eta) + \left(\frac{5}{2} - 5\gamma \right) \beta F_{3/2}(\eta) + \left(\frac{7}{2} - \frac{21}{2}\gamma \right) \beta^2 F_{5/2}(\eta) \\ - \left(\frac{1}{4} + \frac{7}{2}\gamma \right) \beta^3 F_{7/2}(\eta) + \dots \} \quad (\text{II-68})$$

where $\eta = \frac{E_F}{k_B T}$, $\gamma = \frac{m_O^*}{m}$, $\beta = \frac{k_B T}{E_O^*}$

and

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

For the L_1 and X_1 bands, the carrier density is

$$n_i = 4\pi N_i \left(\frac{2m_{di}^* k_B T}{h} \right)^{3/2} F_{1/2}(\eta - \xi_i) \quad (\text{II-70})$$

where

$$\xi_i = \frac{E_i - E_O}{k_B T}$$

E_i gives the energies of the L_1 and X_1 band minima relative to the top of the Γ_{15} state. Similarly the hole concentration is given by

$$p = 4\pi \left(\frac{2m_h^* k_B T}{h} \right)^{3/2} F_{1/2}(\eta - \Delta) \quad (\text{II-71})$$

where

$$\Delta = \frac{E_O}{k_B T}$$

m_h^* 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 Γ point can be taken as spherical. The work of Gold and Roth (57G1) shows that in the cases of the L_1 and X_1 bands, the approximation to an isotropic form of energy surface is satisfactory provided that $\mu B \ll 1$. 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)

$$\begin{aligned} J_x &= F_x \sum_i A_i - F_y \sum_i D_i \\ J_y &= F_y \sum_i A_i + F_x \sum_i D_i \end{aligned} \quad (\text{II-72})$$

where

$$\begin{aligned} A_i &= \frac{\sigma_i}{1 + \sigma_i^2 R_i^2 B^2} \\ D_i &= - \frac{\sigma_i^2 R_i B}{1 + \sigma_i^2 R_i^2 B^2} \end{aligned}$$

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 σ ,

$$R_H = - \frac{1}{B} \frac{\sum_i D_i}{\left(\sum_i A_i \right)^2 + \left(\sum_i D_i \right)^2} \quad (\text{II-73})$$

and

$$\sigma = \frac{\left(\sum_i A_i \right)^2 + \left(\sum_i D_i \right)^2}{\sum_i A_i} \quad (\text{II-74})$$

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.

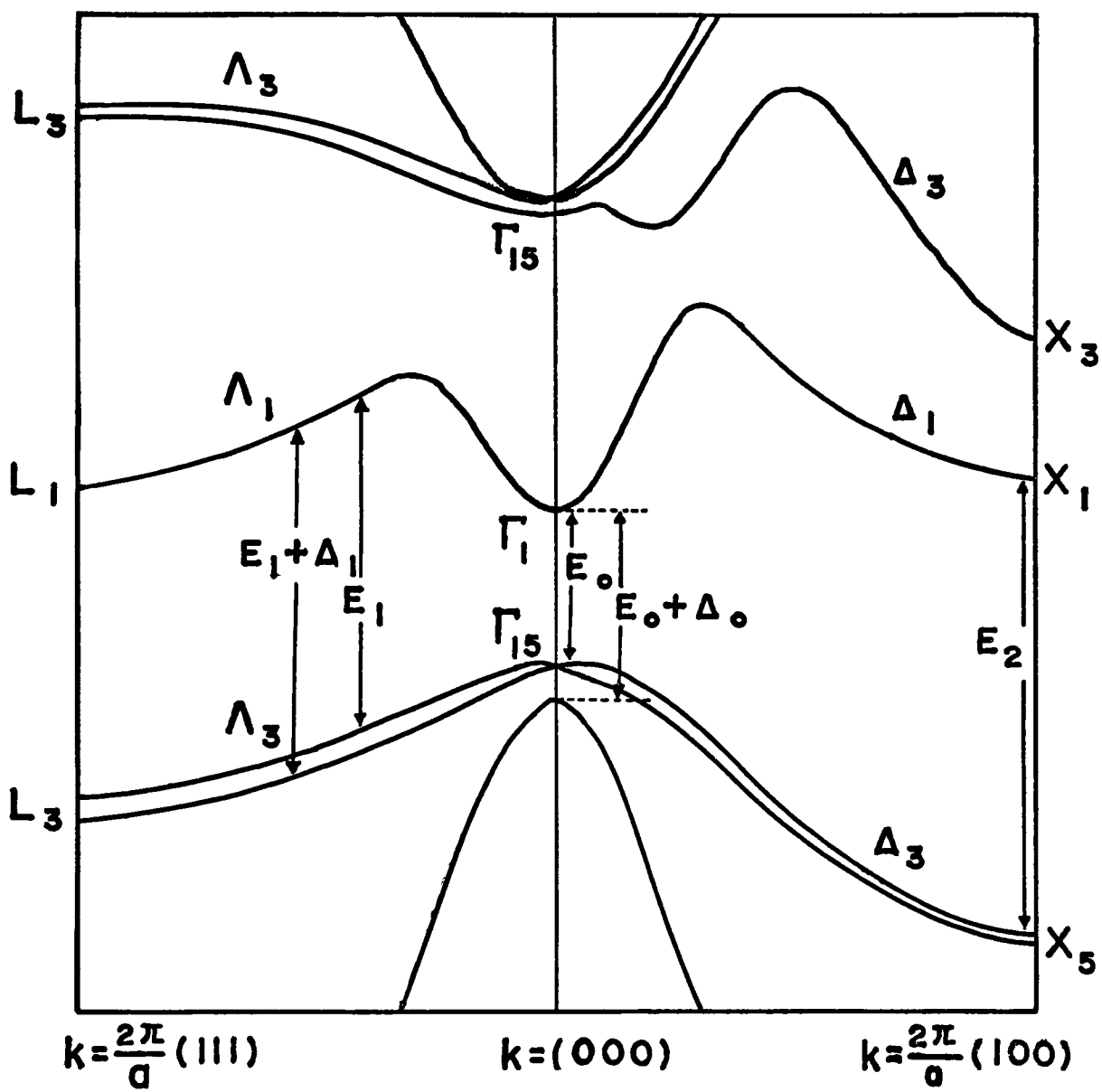


Fig. (II-1) Band Structure of GaAs (66P1).

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 $\pm 0.01^{\circ}\text{C}$ 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 $\pm 0.07^{\circ}\text{C}$ has been observed when $B = 3.0 \text{ Wb/m}^2$. The long term stability is $\sim 0.05^{\circ}\text{C/hr}$. 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 pyrophyllite 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 $1\text{ }\mu\text{V}$, but in conjunction with the nanovolt amplifier, which is used at gains of 10^3 and 5×10^3 , 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 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 parallelepiped 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.

III-3 Material and Sample Preparation

A. Material

The semiconductors used for this work were GaAs, InP and $\text{Ga}_{1-x}\text{Al}_x\text{As}$. 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys were in the form of epitaxial layers grown on Cr-doped semi-insulating GaAs substrates by SpringThorpe et al. (75S1) 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 parallelepiped 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $12 \times 1.5 \times 0.55$ mm and $10 \times 1.2 \times 0.3$ mm, and thus it was not necessary to make corrections to the measured Hall voltages as discussed by Voger (50V1). In the case of $\text{Ga}_{1-x}\text{Al}_x\text{As}$, 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 N_2 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 ($\sim 10 \mu\text{F}$) 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ samples with Au-Ge films evaporated onto the four contact points, we used a furnace preheated up to $\sim 200^\circ\text{C}$ in nitrogen atmosphere. In this way the annealing temperature of 410°C was obtained within 4 minutes, and the samples were annealed for 3 $\sim$ 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 Sauereisen 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloy samples are given in Table (III-2). The correction factor for the measured Hall voltage is given as a function of $\Delta\ell/\ell$ ($\Delta\ell$ 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 $\tan \theta = 0.1$. Correction factor values for resistivity range from 1.005 to 1.016 in the present case.

Table III-1

Magnetic Field at		Gaussmeter Reading	
Sample Site	kG	Normal	Reverse
1		0.9375	0.9325
2		1.873	1.872
3		2.810	2.808
4		3.745	3.744
5		4.682	4.680
6		5.618	5.616
7		6.552	6.551
8		7.490	7.486
9		8.425	8.420
10		9.361	9.356
11		10.296	10.291
12		11.232	11.221
13		12.163	12.157
14		13.096	13.089
15		14.028	14.021
16		14.956	14.953
18		16.807	16.803
20		18.612	18.623
22		20.386	20.384
24		22.275	22.269
26		24.278	24.273
28		26.335	26.325
30		27.990	27.900

Table III-1 Magnetic field calibration

Table III-2

Sample	Sample Dimension	Contact Size	Correction Factor
BL080	2.04-2.50-0.0088	0.221	1.19
BL106	2.52-2.47-0.0065	0.205	1.13
BL130	1.56-1.74-0.0055	0.158	1.15
BL232	1.44-1.46-0.0060	0.190	1.26
BL270	2.44-2.37-0.0060	0.326	1.25
BL300	1.30-1.28-0.0090	0.123	1.15
BL335	1.70-1.60-0.0045	0.168	1.18
BL400	2.20-2.16-0.0055	0.233	1.19
BL520	1.21-1.35-0.0060	0.165	1.27
BL600	2.72-2.62-0.0065	0.242	1.16
BL710	1.36-1.40-0.0065	0.154	1.19
BL950	2.60-2.69-0.0050	0.200	1.11

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

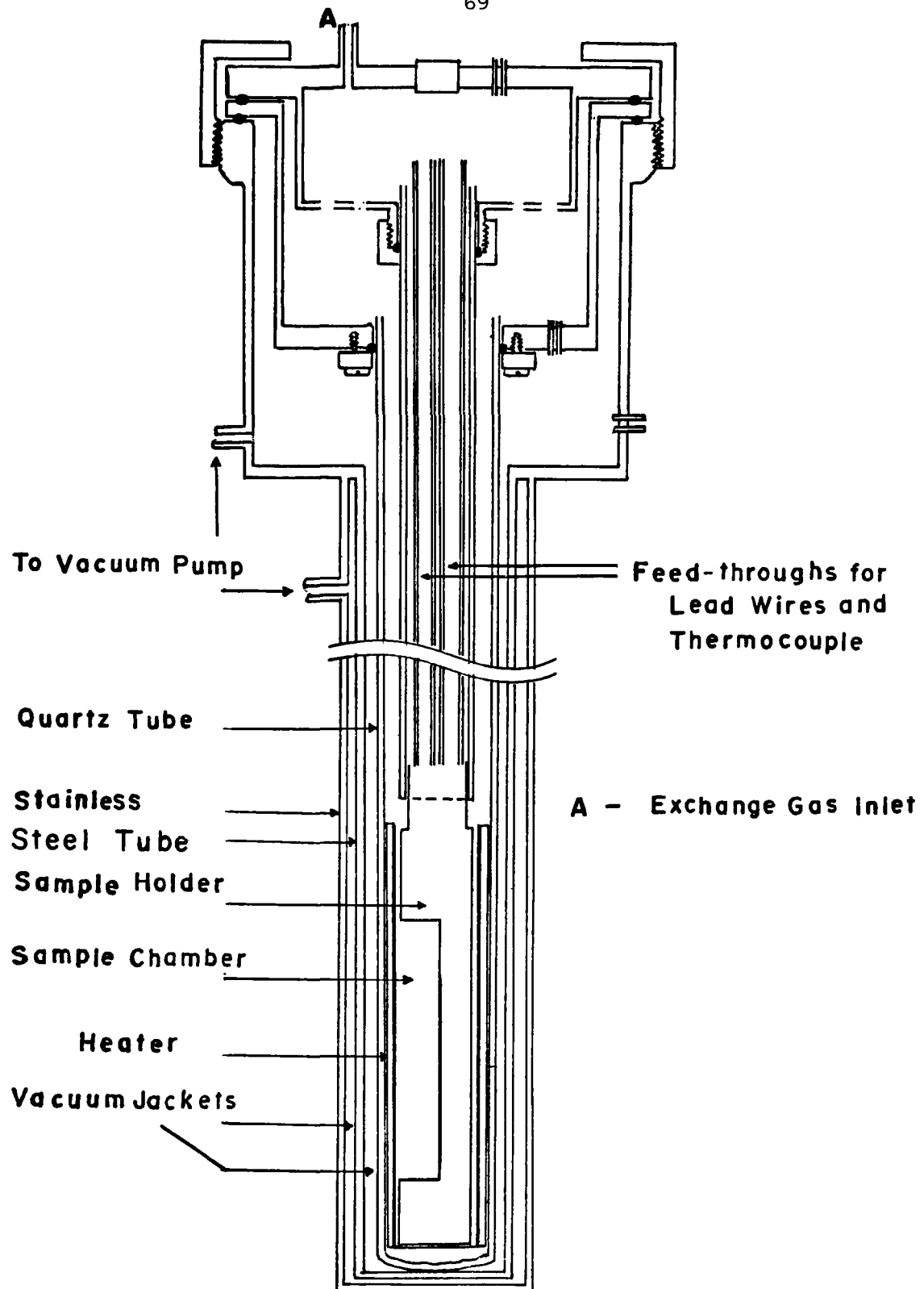


Fig. (III-1) Temperature controlled furnace

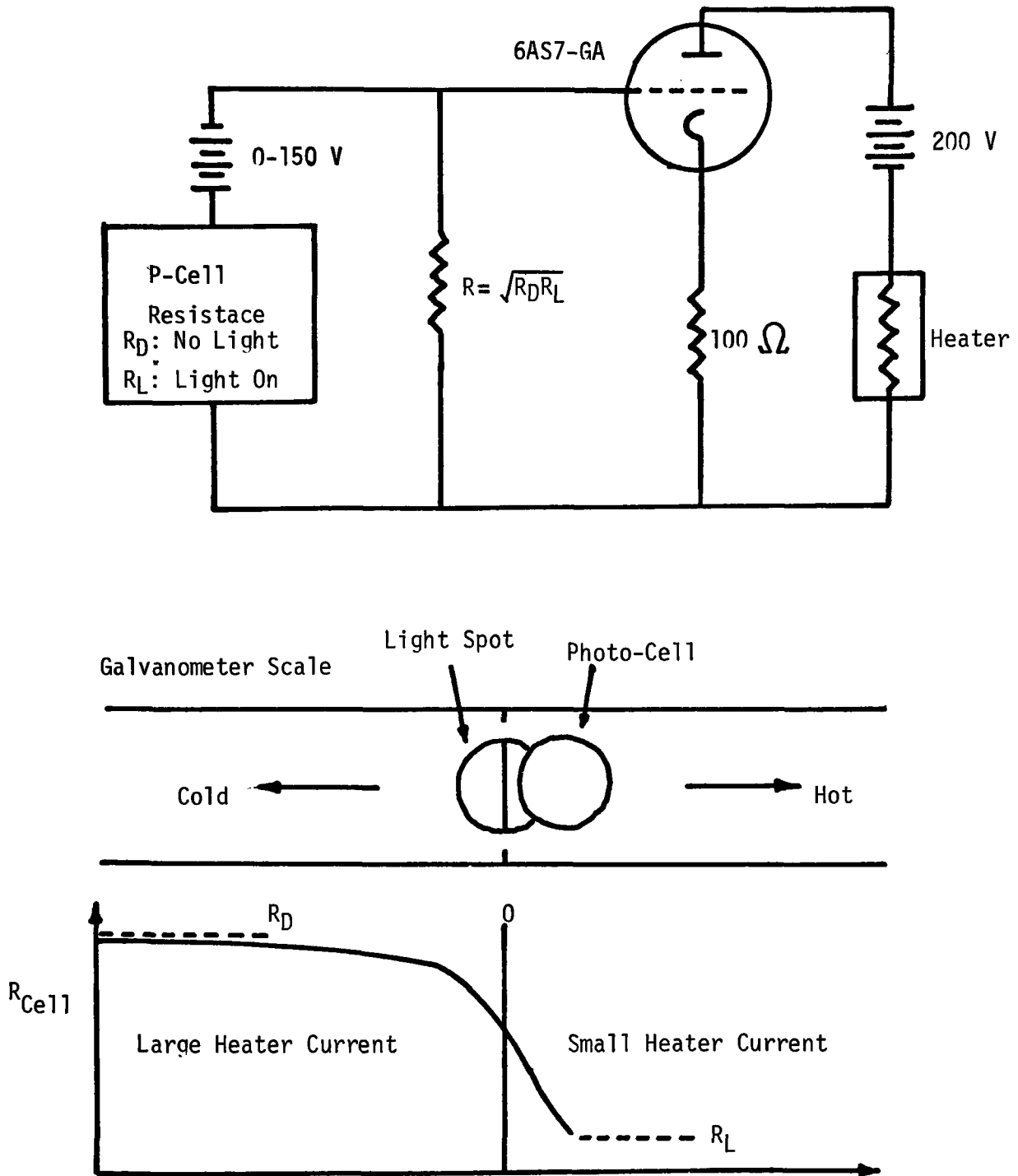


Fig. (III-2) Electro-optical system for temperature control.

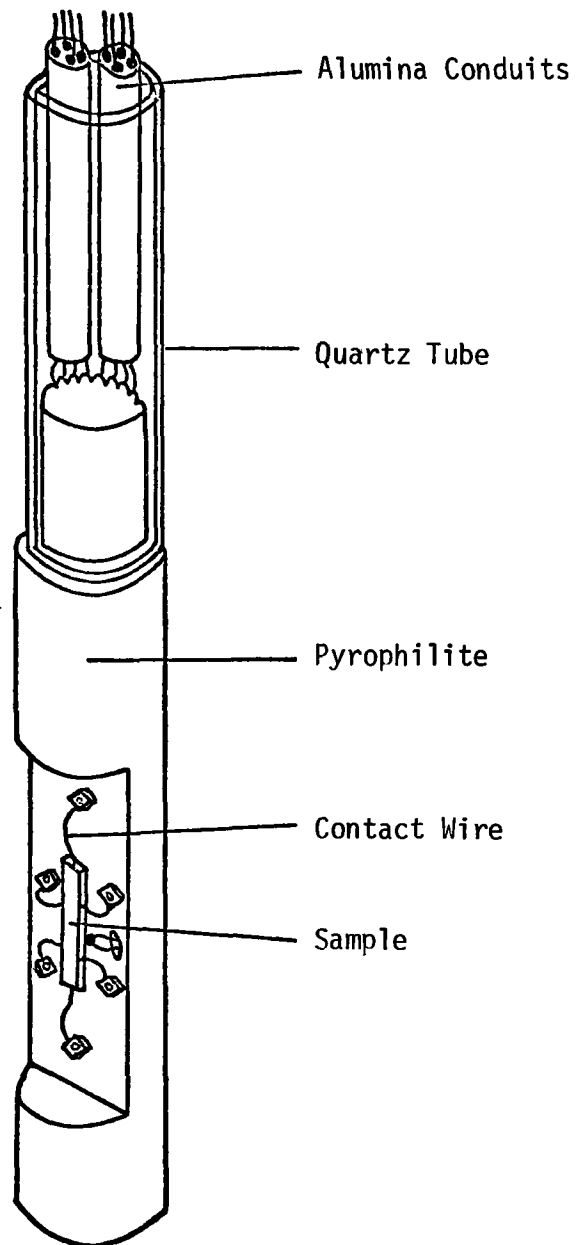


Fig. .(III-3) Sample Holder.

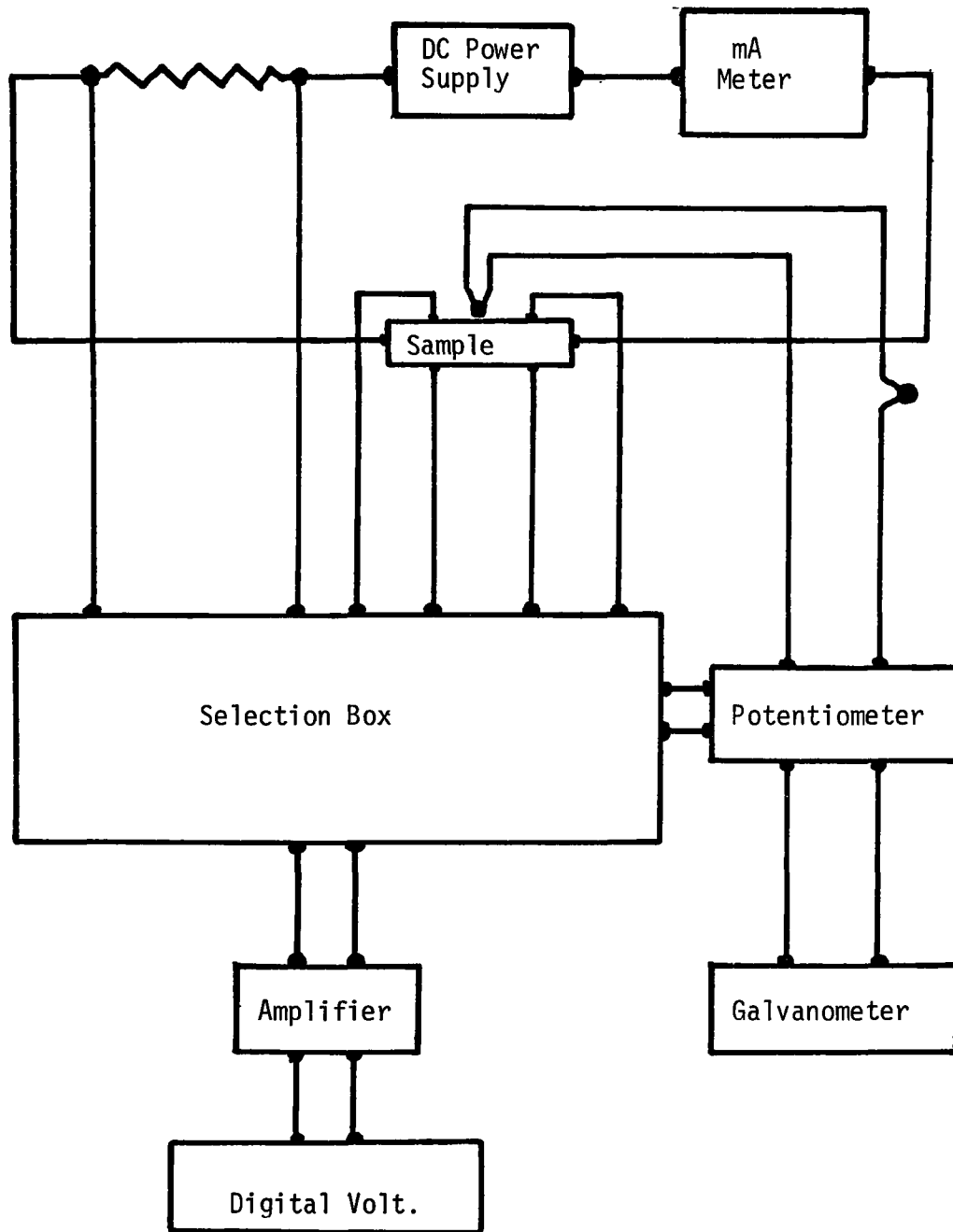
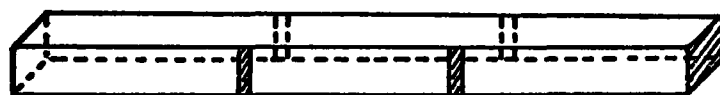
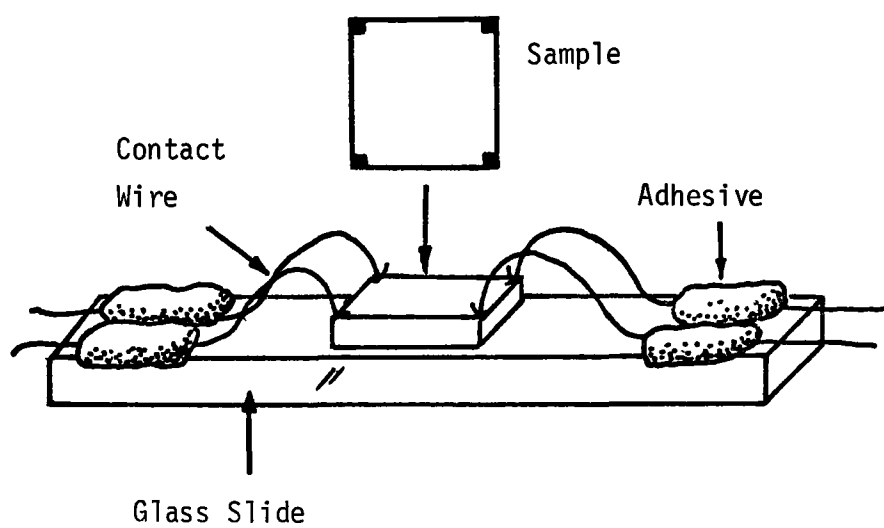


Fig. (III-4) Schematic of the measuring circuit.



(A)



(B)

Fig. (III-5) Sample types; (A) parallelpiped and (B) Van der Pauw.

CHAPTER IV

GaAs

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CHAPTER IV

GaAs

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 X_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 $\langle 111 \rangle$ directions a

few tenths of a volt above the Γ_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 $\langle 100 \rangle$ 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 electro-reflectance measurements, which give various band parameters at the Γ 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 Γ_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 Γ_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 Γ_1 minimum to the subsidiary minima as a function of uniaxial compression along various directions. The results reveal the subsidiary minima in the $\langle 100 \rangle$ 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 $X_1 - \Gamma_1$ separation.

Band structure calculations also have not consistently predicted the relative position of the X_1 and L_1 minima (66C1, 69J1, 70C3, 68H1). Pseudopotential calculations of Cohen and Bergstresser (66C1) gave the L_1 minima to be 0.1 eV below the X_1 minima, whereas Jones and Lettington (69J2), using the same method but a different form of pseudopotential, calculated the L_1 minima to be 0.4 eV above the X_1 minima. The $\underline{k} \cdot \underline{p}$ calculation of Pollak et al. (66P1) placed the L_1 and X_1 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_1 minima are 0.38 eV above the Γ_1 minimum and that the next minima, occurring along $\langle 100 \rangle$ direction, are at 0.82 eV above the Γ_1 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_1 and X_1 minima were taken to lie 0.43 and 0.35 eV respectively above the Γ_1 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_1 minima are located 170 ± 30 meV in energy below the X_1 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 Γ_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 minim are 0.31 and 0.52 eV respectively above the Γ_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 ~ 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 θ 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 Γ_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 ~ 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 ~ 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 Γ_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 $\text{m}^2/\text{V-sec}$ 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 ~ 0.041 $\text{m}^2/\text{V-sec}$ 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}), intervalley scattering coupling coefficient (D_{XX}) and effective space-charge cross section ($N_s Q_s$) 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 L_1 valley in GaAs. Even at high temperatures, most previous authors explained transport effects in terms of the Γ_1 only or the Γ_1 and X_1 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

structure; $\Gamma_1 - \Delta_1$ (or X_1) - L_1 , $\Gamma_1 - \Delta_1$ (or X_1) and $\Gamma_1 - L_1$ band orderings. The best fit to the measured data was obtained with $\Gamma_1 - \Delta_1 - L_1$ ordering by adjusting the energy values of the Δ_1 and L_1 minima.

IV-2 Experimental Results.

Four of the five GaAs samples for this work were doped with Te to a concentration between 4×10^{23} and $5 \times 10^{24} \text{ m}^{-3}$ 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 σ 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 $\sim 200^\circ\text{C}$ and the value increases with temperature above $\sim 200^\circ\text{C}$. 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 σ 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. Γ_1 band

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

$$E_o = 1.519 - \frac{5.405 \times 10^{-4} T^2}{204 + T} \quad (\text{IV-1})$$

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, $E_{D\Gamma} = -(\partial E_g / \partial P)_T / K$, where K is the compressibility and $(\partial E_g / \partial P)_T$ 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 ~ 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 $E_{D\Gamma}$, 7.2 ~ 32 eV, for InSb from various different experimental

analyses. With $E_{D\Gamma} = 14.6$ eV they (71Z1) 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 $E_{D\Gamma}$ 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 $5 \times 10^9 \sim 2 \times 10^{11}$ eV/m. The calculations were made for interaction between the Γ_1 and X_1 bands. With the present band ordering, however, the high field properties need to be calculated in terms of the Γ_1 , L_1 and X_1 minima. Work on this problem has only recently been 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 $\alpha_L = -6.5 \times 10^{-4}$ eV/K and $\theta_L = 204$ K for the $L_1 - \Gamma_{15}$ energy gap

variation from the measured $L_6^C - L_6^V$ 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 α_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, α_L and θ_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), E_d and E_μ being the dilational and shear deformation potentials respectively. The effective deformation potential in the L_1 band is given by (73V1)

$$E_{DL} = E_d + \frac{1}{3} E_\mu - a \quad (IV-2)$$

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_1 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_1 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 Γ_1 and X_1 bands. As a starting point, the coupling coefficient for the interband scattering between the L_1 and X_1 bands is assumed to be equal to $D_{\Gamma L}$.

C. X_1 valley

The X_1 minima are at 1.981 eV above the top of the valence band at 0 K (76A2). Aspnes assumed α_X to be 4.6×10^{-4} eV/K, 85% of α_Γ , 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_1 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 (70Pl).

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°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 Γ_1 carriers. Thus for all doped samples, in this temperature range we are dealing only with the Γ_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 $E_{D\Gamma}$ and N_A , which are the only unknown parameters in these scattering calculations. The ionized impurity concentration is assumed to be

$$N_{cc} = n_t + 2N_A \quad (\text{IV-3})$$

where the compensated acceptors are assumed to be singly ionized. As the temperature increases, the interaction between the Γ_1 and subsidiary bands increases through interband scattering and thus the values of two different interband scattering coupling coefficient $D_{\Gamma L}$ and $D_{\Gamma X}$ should be known for the calculation of the Γ_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 $D_{\Gamma X}$ equal to $D_{\Gamma L}$ for convenience, leaving one unknown parameter $D_{\Gamma L}$ in this case.

In the case of the L_1 valley we have five different unknown parameters, α_L , θ_L , E_{DL} , D_{LL} and D_{LX} . Here D_{LX} is assumed to be equal to $D_{\Gamma L}$ for the same reason as in the case of $D_{\Gamma X}$. As a starting point we have taken $E_{D\Gamma}$ for E_{DL} because there is no good guide to the exact value in this case. 5×10^{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_1 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_1 band have been assumed for the analysis of the X_1 band. However, for a good fit to the experimental results for doped samples above 450°C it was necessary to adjust the X_1 minima variation with temperature.

Pitt and Lees (70Pl) showed that Te-doped GaAs has donor levels associated with the X_1 minima, which are far above the Γ_1 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°C in the doped samples. In the case of the pure sample EM 23/11, the experimental data in the temperature range $18 \sim 190^{\circ}\text{C}$ could be reproduced simply by adjusting $N_{S^0_S}$ and N_A using a one-band (the Γ_1) 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

$$n = N_{DS} - N_A + N_{DD} - N_{DU} \quad (\text{IV-4})$$

where N_{DS} is the concentration of shallow donors, which are assumed to be completely ionized at room temperature, and N_{DD} and N_{DU} are total and unionized deep impurity density respectively. The impurities have been assumed to be associated with the Γ_1 minimum and N_{DD} calculated using $g_1 = 2$ in Eq. (II-67) and neglecting excited states. Then the three-band analysis above 190°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 Γ_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 Γ_1 band to the calculations for the subsidiary bands. We can define an effective relaxation time as (72F2)

$$\tau_{\text{eff}} = - \frac{m^*}{e\hbar} P_3 \quad (\text{IV-5})$$

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 Γ_1 minimum (75W1).

$$E_O^*(P) = E_O^*(O) + a'P + b'P^2 \quad (\text{IV-6})$$

and for the L_1 and X_1 minima,

$$E_i(P) = E_i(O) + a_i'P \quad (\text{IV-7})$$

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 Γ_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 Γ_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

$$n_t = N_d - N_A = n_{\Gamma} + n_L + n_X + n_d \quad (\text{IV-8})$$

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} 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_o^* is estimated by the lattice dilatation only and the variation of E_o^* with temperature is given by

$$\left(\frac{\partial E_o^*}{\partial T}\right)_P = -\frac{3\alpha}{K} \left(\frac{\partial E_o}{\partial P}\right)_T \quad (\text{IV-9})$$

where α 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 -1.2×10^{-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 ~ 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., $\mu_{ac} \propto m_o^{*-5/2}$, 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 $E_D = (\partial E_o / \partial P)_T / K$ would be too low in the present case.

The N_A values obtained from the present analysis are negligible for the three samples MO572/8, NE22/1 and MO807/8. 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 $D_{\Gamma L}$ 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 $E_{D\Gamma}$. Here the same question arises in the determination of E_{DL} as for the $E_{D\Gamma}$. Pickering and Adams (77P1) found $E_d - a = -11 \pm 3$ eV and $E_\mu = 22 \pm 7$ eV in their stress experiments, while Aspnes and Cardona (78A1) determined $E_\mu = 25 \sim 30$ 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 E_μ and $E_d - a$ 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 'a' = 1.64 and $E_{D\Gamma} = 16.1$ 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 3×10^{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.

1.8×10^{10} eV/m (77A1) and 1×10^{11} eV/m (77L1) for GaAs, 5.8×10^{10} eV/m (74B1) for GaSb and 3×10^{10} eV/m (72R2) for Ge, the values of $7 \sim 10 \times 10^{10}$ eV/m appear to be high and thus 6 eV is considered low for E_{DL} . Also, the assumption that $E_{DL} = E_{D\Gamma}$ does not seem to be unreasonable, since recent work (77A1, 77L1) has reported the same or similar values for $E_{D\Gamma}$ 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_1 band. Recent three-band analysis of high field transport properties in GaAs gave $D_{\Gamma L} = D_{\Gamma X} = 1 \times 10^{11}$ eV/m (77L1, 78K1) which is in good agreement with the present results. the $E_{D\Gamma}$ 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 $N_S Q_S = 1.05 \times 10^6 \text{ m}^{-1}$. From the resulting variation of carrier density with temperature we obtained $E_d = 0.09 \pm 0.002 \text{ eV}$, $N_{DD} = 1.1 \times 10^{22} \text{ m}^{-3}$ and $N_{DS} - N_A = 3.07 \times 10^{21} \text{ m}^{-3}$ 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 7×10^{10} eV/m is used for D_{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 Γ_1 band. Thus the true value for N_{cc} would be between $n_t + 2N_A$ and $n_t + 2N_A + \sum n_i$, 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 (70Pl), LE11, CL17/8, and G62A for this re-examination. In this work we assumed 'a' = 1.64, $E_{D\Gamma} = E_{DL} = 16.1$ eV, $D_{\Gamma L} = D_{\Gamma X} = 8 \times 10^{10}$ eV/m, $\alpha_L = -7.82 \times 10^{-4}$ eV/K, $\theta_L = 490$ K, $\alpha_X = -6.88 \times 10^{-4}$ eV/K and $\theta_X = 550$ 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 $N_D - N_A$ given in the literature (70Pl). 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 $R_H(P)/R_H(0)$ and thus E_L has been adjusted to fit the pressure value, 33 Kbar, showing maximum $R_H(P)/R_H(0)$. To make a fit to the maximum $R_H(P)/R_H(0)$ data, we have tried varying D_{LX} , $D_{\Gamma X}$ and E_{DX} values and the latter two parameters have proved to have negligible effects on this fit. The experimental maximum values of $R_H(P)/R_H(0)$ have been reproduced by adjusting only D_{LX} . E_{DX} has been found to be important to make a fit to the reduced resistivity data $\rho(P)/\rho(0)$ above 40 Kbar. The activation energy of the impurity level has been determined simply by adjusting it to fit the $R_H(P)/R_H(0)$ 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, $R_H(P)/R_H(0)$, $\mu_H(P)/\mu_H(0)$ and $\rho(P)/\rho(0)$, 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_1 minima data of the $Ga_{1-x}Al_xAs$ alloys to be treated in the next Chapter.

The D_{LX} values show considerable scatter and are very high compared with recently reported data, 5.5×10^{10} eV/m (77A1) and 5×10^{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_1 band at high pressures. The present analysis indicates that the interband scattering between the L_1 and X_1 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 Γ_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 5×10^{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, 1.14×10^{11} eV/m (74B1). The E_{DX} values obtained are in the range 12 ~ 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 5.5×10^{10} eV/m of Herbert (73H1). However previous work (68C2, 73V1, 73F1) used 1×10^{11} eV/m for D_{XX} and ~ 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 (1×10^{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 1×10^{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 (VV-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 Γ_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 $dm^*/dP = 0.007 m^*(0)/\text{kbar}$ (73Pl) 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 1.1×10^{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 α_x values by $\sim 1.5\%$ from those given in Table (IV-3). This reduction in the α_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_{LX} and α_x replaced by 12.5 eV, 1.1×10^{11} eV/m and -6.77×10^{-4} 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 Γ_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 Γ_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. Piezo-electric 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 Γ_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 Γ_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 Γ_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 Γ_1 band is completely negligible because the effective mass in the Γ_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 Γ_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^2V/sec for the Γ_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

"F" exhibit theoretical Hall mobility values quoted by Blood from the literature (70R1, 70F2) for comparison with his data. At room temperature the μ_H values for these samples are $0.7 \sim 0.76 \text{ m}^2/\text{V-sec}$, which are in good agreement with those of Stillman et al. (70S1) and Ikoma (70I1) for the samples of similar carrier concentrations.

In epitaxially grown samples, space charge scattering would be negligible (70I1, 68C2). Thus the values of μ_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 μ_H values which are in good agreement with the experimental data as shown in Fig. (IV-15). In these predictions of μ_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 μ , 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 Γ_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 Γ_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 $\text{m}^2/\text{V-sec}$ at 300 K for samples with $n_t = 1.1 \times 10^{21}$, 4.4×10^{23} and $1.27 \times 10^{24} \text{ m}^{-3}$ 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 $\text{m}^2/\text{V-sec}$ and the corresponding Hall mobility is 0.721 $\text{m}^2/\text{V-sec}$ for $n_t = 1.1 \times 10^{21} \text{ m}^{-3}$. Rode and Knight (71R1) considered all the scattering mechanisms used in the present work for their calculation on a pure GaAs sample and the results gave $\mu = 0.79 \text{ m}^2/\text{V-sec}$ and $\mu_H = 0.84 \text{ m}^2/\text{V-sec}$, 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 $E_{\text{D}\Gamma}$, that of ZnSe.

E. Carrier Mobility and Hall Scattering Coefficient.

In the Γ_1 band the carrier mobility at room temperature is in the range $0.22 \sim 0.67 \text{ m}^2/\text{V-sec}$ for the samples considered in this work, while the values for the L_1 and X_1 bands are $0.053 \sim 0.14 \text{ m}^2/\text{V-sec}$ and $0.01 \sim 0.02 \text{ m}^2/\text{V-sec}$ respectively. In estimating multiband transport properties it has previously been assumed that the mobility ratio μ_{Γ}/μ_x (or μ_{Γ}/μ_L) is constant with temperature or pressure (60A1, 70I1, 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 μ_T/μ_L and μ_T/μ_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 μ_T/μ_L values are in the range $3.5 \sim 4.9$ and μ_T/μ_x in the range $21 \sim 33$ 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 Γ_1 band. The temperature dependence is partly related to the effective mass variation with temperature; when the temperature increases from room to 500°C , m_O^* 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 , μ , 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 LE11 of Pitt and Lees (70P1). The mobility values show significant changes at pressures around which a band crossover occurs, and μ_{Γ}/μ_L and μ_{Γ}/μ_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 Γ_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 μ_H value in the X_1 band is $0.0312 \text{ m}^2/\text{V-sec}$ 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 μ_H variation at high pressures by Pitt and Lees. However, when this interband scattering is included in the calculation, $\mu_{HX} = 0.025 \text{ m}^2/\text{V-sec}$ and $\mu_{H\Gamma}/\mu_{HX} = 28$. The values of μ_X derived from experimental data cover a wide range of values, 0.011 (67H1) $\sim 0.04 \text{ m}^2/\text{V-sec}$ (70P1). Theoretical calculations (69J1, 73V1, 73F1) give values much closer to the higher end of this range. These estimated values of μ_X are high because the L_1 band effects were neglected in the calculations. The results of the present calculations for sample EL11 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_H with temperature in the higher temperature range indicates the increasing effect of interband scattering with increasing temperature. In Fig. (IV-18), r_H 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 Γ_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 Γ_1 conduction band and Γ_{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 Γ_1 band,

$$E = \frac{\hbar^2 k^2}{2m} - \frac{\chi - E_o}{2} + a \frac{\chi + E_o}{2\chi} \frac{\hbar^2 k^2}{2m} + \frac{\chi - E_o}{2\chi} \frac{\hbar^2 k^2}{2m} \left(b + \frac{c}{5}\right) \quad (\text{IV-10})$$

where χ , 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 Γ_1 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 MO241/44/2 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 $\Gamma_1 - L_1 - X_1$ conduction band model. The temperature dependences of the subsidiary band minima and the effective masses in the Γ_1 and L_1 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 Γ_1 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_1 minima 304 meV above the Γ_1 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 ~ 200 and $\sim 400^\circ\text{C}$ respectively for a pure sample. Below $\sim 400^\circ\text{C}$ intrinsic effects can be neglected for a pure sample with $n \sim 1 \times 10^{21} \text{ m}^{-3}$.

The values of acoustic deformation potential are $16.0 \pm 0.5 \text{ eV}$ and $12.5 \pm 0.5 \text{ eV}$ for the Γ_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 Γ_1 , the interband and intervalley scattering coefficients $D_{\Gamma L}$ and D_{LL} are in the ranges $7 \sim 9 \times 10^{10} \text{ eV/m}$ and $3 \sim 7 \times 10^{10} \text{ eV/m}$ respectively. The interband scattering coefficient D_{LX} obtained from the high pressure experimental data has a value of $(1.1 \pm 0.2) \times 10^{11} \text{ eV/m}$. The assumption that $D_{XX} = D_{LL}$ and $D_{\Gamma X} = D_{\Gamma L}$ has been found to be satisfactory in the present analysis.

In the Γ_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 Γ_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

Sample	T	R_H	σ	n_t	N_A
	$^{\circ}\text{C}$	$10^{-5} \text{ m}^3/\text{Coul}$	$10^4 \text{ Ohm}^{-1} \text{ m}^{-1}$	10^{23} m^{-3}	10^{22} m^{-3}
EM23/11	18.4	84.2	0.0599	0.0795	0.88
MO572/8	20.1	1.49	2.42	4.24	0.025
NE22/1	21.5	0.985	3.20	6.35	1.70
MO807/8	20.0	0.515	5.80	12.30	-
MO241/44	23.0	0.142	15.00	44.50	43.0

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/m^2 for EM23/11 and at 0.8 Wb/m^2 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

Parameter	Value	Reference
$E_o(0)$	1.519 eV	75T1
$m_o(0)$	0.066 m	70S2,71S1,75P1,75R2
$m_o^*(295)$	0.0638 m	70S2,65M1
Δ_o	0.341 eV	75A1
α_o	-5.405×10^{-4} eV/K	75T1
θ_o	204 K	75T1
m_{1L}	1.9 m	76A2
m_{tL}	0.0754 m	76A2
$E_L(0)$	1.815 eV	76A1
Δ_1	0.22 eV	73A1
E_1	3.041 eV	73A1
$E_X(0)$	1.981 eV	76A2
m_{1X}	1.3 m	68C2
m_{tX}	0.23 m	66P2
K_∞	10.91	75R2
K_o	12.91	75R2
$\hbar\omega_o$	0.0362 eV	70I2
$\hbar\omega_{ij}$	$0.8 \hbar\omega_o$	68C2
C_1	1.397×10^{11} N/m ²	71C1
ρ	5307 Kg/m ³	71N1
P_e	0.052	75R2

Table IV-2 Material parameters of GaAs.

Table IV-3

Case No.	$m_o(O)$ m	$m^*(room)$ m	a	$E_{D\Gamma}$ eV	$D_{\Gamma L}$ 10^{10} eV/m	D_{LL} 10^{10} eV/m	α_L 10^{-4} eV/K	θ_L	α_X 10^{-4} eV/K	θ_X K
1	0.066	0.064	1.84	15.2	10.0	3.0	-7.72	485	-6.90	550
2	"	"	"	"	"	5.0	-7.68	"	"	"
3	"	"	"	"	8.0	7.0	-7.75	490	-6.85	"
4	"	0.0638	1.64	16.1		3.0	-7.87	"	"	"
5	"	"	"	"		5.0	-7.82		-6.88	"
6	"	"	"	"	7.0	7.0	-7.80	"	-6.87	"
7	0.0665		1.36	16.4	8.0	3.0	-7.89	"	-6.97	"
8			"	"	7.0	5.0		495	-6.95	"
9	"	"	"	"	7.0	6.0	-7.84	490	-6.85	"
10	"	0.0629	1.00	18.4	-	-	-	-	-	-

Table IV-3 Parameter values determined as a function of effective mass of the Γ_1 band. These results were obtained under the assumption that $E_{DL} = E_{DX} = E_{D\Gamma}$, $D_{\Gamma X} = D_{LX} = D_{\Gamma L}$ 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 α_X by $\sim 1.5\%$ of those given here.

Table IV-4

Pressure Coefficient	Γ_1	L_1	X_1
a_i (eV/Kbar)	1.26×10^{-2} (75W1)	3.55×10^{-3} (71C1, 76A2)	-1.75×10^{-3} (71C1, 76A2)
b (eV/Kbar ²)	-3.77×10^{-5} (75W1)	--	--
$\left(\frac{\partial \omega_o}{\partial P}\right)_T$ (%/Kbar)	0.16 (73P3)	--	--

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

Table IV-5

Sample	N_A 10^{21} m^{-3}	E_{DX} eV	D_{LX} 10^{10} eV/m	E_d eV	μ_X $10^{-2} \text{ m}^2/\text{V-sec}$		μ_T/μ_L		μ_T/μ_X	
					0 Kbar	50 Kbar	0 Kbar	50 Kbar	0 Kbar	50 Kbar
EL11	0	12.2	9.5	0	2.20	3.35	4.91	1.78	29.0	3.53
G62A	1.6	13.0	13.0	0.148	1.74	3.23	5.05	2.49	37.8	3.75
CL17/8	35.0	12.0	9.5	0.018	1.48	2.45	3.71	1.51	18.9	3.25

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

Table IV-6

T °C	E _F eV	Γ ₁			L ₁			X ₁		
		μ	r	n 10 ²³	μ	r	n 10 ²²	μ	r	n 10 ²¹
20	0.0105	0.3510	1.010	4.240	0.0992	1.048	0.008	0.0164	1.116	0.0001
100	-0.0017	0.3103	1.010	4.318	0.0775	1.050	0.116	0.0118	1.113	0.006
150	-0.0105	0.2908	1.010	4.343	0.0680	1.055	0.364	0.0100	1.111	0.035
200	-0.0203	0.2728	1.012	4.288	0.0603	1.063	0.902	0.0086	1.109	0.135
250	-0.0313	0.2559	1.017	4.188	0.0541	1.071	1.881	0.0075	1.107	0.406
300	-0.0440	0.2399	1.026	4.028	0.0490	1.079	3.421	0.0067	1.104	0.999
350	-0.0585	0.2249	1.040	3.803	0.0448	1.088	5.562	0.0060	1.102	2.098
400	-0.0752	0.2108	1.058	3.518	0.0413	1.097	8.228	0.0054	1.100	3.869
450	-0.0942	0.1967	1.081	3.192	0.0384	1.104	11.24	0.0049	1.097	6.392
500	-0.1157	0.1841	1.110	2.846	0.0359	1.111	14.38	0.0045	1.095	9.661

Table IV-6 Results of the analysis of the experimental data for sample MO572/8 ($N_A = 2.5 \times 10^{20} \text{ m}^{-3}$).
Unit of μ used in the table is $\text{m}^2/\text{V-sec}$ and carrier density is given per m^3 .

Table IV-7

T	E _F	Γ_1			L_1			X_1		
^o C	eV	μ_Γ	r_Γ	$n_\Gamma 10^{24}$	μ_L	r_L	$n_L 10^{23}$	μ_X	r_X	$n_X 10^{22}$
20	0.1394	0.2156	1.009	4.435	0.0533	1.017	0.140	0.0097	1.015	0.002
100	0.1363	0.1990	1.012	4.455	0.0494	1.012	0.840	0.0083	1.012	0.004
150	0.1327	0.1888	1.017	4.374	0.0466	1.014	1.837	0.0075	1.015	0.175
200	0.1274	0.1799	1.024	4.219	0.0440	1.019	3.359	0.0068	1.018	0.505
250	0.1203	0.1700	1.035	4.009	0.0413	1.027	5.393	0.0062	1.022	1.173
300	0.1112	0.1615	1.049	3.752	0.0390	1.036	7.846	0.0057	1.027	2.317
350	0.1003	0.1527	1.067	3.462	0.0367	1.046	10.57	0.0052	1.031	4.041
400	0.0876	0.1439	1.087	3.153	0.0346	1.056	13.43	0.0048	1.034	6.400
450	0.0732	0.1353	1.111	2.840	0.0327	1.065	16.26	0.0045	1.036	9.380
500	0.0572	0.1278	1.138	2.535	0.0311	1.073	18.96	0.0042	1.039	12.91

Table IV-7 Results of the analysis of the experimental data for sample MO241/44/12 ($N_A = 4.3 \times 10^{23} \text{ m}^{-3}$).
Unit of μ used in the table is $\text{m}^2/\text{V-sec}$ and carrier density is given per m^3 .

Table IV-8

T °C	E _F eV	Γ_1			L_1			X_1		
		μ	r	n 10 ²¹	μ	r	n 10 ²⁰	μ	r	n 10 ¹⁹
20	-0.1497	0.6675	1.133	1.100	0.1353	1.166	0.002	0.0202	1.250	-
100	-0.2021	0.4973	1.093	1.098	0.0952	1.147	0.022	0.0134	1.224	0.001
150	-0.2362	0.4323	1.076	1.092	0.0800	1.141	0.074	0.0110	1.206	0.007
200	-0.2712	0.3835	1.067	1.081	0.0689	1.138	0.191	0.0093	1.190	0.028
250	-0.3074	0.3451	1.063	1.058	0.0605	1.138	0.412	0.0080	1.176	0.089
300	-0.3451	0.3136	1.066	1.021	0.0539	1.140	0.769	0.0070	1.165	0.225
350	-0.3847	0.2867	1.077	0.967	0.0487	1.143	1.279	0.0062	1.155	0.483
400	-0.4264	0.2632	1.094	0.898	0.0444	1.146	1.931	0.0056	1.146	0.907
450	-0.4704	0.2423	1.117	0.816	0.0409	1.150	2.686	0.0051	1.139	1.525
500	-0.5169	0.2234	1.147	0.728	0.0381	1.153	3.487	0.0047	1.132	2.338

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

Table IV-9

P	E _F	Γ_1			L_1			X_1		
kbar	eV	μ	r	$n \cdot 10^{21}$	μ	r	$n \cdot 10^{21}$	μ	r	$n \cdot 10^{21}$
0.0	-0.0971	0.6372	1.104	9.248	0.1295	1.166	-	0.0199	1.249	-
10.0	-0.0997	0.5815	1.110	9.228	0.1240	1.212	0.019	0.0202	1.250	-
20.0	-0.1032	0.5308	1.130	8.804	0.1008	1.350	0.370	0.0206	1.252	0.075
25.0	-0.1091	0.4945	1.167	7.288	0.0749	1.283	1.251	0.0209	1.252	0.638
30.0	-0.1293	0.4146	1.290	3.440	0.0579	1.323	2.243	0.0211	1.253	3.566
33.0	-0.1526	0.3009	1.397	1.412	0.0552	1.324	1.981	0.0229	1.245	5.853
35.0	-0.1716	0.2093	1.326	0.679	0.0553	1.324	1.563	0.0242	1.234	7.003
40.0	-0.2243	0.1312	1.350	0.089	0.0557	1.324	0.676	0.0280	1.236	8.483
45.0	-0.2786	0.1186	1.366	0.011	0.0565	1.323	0.255	0.0311	1.226	8.982
50.0	-0.3320	0.1177	1.366	-	0.0569	1.322	0.092	0.0325	1.197	9.151
60.0	-0.4338	0.1164	1.364	-	0.0576	1.322	0.012	0.0337	1.175	9.237

Table IV-9 Results of the analysis of the high pressure data of Pitt and Lees (70Pl) for sample

EL11 ($N_A = 0.0$, $B = 0.625 \text{ Wb/m}^2$).

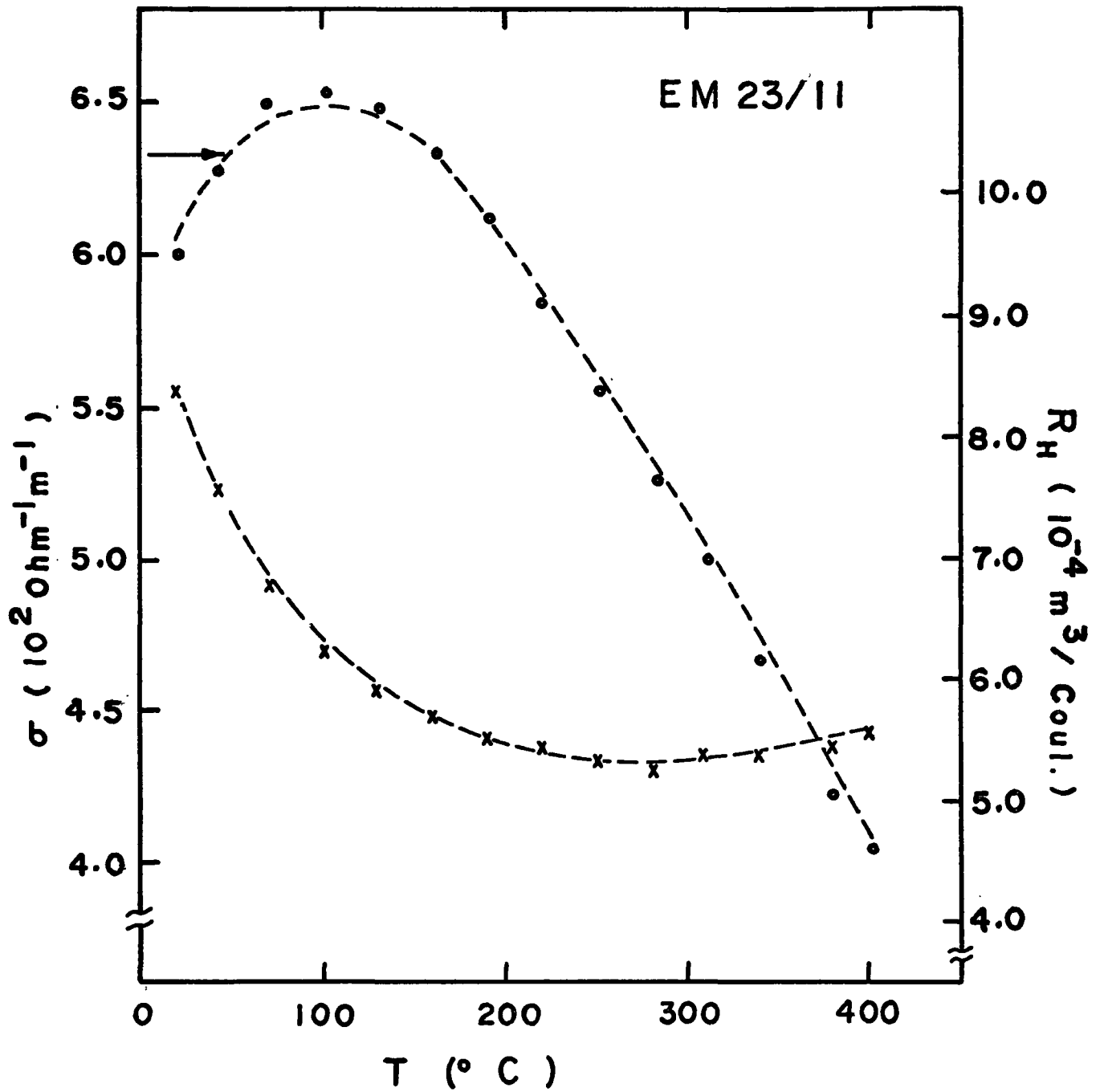


Fig. (IV-1) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample EM23/11 of GaAs.

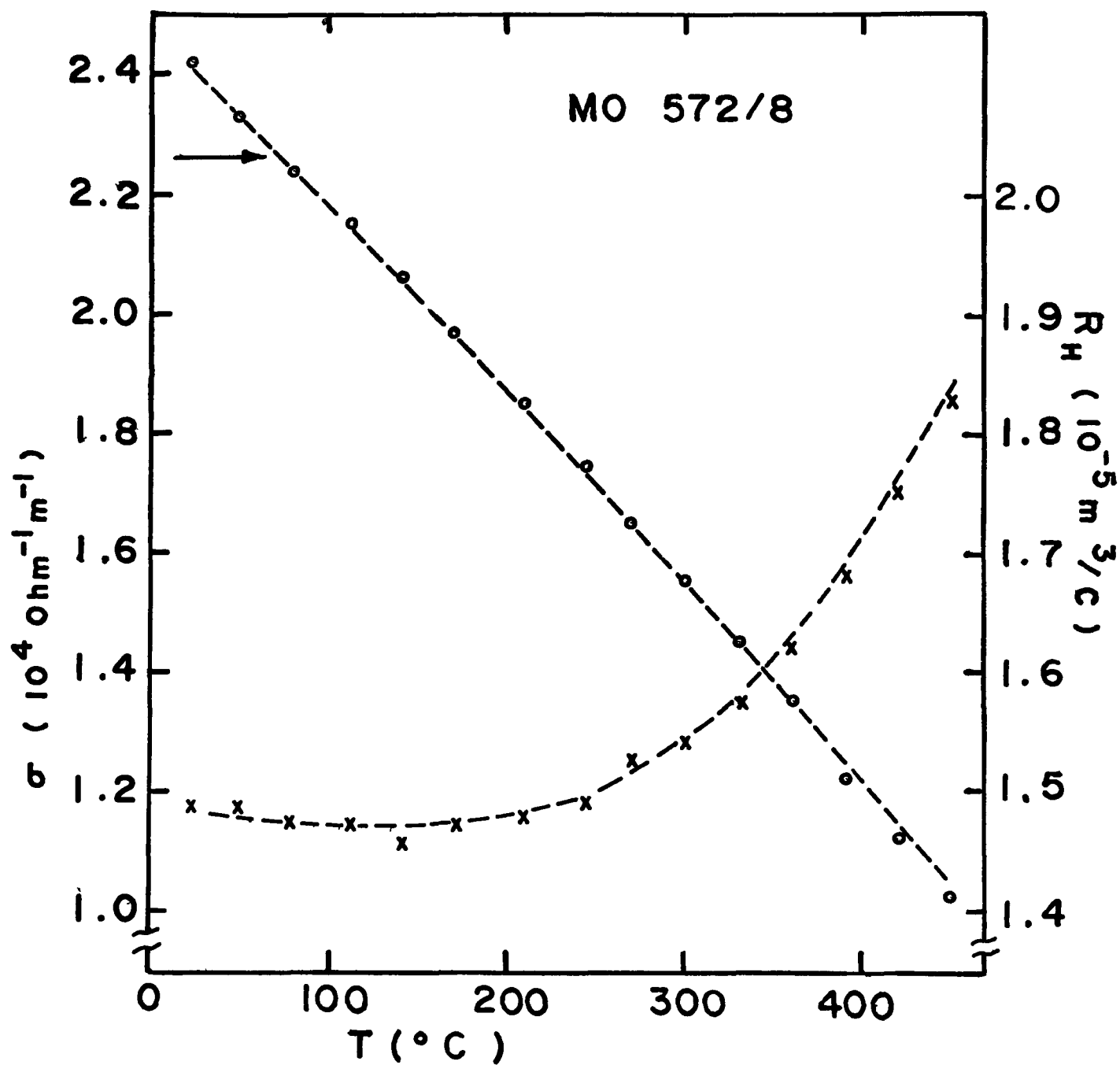


Fig. (IV-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO572/8 of GaAs.

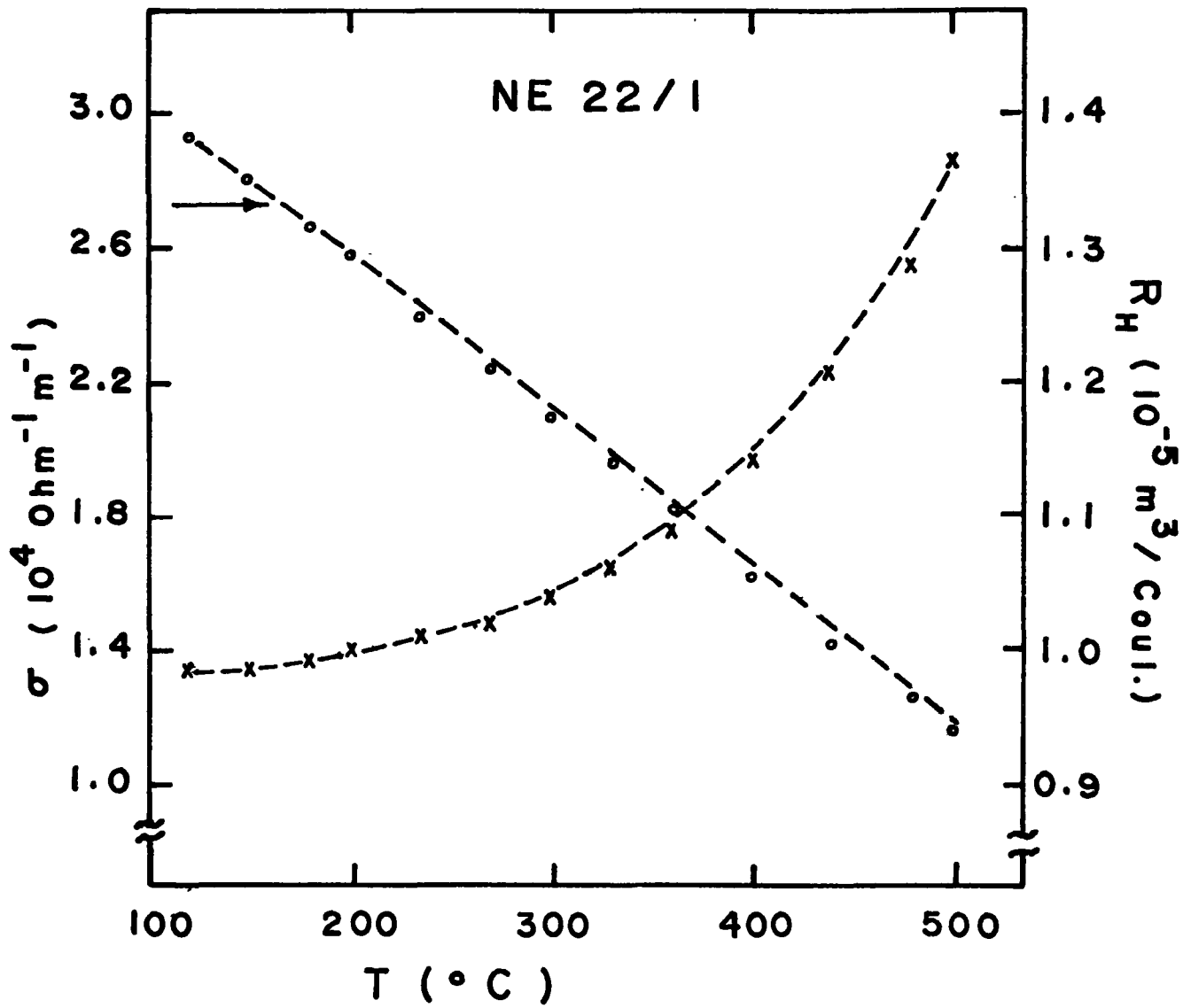


Fig. (IV-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample NE22/1 of GaAs.

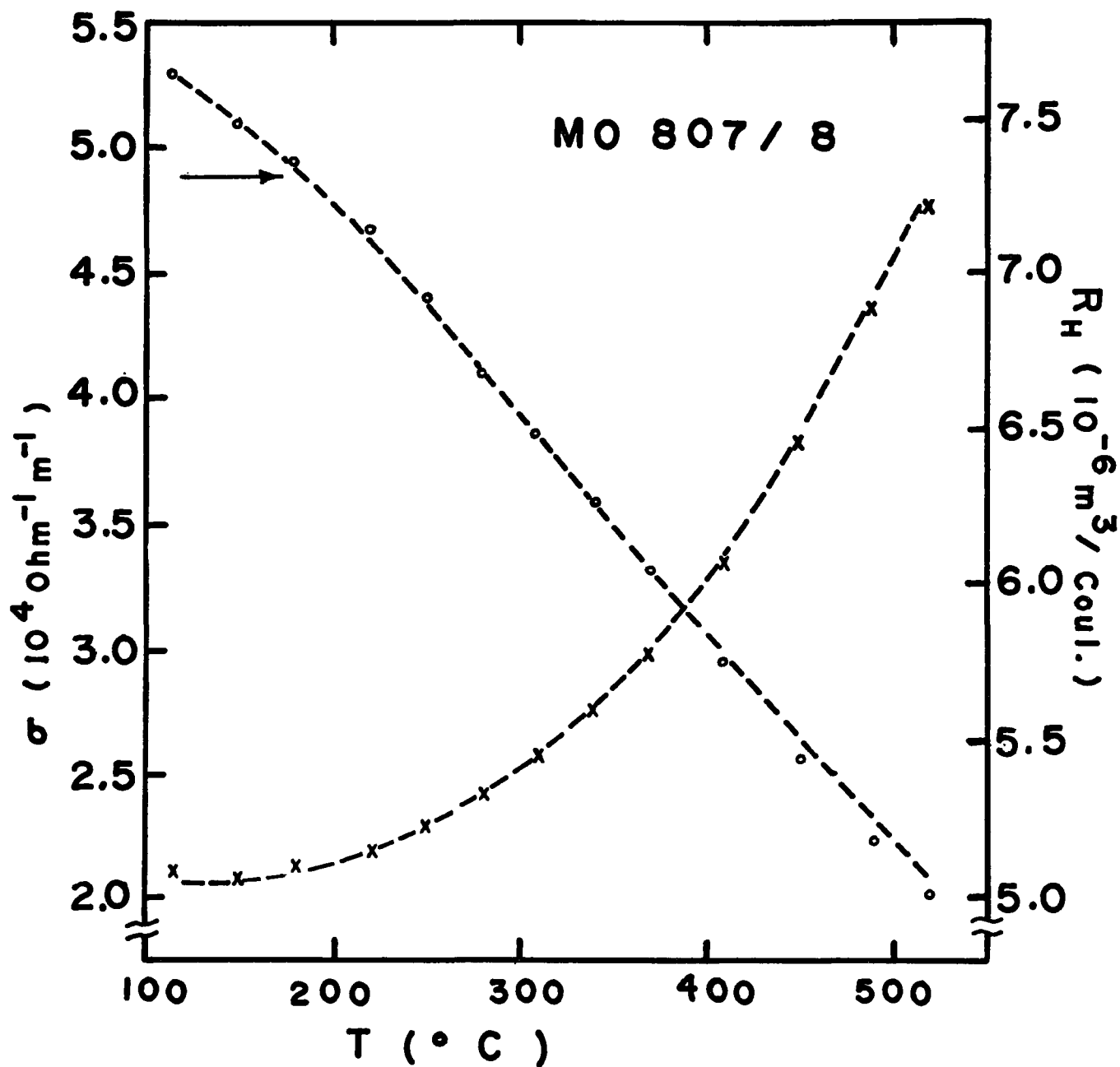


Fig. (IV-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO807/8 of GaAs.

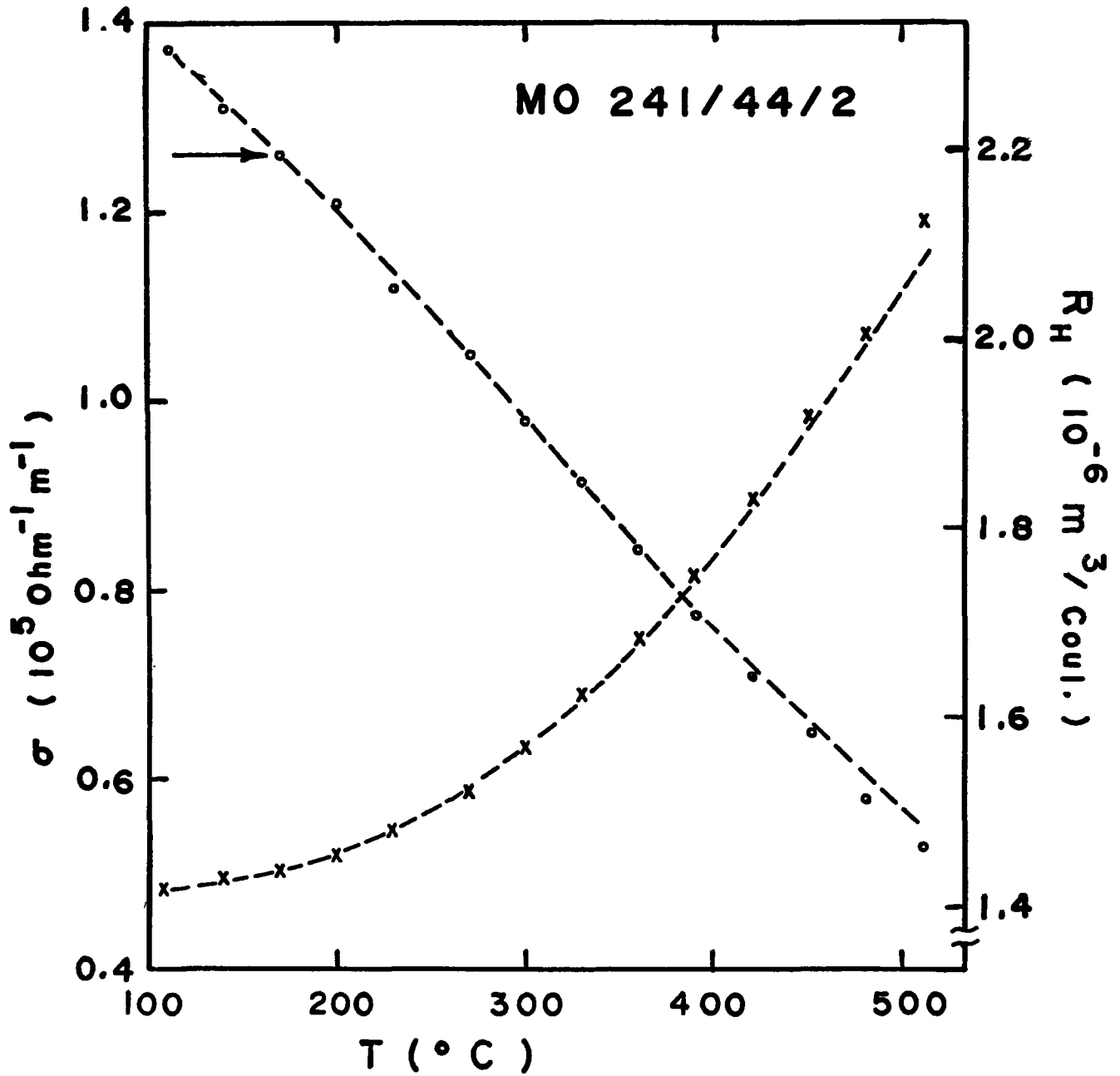


Fig. (IV-5) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample MO241/44/2 of GaAs.

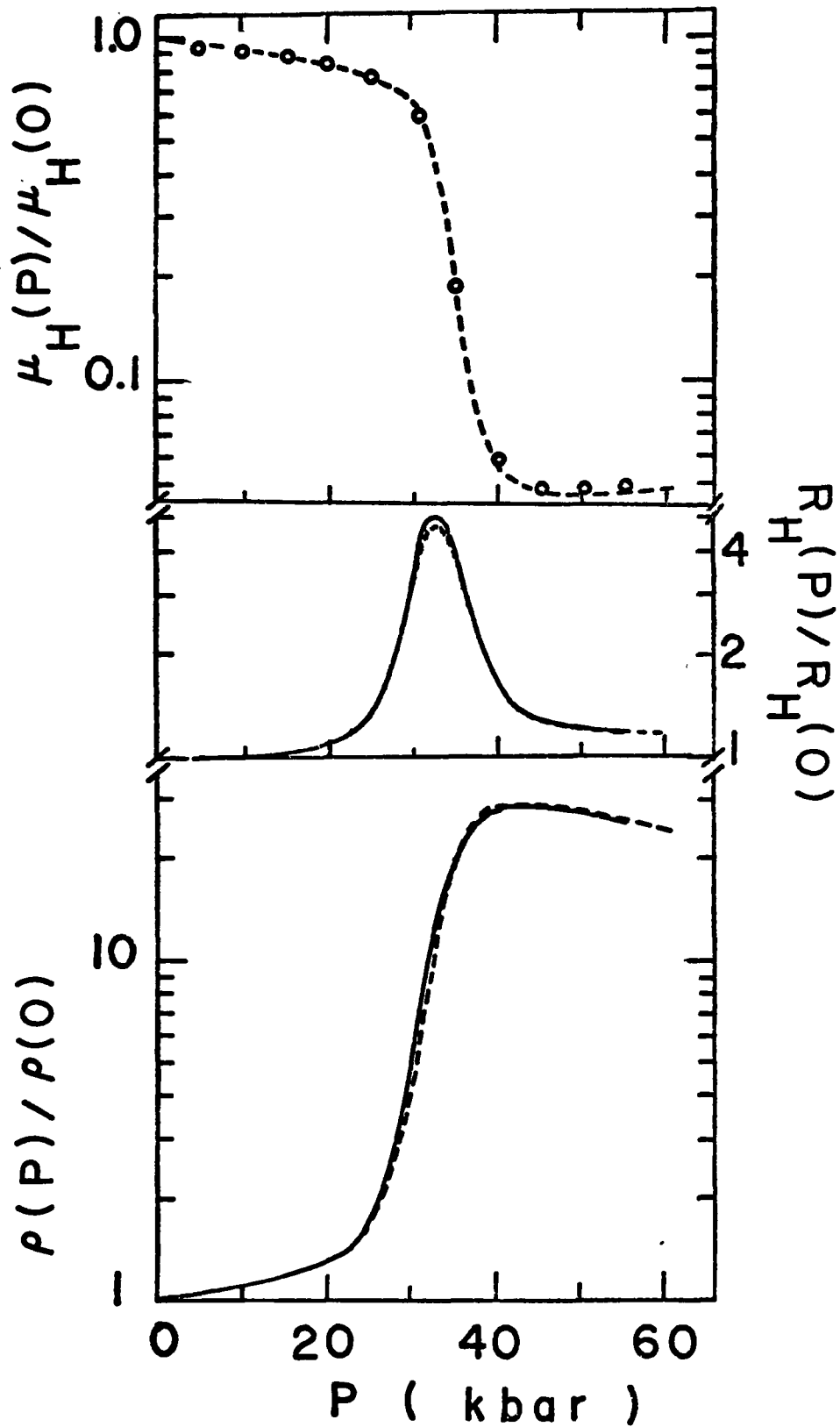


Fig. (IV-6) Normalized Hall mobility, Hall coefficient and resistivity measured as a function of pressure for sample G62A of Pitt and Lees (70Pl) and curves fitted to the data.

— and o experimental data
 ----- fitted curves.

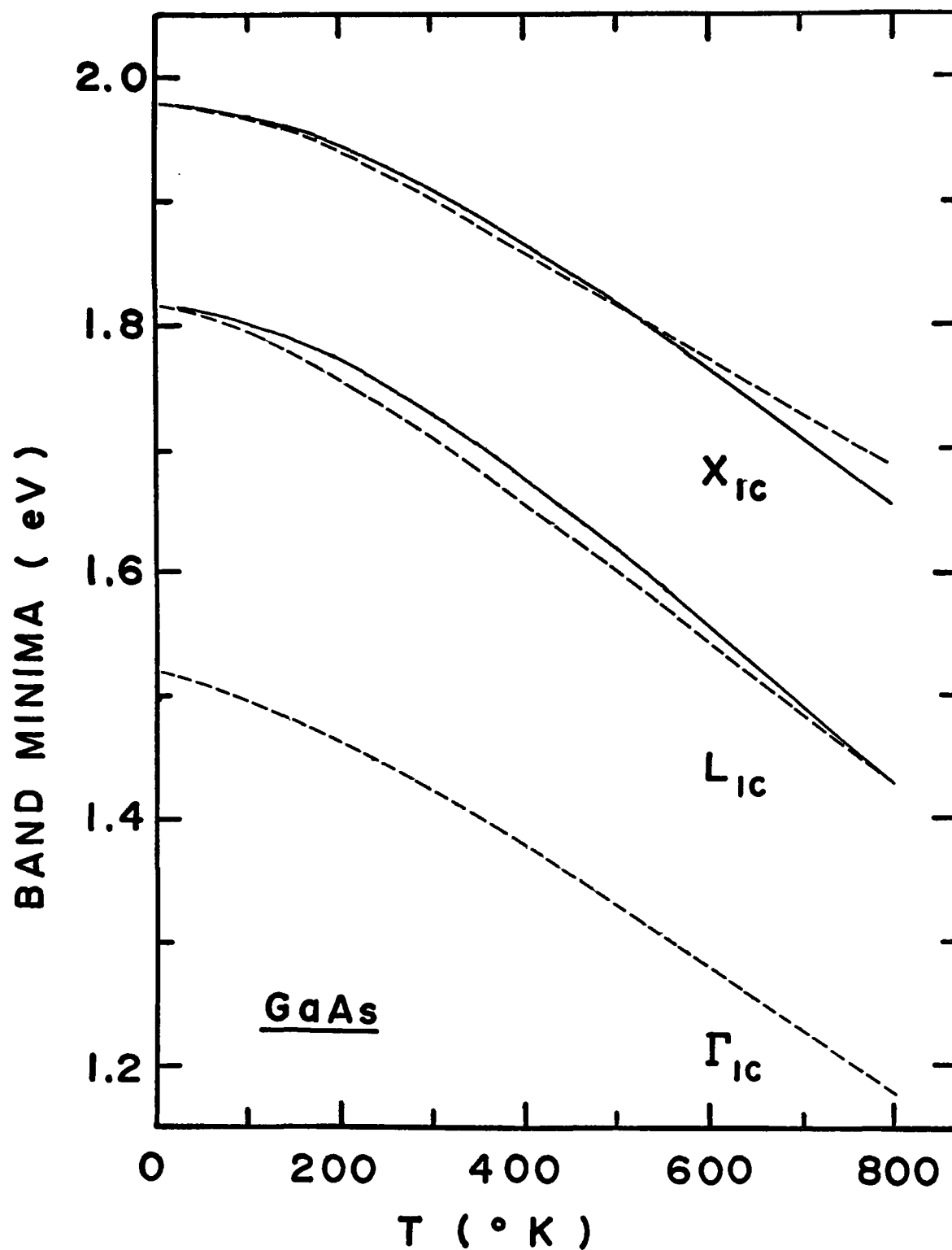


Fig. (IV-7) Band gap variation with temperature for GaAs.
 ---- Aspnes (76A2),
 — present results ($\alpha_L = -7.82 \times 10^{-4}$ eV/K and
 $\theta_L = 490$ K for the L_1 minima, and $\alpha_X = -6.77 \times 10^{-4}$ eV/K and
 $\theta_X = 550$ K for the X_1 minima.

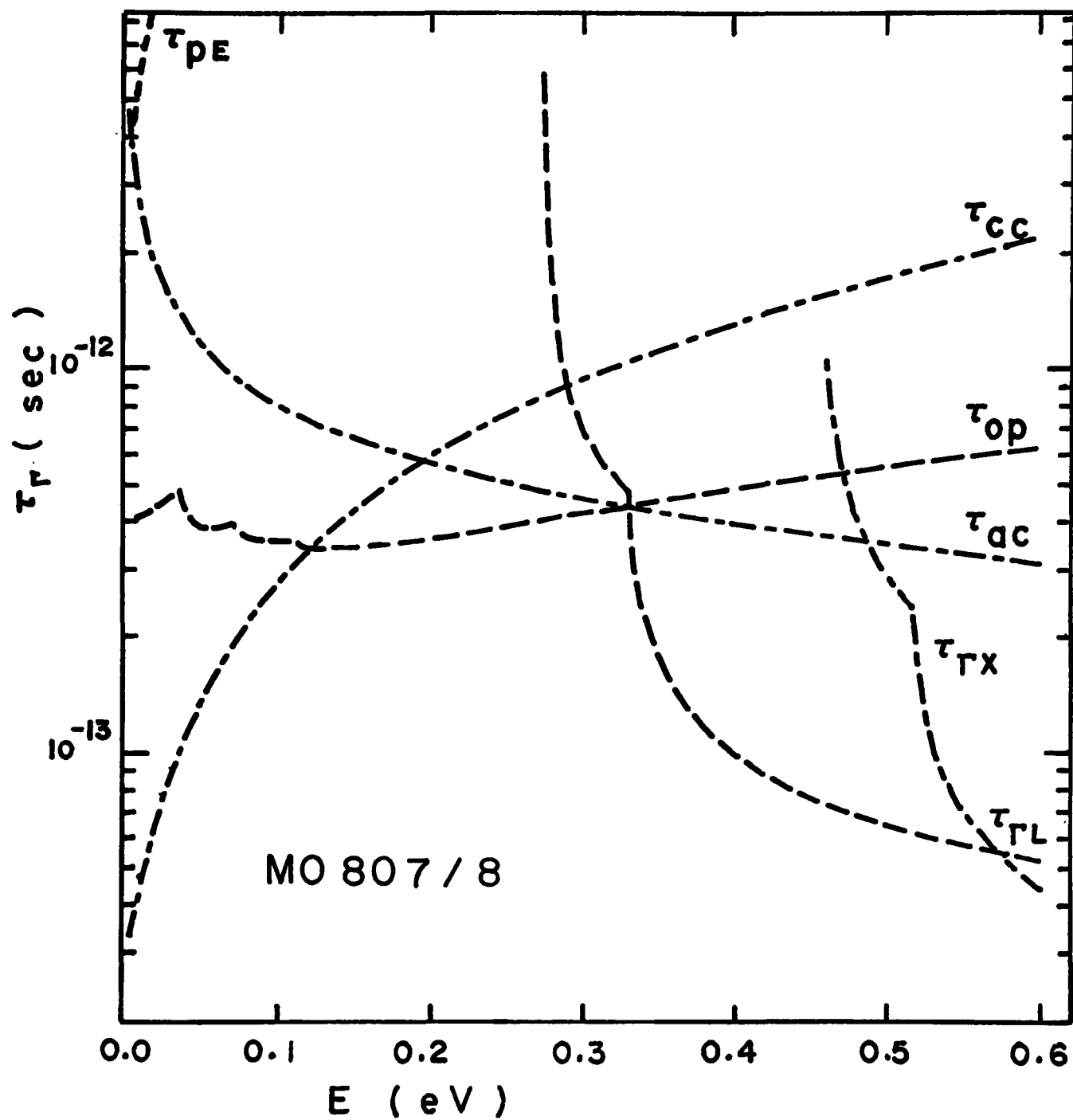


Fig. (IV-8) Relaxation times as a function of energy in the Γ_1 band with $E_{D\Gamma} = 16.1$ eV, $D_{\Gamma L} = 8 \times 10^{10}$ eV/m, $a = 1.64$ and the band minima variation with temperature as given in Fig. (IV-7).

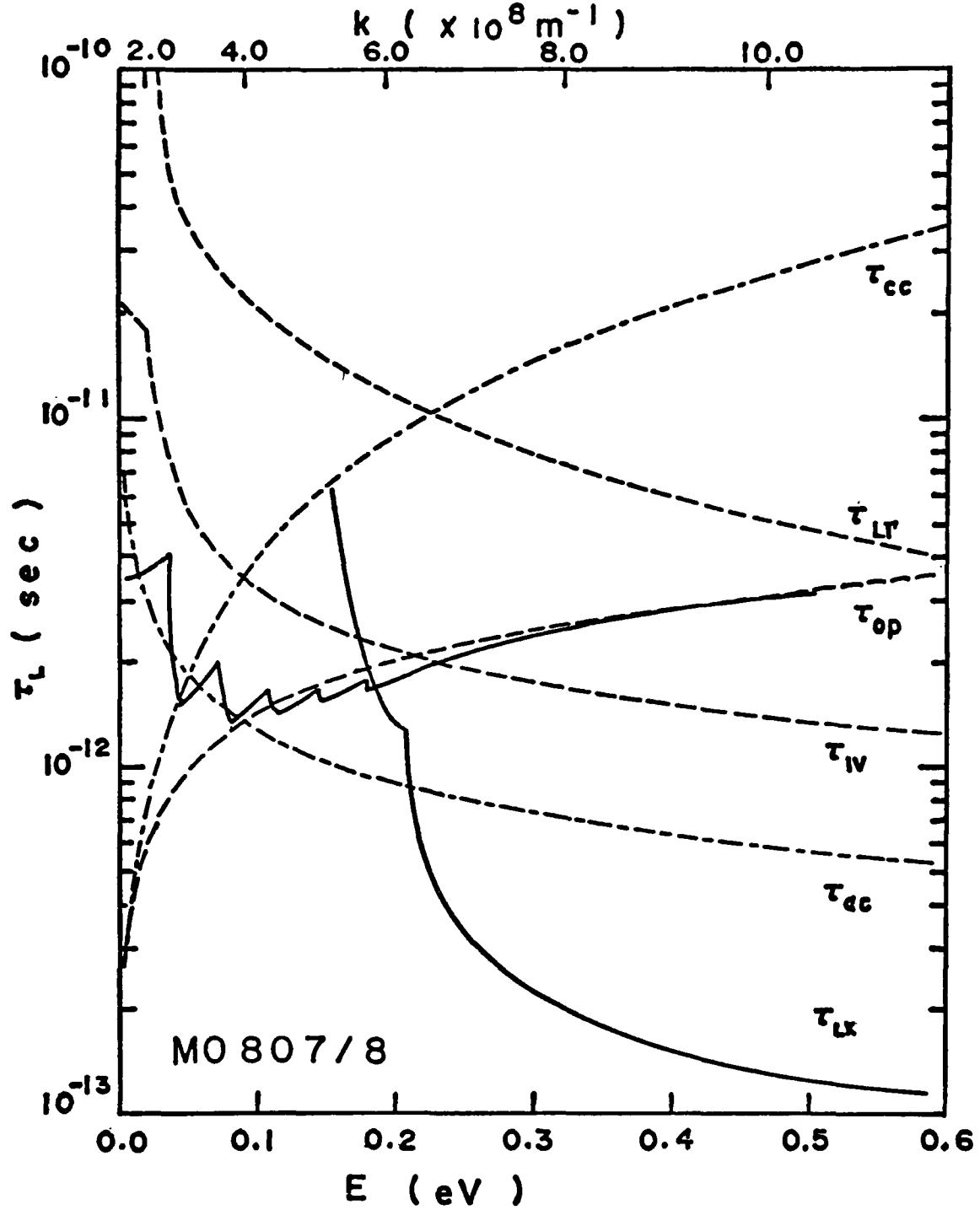


Fig. (IV-9) Relaxation times as a function of energy in the L_1 band with $E_{DL} = 16.1$ eV, $D_{LL} = 5 \times 10^{10}$ eV/m, $D_{LX} = 1.1 \times 10^{10}$ eV/m and the other parameters as used for the calculation of τ_T in Fig. (IV-8). The values of τ_{op} given by the full and dotted lines were calculated using the Fletcher and Butcher method (72F2) and the relaxation time approximation respectively.

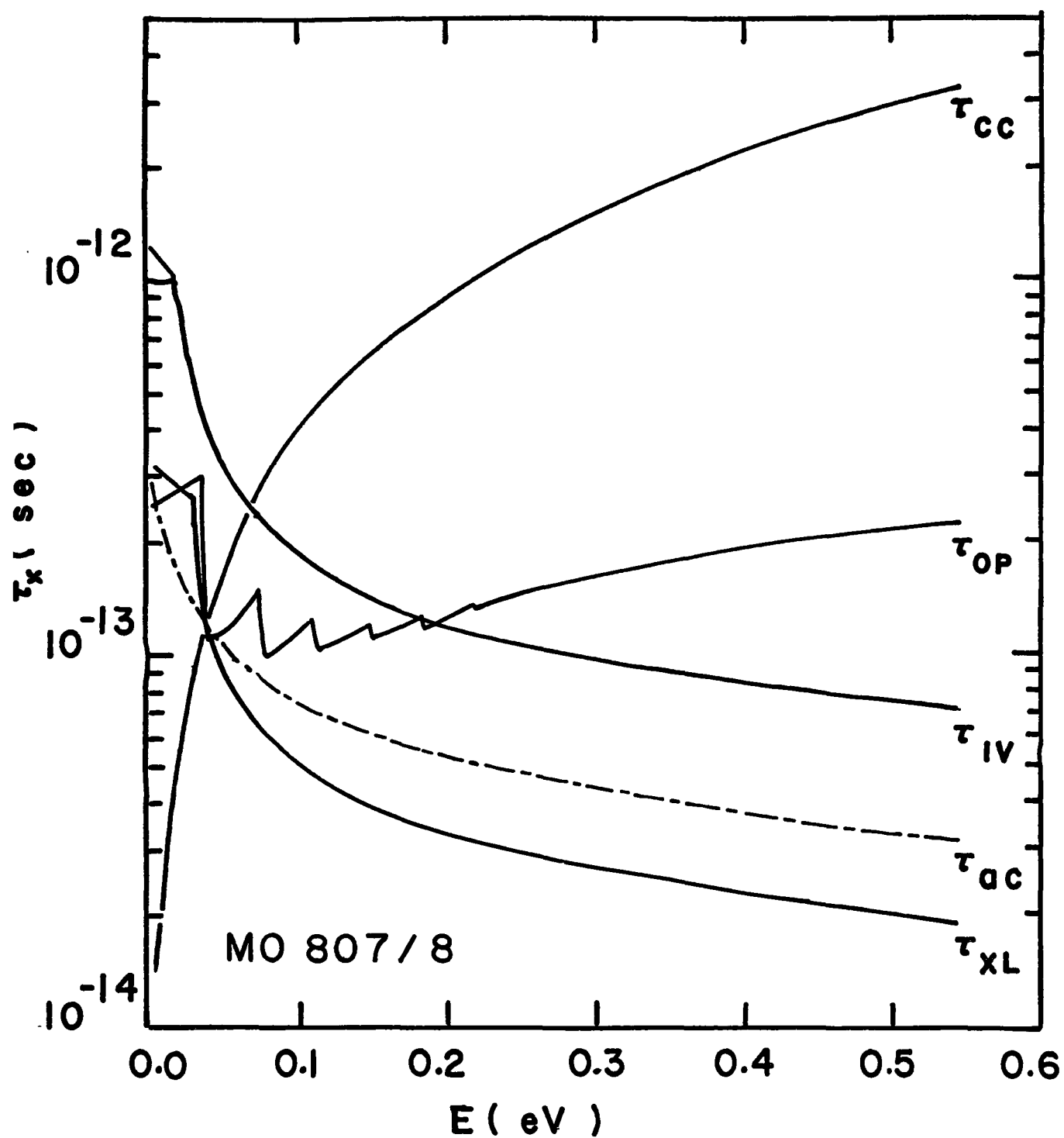


Fig. (IV-10) Relaxation times as a function of energy in the X_1 band with $E_{DX} = 12.5$ eV, $D_{XX} = 5 \times 10^{10}$ eV/m and the other parameter values as used for the calculation of τ_L in Fig. (IV-8).

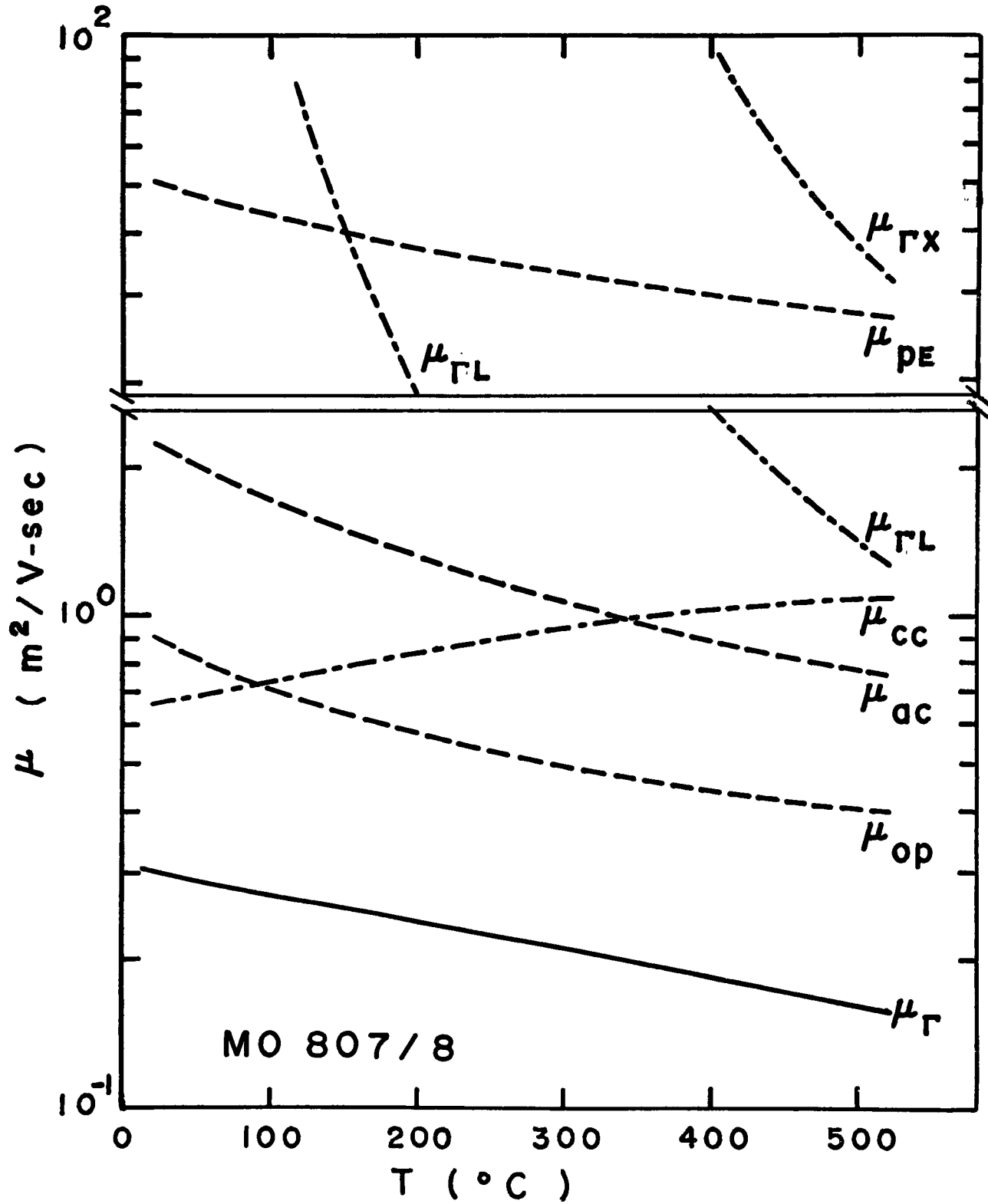


Fig. (IV-11) Carrier mobility as a function of temperature in the Γ_1 band. Calculation was made using the data given in Fig. (IV-8).

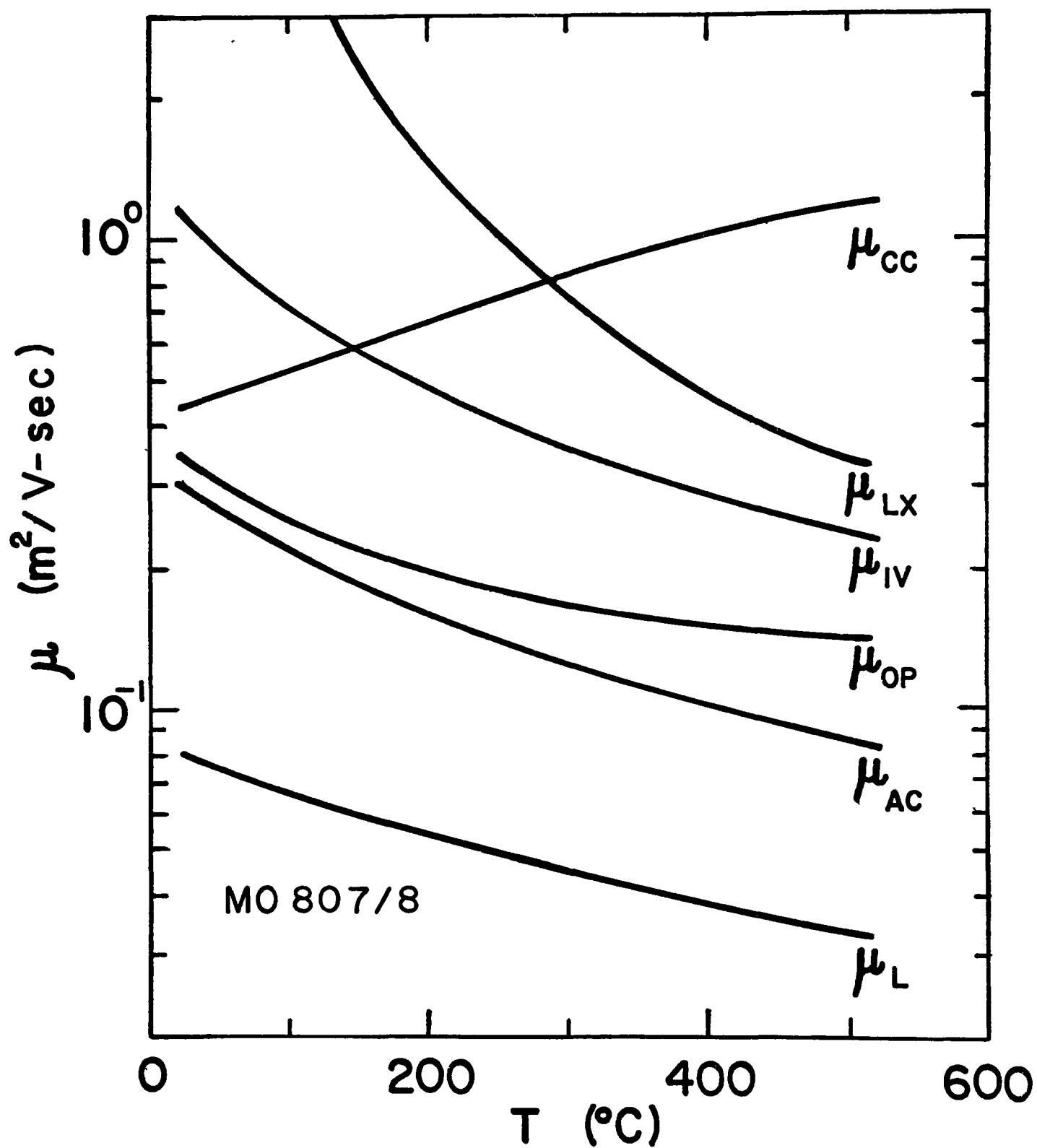


Fig. (IV-12) Carrier Mobility as a function of temperature in the L_1 band
 Calculation was made using the data given in Fig. (IV-9).

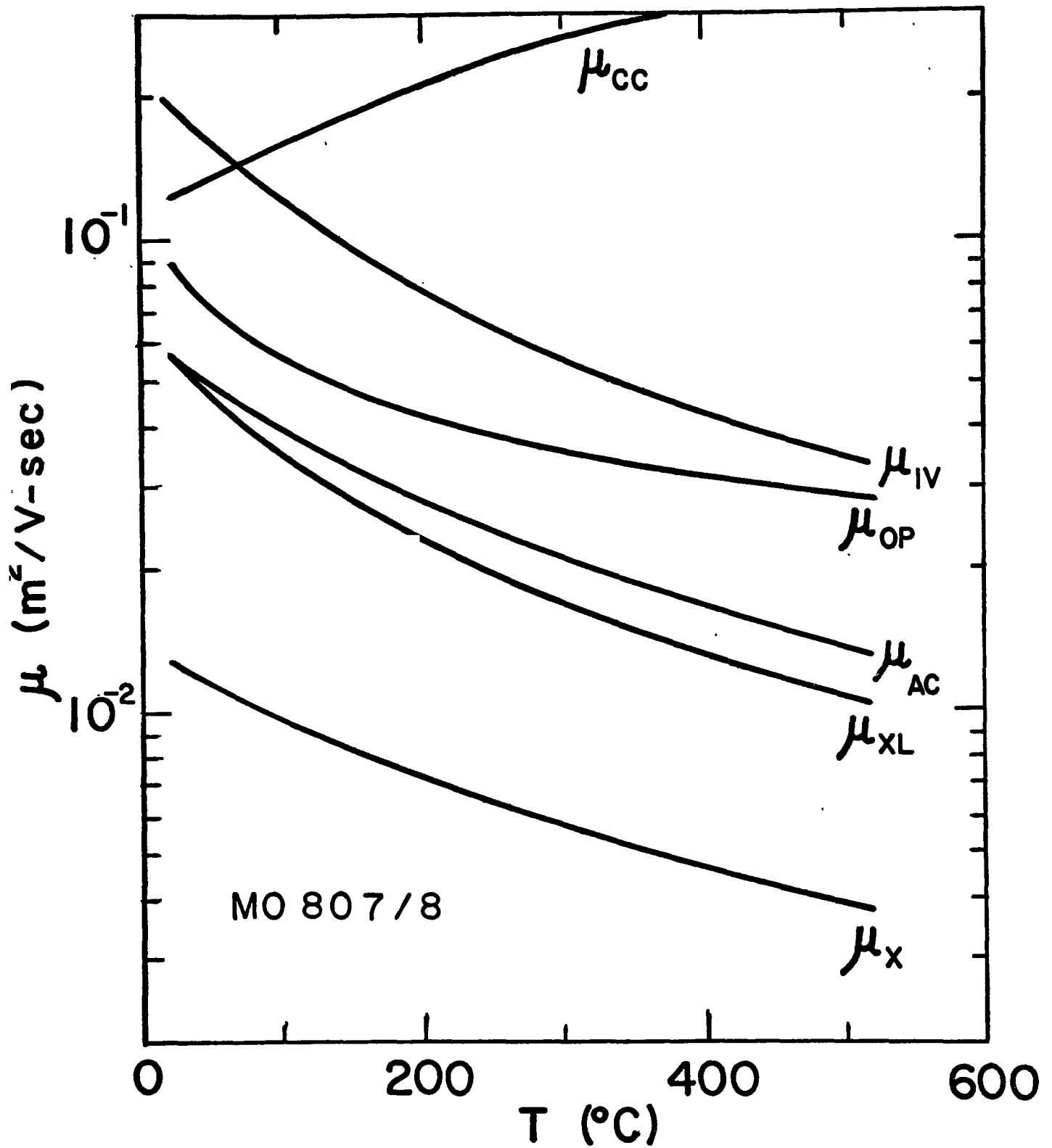


Fig. (IV-13) Carrier mobility as a function of temperature in the X_1 band
Calculation was made using the data given in Fig. (IV-10).

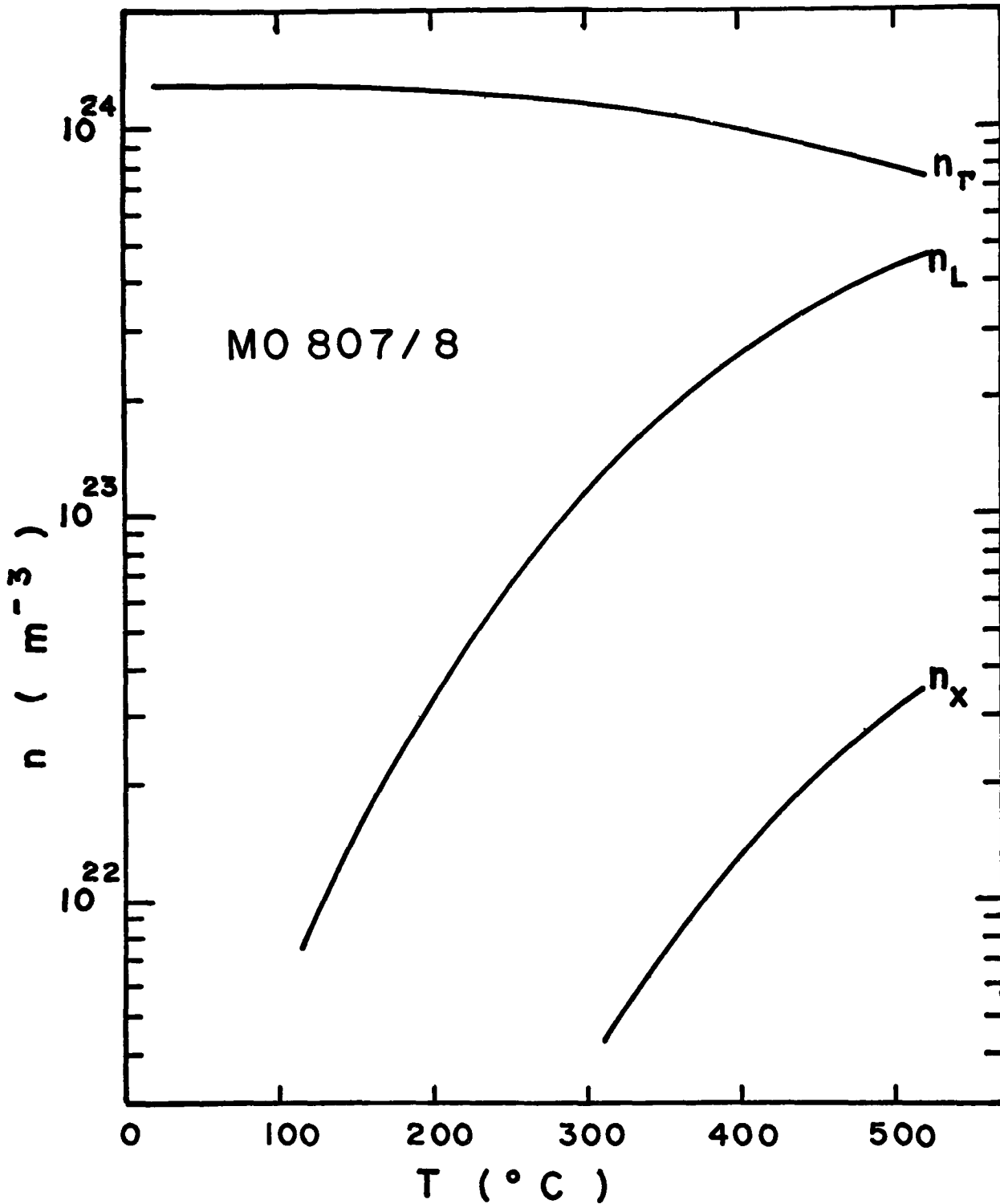


Fig. (IV-14) Carrier distribution in the three conduction bands of GaAs. Calculations carried out for sample MO807/8 using the following temperature variation of band minima: Γ_1 minimum, Thurmond (75T1) L_1 and X_1 minima, present analysis as shown in Fig. (IV-7).

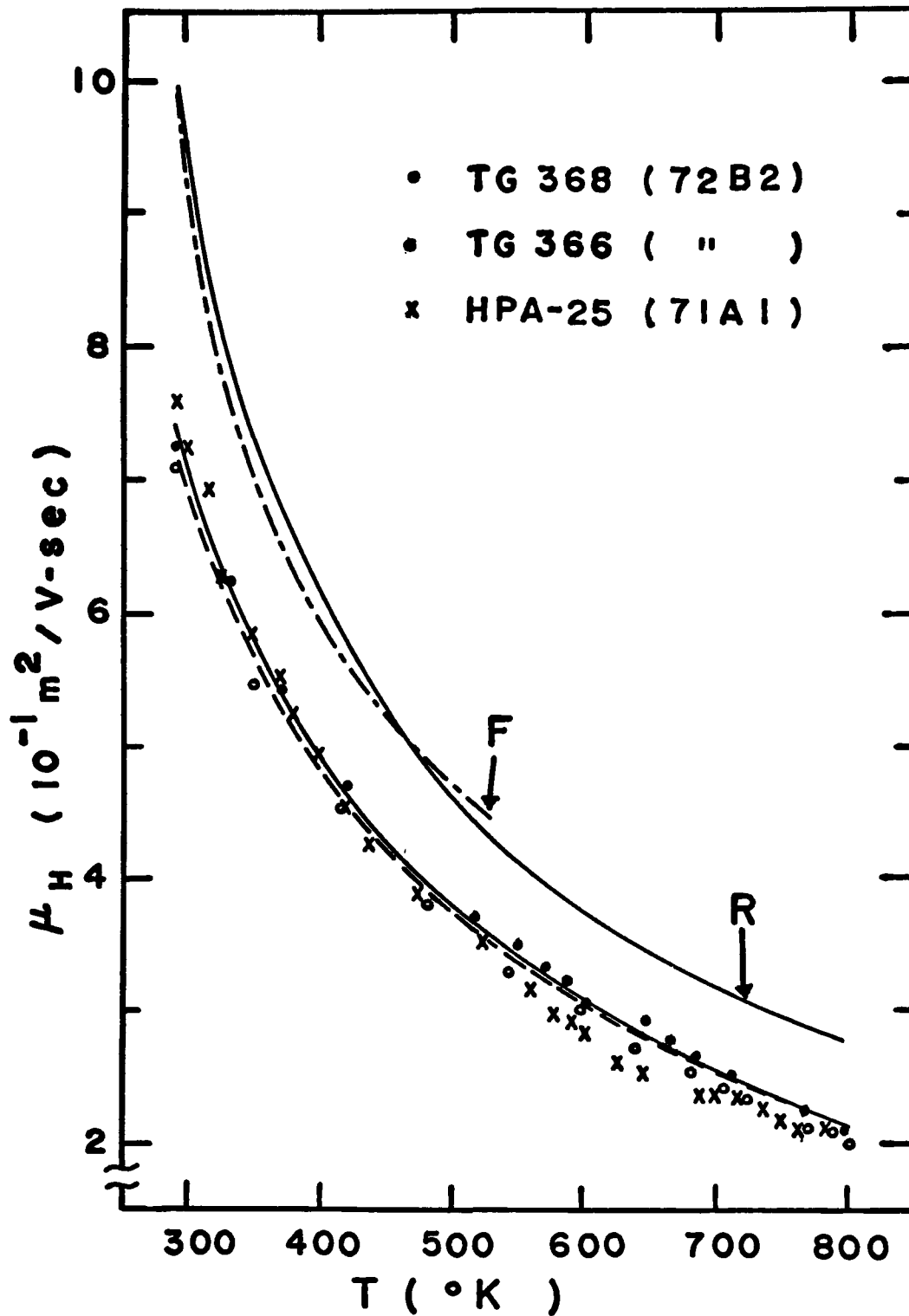


Fig. (IV-15) Comparison of theoretical curves with experimental Hall mobility data of Blood (72B2) and Akita et al. (71A1) for pure GaAs samples.

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——

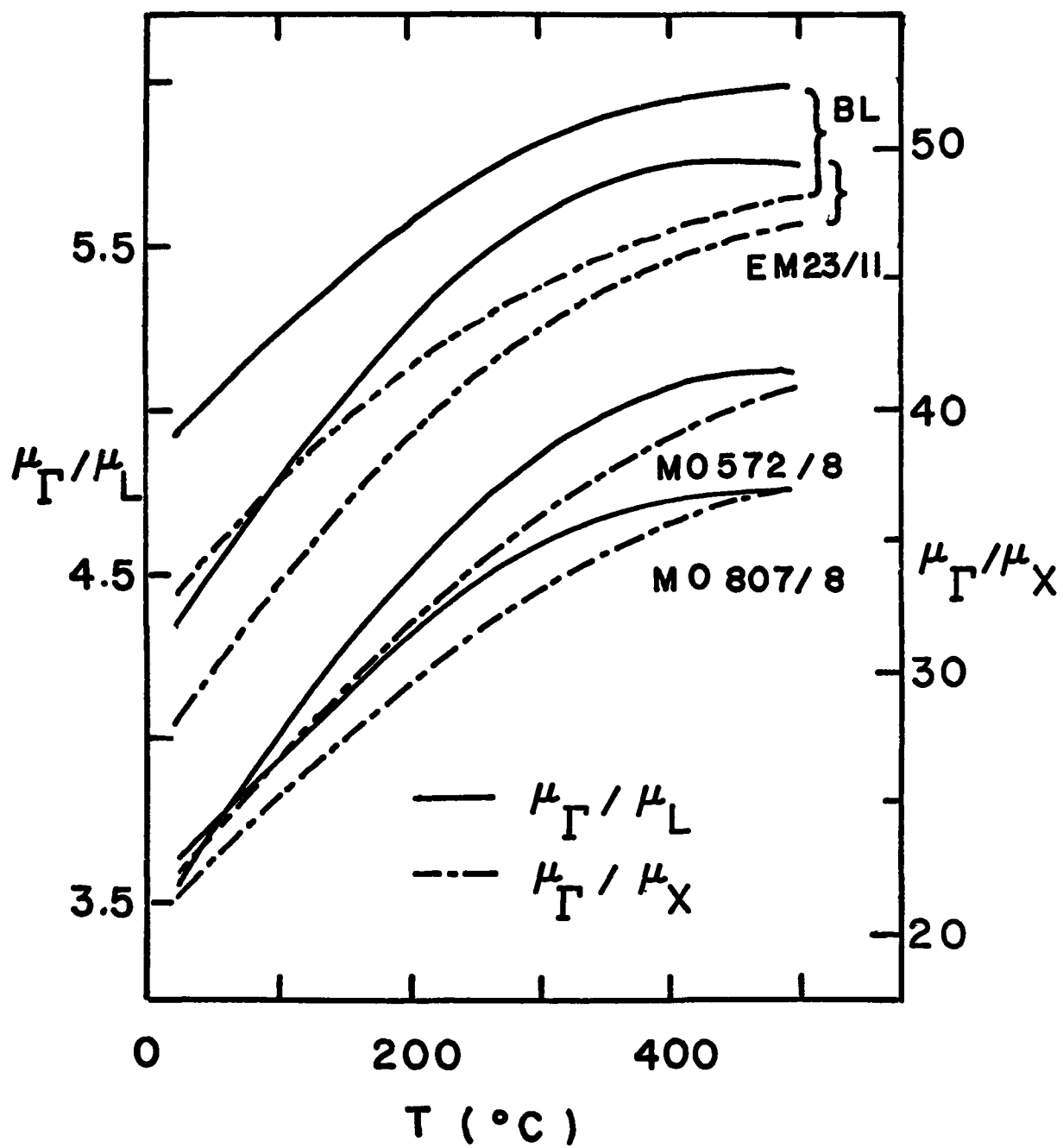


Fig. (IV-16) Mobility ratios μ_{Γ}/μ_L and μ_{Γ}/μ_X vs temperature for GaAs.

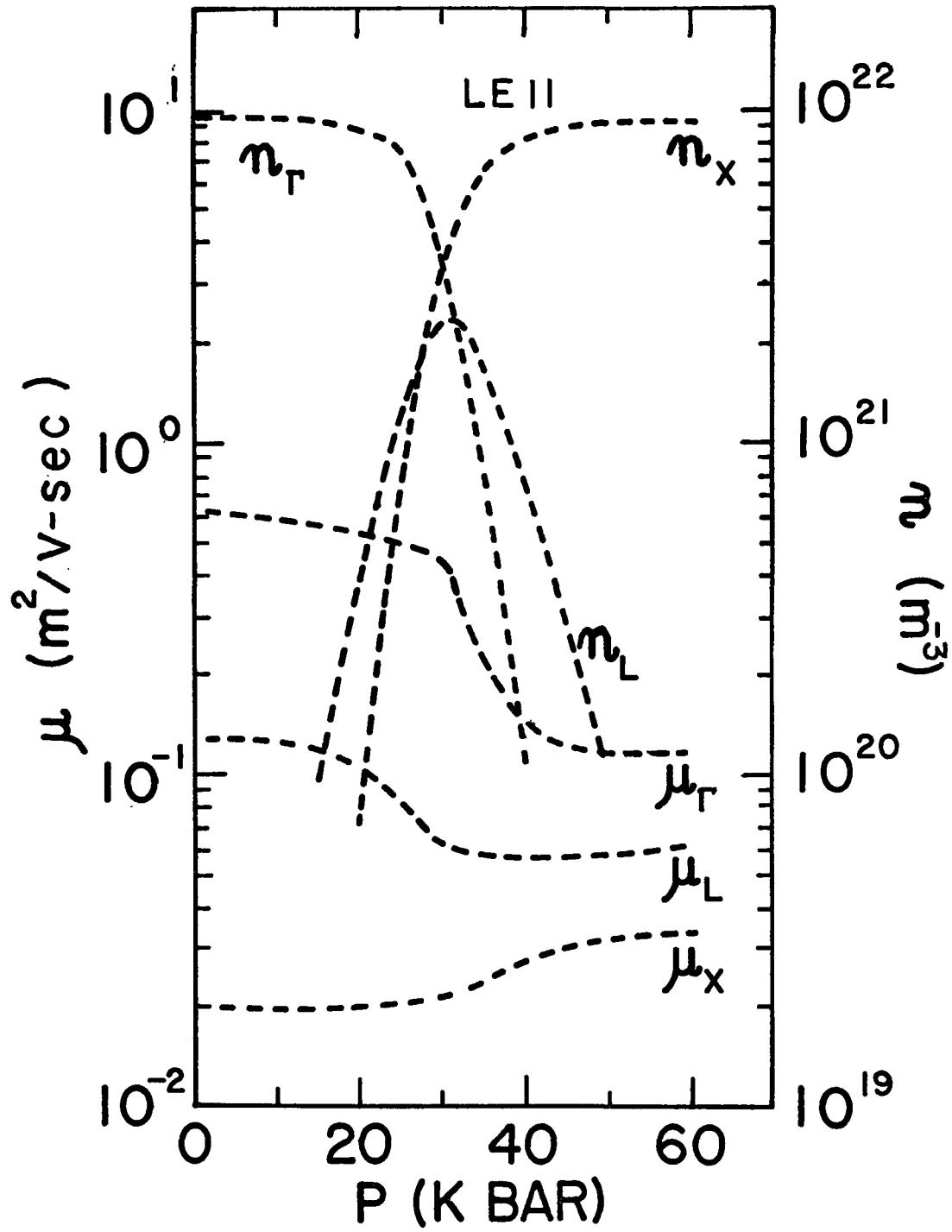


Fig. (IV-17) Mobility and carrier density variations with pressure in the three conduction bands for GaAs.

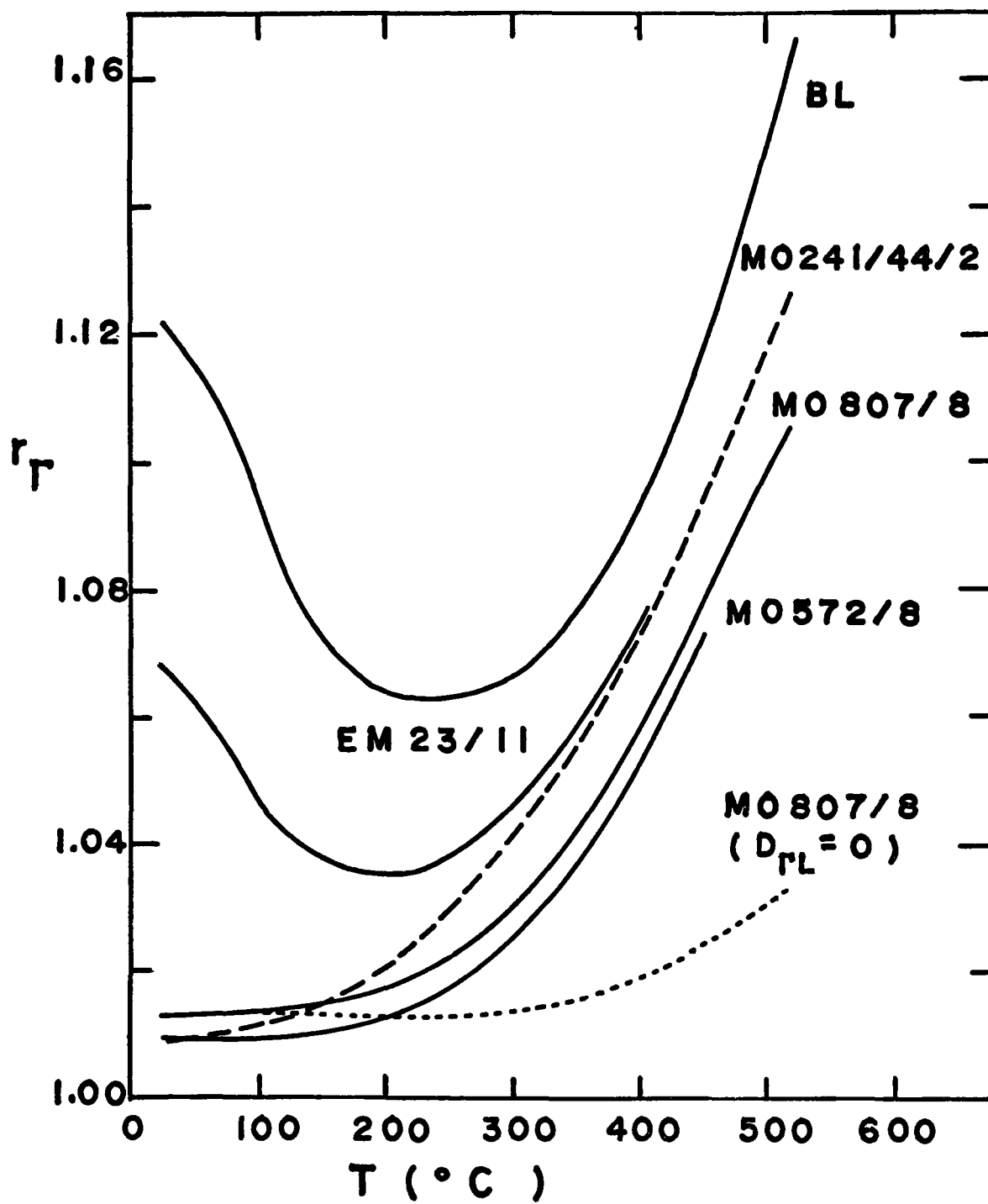


Fig. (IV-18) Hall scattering coefficient r_H vs. temperature for GaAs.

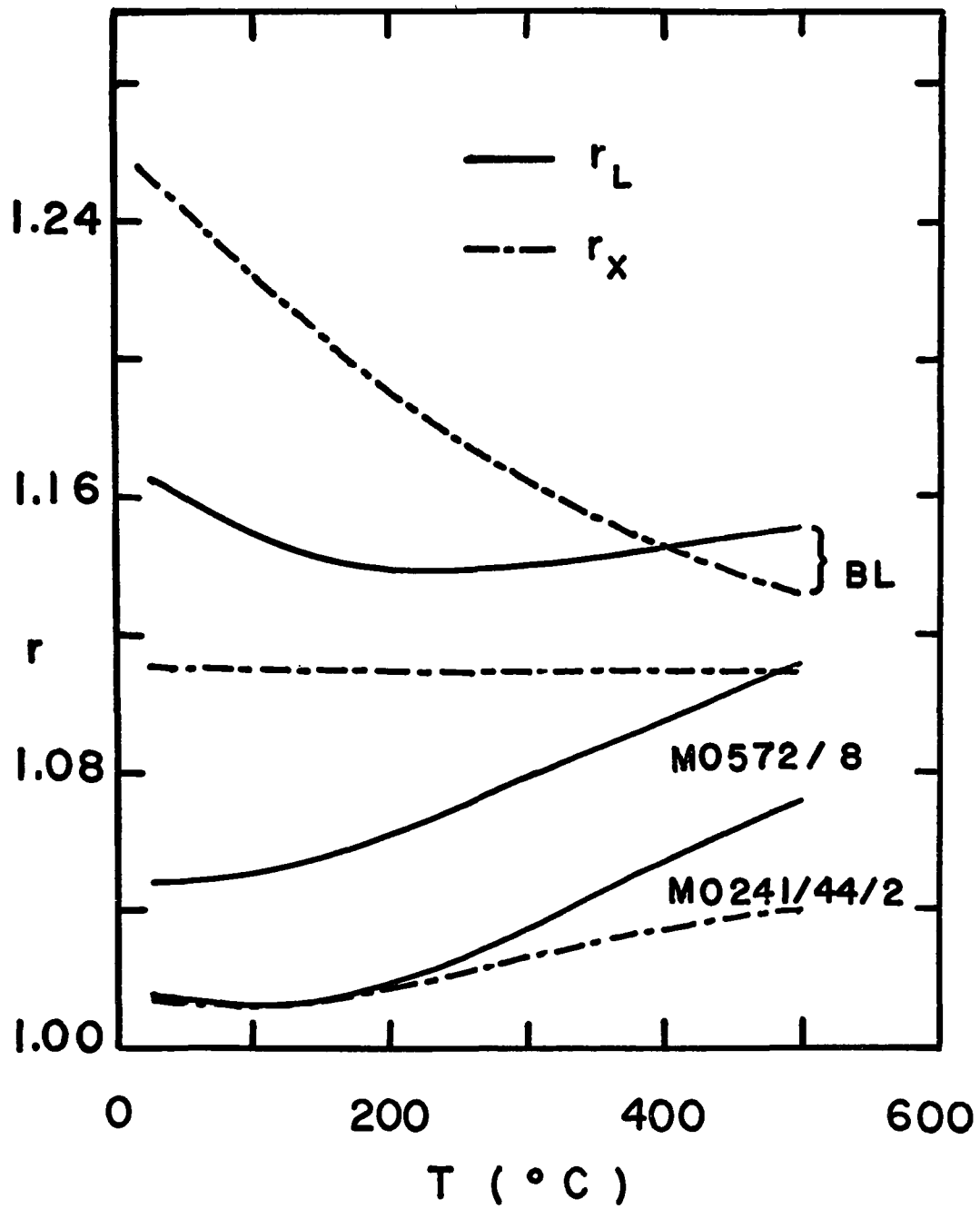


Fig. (IV-19) Hall scattering coefficients r_L and r_X vs. temperature for GaAs.

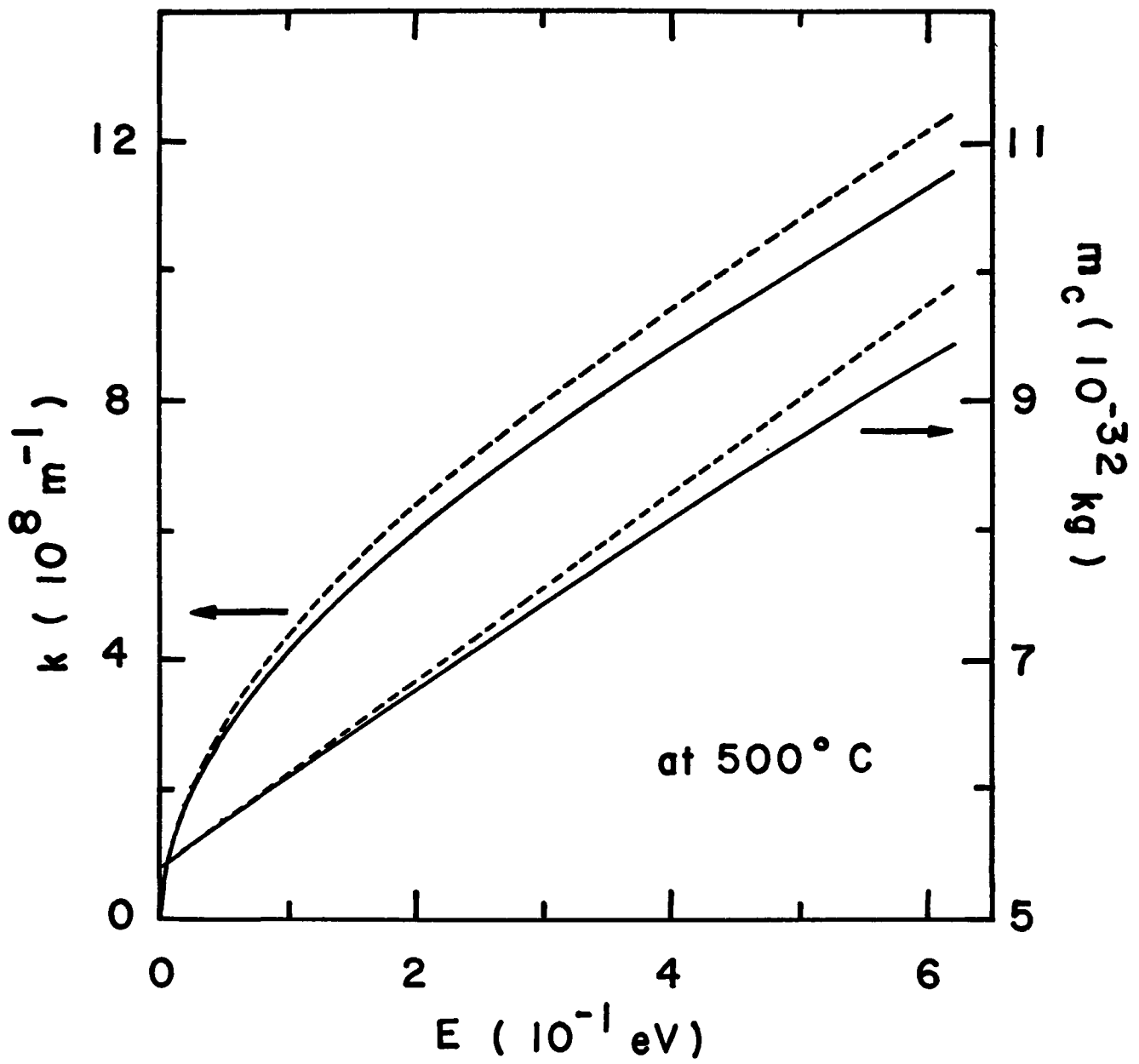
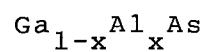


Fig. (IV-20) Energy and cyclotron effective mass as a function of wave vector near the Γ_1 point for GaAs;

— present model (small gap approximation)

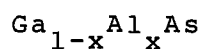
---- model with higher and lower bands included (66K1).

CHAPTER V



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CHAPTER V

V-1 Introduction

$\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 (66K4), optical absorption (69P1, 76M2), photoresponse (69C1) and electrophotorelectance (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_1 minima.

Onton et al. (71O1) measured the alloy composition dependence of the direct band gap in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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_1 minima they determined the direct-indirect

band crossover to be at $x = 0.44$ and $E_0 = 1.99$ 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 Γ_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 $dE_x/dT = -(4.2 \pm 0.3) \times 10^{-4}$ 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 $E_0 = 1.433 + 1.281x + 0.194x^2$. The temperature dependence of E_0 measured between 77 and 300 K shows $dE/dT = -(4.3 \pm 0.3) \times 10^{-4}$ 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 Γ_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 ± 0.01 at 4 and 293 K respectively. The effective mass variation of the Γ_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 $E_o = 1.424 + 1.266x + 0.26x^2$ (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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$. 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $10^{23} \sim 10^{25} \text{ m}^{-3}$. Analysis of the measured Hall coefficient shows that donor levels are located at $36 \sim 60$ meV below Δ_1 minima and that the density of states effective mass ranges between 1.45 and $1.84 m$. The measured mobilities were $0.007 \sim 0.015 \text{ m}^2/\text{V-sec}$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $Ga_{1-x}Al_xAs$ 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 Euvema (69S1) calculated the band structure of AlAs and the resultant indirect band gap was 2.38 eV. The same calculation locates the Γ_1 and L_1 minima at 2.5 and 2.57 eV respectively above the Γ_{15} state. Hess et al. (73H2) also calculated the band structure using a combination of the pseudopotential method with the k.p method. The Γ_1 , L_1 , and X_1 minima were shown to be at 3.21, 2.76 and 2.25 eV above the Γ_{15} in the calculation. The theoretical band structure locates the subsidiary band minima along Δ and Λ . The calculated

effective masses are $m_o = 0.15 m$, $m_t(\Delta) = 0.15 m$, $m_\ell(\Delta) = 1.32$, $m_t(\Delta) = 0.24 m$ and $m_\ell(\Delta) = 1.48 m$. Rheinlander et al. (72R1) measured the effective mass at the X_1 point in k-space in AlAs using the Faraday rotation experiment and the values obtained are $m_t = 0.19 m$ and $m_\ell = 1.1 m$.

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 σ 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 Γ_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 σ as is shown in Figs. (V-3, 4, 5); R_H increases and σ 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 σ 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 σ 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 σ 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 Γ_1 and X_1 (or Δ_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 $\langle 111 \rangle$ minima are not far above the $\langle 100 \rangle$ 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 Γ_1 and X_1 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ while designing a laser system; $m_o^* = 0.0636 + 0.0552x + 0.0092x^2$ (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_o^* 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 $m_t = 0.15$ m and $m_\ell = 1.32$ m in the L_1 band (73H2) and $m_t = 0.19$ m and $m_\ell = 1.1$ 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 Γ_1 minima are of critical importance in the transport calculation, and so the minima energy values have been treated as adjustable with the Γ_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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$, 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 $\text{InAs}_{1-x}\text{P}_x$, 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 $E_{D\Gamma}$, E_{DL} , E_{DX} , $D_{\Gamma L}$, $D_{\Gamma X}$, D_{LX} , D_{LL} and D_{XX} . To simplify the analysis, we have assumed that $E_{D\Gamma} = E_{DL}$ and $D_{LL} = D_{XX}$, 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 $\text{InAs}_{1-x}\text{P}_x$.

E_{DX} and D_{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

$$\mu_{A\ell\ell} = \frac{\sqrt{2\pi} e \hbar^4 N_o}{3m^*{}^{5/2} \sqrt{k_B T} x(x-1) (E_A - E_B)^2} \quad (V-1)$$

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.

$$\frac{1}{\tau_{A\ell\ell}} = m^{*3/2} x(x-1) E^{1/2} A_p \quad (V-2)$$

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 κ_∞ . The value of κ_∞ 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 κ_∞ value for the alloys while the low-frequency dielectric constant κ_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 Γ_1 minimum are more important than the values of Γ_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 Γ_1 band in this case. However, for the determination of the absolute energy values of the subsidiary band minimum, the energy value of the Γ_1 minimum needs to be known, but the experimental data on the Γ_1 minimum show considerable scatter as is shown in Fig. (V-1). The data on the Γ_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 Γ_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 Γ_1 and L_1 minima required adjustment to give a fit to the experimental R_H and σ data. The results place the Γ_1 minimum at 1.601, 1.635 and 1.662 eV above the Γ_{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 upto ~ 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 Γ_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_t 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 Γ_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 $\sim$ 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, $E_{D\Gamma}$, $D_{\Gamma L}$, 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 ,

g_1 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_{eff} " to determine n from $n = r_{\text{eff}}/R_H e$ at each temperature of observation. " r_{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 $\kappa_{\infty} = 10.91 - 2.31x$, $D_{XX} = (5 - x) 10^{10}$ and $E_{DX} = 12.5 - 10.75x$ and $A_p = 4.6 \times 10^{68}$. The expression for κ_{∞} gives a value of 8.6 ± 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 $Ga_{1-x}Al_xAs$ 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 ~ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $N_S Q_S = 9.6 \times 10^6 \text{ m}^{-1}$.

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 $E_{D\Gamma}$ and D_{LX} values given approximately by $E_{D\Gamma} = 16.1 - 13.5x$ and $D_{LX} = (11.0 - 10.5x) \times 10^{10}$ 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 $\pm 3\%$ from the above linear variation and the values are shown in Table (V-3). In the case of $D_{\Gamma L}$, 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 $D_{\Gamma L}$ for these last three compositions; $2.2 \sim 2.7 \times 10^{10}$ eV/m, are far lower than that for GaAs, but a similar low value, $D_{\Gamma X} = 3 \times 10^{10}$ eV/m, has been quoted by Neumann and Flohrer (74N1) for Hall mobility calculations in the direct-indirect transition region of $\text{Ga}_{1-x}\text{Al}_x\text{As}$. 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 Γ_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 $0.154 \pm 0.005 m$ 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_1 minima with temperature than that for GaAs which we assumed for the present analysis, and thus only α_x was adjusted and a value of $-(6.15 \pm 0.15) \times 10^{-4}$ eV/K gave the best fit for the two samples with $x = 0.40$ and 0.60. This value of α_x gives a 64.7 ± 1.6 meV change in the X_1 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 α_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 α_x for the best fit were a little different from that above, while the X_1 band contribution was not sufficient to determine α_x for lower Al-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 α_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 Γ_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 Γ_1 minimum still indicate the experimental data on the Γ_1 minima which show bowing are more consistent with the present work.

The values of "effective scattering factor r_{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_{eff} varies from 1.265 to 1.695 when the temperature is increased from 18.5 to 225^oC. Similarly the sample with $x = 0.335$ shows an r_{eff} variation from 1.46 to 1.865 over a similar temperature range, but r_{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 $N_{\text{cc}} = n_t + 2N_A$ 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 $\sim 1.5\%$ for the samples near the two compounds. Some discrepancies are observed for the samples of intermediate compositions and the worst fits, $\sim 3\%$ 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_1 in Eq. (II-67) has been assumed to be 2 in one analysis as in the case of GaAs (70P1) and $\text{GaAs}_{1-x}\text{P}_x$ (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 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 (70Pl), 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 (49Pl, 70Pl) 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 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 Γ_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

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

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 $E_X - E_d (=E_I)$ 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 $\text{GaAs}_{1-x}\text{P}_x$ (76A2).

C. Band Structure.

For no other III-V alloy system has the band structure been investigated so thoroughly as for $\text{Ga}_{1-x}\text{Al}_x\text{As}$. Most of the experimental data on the Γ_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 Γ_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 Γ_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 Γ_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 Γ_1 minimum used in the calculation for the alloys are shown for 0 and 295 K in Table (V-4). The value of the Γ_1 minimum energy at 295 K for AlAs is quoted from Onton's experimental data (70O1). The value for the Γ_1 minimum for GaAs is the one used in Chapter IV. A least squares fit to these data gives an expression for the Γ_1 minimum variation with x at 295 K as

$$E_o(295\text{ K}) = 1.425 + 1.155x + 0.37x^2 \quad (\text{V-5})$$

This bowing parameter is effectively an average value of those of two previous works (71O1, 71B1). Eq. (V-5) gives the energies of the Γ_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 $E_o(297\text{K}) = 1.424 + 1.247 x$ in the direct gap region,

which gives the Γ_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 Γ_1 minimum is very sensitive to the value of the Γ_1 minimum energy for AlAs. Mead and Spitzer (63M1) measured the Γ_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, $E_O(295\text{ K}) = 1.425 + 1.192x + 0.285x^2$. 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

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

Here the bowing parameter value is very low compared with that for the Γ_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 Γ_{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 $E_L = 2.363$ eV for AlAs which is a little higher than the estimated value by Dingle et al., $E_L = 2.25 \sim 2.35$ eV at 297 K (78C1), while theoretical calculations gave $E_L = 2.57$ 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

$$E_X(295 \text{ K}) = 1.911 + 0.005x + 0.245x^2 \quad (\text{V-7})$$

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;	$x = 0.432,$	$E_O = 1.992$ eV
	$\Gamma_1 - X_1$ crossover;	$x = 0.405,$	$E_O = 1.953$ eV
and	$L_1 - X_1$ crossover;	$x = 0.35,$	$E_L = 1.942$ 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,

$$\begin{array}{lll} \Gamma_1 - L_1 \text{ crossover;} & x = 0.424, & E_O = 2.075 \text{ eV} \\ \Gamma_1 - X_1 \text{ crossover;} & x = 0.38, & E_O = 2.011 \text{ eV} \\ \text{and } L_1 - X_1 \text{ crossover;} & x = 0.30, & E_L = 1.998 \text{ eV} \end{array}$$

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

$$\begin{aligned} E_L^V (L_3 - \Gamma_{15} \text{ energy difference}) &= -1.236 + 0.034x - 0.395x^2 \\ E_X^V (X_5 - \Gamma_{15} \text{ energy difference}) &= -3.089 + 0.135x + 0.225x^2 \end{aligned}$$

The two valence band points show opposite band bowing.

As has been indicated, Rode's estimated value of the effective mass for the Γ_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

$$m_o(0) = 0.066 + 0.088x \quad (V-9)$$

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

D. Multiplicity of Equivalent Valleys in the $\langle 111 \rangle$ and $\langle 100 \rangle$ Directions.

Theoretical prediction (73H2) and experimental analysis (73H3) of the optical data for AlAs suggest that the band minima to be found in the $\langle 100 \rangle$ and $\langle 111 \rangle$ 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 4.05×10^{10} to 2.4×10^{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 Λ_1 minima energy is 6 meV higher than that for the L_1 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 reasonable 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 Λ_1 and Δ_1 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 Λ_1 and Δ_1 band minima were required for a fit because the Γ_1 band plays an important role at this composition and when the energy values determined for the lower multiplicity case are used in the calculation with high multiplicity, the values of carrier density and mobility in the Γ_1 band are much reduced as compared with the values determined for the lower multiplicity case. With this resulting band structure, the carrier density in the Λ_1 band is only ~7% of the total density at the highest experimental temperature and thus a two-band model comprising

the Γ_1 and Λ_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 Λ_1 and Δ_1 minima are 2.01 and 2.008 eV respectively above the top of the Γ_{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 Λ_1 minima increases with x at approximately the same rate as the Γ_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 Λ_1 band calculation, the high values of the Λ_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 Γ_1 , L_1 and X_1 bands for these alloys. This recent report supports the lower multiplicity of the bands in the $\langle 111 \rangle$ and $\langle 100 \rangle$ 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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys and GaAs.

E. Some Scattering Parameter Values and Carrier Mobility

Some of the more important scattering parameters are the deformation potential E_{Di} , the interband scattering coupling coefficient D_{ij} and the intervalley scattering coupling coefficient D_{ii} . No work has been reported on these parameters for $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $E_{D\Gamma} = E_{DL}$, $D_{LL} = D_{XX}$ and $D_{\Gamma X} = D_{\Gamma L}$, 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

$$\begin{aligned}
 E_{D\Gamma} &= 16.1 - 13.5x & (\text{eV}) \\
 E_{DX} &= 12.5 - 10.75x & (\text{eV}) \\
 D_{LL} &= 5.0 - 1.0x & (10^{10} \text{ eV/m}) \\
 \text{and } D_{LX} &= 11.0 - 10.5x & (10^{10} \text{ eV/m}) \quad (\text{V-10})
 \end{aligned}$$

The values for $E_{D\Gamma}$ 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_{Γ_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 cross-overs occur. In the Γ_1 and X_1 bands, polar optical scattering is the dominant mechanism. Though the value of D_{Γ_L} is very low compared with that of GaAs, interband scattering plays a more important role in the Γ_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°C in the Γ_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 Γ_1 band. For the X_1 and L_1 bands, interband scattering into the Γ_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 μ_Γ 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 μ_Γ for $x > 0.4$, the alloys in this range have been assumed to have the same $D_{\Gamma L}$ 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 Γ_1 band for all compositions which required the Γ_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 μ_Γ 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_d^* values are 0.4097 and 0.341 m for GaAs and AlAs respectively. Thus the rapid increase in the μ_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 $r_{\text{eff}} = n_t R_H e$ has a maximum value, 2.4, at $x \sim 0.36$ 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 $3 \sim 4.5$ for the samples (70P1) treated in Chapter IV. The low maximum value of r_{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 $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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 $m_d = 1.32 \text{ m}$, 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

$m_t = 0.12 m$ was obtained. With this trial value ($m_t = 0.12 m$ for AlAs), the density of states effective mass for $x = 0.4$ is $0.24 m$, which is lower by 7.7% than that given by $m_t = 0.15 m$ for AlAs. With this lower value of m_d^* for $x = 0.4$, a fit was recovered by replacing 2.8×10^{10} with 3.0×10^{10} eV/m for $D_{\Gamma L}$, 6.8×10^{10} with 7.4×10^{10} eV/m for D_{LX} , 2.057 with 2.06 eV for $E_L(0)$ and 2.015 with 2.013 eV for $E_X(0)$. A considerable change (9%) is seen only for the value of D_{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 6.8×10^{10} to 6.5×10^{10} eV/m for D_{LX} , from 2.015 to 2.017 eV for $E_X(0)$. 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 (74C1). 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, $E_{D\Gamma} = 12.4$ 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_1 and X_1 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_1 and X_1 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_1 minima at 2.363 eV above the top of the Γ_{15} state at 295 K.

The assumption of the band minima at general points in the Λ_1 and Δ_1 directions gives results which are less satisfactory than those obtained assuming minima at the L_1 and X_1 points.

Scattering parameter values of $E_{D\Gamma}$ ($= E_{DL}$), E_{DX} and D_{LX} 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 $D_{\Gamma L}$ ($= D_{\Gamma X}$) for the samples with $x < 0.3$, but the best fits to the experimental data require almost constant value of $D_{\Gamma L}$ 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 Γ_1 band at all compositions considered and also in the X_1 band for the alloys of $x \geq 0.4$. For the samples near GaAs, acoustic deformation potential and interband scattering between the L_1 and X_1 bands are more important in the calculations for the X_1 band than is polar optical. In the L_1 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_1 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

Sample	T	R_H	σ	n_t	N_A
	$^{\circ}\text{C}$	$10^{-5} \text{ m}^3/\text{Coul}$	$10^3 \text{ Ohm}^{-1} \text{ m}^{-1}$	10^{23} m^{-3}	10^{23} m^{-3}
BL080	18.0	126.2	0.329	0.052	0.22
BL106	18.0	0.405	51.50	15.84	2.30
BL130	21.3	0.525	39.60	12.23	1.90
BL232	21.5	0.512	29.89	13.20	4.13
BL270	19.5	0.729	17.20	8.796	5.10
BL300	18.5	2.025	5.26	3.896	7.15
BL335	19.0	2.55	4.32	3.574	6.20
BL400	18.0	7.39	1.09	1.406	
BL520	19.0	3.58	1.16	1.681	-
BL600	21.0	2.30	1.85	2.584	
BL710	18.5	1.725	1.938	3.285	0.45
BL950	21.0	1.80	3.003	3.414	

Table V-1 Room temperature values of the Hall coefficient, conductivity and carrier density for the twelve samples of the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ 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

Parameter	Value	Ref.
$m_o(0)$	0.154 m	*
m_{tl}	0.15 m	(73H2)
m_{lL}	1.32 m	(73H2)
Δ_o	0.275 eV	(70O1)
Δ_l	0.2 eV	(70O1)
m_{tX}	0.19 m	(72R1)
m_{lX}	1.1 m	(72R1)
$h\omega_o$	0.0474 eV	(70I2)
C_l	$13.4 \times 10^{10} \text{ N/m}^2$	(75W2)
κ_s	10.0	(70M1)
κ_∞	9.5 ± 0.1	*
E_{DX}	$1.8 \pm 0.3 \text{ eV}$	*
D_{XX}	$(4.0 \pm 0.2) \times 10^{10} \text{ eV/m}$	*
ρ	3598 kgm/m^3	(75w2)

Table V-2 Material parameters of AlAs. *-determined
in the present analysis.

Table V-3

Sample	$E_{D\Gamma}$ eV	$D_{\Gamma L}$ 10^{10} eV/m	D_{LX} 10^{10} eV/m	α_X 10^{-4} eV/K
BL080	15.1	6.4	10.2	-6.65
BL106	14.5	5.9	10.0	-6.53
BL130	14.2	5.4	9.6	-6.47
BL232	13.0	3.7	8.7	-6.28
BL270	12.3	3.0	8.3	-6.23
BL300	11.7	2.5	8.1	-6.20
BL335	11.2	2.2	7.5	-6.17
BL400	10.8	2.7	6.8	-6.15
BL520	9.0	-	5.8	-6.15
BL600	7.8	-	4.8	-6.15

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

Table V-4

Composition x	E _O eV		E _L eV		E _X eV	
	0 K	295 K	0 K	295 K	0 K	295 K
0.000	1.519	1.425	1.821	1.734	1.981	1.911
0.081	1.608	1.514	1.873	1.786	1.981	1.913
0.106	1.639	1.545	1.882	1.795	1.981	1.914
0.130	1.674	1.580	1.898	1.811	1.982	1.915
0.232	1.802	1.708	1.951	1.864	1.994	1.929
0.270	1.855	1.764	1.976	1.889	1.994	1.929
0.300	1.899	1.805	1.994	1.907	1.998	1.934
0.335	1.938	1.844	2.033	1.946	2.003	1.940
0.400	2.040	1.946	2.057	1.970	2.015	1.952
0.520	2.220	2.126	2.157	2.070	2.043	1.979
0.600		-	2.177	2.090	2.066	2.002
0.710	-				2.102	2.038
0.950	-	-		-	2.200	2.136
1.000	3.044	2.950	2.450	2.363	2.224	2.160

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

Table V-5

X	$g_1 = 2$		$g_1 = 6$		N_A 10^{23} m^{-3}
	N_D	E_d eV	N_D	E_d eV	
0.335	17.7	0.102	19.0	0.081	6.2
	11.6	0.126	13.8	0.103	-
0.40	5.3	0.133	6.9	0.115	-
0.52	6.9	0.118	9.7	0.102	-
0.60	7.5	0.102	10.4	0.083	-
0.71	7.4	0.070	9.1	0.054	0.45
	6.8	0.075	8.4	0.058	-
0.95	7.3	0.086	9.1	0.065	-

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

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

T °C	E _F eV	Γ_1			L_1			X_1		
		μ	r	n 10 ²⁴	μ	r	n 10 ²³	μ	r	n 10 ²¹
18	0.0546	0.2045	1.021	1.58	0.0613	1.020	0.043	0.0133	1.032	0.067
60	0.0512	0.1958	1.022	1.57	0.0560	1.027	0.130	0.0118	1.033	0.32
100	0.0472	0.1881	1.022	1.55	0.0515	1.033	0.302	0.0106	1.035	1.03
140	0.0424	0.1804	1.022	1.52	0.0474	1.043	0.597	0.0096	1.037	2.66
180	0.0364	0.1735	1.023	1.47	0.0439	1.054	0.040	0.0087	1.040	5.77
225	0.0280	0.1648	1.025	1.40	0.0404	1.066	1.730	0.0079	1.043	1.17

Table V-6 Results of the analysis for sample BL106. Unit of μ is m²/V-sec and carrier density is given per m³. E_F was calculated with respect to the Γ_1 minimum.

Table V-7

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

Table V-7 Results of the analysis for sample BL232. Unit of μ is $m^2/V\text{-sec}$ and carrier density is given per m^3 . E_F was calculated with respect to the Γ_1 minimum.

Table V-8

T °C	E _F eV	Γ_1			L ₁			X ₁		
		μ	r	n 10 ²³	μ	r	n 10 ²³	μ	r	n 10 ²³
18.5	-0.0213	0.1111	1.060	2.553	0.0408	1.034	0.913	0.0157	1.029	0.433
60	-0.0314	0.1076	1.055	2.494	0.0368	1.034	1.504	0.0141	1.024	0.692
100	-0.0449	0.1038	1.052	2.232	0.0336	1.035	2.021	0.0128	1.022	0.903
140	-0.0615	0.0999	1.050	1.903	0.0309	1.038	2.423	0.0116	1.021	1.053
180	-0.0810	0.0978	1.043	1.568	0.0280	1.043	2.683	0.0107	1.022	1.137
225	-0.1049	0.0943	1.039	1.260	0.0270	1.049	2.879	0.0098	1.022	1.192

Table V-8 Results of the analysis for sample BL300. Unit of μ is m²/V-sec and carrier density is given per m³. E_F was calculated with respect to the Γ_1 minimum.

Table V-9

T °C	E _F eV	Γ_1			L_1			X_1		
		μ	r	$n \cdot 10^{22}$	μ	r	$n \cdot 10^{23}$	μ	r	$n \cdot 10^{23}$
18.5	-0.1236	0.2167	1.094	0.567	0.0632	1.173	0.351	0.0324	1.150	0.999
60.5	-0.1332	0.1742	1.066	0.919	0.0503	1.148	0.675	0.0254	1.133	1.461
104.0	-0.1468	0.1463	1.046	1.236	0.0416	1.127	1.063	0.0206	1.117	1.837
125.0	-0.1555	0.1373	1.042	1.318	0.0385	1.121	1.214	0.0189	1.109	1.917
127.0	-0.1768	0.1213	1.034	1.437	0.0334	1.112	1.533	0.0160	1.093	2.024
222.0	-0.2041	0.1093	1.032	1.414	0.0301	1.114	1.734	0.0140	1.087	1.961

Table V-9 Results of the analysis for the sample BL400. Unit of μ is $\text{m}^2/\text{V-sec}$ and carrier density is given per m^3 . E_F was calculated with respect to the Γ_1 minimum.

Table V-10

T °C	E _F eV	Γ_1	L ₁			X ₁		
			μ	r	n 10 ²²	μ	r	n 10 ²³
21	-0.1057		0.0676	1.123	0.69	0.043	1.110	2.50
60	-0.1160		0.0552	1.098	1.68	0.035	1.090	3.45
100	-0.1297		0.0470	1.081	3.20	0.030	1.076	4.12
140	-0.1464		0.0413	1.069	5.05	0.026	1.067	4.44
180	-0.1654		0.0370	1.062	7.02	0.023	1.061	4.50
225	-0.1894		0.0336	1.057	9.10	0.021	1.057	4.36

Table V-10 Results of the analysis for sample BL600. Unit of μ is m²/V-sec and carrier density is given per m³. E_F was calculated with respect to the X₁ minima.

Table V-11

T °C	E_F eV	Γ_1	L_1	x_1		
				μ	r	$n \cdot 10^{23}$
21	-0.0957			0.061	1.112	3.40
60	-0.1084			0.051	1.085	4.12
100	-0.1223			0.044	1.063	4.43
140	-0.1380			0.040	1.049	5.16
180	-0.1540			0.036	1.038	5.37
225	-0.1734			0.033	1.030	5.61

Table V-11 Results of the analysis for sample BL950. Unit of μ is $m^2/V\text{-sec}$ and carrier density is given per m^3 . E_F was calculated with respect to the Γ_1 minimum.

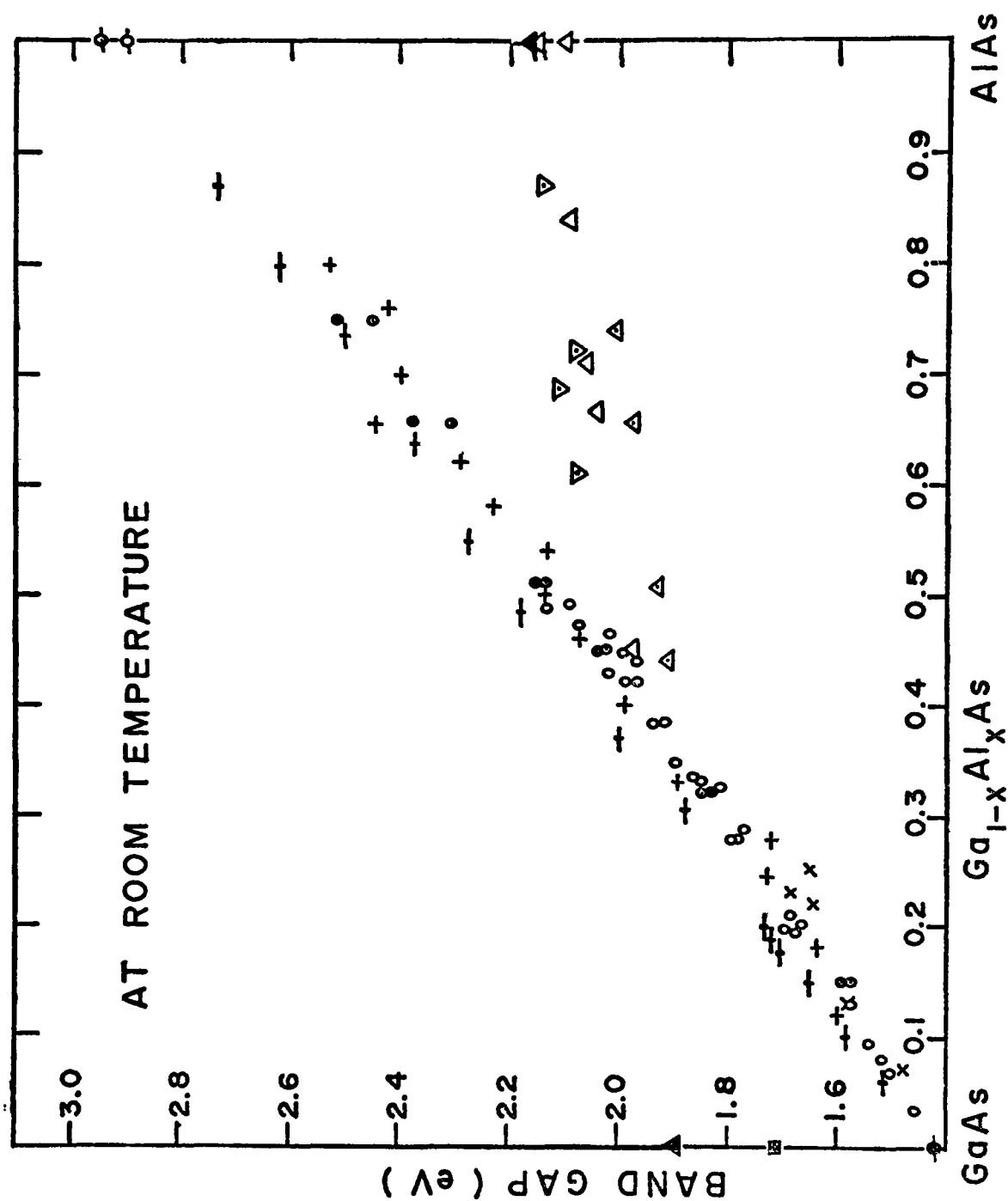


Fig. (V-1) Experimental data on the band gap in the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ system;
 O (73P1), $\odot$ and Δ (69C1), $\bullet$ (71B1), + (75K1), X and ∇ (66B2),
 + (76M2), Δ (76N2), $\oplus$ (76O1), $\ominus$ and $\uparrow$ (63M1), $\blacktriangle$ (70L1),
 $\triangle$ (71Y1) and $\clubsuit$, $\blacksquare$ and $\blacktriangle$ (see chapter IV).

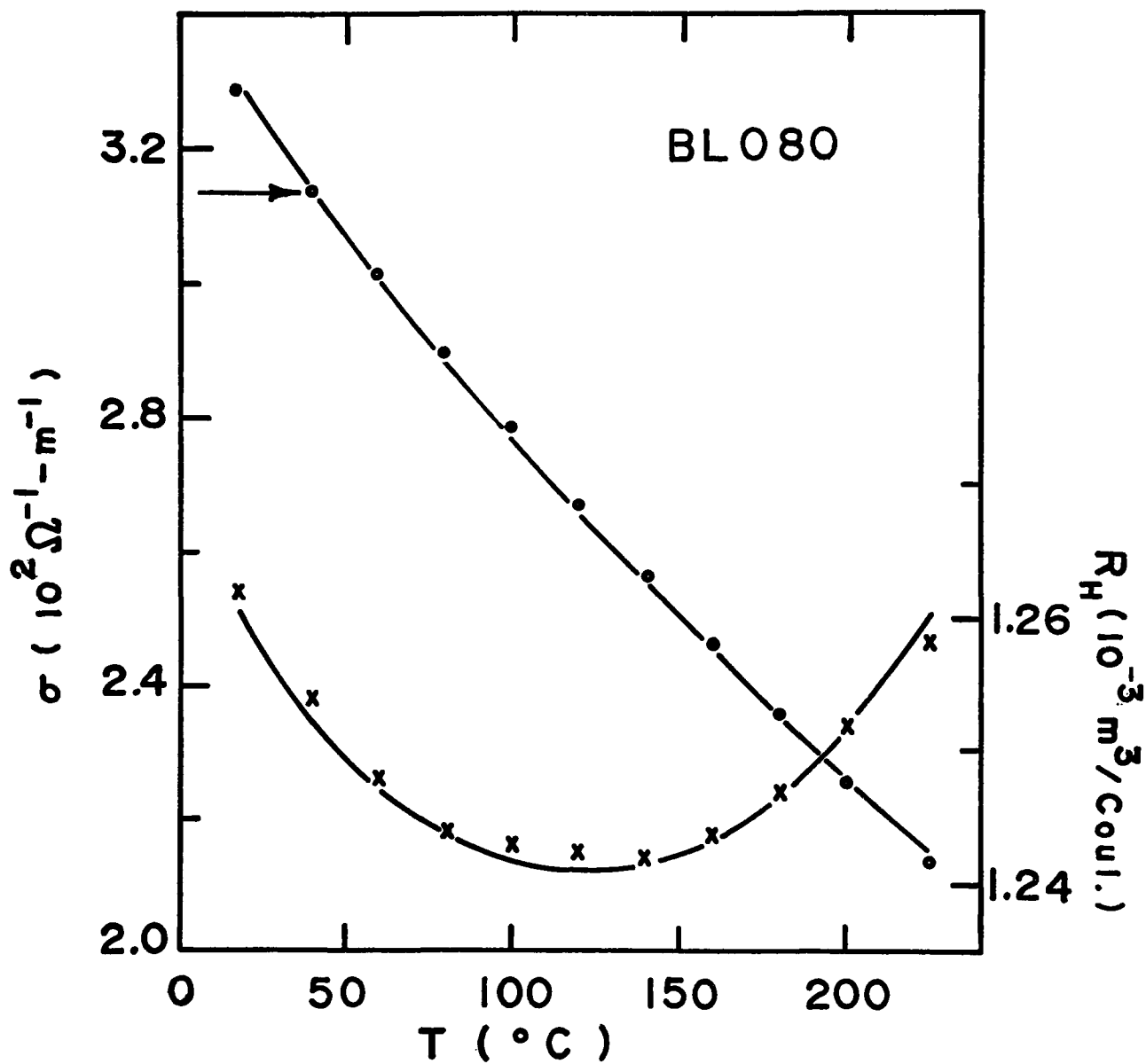


Fig. (V-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL080 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

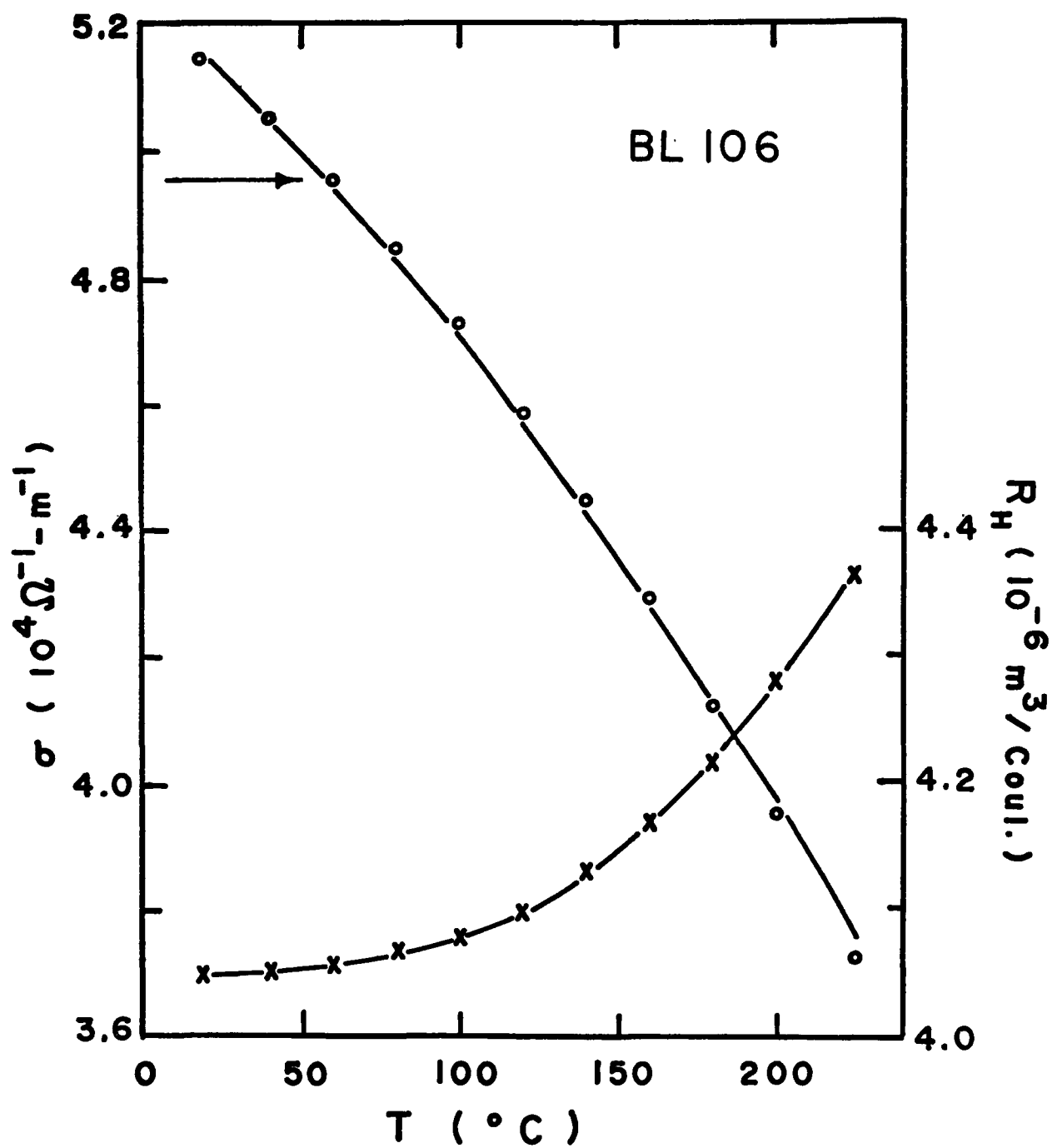


Fig. (V-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL106 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$

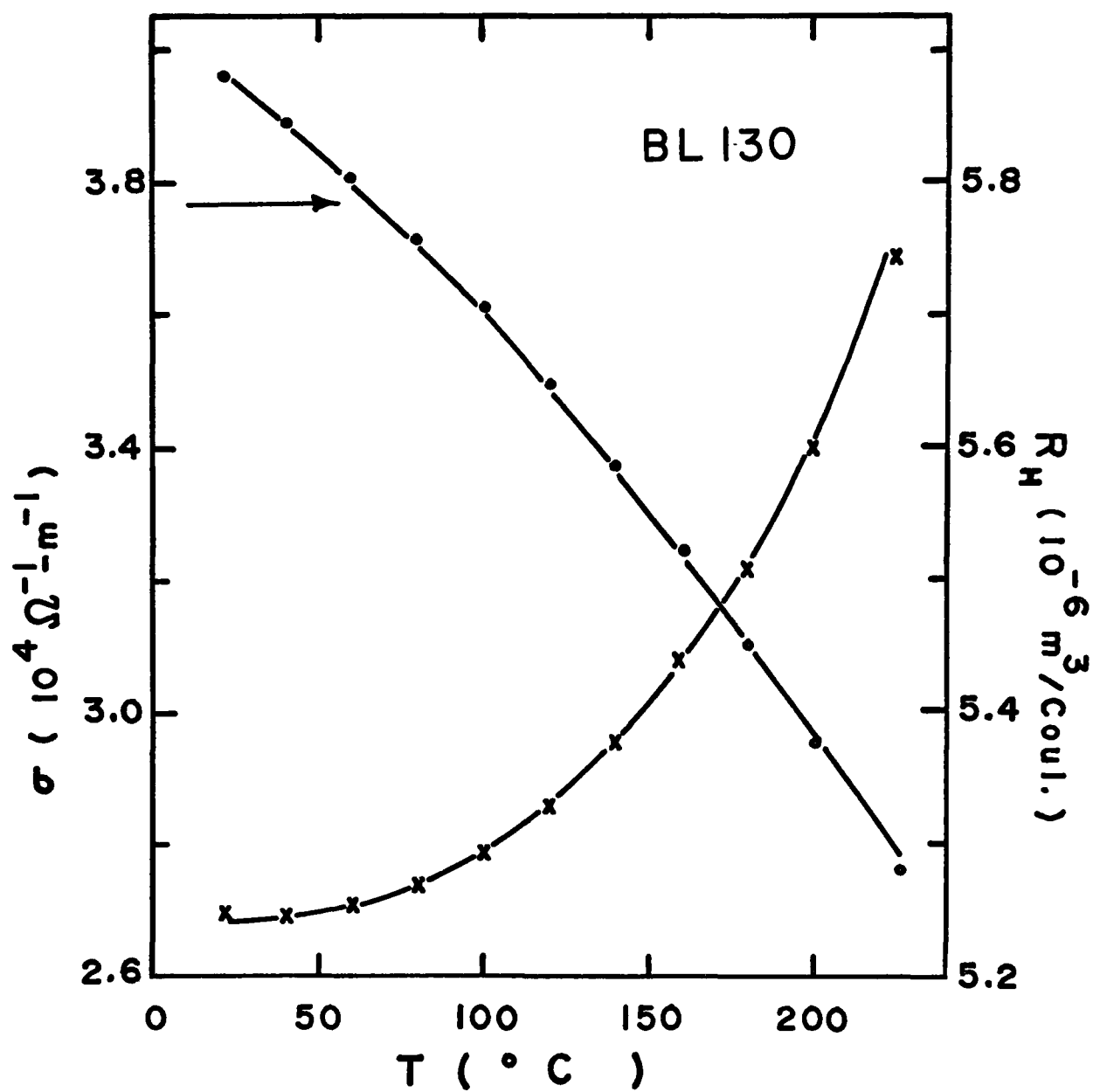


Fig. (V-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL130 of $Ga_{1-x}Al_xAs$

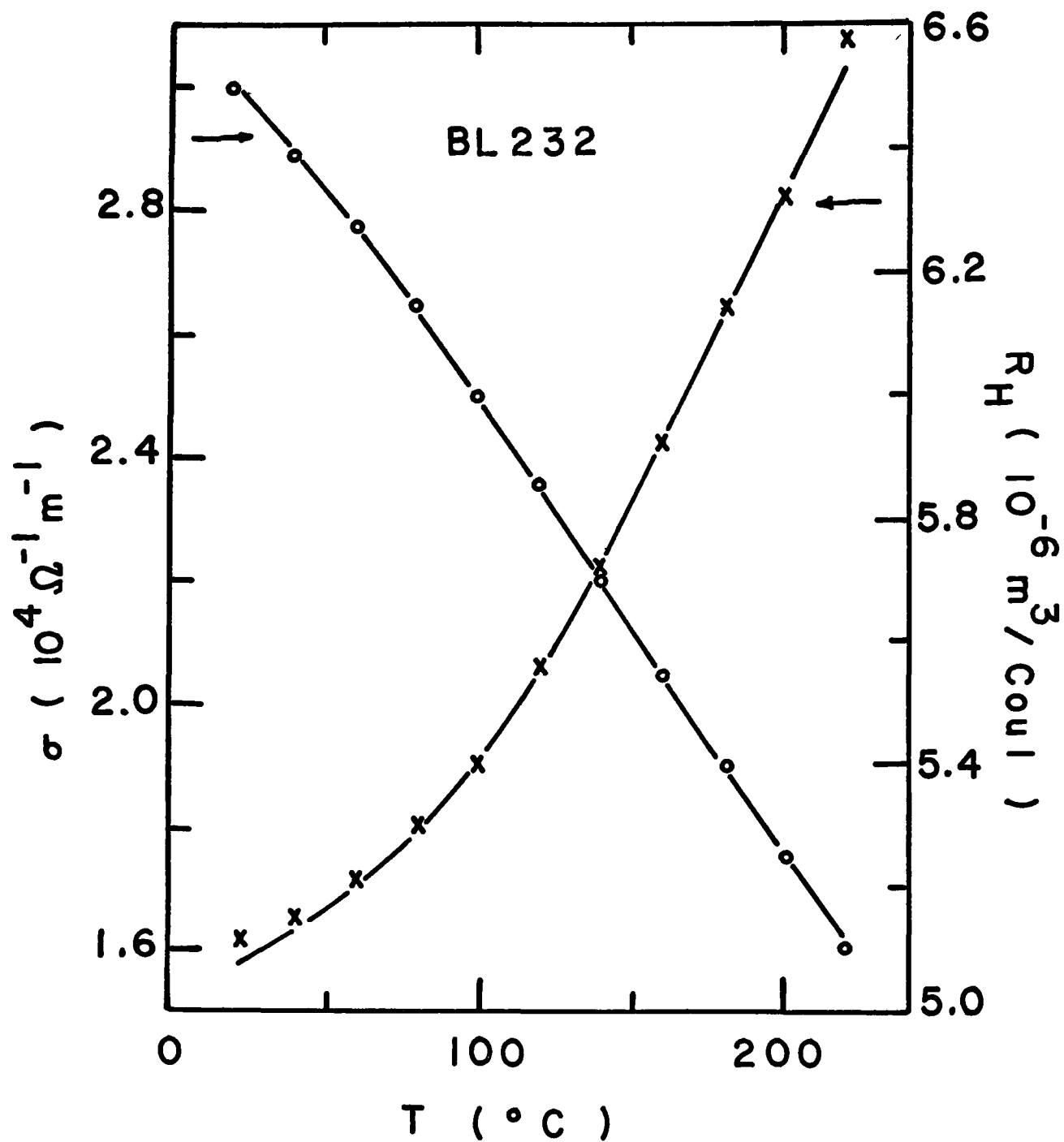


Fig. (V-5) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL232 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

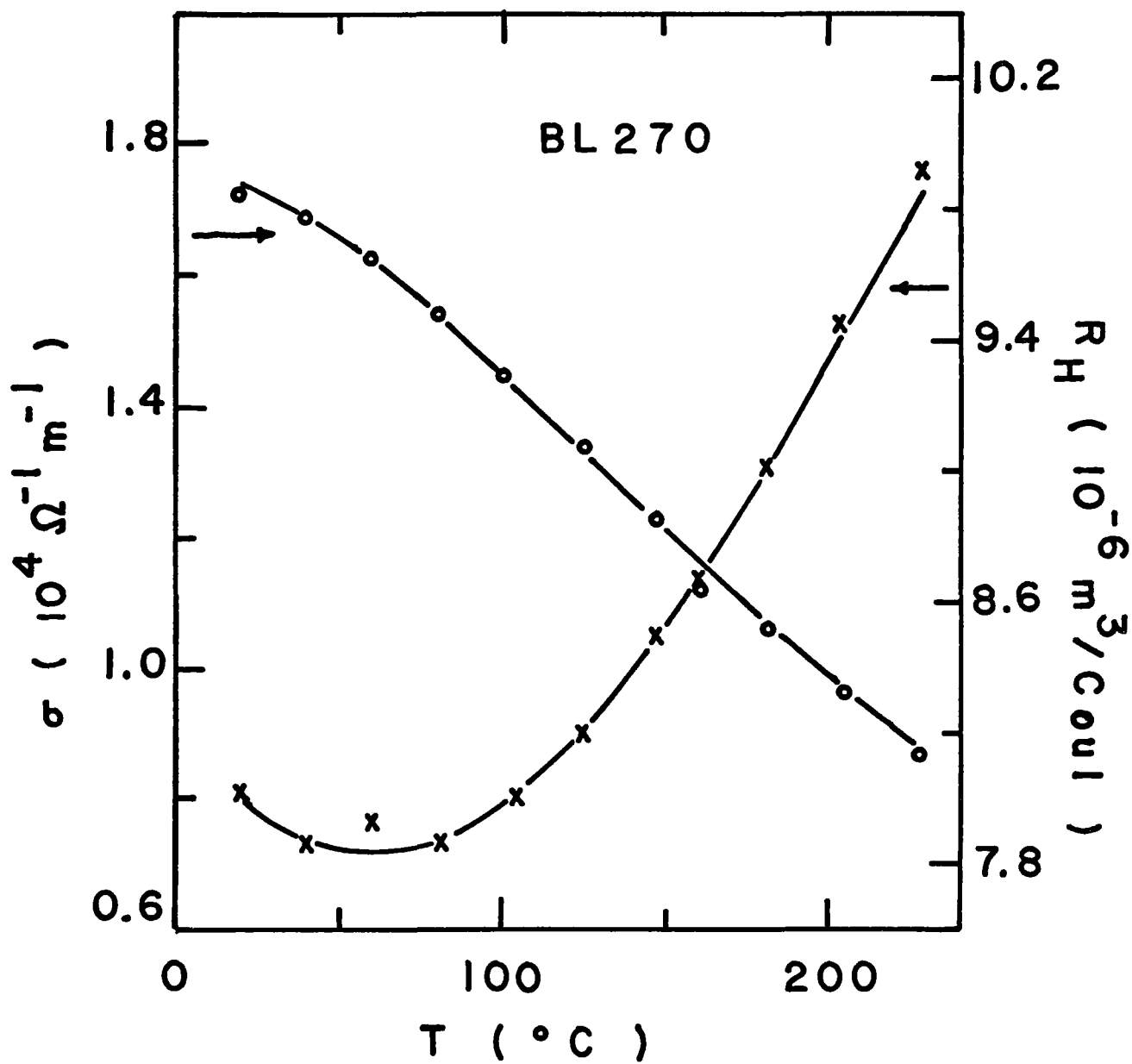


Fig. (V-6) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL270 of $Ga_{1-x}Al_xAs$.

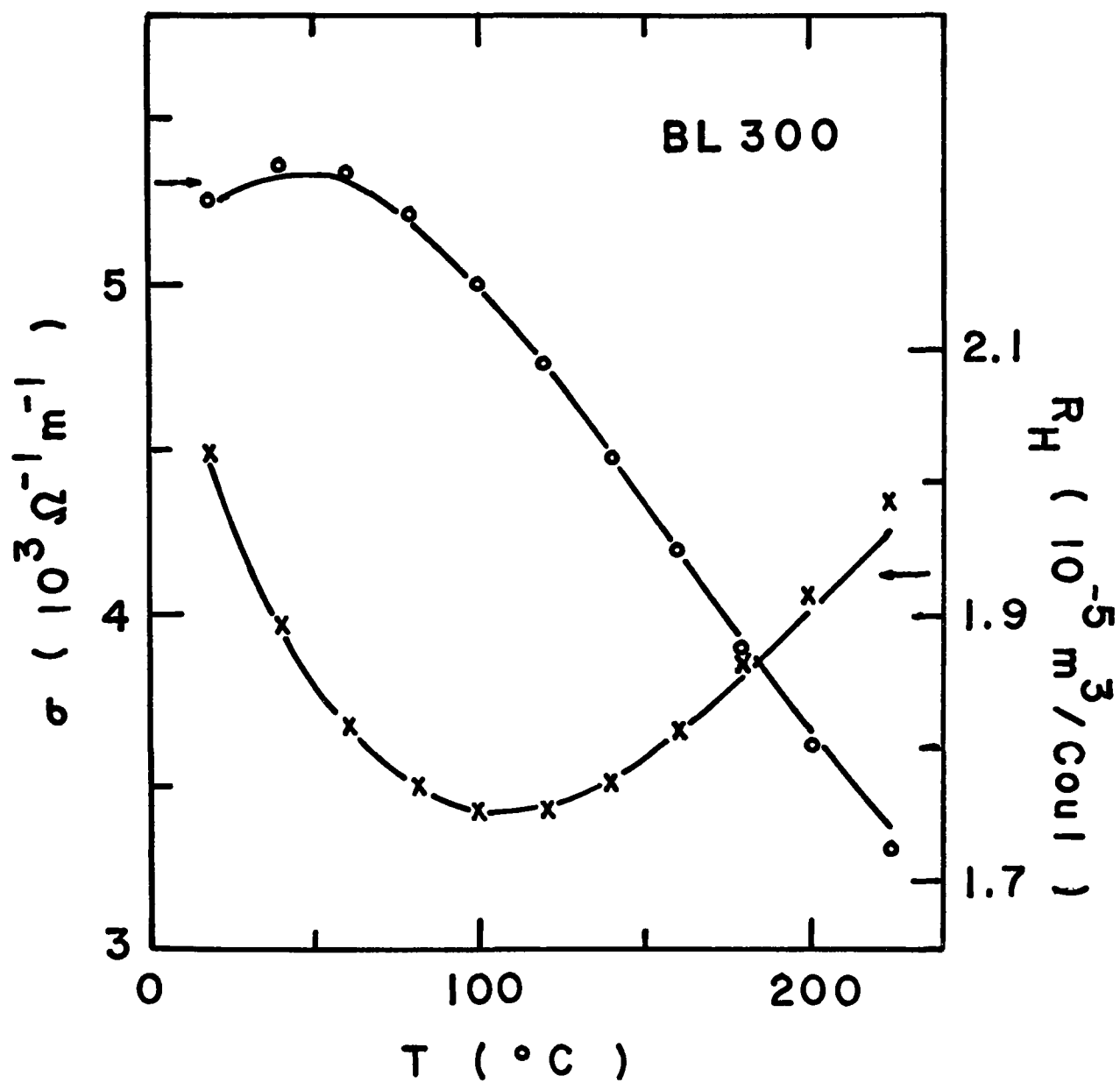


Fig. (V-7) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL300 of $Ga_{1-x}Al_xAs$.

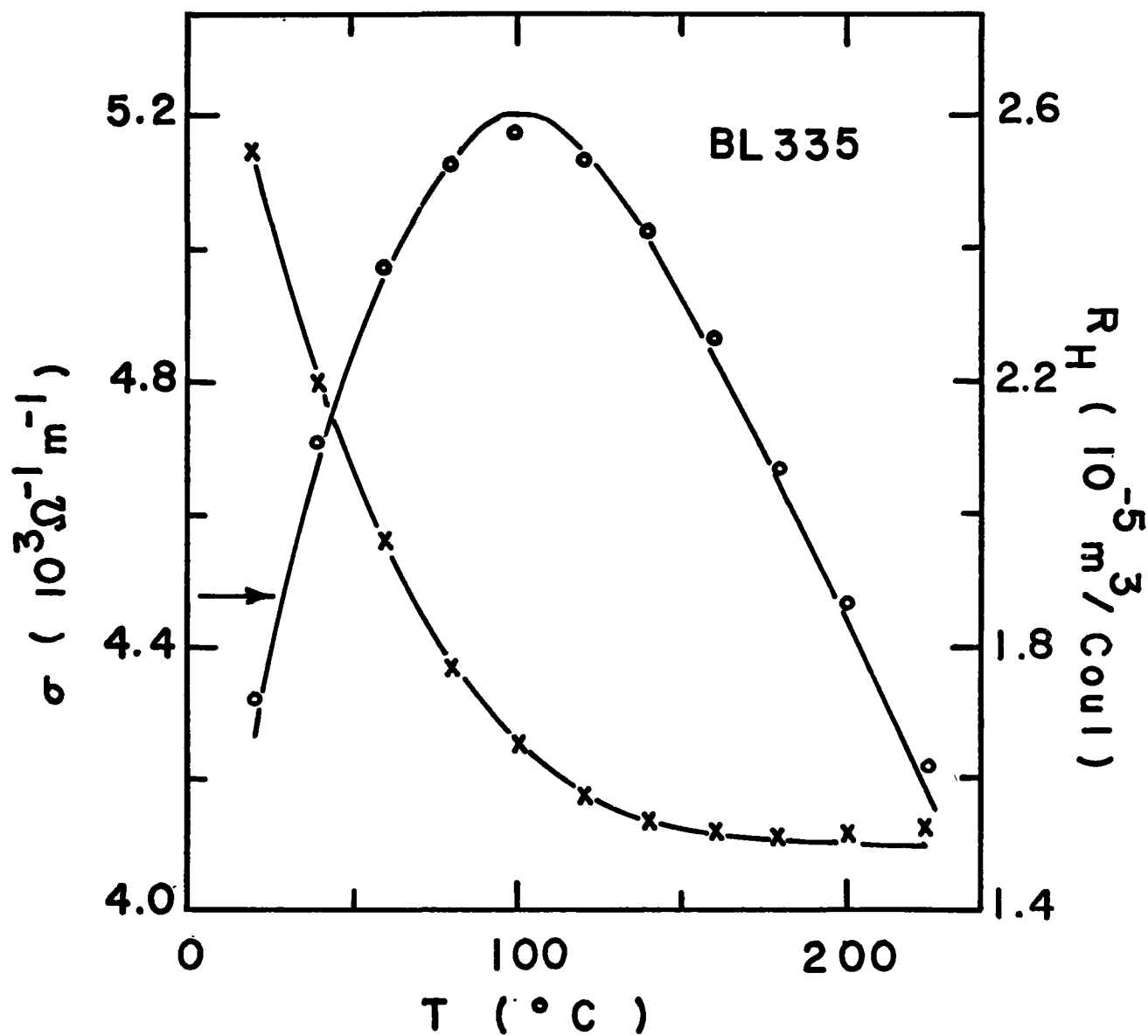


Fig. (V-8) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL335 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

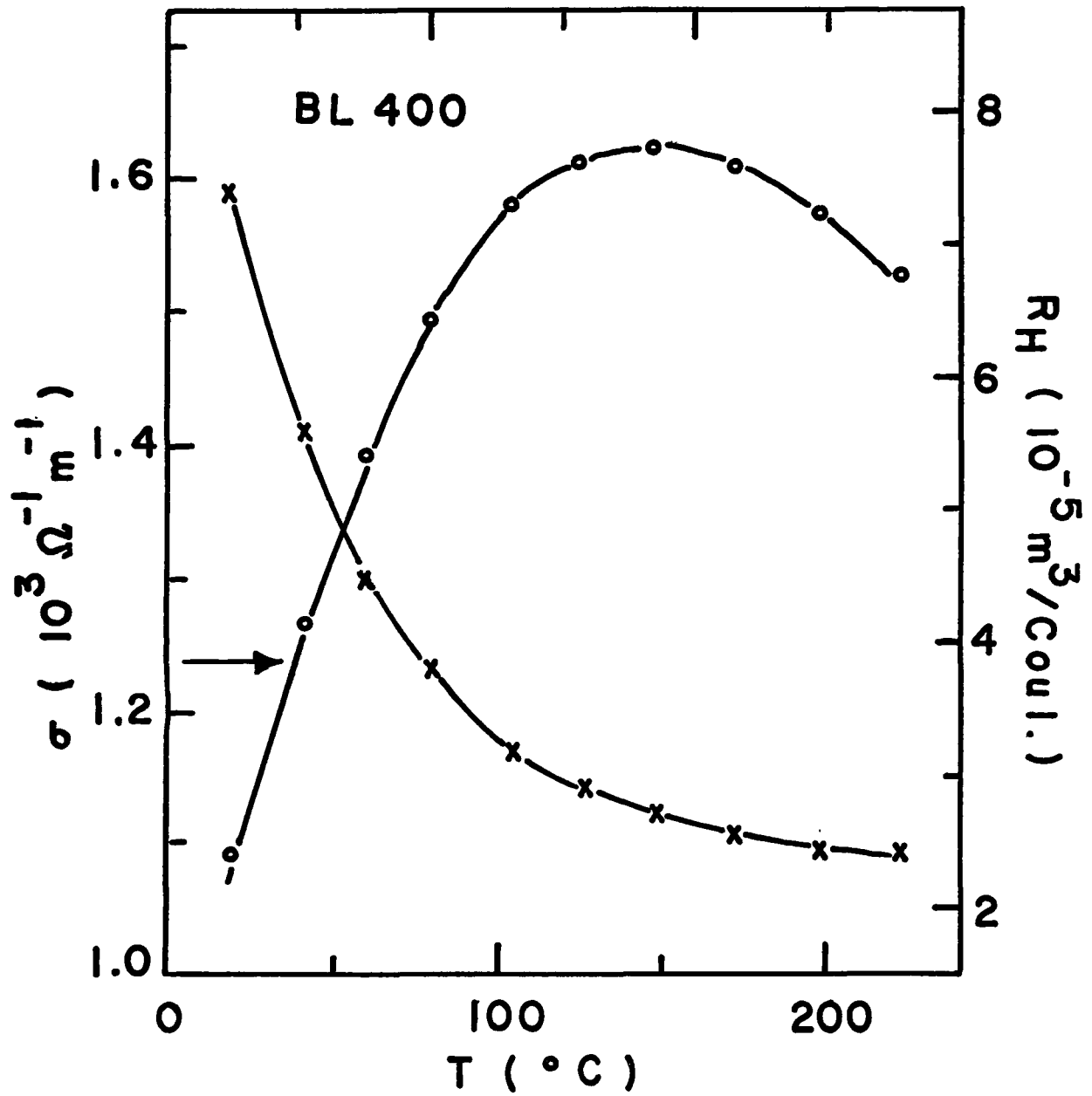


Fig. (V-9) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL400 of $Ga_{1-x}Al_xAs$.

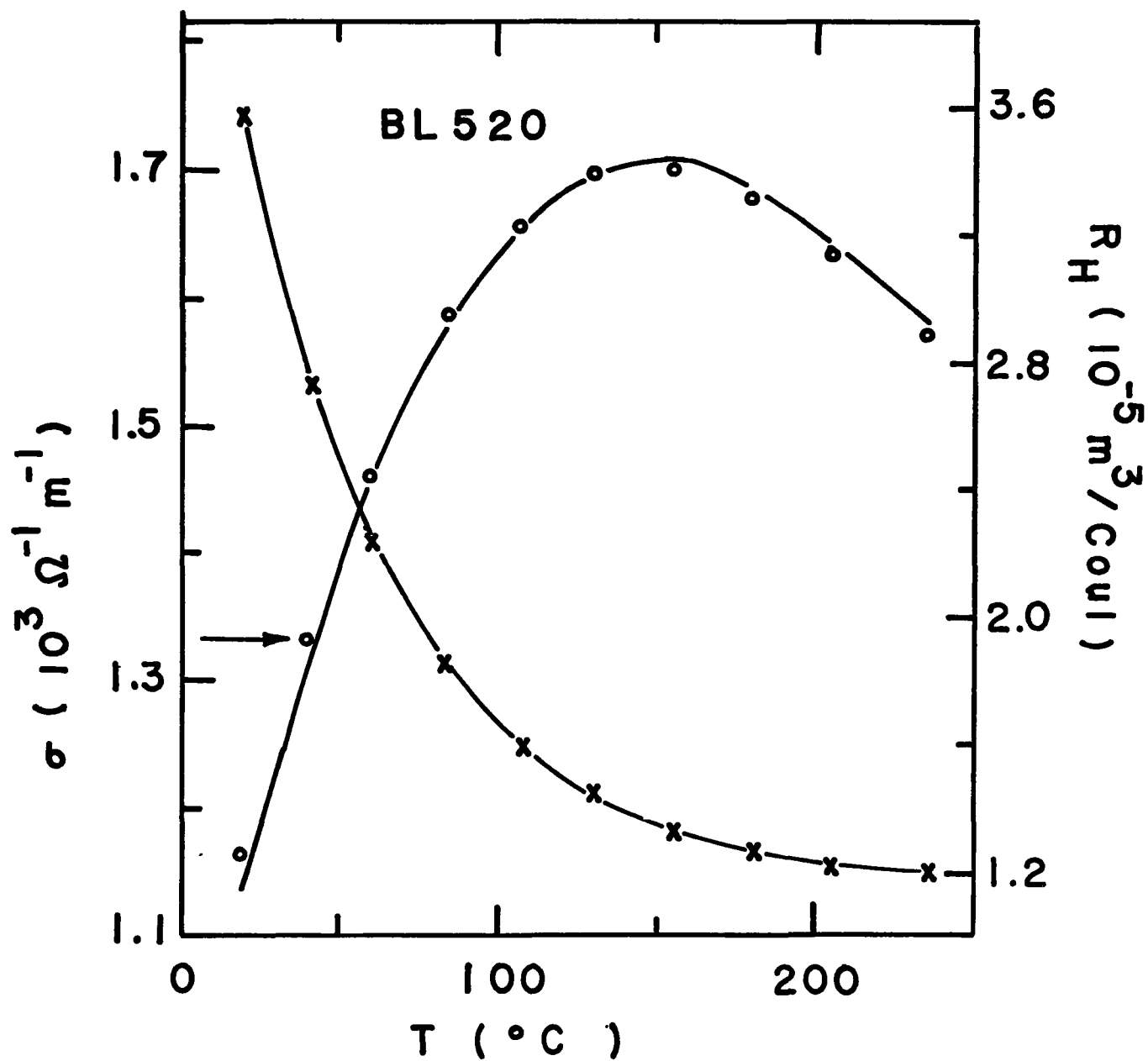


Fig. (V-10) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL520 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

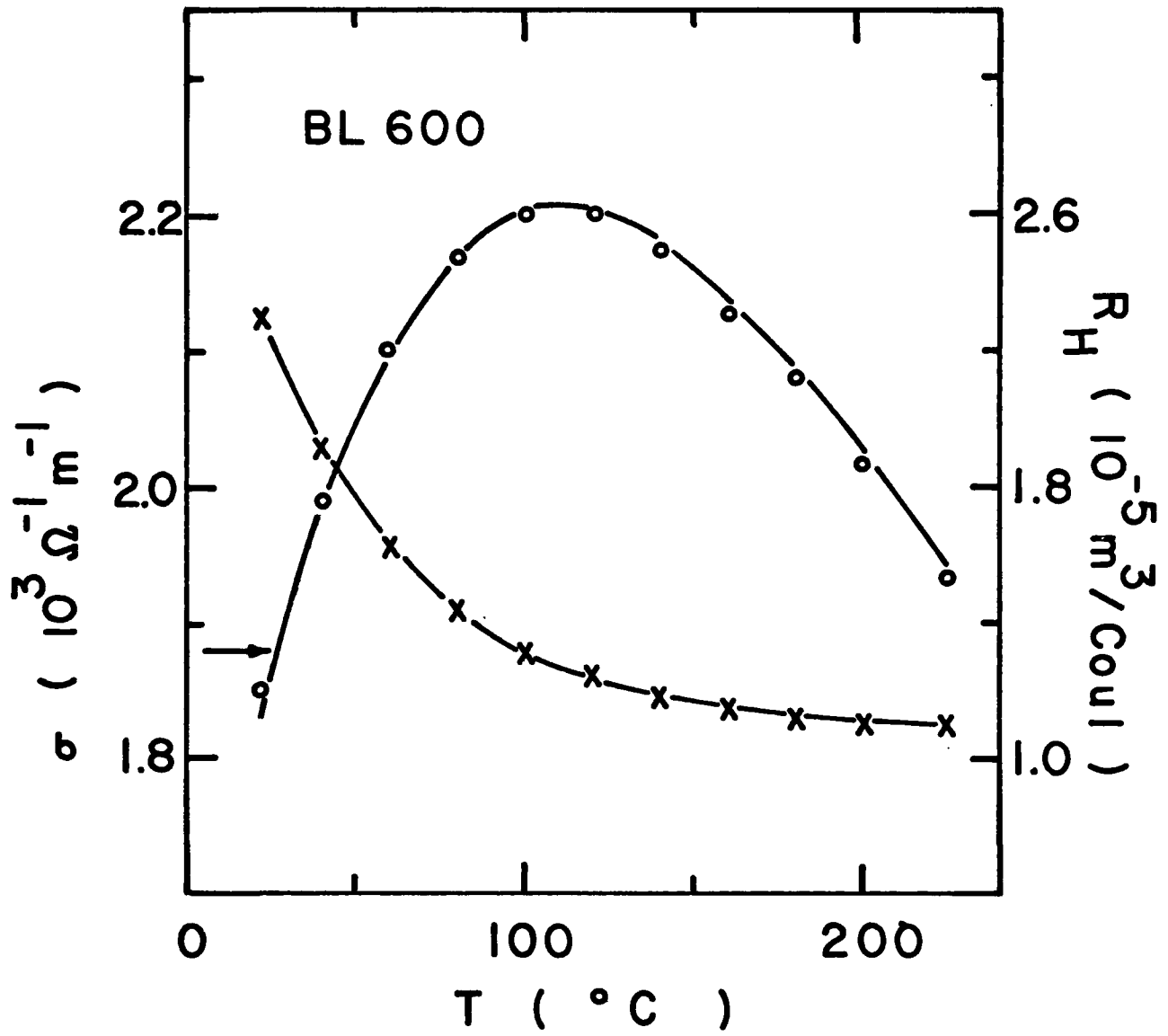


Fig. (V-11) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL600 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

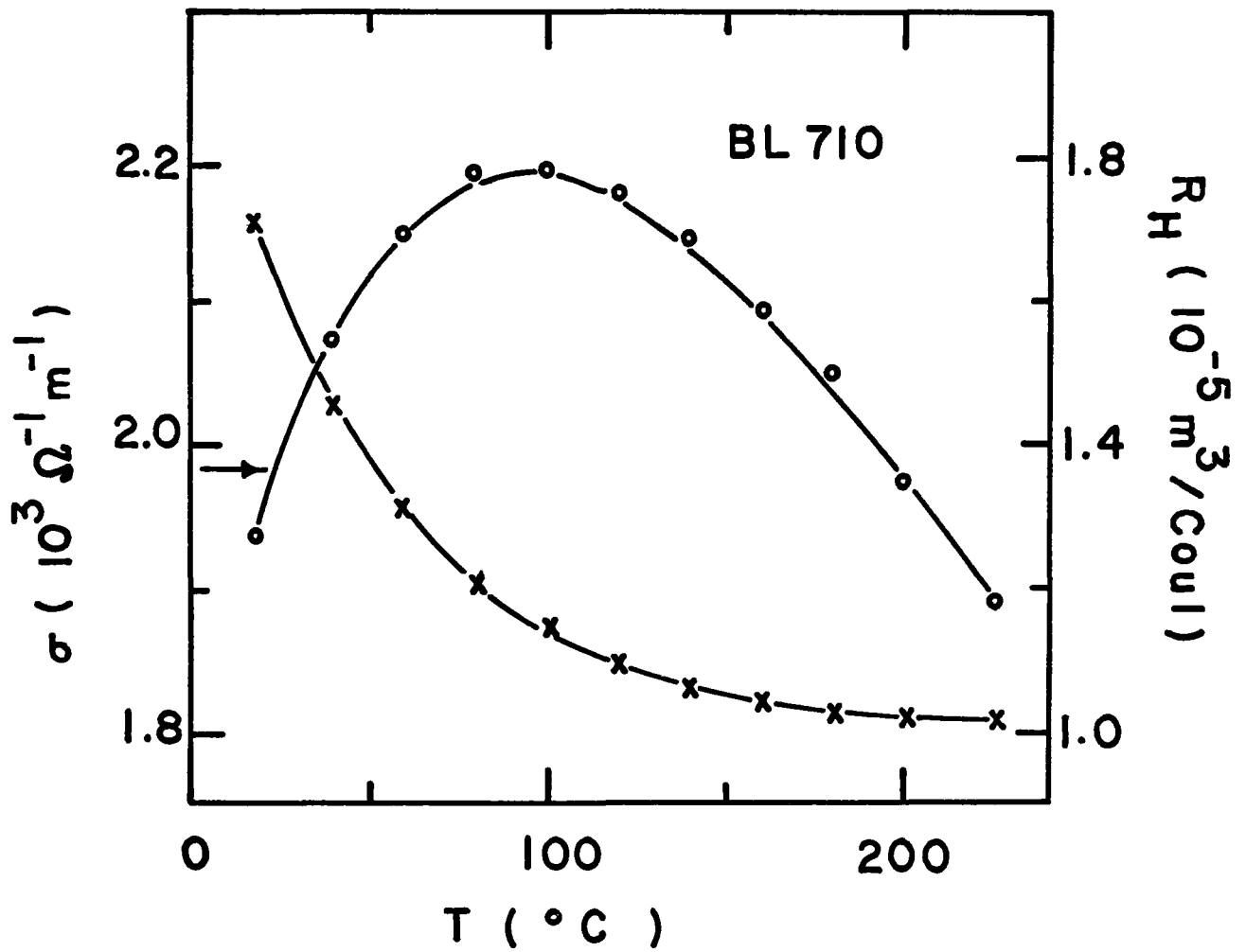


Fig. (V-12) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL710 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

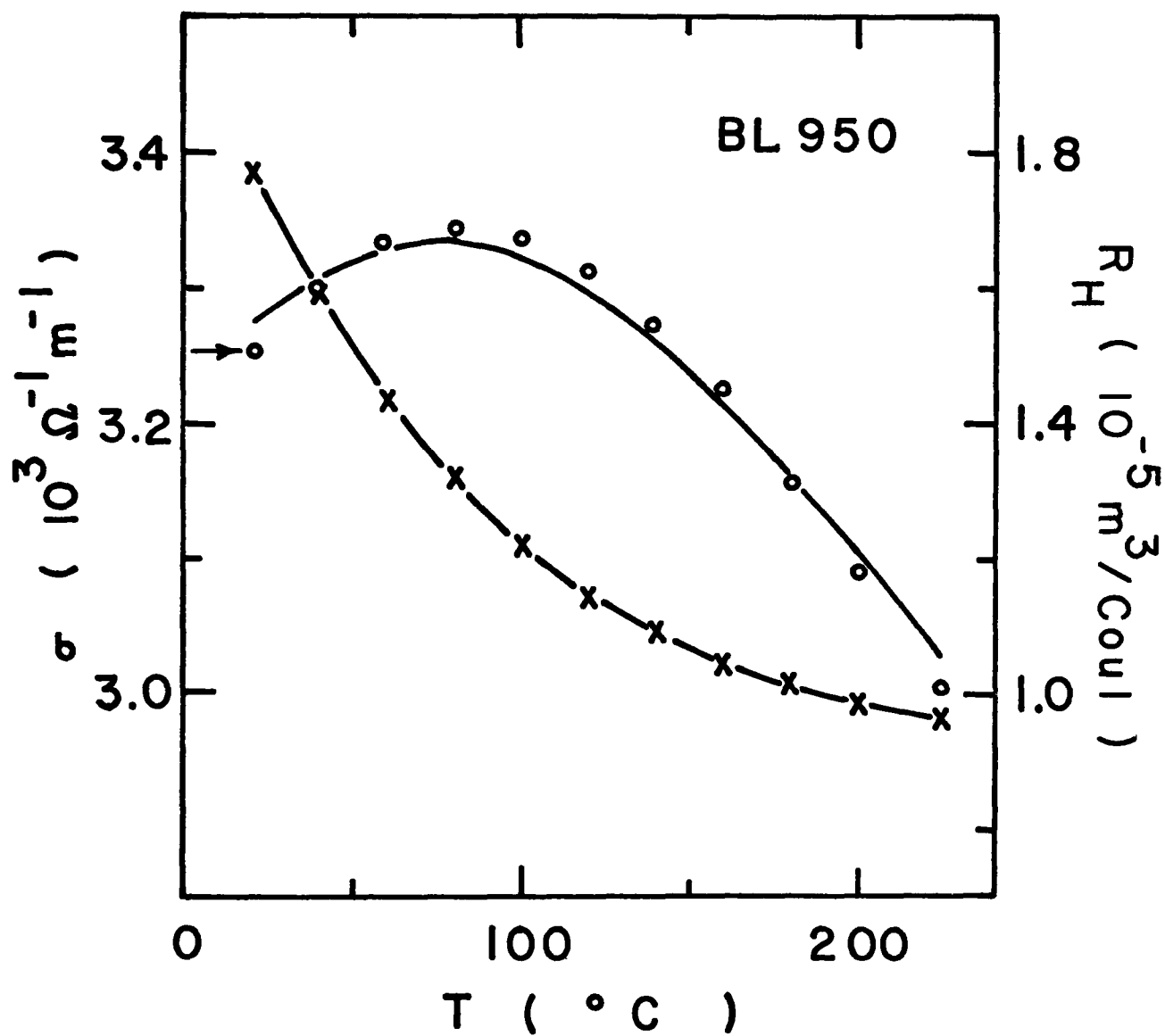


Fig. (V-13) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample BL950 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

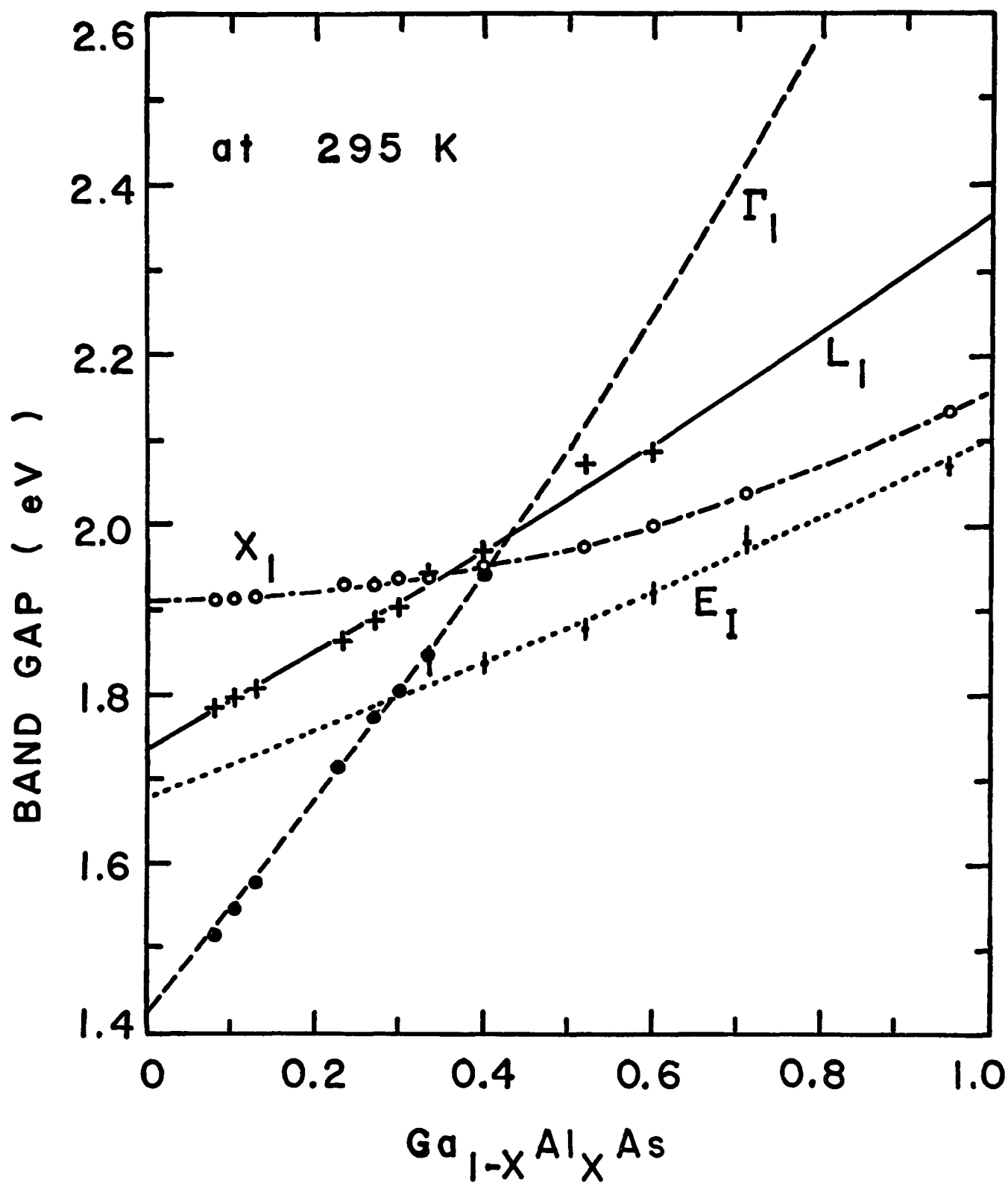


Fig. (V-14) Band gap and impurity level energy as a function of x in the $Ga_{1-x}Al_xAs$ system. The curves are given by Eqs. (V-5, 6, 7, and 4).

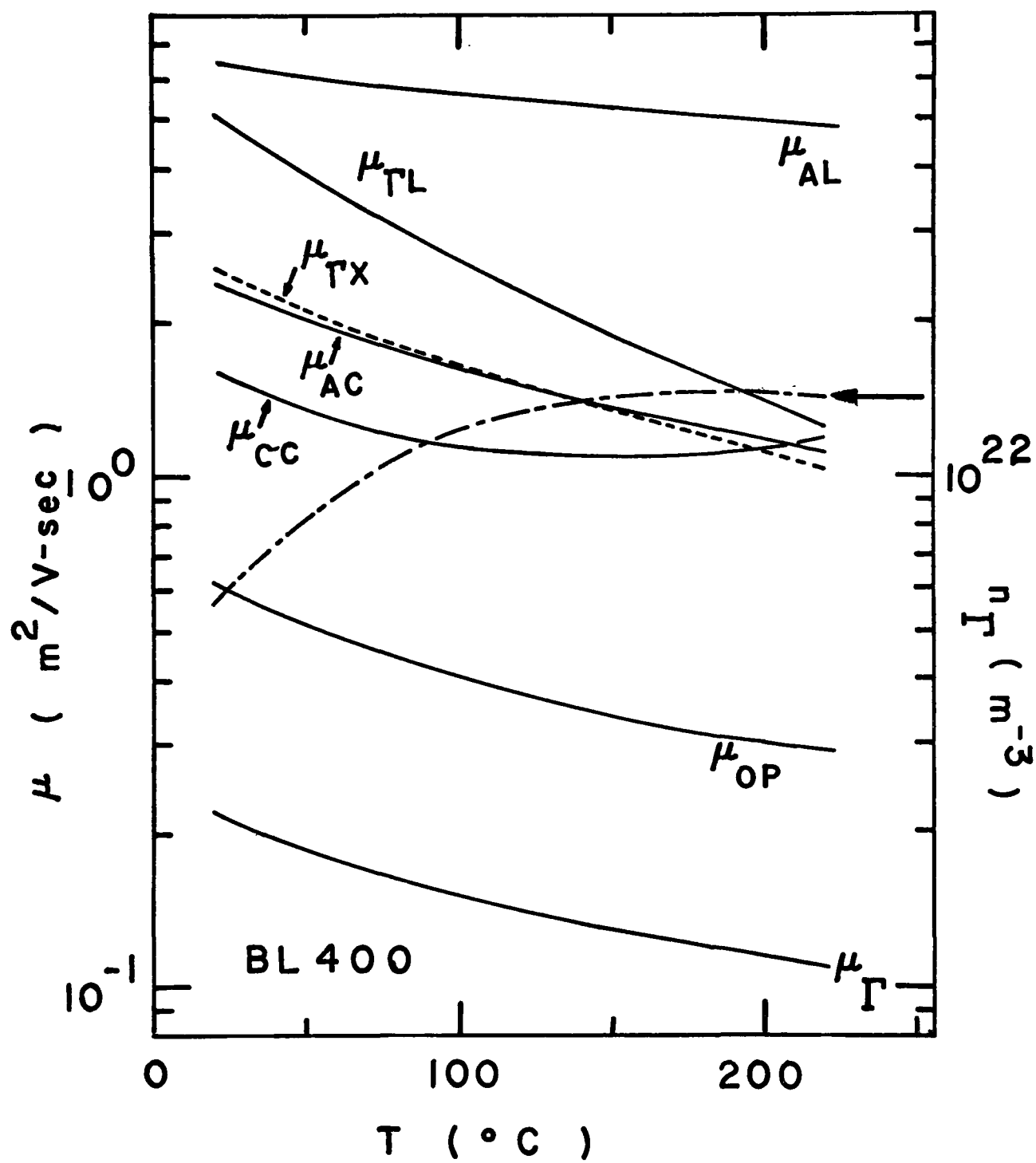


Fig. (V-15) Carrier mobility and carrier density variations with temperature in the Γ_1 band for sample BL400 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

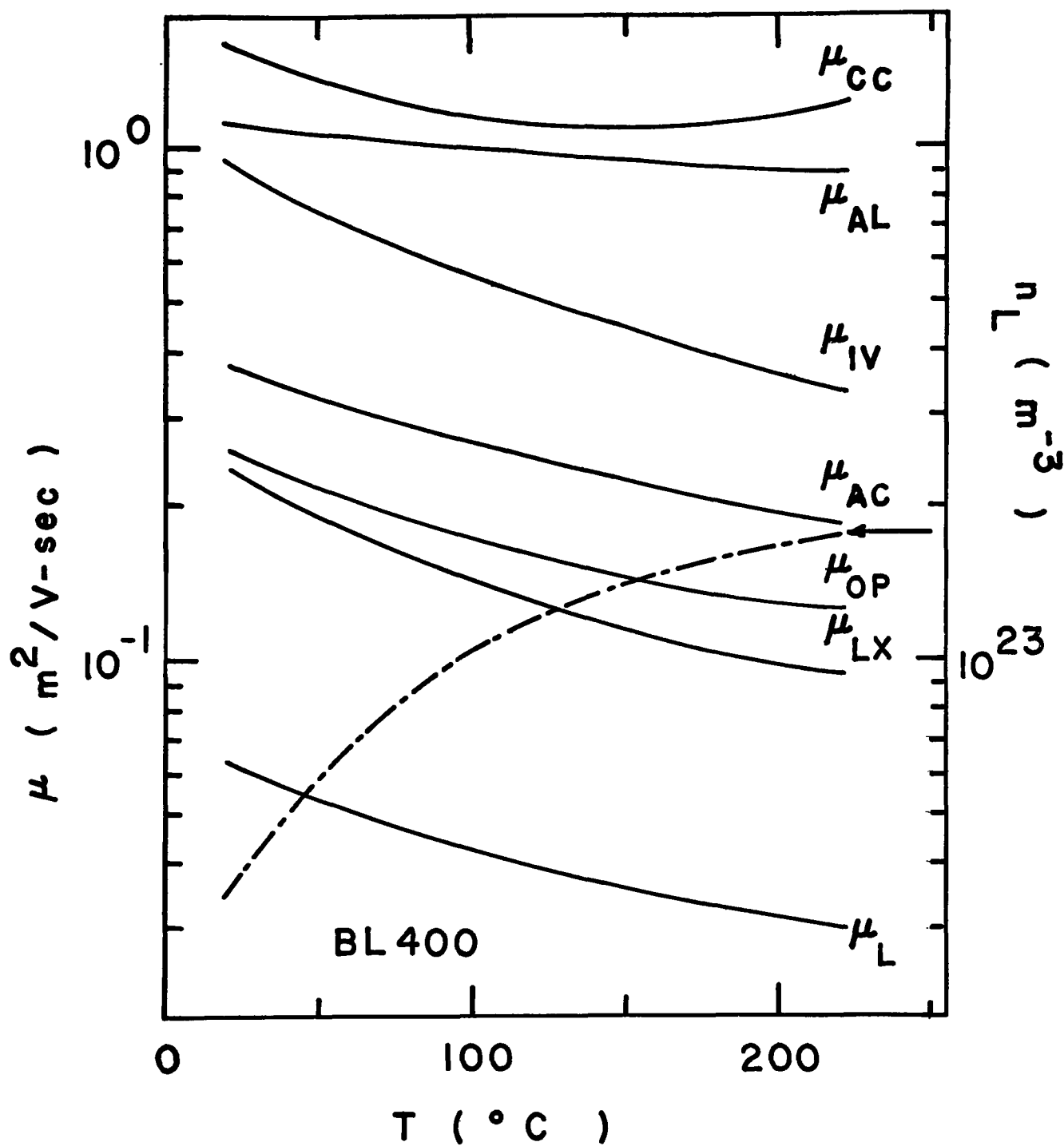


Fig. (V-16) Carrier mobility and carrier density variations with temperature in the L_1 band for sample BL400 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

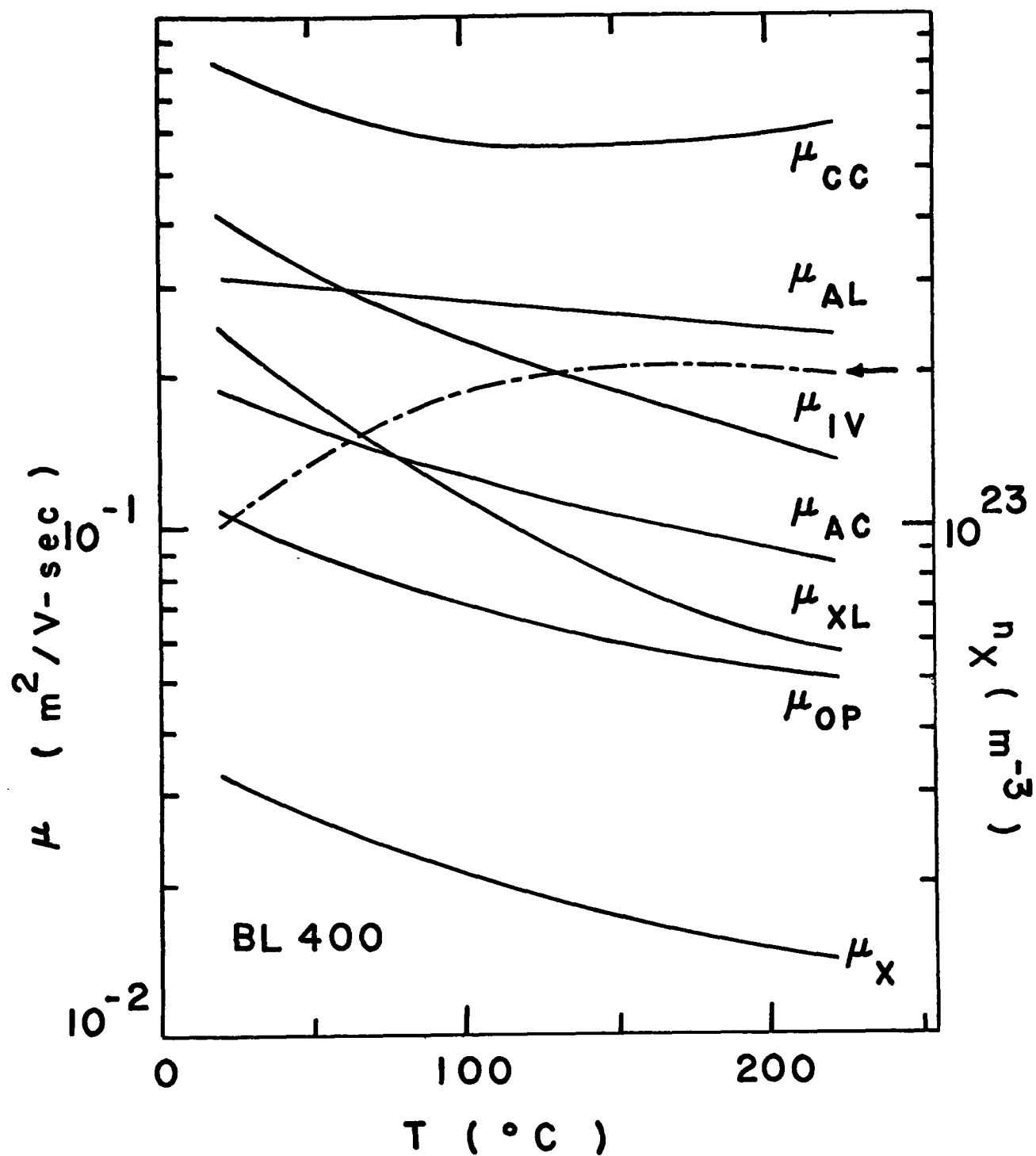


Fig. (V-17) Carrier mobility and carrier density variations with temperature in the X_1 band for sample BL400 of $\text{Ga}_{1-x}\text{Al}_x\text{As}$.

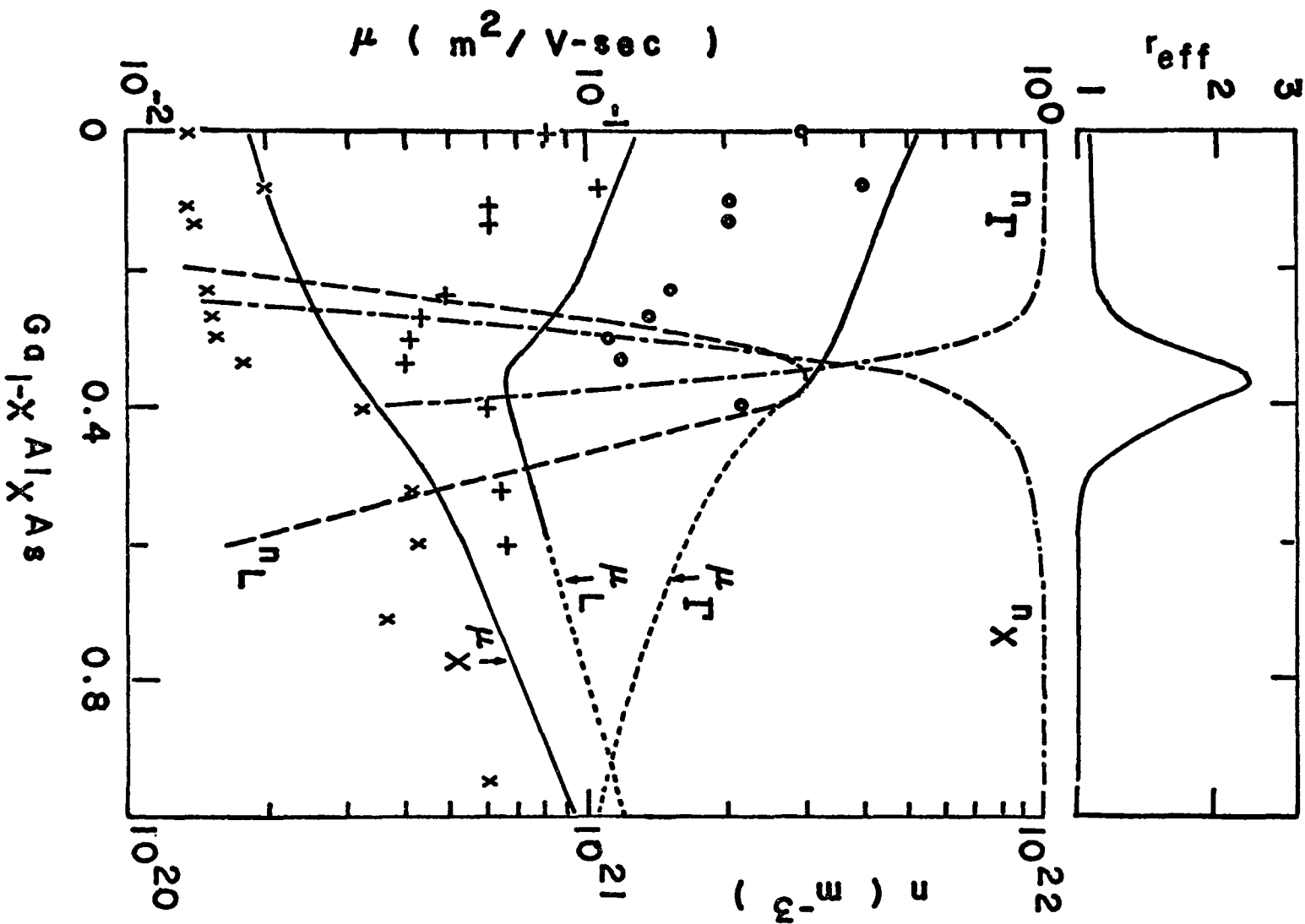


Fig. (V-18) Carrier mobility, carrier density and "effective Hall scattering coefficient" vs. temperature for the $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys at 295 K. 0, + and x show values of μ_{Γ} , μ_L and μ_X respectively obtained for the alloys considered here. Theoretical curves for the three different mobility values were calculated for the case of $n_t = 10^{21} \text{ m}^{-3}$ and $N_A = n_t$.

CHAPTER VI

InP

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CHAPTER VI

InP

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

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

The experimental values obtained by various authors for the effective mass at the bottom of the Γ_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 Γ_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 $0.48 \text{ m}^2/\text{V-sec}$ 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 $n = 1.9 \sim 8 \times 10^{21} \text{ m}^{-3}$ were between 0.427 and $0.528 \text{ m}^2/\text{V-sec}$ at 300 K. Rode (75R2) calculated theoretically the drift mobility using polar optical, acoustic deformation potential, ionized impurity and piezoelectric mode scattering and obtained $0.515 \text{ m}^2/\text{V-sec}$ 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 2~8 % 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 Γ_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 magnetoresistance (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 κ_0 is varied while κ_∞ constant at 9.55 (75R2). The values of E_D , N_A and $N_S Q_S$ 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 Γ_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, ~ 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,

$$E_O^* = E_O(0) - \frac{3\alpha T}{K} \left(\frac{\partial E_O}{\partial P} \right)_T \quad (\text{VI-1})$$

and a Kane form (67K1) for the effective mass variation at the bottom of the band,

$$\frac{1}{m_O^*} = 1 + \frac{P^2}{3} \left(\frac{2}{E_O^*} + \frac{1}{E_O^* + \Delta_O} \right) \quad (\text{VI-2})$$

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 $\frac{3\alpha}{K} \left(\frac{\partial E_O}{\partial P} \right)_T = 5 \times 10^{-5} \text{ eV/K}$ (70R1). The spin-orbit splitting Δ_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 $m_O^*(0) = 0.082 m$. 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. (II-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 RRE1, the most heavily doped sample in this work, require 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 $Q_{||}$ and $Q_{\perp}$ can be calculated. $Q_{||}$ as a function of magnetic field is given by (73D1)

$$Q_{||}(B) = |\alpha(B)| - |\alpha(0)| \quad (\text{VI-3})$$

where

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

and thermoelectric power is defined as

$$\alpha(0) = \frac{\theta_{zz}}{\sigma_{zz}} - \frac{E_F}{eT} \quad (\text{VI-4})$$

The transverse coefficient Q_1 is expressed by

$$Q_1(B) = \frac{1}{B} \frac{\sigma_{xy} \theta_{xx} - \sigma_{xx} \theta_{xy}}{\sigma_{xx}^2 + \sigma_{xy}^2} \quad (\text{VI-5})$$

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

$$\begin{aligned} \theta_{xx} &= \left\langle \frac{EP_1}{T} \right\rangle \\ \theta_{xy} &= \left\langle \frac{EP_2}{T} \right\rangle \\ \theta_{zz} &= \left\langle \frac{EP_3}{T} \right\rangle \end{aligned}$$

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

VI-4 Results and Discussion

As with the "a" parameter, the sample RRE1 requires also a lower κ_0 value for the best fit than those for the samples of low carrier density. Here again we determined a compromise value of $\kappa_0 = 12.5 \pm 0.1$, which is to be compared with published values of 12.9 ($\kappa_\infty = 10.9$) (71N1), 12.38 ($\kappa_\infty = 9.55$) (72R2) and 15.0 ($\kappa_\infty = 10.6$) (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 ± 0.7 eV, which compares well with those of GaAs (16.1 ± 0.5 eV) (see Chapter IV) and of InSb (14.6 eV) (71Z1).

Zawadzki and Szymanska (71Z1) 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 $N_s Q_s$ 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 $N_s Q_s$ 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 RRE1. This lower compensation ratio can be observed in previous transport work (70G1, 74B2, 71B2). Resulting theoretical curves for R_H and σ calculated using the parameter values shown in Table (VI-2) and determined here are compared with the measured variations of R_H and σ 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 σ data, i.e., the calculated R_H increased with temperature at high temperature range when calculations were made to fit the σ 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 $\text{m}^2/\text{V-sec}$ 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 μ_{op} due to polar optical scattering is $0.56 \text{ m}^2/\text{V-sec}$, which is low compared with that of GaAs ($\mu_{\text{op}} = 0.95 \text{ m}^2/\text{V-sec}$). Two scattering mechanisms, viz. acoustic deformation potential and space charge, give similar mobility values throughout the experimental temperature range. The mobility value μ_{ac} due to acoustic deformation potential mode scattering is calculated to be $2.15 \text{ m}^2/\text{V-sec}$ 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 $\sim 0.44 \text{ m}^2/\text{V-sec}$, which is lower by 15% than the theoretical value $0.515 \text{ m}^2/\text{V-sec}$ 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 (70G1, 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

$\mu = 0.515 \text{ m}^2/\text{V-sec}$, giving $r = 1.237$, 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 variation measured in the other four samples is due to the r variation with temperature. The most heavily doped sample RRE1 shows $\sim 3\%$ 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 (70G1)

$\Delta\rho/\rho_0$ 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 . 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 (59G1), the discrepancies shown by the two other samples are not unreasonable.

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 $\alpha(0)$ 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 in the figure) which is in good agreement

with the calculated value $-177 \mu\text{V/K}$. The data points denoted by X and 0 are those for samples with $n = 7.1 \times 10^{21}$ and $2.1 \times 10^{23} \text{ m}^{-3}$ respectively, measured by Kudman and Steigmeier (64K1). The other experimental points were obtained by Kesamanly et al. (69K1) and are shown by $\bullet$, $\circ$ and $+$ in Fig. (VI-9) for three different samples with $n = 2.2 \times 10^{23}$, 9×10^{23} and $7.3 \times 10^{24} \text{ m}^{-3}$ 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 $-612 \mu\text{V/K}$, the Fermi energy term giving $-436 \mu\text{V/K}$, while in the case of RRE1, the calculated $\alpha(0)$ is $-177 \mu\text{V/K}$ and the Fermi energy term is $121 \mu\text{V/K}$. 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 m respectively for the two samples. This unreasonable result may be due partially to the effects discussed above. Also this experimental $\alpha(0)$ 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 $Q_{||}$ and $Q_{\perp}$ values respectively. The data denoted by $\circ$ and $\bullet$ in the figure are $Q_{||}$ values measured by Demars for the two samples cut from the same crystal slices as RRE1 and RRE2 respectively. $Q_{||}$ 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 $\times$ and $+$ respectively in Fig. (VI-10). The disagreement between the theoretical and experimental values in $Q_{||}$ 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 $\odot$ 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 $\mu_m = (\Delta\rho/\rho_0)^{1/2}/B$ 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 μ_H data using the rather high theoretical μ_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 distribution of mobility values should not exceed $\pm 3\%$ at room temperature. The measured μ_m values at 300 K for five of the samples lie within a range of $\pm 5.5\%$ around the average value of $0.44 \text{ m}^2/\text{V-sec}$, while the corresponding μ_H values are spread through a wide range of $0.45 - 0.53 \text{ m}^2/\text{V-sec}$. For the single sixth sample, the measured values of μ_m and μ_H are 0.528 and $0.53 \text{ m}^2/\text{V-sec}$ respectively. The larger scatter in the μ_H data may be due to substrate effects indicated by Blood and Orton (74B2). Thus from our above estimate, it would appear that the μ_m values of the five samples are the more reliable data.

Measurements on GaAs (71B2,7301) gave experimental values of μ_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 μ_m should be equal to μ_H , although, as indicated above, for five samples μ_m was lower than μ_H by up to 15% and only in a single sample were the values of μ_m and μ_H close. They attributed the low μ_m values for the five

to the presence of parasitic resistance associated with the metal contacts.

Here we have calculated μ_H and μ (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 μ_m data for the five samples show good agreement with the theoretical μ curve, while for the single sixth sample the measured μ_m value agrees with μ_H curve. If, as indicated above, the μ_m data on the five samples are the more reliable data, this would indicate that μ_m is more likely to be equal to μ and hence less than μ_H . However, this is to be contrasted with the theoretical calculations (63B1) showing that μ_m is greater than both μ_H and μ . 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 Γ_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 σ simultaneously.

To fit the experimental data of effective mass variation with temperature (70E1, 70C1), 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 σ 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 ± 0.1 and 14.2 ± 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 magnetoresistance 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

Sample	T	R_H	σ	n_t	N_A	$N_S Q_S$
	$^{\circ}\text{C}$	$10^{-4} \text{ m}^3/\text{Cou1}$	$10^3 \text{ Ohm}^{-1} \text{ m}^{-1}$	10^{22} m^{-3}	10^{22} m^{-3}	10^6 m^{-1}
RRE1	18.0	0.055	32.30	113.0	3.80	-
RRE2	22.4	20.74	0.1624	0.3514	-	3.2
RRE4	18.3	21.51	0.2149	0.347	-	1.4
ISM2	18.0	1.333	2.467	5.20	-	1.65
ISM3	22.0	0.4793	5.59	13.90	-	0.98

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 $N_S Q_S$ and N_A were obtained from the analysis of the experimental data.

Table VI-2

Parameter	Value	Ref.
$E_O(0)$	1.423 eV	(75R1)
$m_O(0)$	0.079 m	(75R1)
Δ_O	0.108 eV	(75R1)
α_Γ	-4.91×10^{-4} eV/K	(67V1)
θ_Γ	327 K	(67V1)
$\hbar\omega_O$	0.0429 eV	(66M1, 72A1)
κ_∞	9.55	(70R1)
κ_O	12.5 ± 0.1	*
C_ℓ	12.1×10^{10} N/m ³	(75R2)
E_D	14.2 ± 0.7 eV	*

Table VI-2 Material parameters of InP

*-determined in the present work.

Table VI-3

T	E_F	μ	r	$\Delta\rho/\rho_o \quad 10^{-4}$		$\alpha(0)$	$Q_{ } \quad \mu V/K$		$Q_{\perp} \quad 10^{-6} m^2/K.S.$	
$^{\circ}C$	eV	$m^2/V\text{-sec}$	1.09 T	1.09 T	2.8 T	$\mu V/K$	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. $\Delta\rho/\rho_o$, $Q_{||}$ and $Q_{\perp}$ were calculated using $B = 0.3$ and 2.8 Wb/m^2 respectively.

Table VI-4

T	E_F	μ	r	$\Delta\rho/\rho_o$	$\alpha(O)$	$Q_{ }$	$Q_{\perp}$
$^{\circ}\text{C}$	eV	$\text{m}^2/\text{V-sec}$		10^{-2}	$\mu\text{V/K}$	$\mu\text{V/K}$	$10^{-5} \text{m}^2/\text{K.S.}$
18.0	-0.0580	0.2909	1.112	0.9618	393.0	1.582	0.6115
60.0	-0.0724	0.2500	1.099	0.6733	413.6	1.376	0.5529
100.0	-0.0869	0.2211	1.088	0.4845	431.6	1.157	0.4883
140.0	-0.1020	0.1989	1.076	0.3539	448.0	0.956	0.4247
180.0	-0.1173	0.1814	1.066	0.2622	462.5	0.786	0.3666
220.0	-0.1330	0.1673	1.057	0.1975	475.2	0.644	0.3163
260.0	-0.1493	0.1558	1.050	0.1513	486.9	0.534	0.2741

Table VI-4 Results of analysis for sample ISM2. r , $\Delta\rho/\rho$, $Q_{||}$ and $Q_{\perp}$ were calculated using $B = 1.09 \text{ Wb/m}^3$.

Table VI-5

T °C	E_F eV	μ $m^2/V\text{-sec}$	r 1.09 T	$\Delta\rho/\rho_0$ 10^{-4}		$\alpha(0)$ $\mu V/K$	$Q_{ }$ $\mu V/K$		$Q_{\perp}$ $10^{-6} m^2/K.S.$	
				1.09 T	2.8 T		1.09 T	2.8 T	1.09 T	2.8 T
18.0	0.0358	0.1815	1.0032	0.706	4.234	177.1	-0.0694	-0.3865	-0.493	-0.439
60.0	0.0329	0.1674	1.0029	0.601	3.500	191.8	-0.1013	-0.5604	-0.670	-0.597
100.0	0.0292	0.1569	1.0029	0.563	3.319	205.0	-0.1120	-0.6561	-0.783	-0.702
160.0	0.0220	0.1443	1.0031	0.563	3.371	223.6	-0.1206	-0.7295	-0.864	-0.787
220.0	0.0138	0.1345	1.0032	0.505	3.090	239.6	-0.1129	-0.6997	-0.862	-0.792
250.0	0.0095	0.1302	1.0032	0.4864	2.829	246.5	-0.1073	-0.665	-0.839	-0.774

Table VI-5 Results of analysis for sample RRE1, $\Delta\rho/\rho_0$, $Q_{||}$ and $Q_{\perp}$ were calculated using $B = 1.09$ and 2.8 Wb/m^2 respectively.

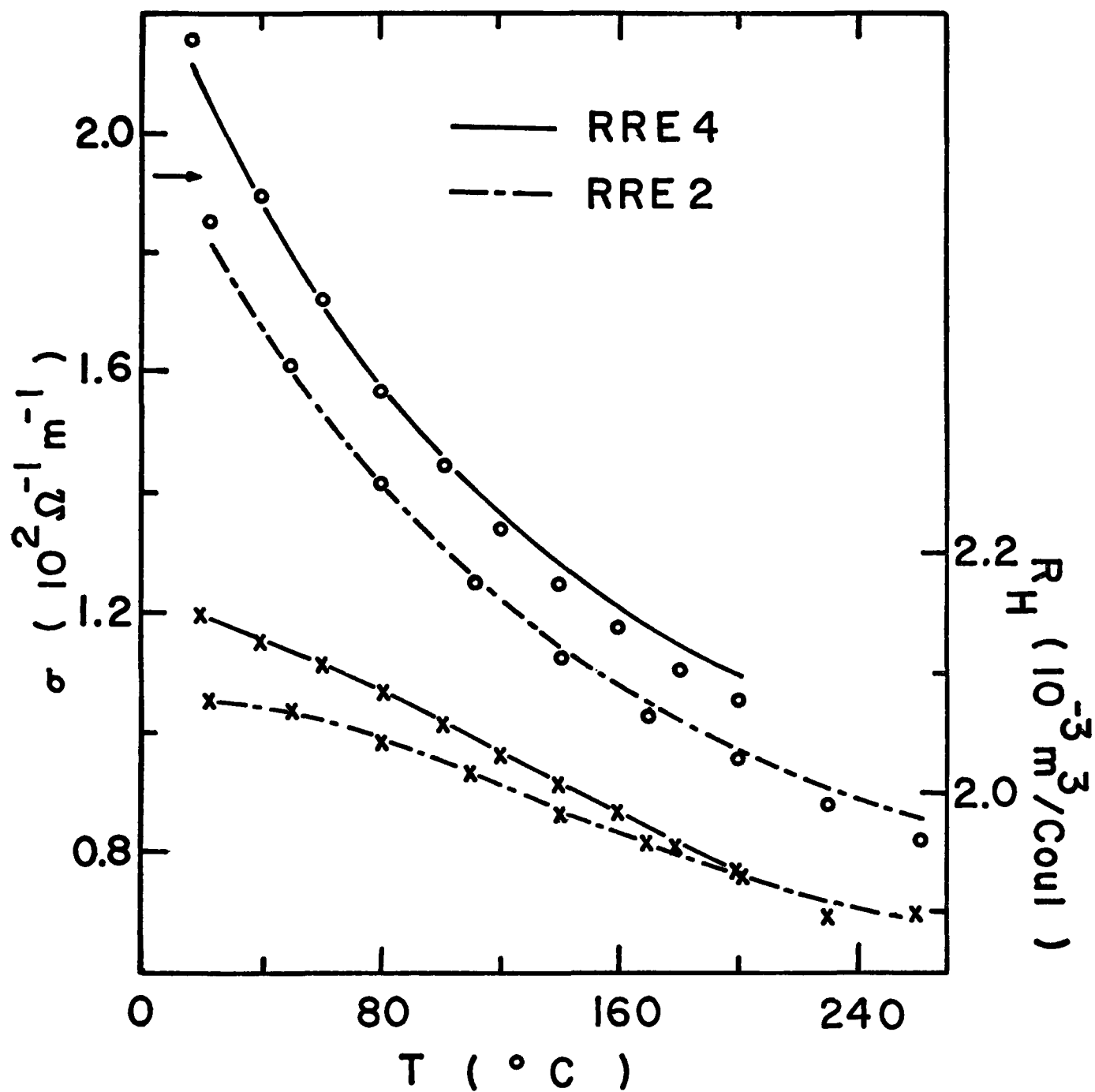


Fig. (VI-1) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for samples RRE2 and RRE4 of InP.

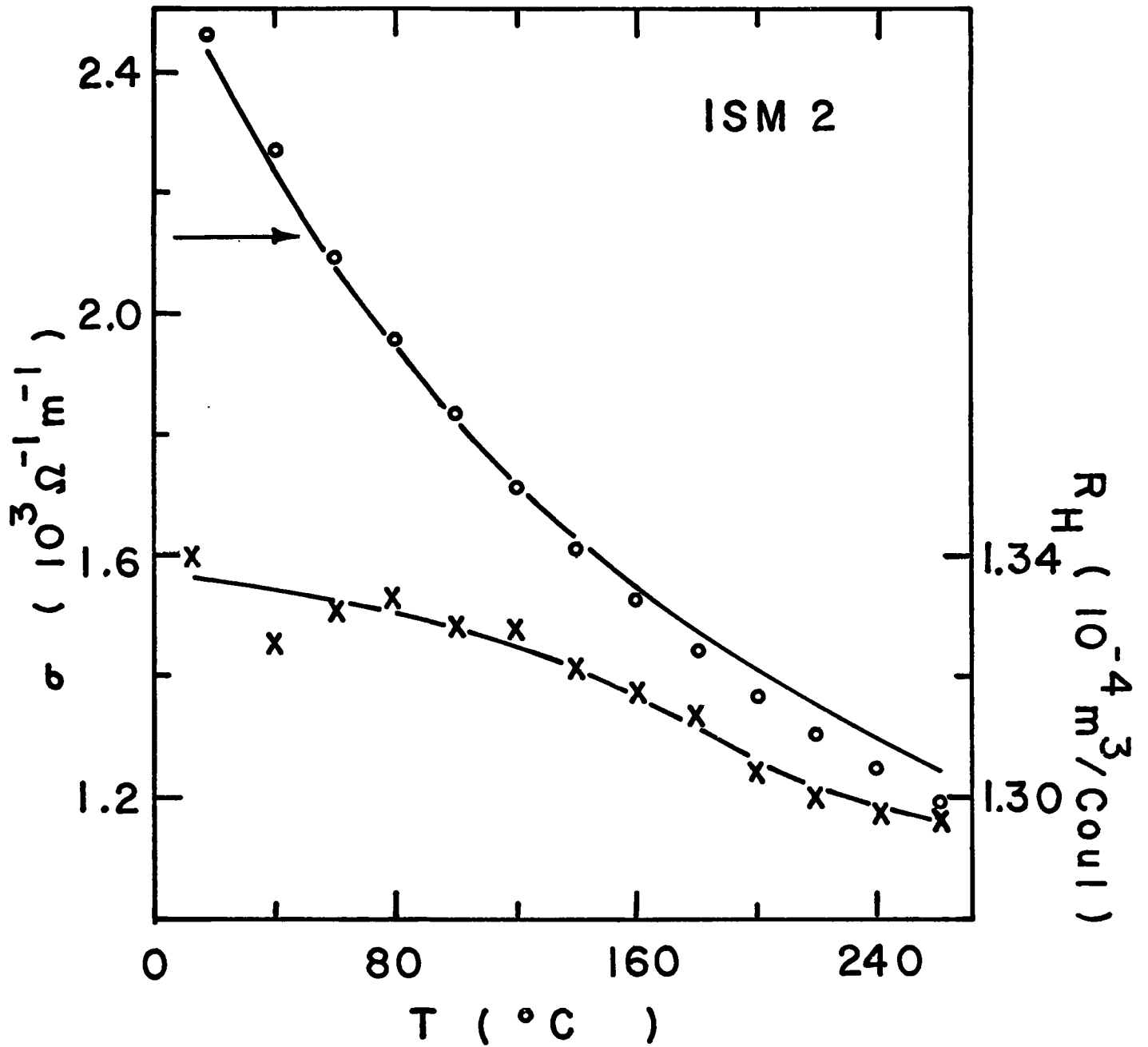


Fig. (VI-2) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample ISM2 of InP.

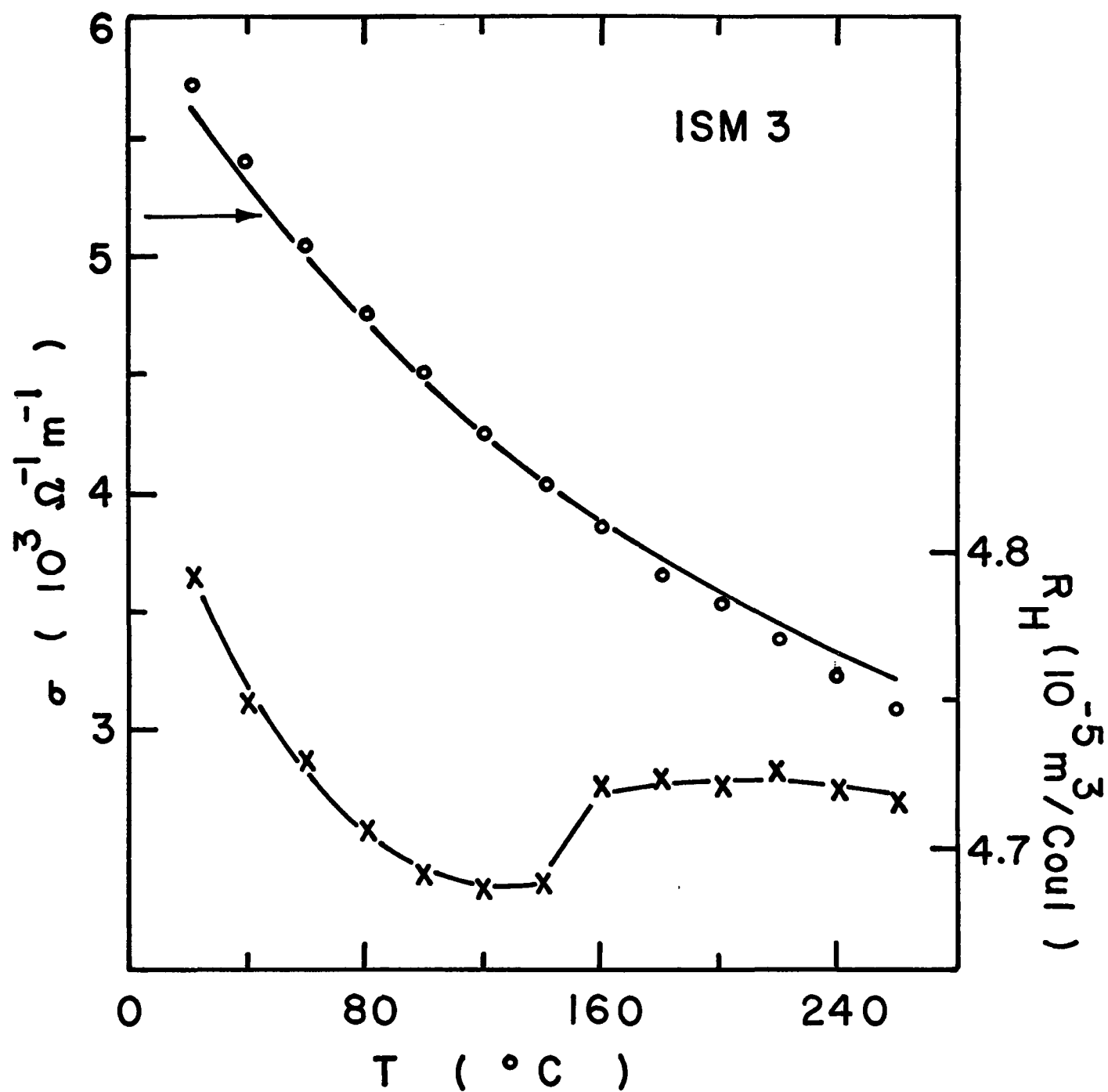


Fig. (Vi-3) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample ISM3 of InP.

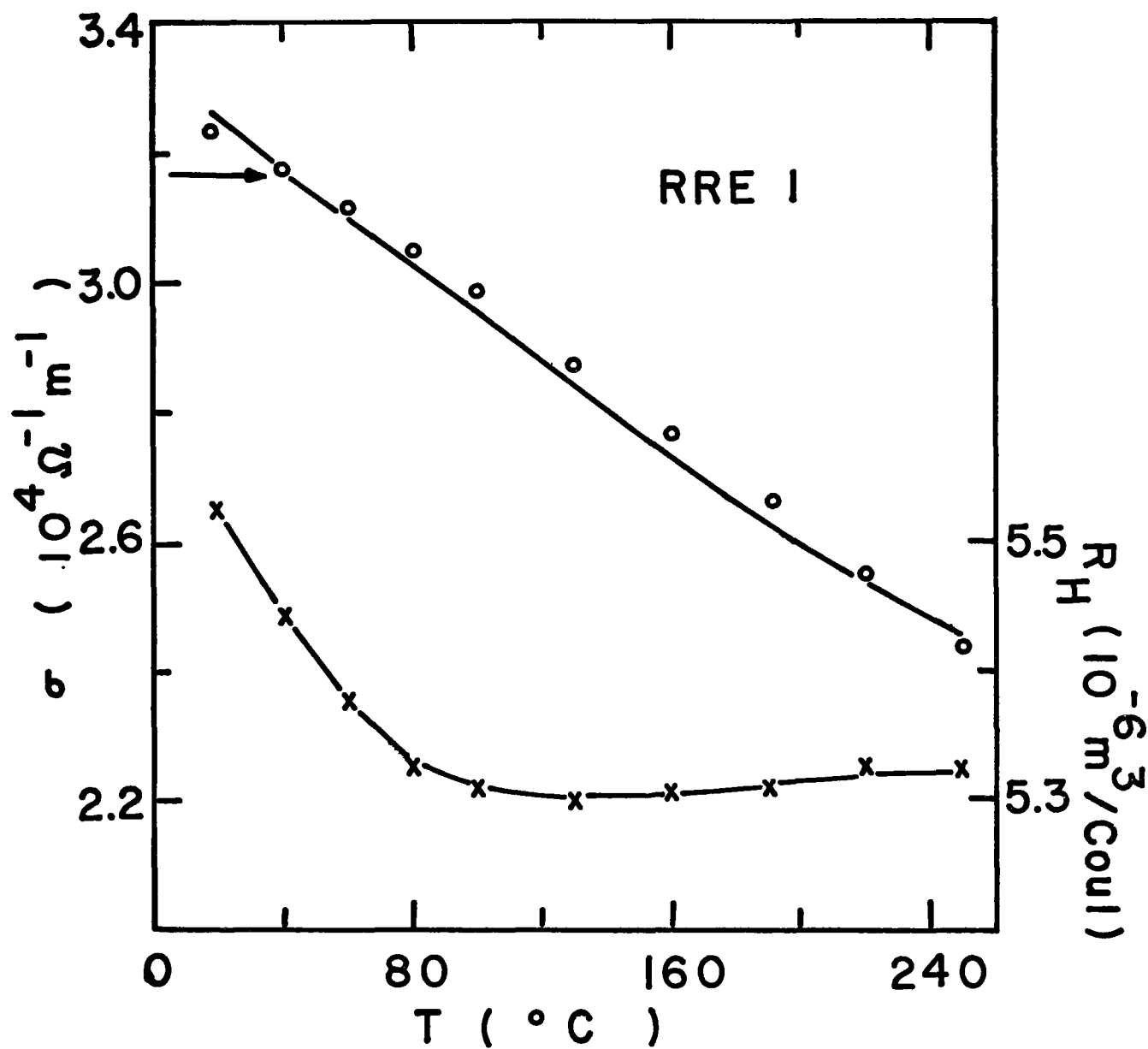


Fig. (VI-4) Experimental values of Hall coefficient and conductivity as a function of temperature and theoretically fitted curves for sample RRE1 of InP.

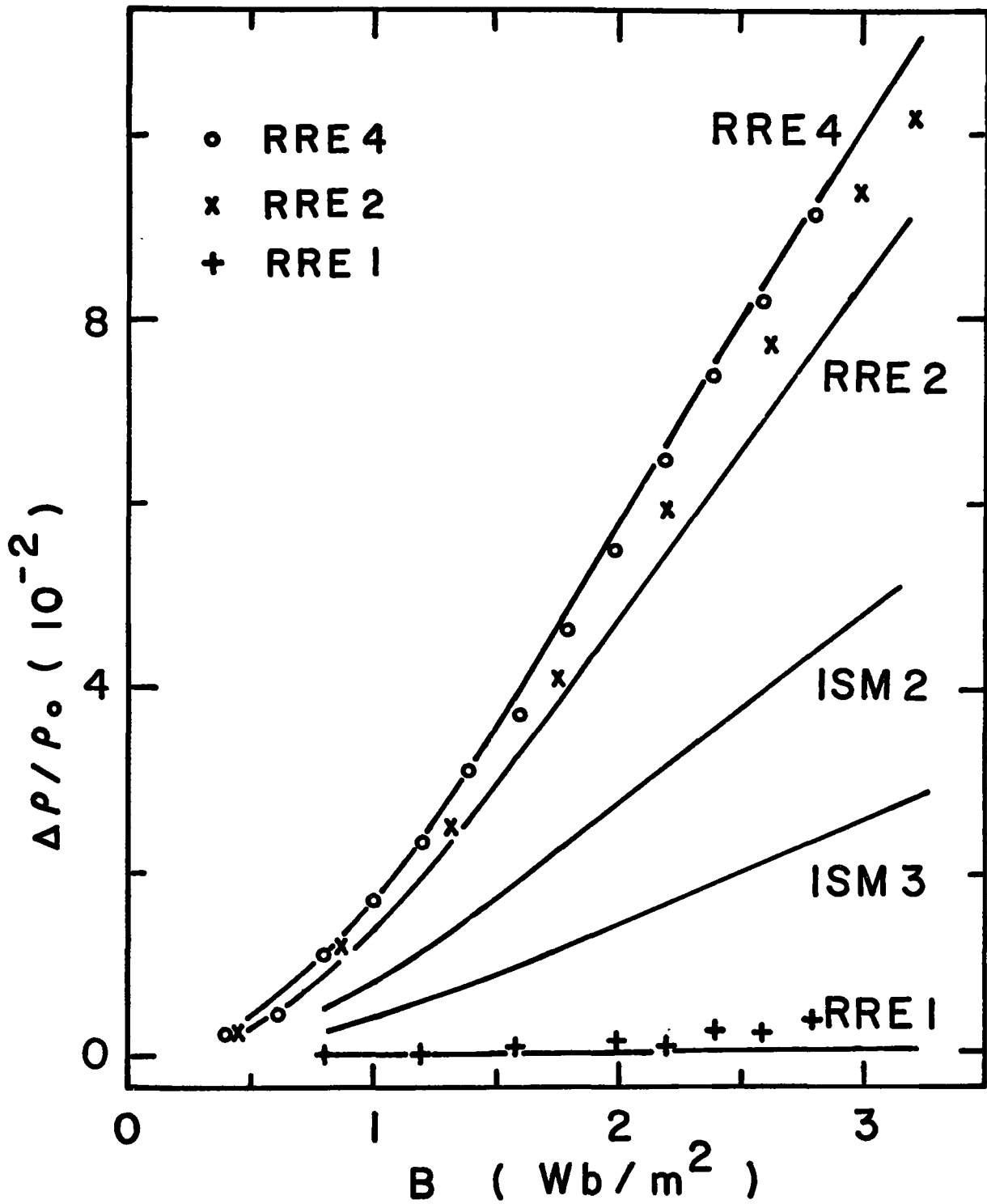


Fig. (VI-5) Magnetoresistivity measured as a function of magnetic field for the three samples, RRE1, RRE2 and RRE4 and theoretically predicted curves. Measurements have been made at room temperature.

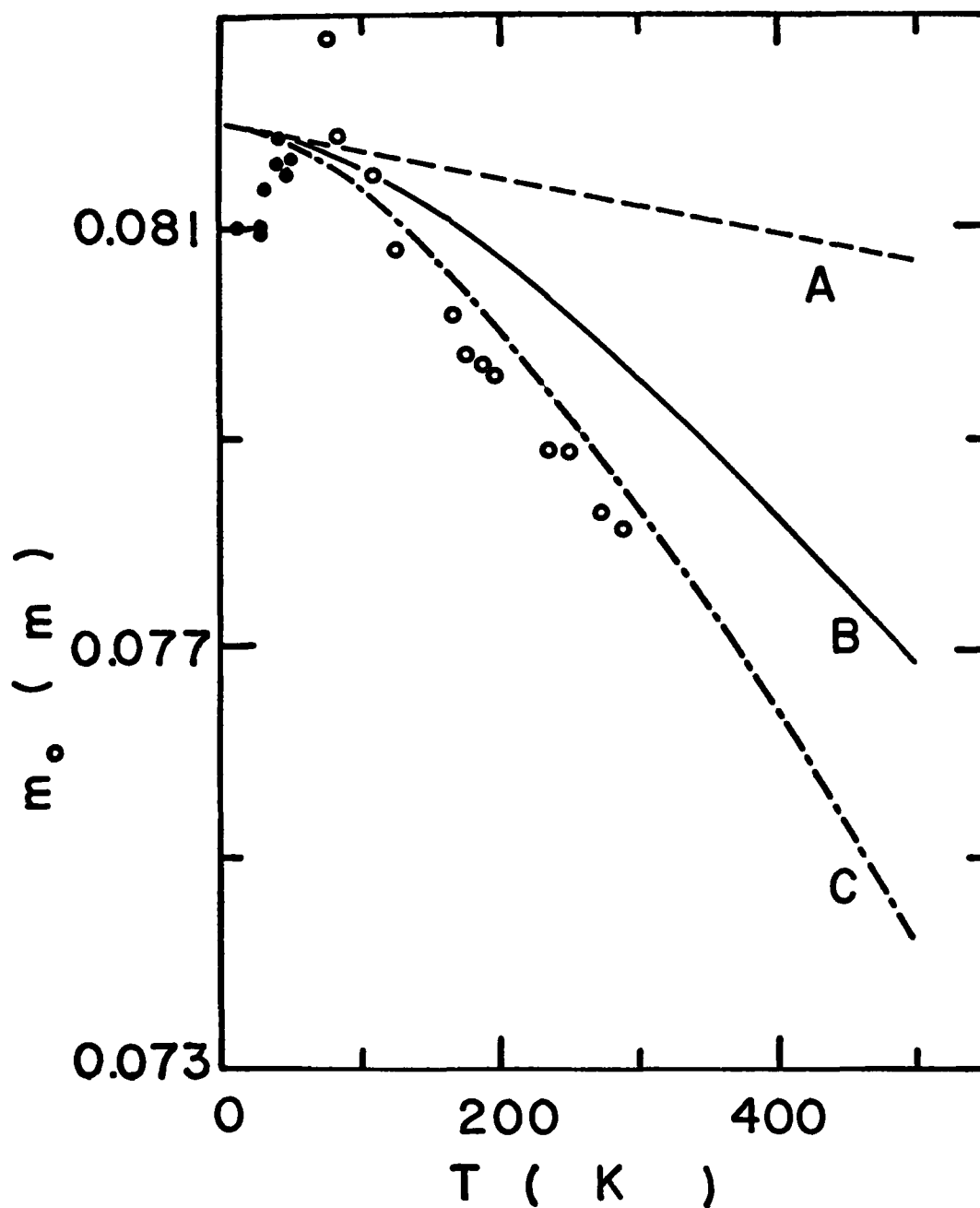


Fig. (VI-6) Variation with temperature of experimental value of effective mass

• (70C1) ○ (70E1) Experimental values
 --- }
 -.- } Theoretical curves (see text)
 ——— }

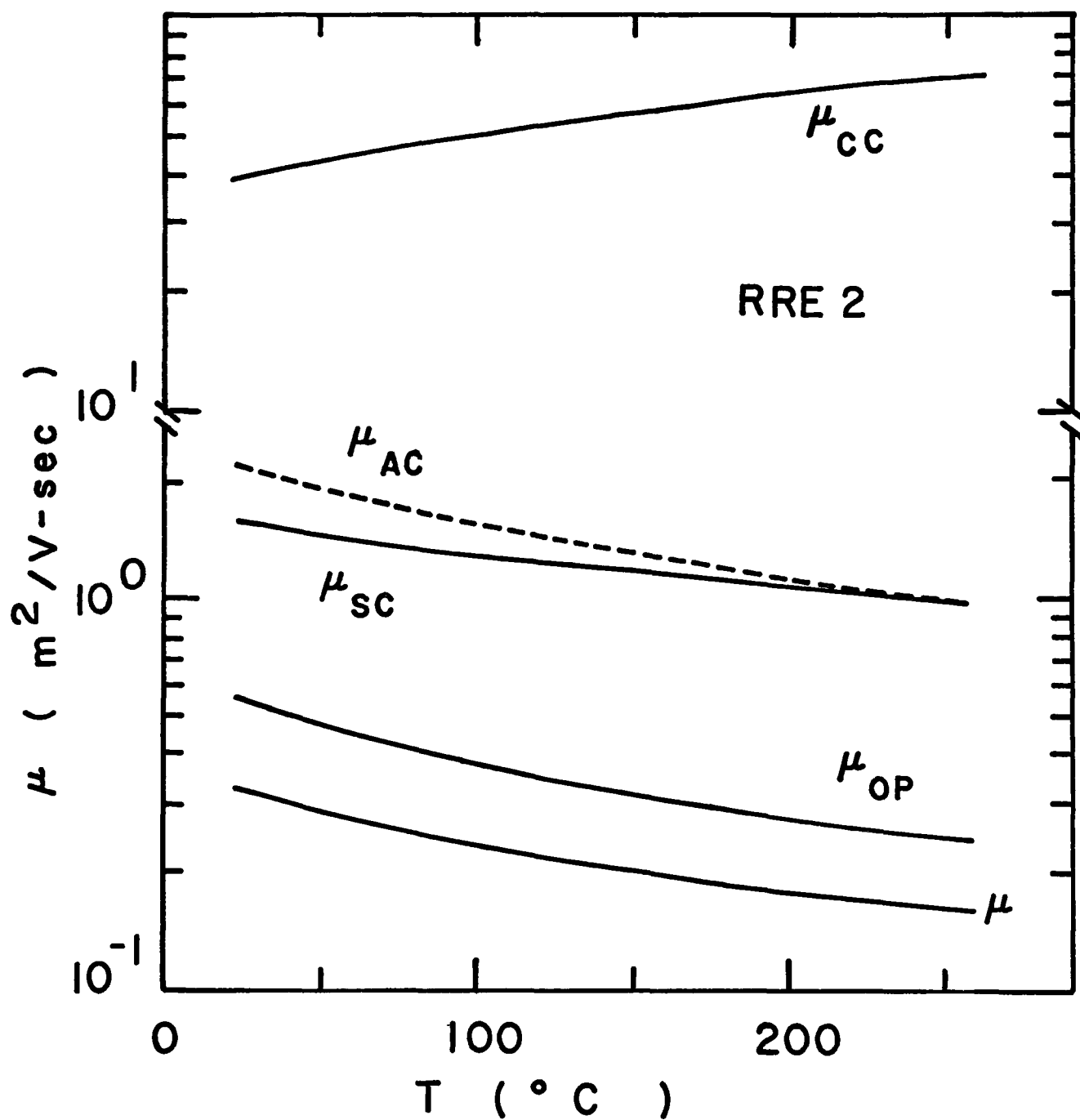


Fig. (VI-7) Mobility calculated as a function of temperature for each scattering mechanism for InP.

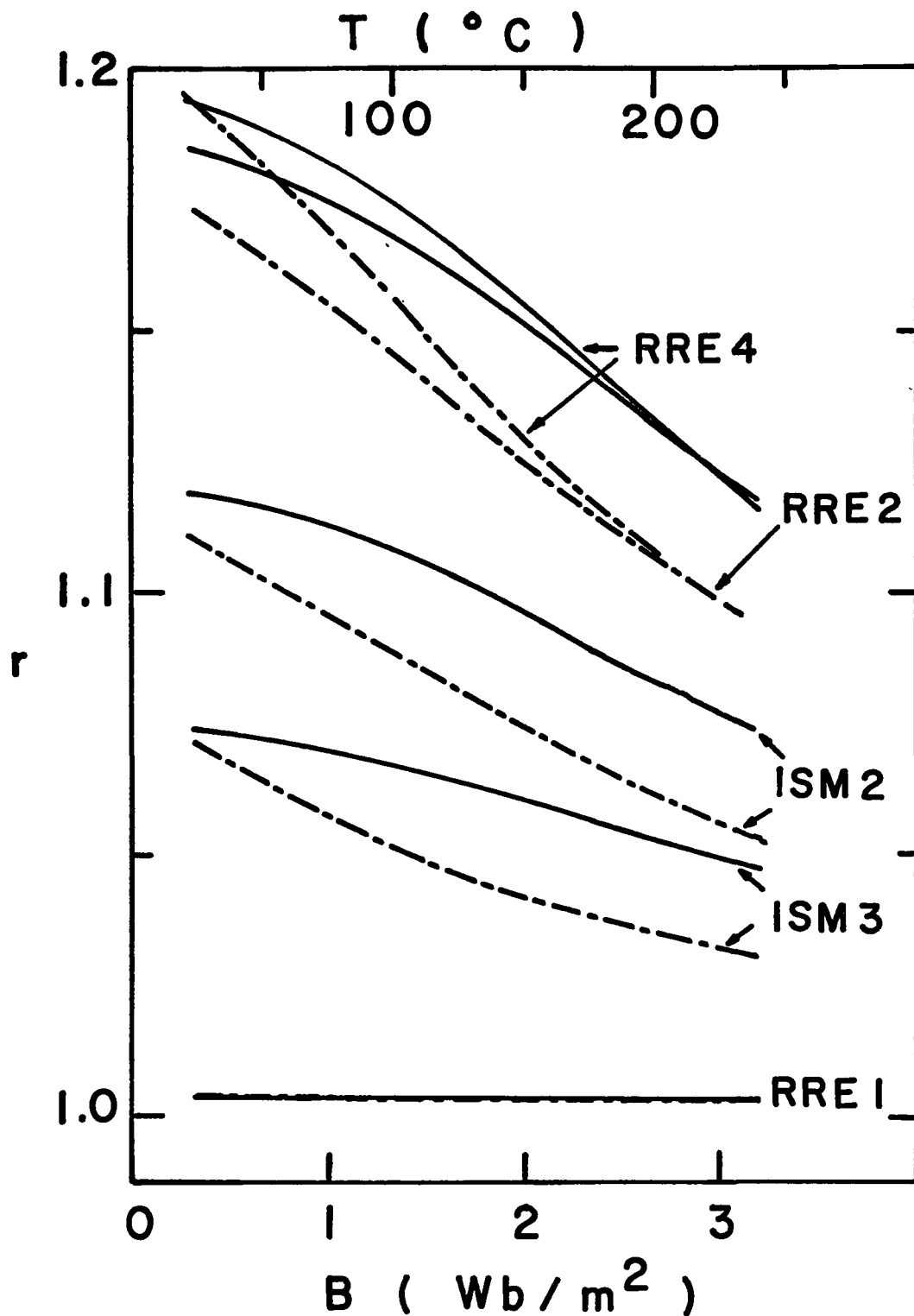


Fig. (VI-8) Hall scattering coefficient as a function of magnetic field at room temperature and of temperature at the magnetic field used for the measurements of Hall coefficient. Full line denotes r vs. T relation.

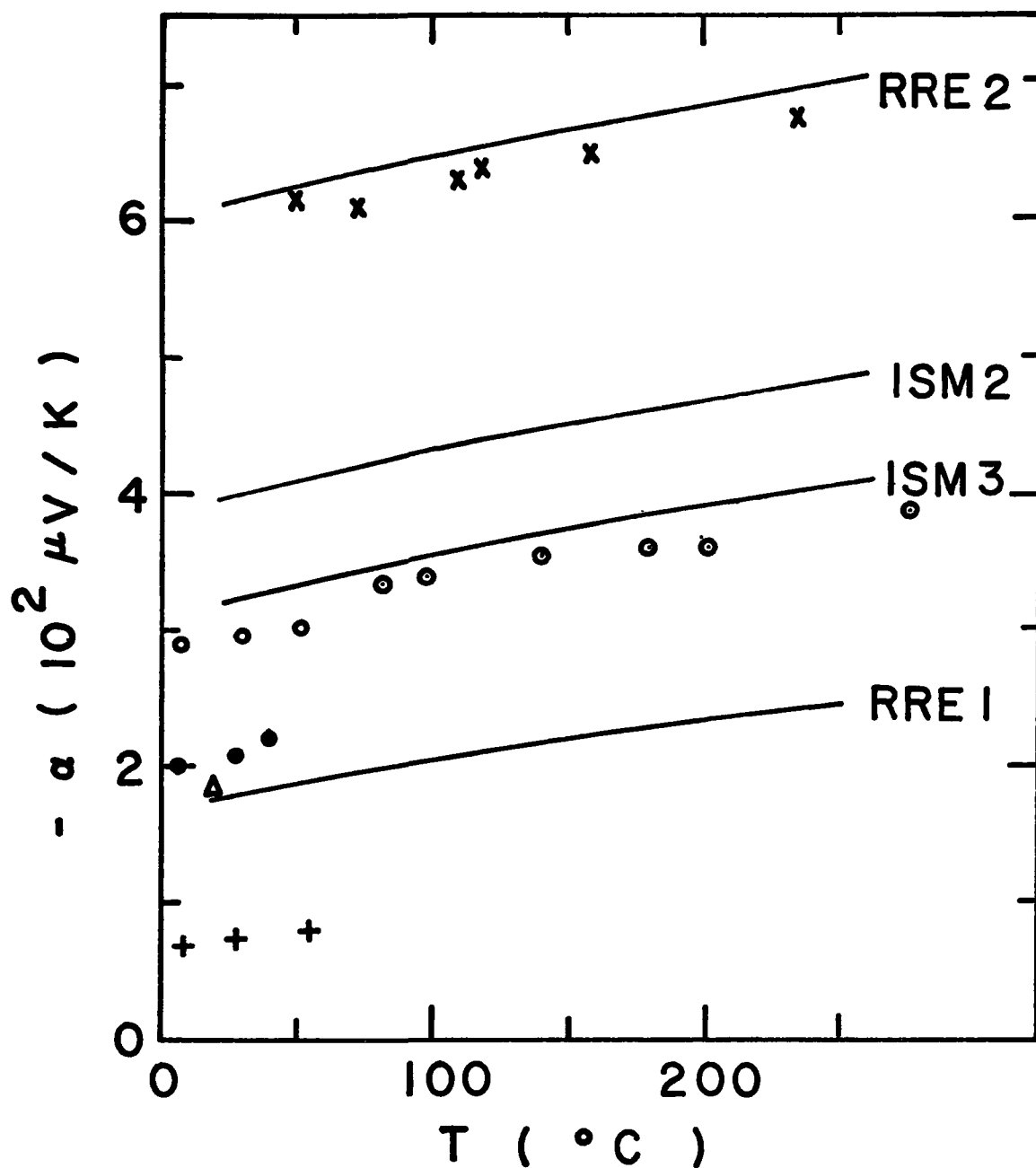


Fig. (VI-9) Theoretically predicted variation of thermoelectric power with temperature. Experimental points are: Δ measured by Demars for a sample cut from the same crystal slice as RRE1, x and $\odot$ by Kudman and Steigmeier (64K1) for samples with $n = 7.1 \times 10^{21}$ and $2.1 \times 10^{23} \text{ m}^{-3}$ respectively and $\circ$, $\bullet$ and $+$ by Kesamanly et al. (69K1) for three different samples with $n = 2.2 \times 10^{23}$, 9×10^{23} and $3.2 \times 10^{24} \text{ m}^{-3}$ respectively.

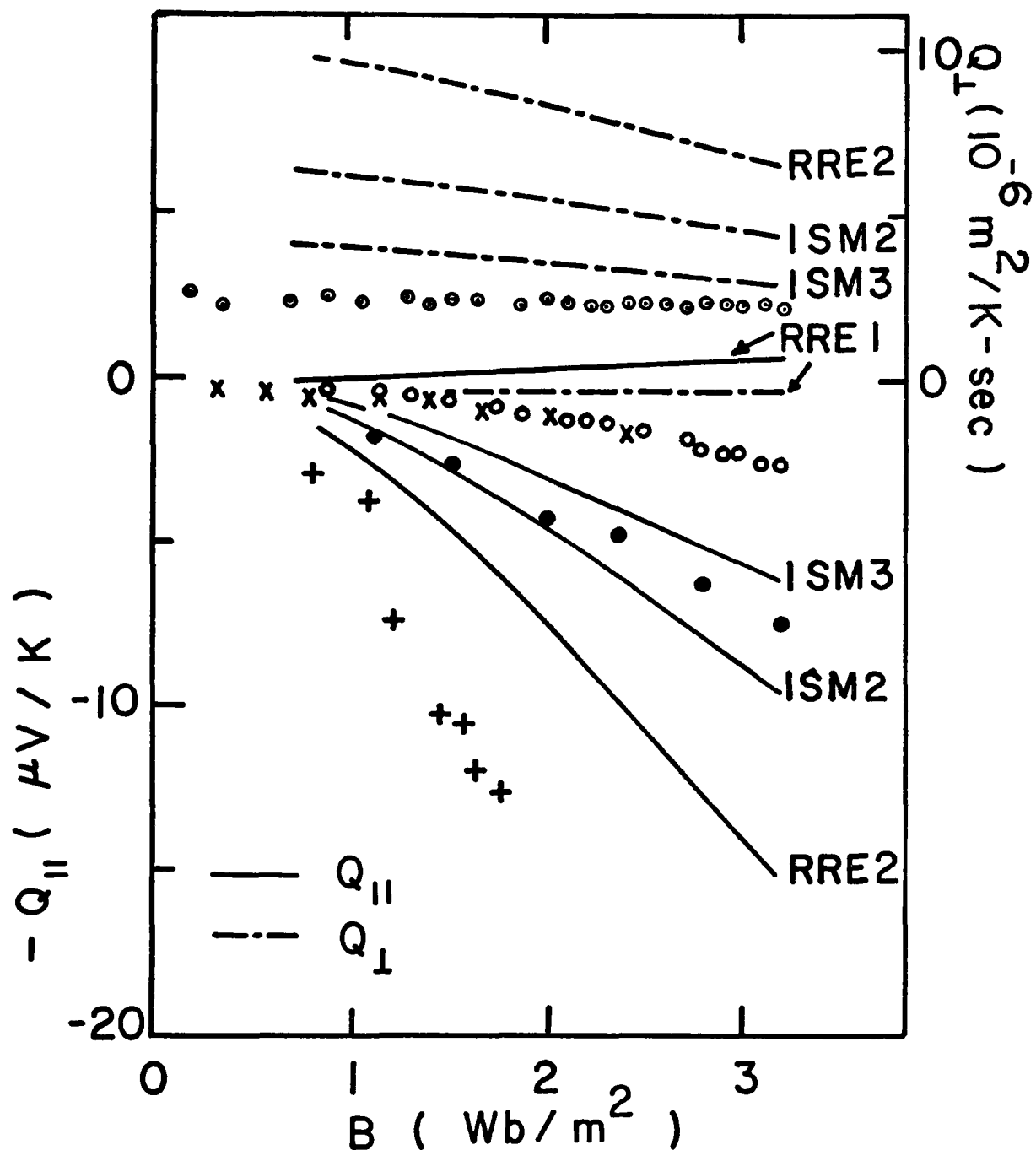


Fig. (VI-10) Longitudinal and transverse Nernst-Ettingshausen coefficient curves predicted as a function of magnetic field for InP. Experimental data to be compared with theoretical curves are:

○ $Q_{\perp}$ value by Demars for a sample cut from the same crystal slice as RRE1, 0 and ● $Q_{||}$ dat by Demars for two different samples cut from the same slice as RRE1 and RRE2 respectively, X and + $Q_{||}$ values by Kesamanly et al. (69K1) for samples with $n = 9 \times 10^{23}$ and $7.7 \times 10^{22} \text{ m}^{-3}$ respectively.

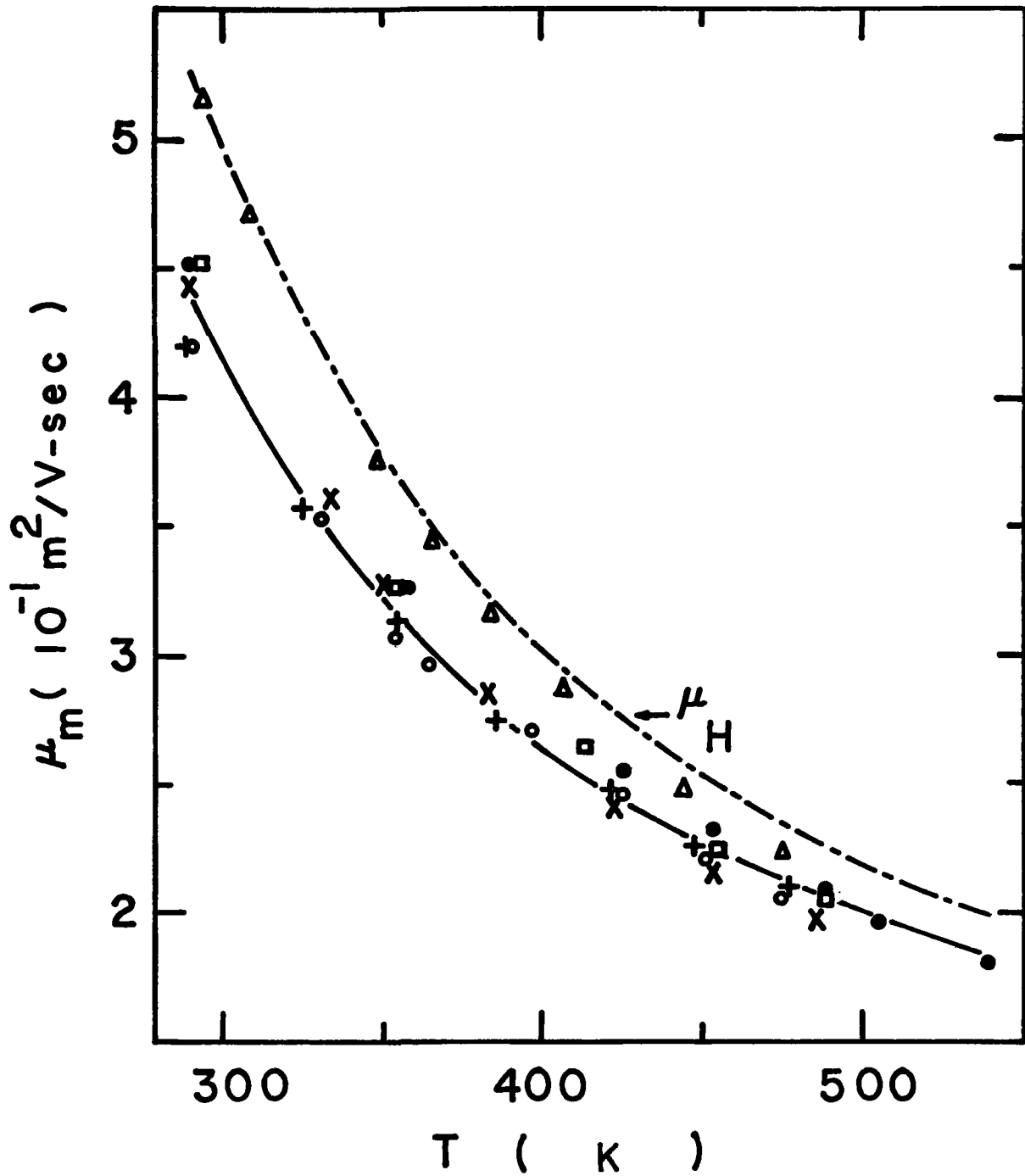


Fig. (VI-11) Theoretical comparison with geometrical magnetoresistance mobility measured by Blood and Orton (74B2). The values of carrier density are: $1.9 \times 10^{21} \text{ m}^{-3}$ (Δ and $\bullet$), $4.9 \times 10^{21} \text{ m}^{-3}$ ($\square$), $5 \times 10^{21} \text{ m}^{-3}$ ($+$), $7 \times 10^{21} \text{ m}^{-3}$ ($\circ$) and $8 \times 10^{21} \text{ m}^{-3}$ ($\times$). ----- and ——— present theoretical curves of μ_H and μ 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_0^* for the Γ_1 band. This parameter, introduced in a semi-empirical way by Ehrenreich, has never been put on a firm theoretical

basis. Here E_O^* has been used as a normalizing parameter to relate known values of Γ_1 band effective mass to the known E_O 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_O^* 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 Γ_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_1 and L_1 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_1 band from the present transport results while at high x values nothing could be determined concerning the L_1 and Γ_1 bands. However as was seen in the case of GaAs, data determined at high pressure gave useful results on the X_1 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

$\text{Ga}_{1-x}\text{In}_x\text{P}$, $\text{GaAs}_{1-x}\text{P}_x$, $\text{GaAs}_x\text{Sb}_{1-x}$ and some quaternary III-V alloys.

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