

TRANSPORT CHARACTERISTICS OF
EPITAXIALLY GROWN $\text{InAs}_{1-x}\text{P}_x$

By

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To my parents
my best teachers

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Although several people have added their time and knowledge to this work, I feel two should be singled out to whom I am especially indebted.

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by

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An experimental study has been made of the transport properties of $\text{InAs}_{1-x}\text{P}_x$ grown epitaxially from the vapor phase onto semi-insulating GaAs substrates. The hydrogen carrier gas flow rate was varied for four sets of samples of $\text{InAs}_{0.61}\text{P}_{0.39}$ with changing thickness between sets. A fifth set was investigated with varying composition. Resistivity and Hall effect measurements from 3K to 300K yielded electron mobilities as high as 13,100 $\text{cm}^2/\text{volt-sec}$ at 77K and electron concentrations from $1.5 \times 10^{16} \text{cm}^{-3}$ to $8 \times 10^{16} \text{cm}^{-3}$ at 300K. Transport at low temperatures ($T < 30\text{K}$) is attributed to the formation of a donor impurity band.

CHAPTER I
INTRODUCTION

There has been an active interest in the development and properties of III-V compounds. Lately, much of this effort has been directed toward III-V ternary compounds, especially the $\text{InAs}_{1-x}\text{P}_x$ system because of its many useful characteristics such as high electron mobility and broad range of energy band gaps (0.36eV for InAs to 1.29eV for InP). These characteristics indicate that the $\text{InAs}_{1-x}\text{P}_x$ system has several device applications such as injection laser diodes¹ and detecting devices operable in the infrared region with wavelengths from 0.96 to 3.45 μm . Highly efficient photocathodes operating at 1.06 μm have been fabricated^{2,3} from the $\text{InAs}_{1-x}\text{P}_x$ system. The band structure and high mobility also indicate the possibility of high frequency applications such as Gunn oscillators.^{4,5}

Folberth⁶ first reported both the $\text{InAs}_{1-x}\text{P}_x$ and the $\text{GaAs}_{1-x}\text{P}_x$ systems in 1955. However, the $\text{InAs}_{1-x}\text{P}_x$ system was almost totally ignored since research at that time was directed more toward materials, such as $\text{GaAs}_{1-x}\text{P}_x$, whose band gaps were in the visible light range. Now with the interest in infrared emission and detection there is a renewed interest in $\text{InAs}_{1-x}\text{P}_x$. All work, until recently,

on $\text{InAs}_{1-x}\text{P}_x$ has been attempts to grow pure single crystals using standard bulk techniques previously successful with group IV semiconductors.^{7,8} The resulting crystals were typically inhomogenous and polycrystalline. Vapor-deposited epitaxial layers of $\text{InAs}_{1-x}\text{P}_x$ were first reported by Tietjen et al.⁹ in 1969. The layers were grown on conducting InAs substrates which had to be mechanically removed before measurements could be made on the epilayers. Thus, layers of at least 100 μm thicknesses had to be grown to insure mechanical strength. Later, Allen and Mehal^{10,11} deposited $\text{InAs}_{1-x}\text{P}_x$ on substrates of both GaAs and GaP for their insulating nature and for their utility as optical windows in photocathodes.

Epitaxially grown $\text{InAs}_{1-x}\text{P}_x$ is limited, as yet, by impurity content, surface states, and low mobility. There is then a need to broaden the knowledge of not only the electrical characteristics of epitaxial $\text{InAs}_{1-x}\text{P}_x$ but also how those characteristics may be enhanced by altering the growth conditions. These are the basic intentions of this research.

A general discussion of some theoretical aspects is presented in Chapter II. The effects of different scattering modes, especially those important to $\text{InAs}_{1-x}\text{P}_x$, are considered. Also the idea of conduction within an impurity band is developed.

The samples used for this research were epitaxially deposited using the hydride system similar to Tietjen's. The

growth procedure is presented in Chapter III along with a summary of the experimental methods used in measuring the transport properties.

The experimental results obtained for samples of $\text{InAs}_{0.61}\text{P}_{0.39}$ grown with different flow rates and varying epitaxial thicknesses are presented in Chapter IV. The results for samples of varying composition ($\text{InAs}_{1-x}\text{P}_x$) are presented in Chapter V. In both chapters the results are compared to the theory of Chapter II.

In the last chapter some conclusions are made concerning the properties of these epitaxial samples.

CHAPTER II

THEORY OF ELECTRON TRANSPORT IN $\text{InAs}_{1-x}\text{P}_x$

2.1 Crystal Properties

The ternary semiconductor $\text{InAs}_{1-x}\text{P}_x$ crystallizes, like most III-V compounds, into the cubic zinc-blende structure. The band structures of InAs and InP are very similar in nature and Oswald¹² has shown that for mixed crystals in the form $\text{InAs}_{1-x}\text{P}_x$, the energy gap, E_g , varies linearly as a function of x . This linear variation will be used as an approximation to determine other constants needed for theoretical analysis such as the effective mass, dielectric constant, and lattice constant. As further justification for this approximation the distance between centers of III-V atom may be given quite accurately by the sum of their tetrahedral radii. Using the values given by Hilsum and Rose-Innes¹³ of 1.44\AA for In, 1.18\AA for As, and 1.10\AA for P, then interpolating between the radii for As and P, a value for the cube edge of the unit cell ($2.31 \times$ III-V distance) may be obtained for $\text{InAs}_{0.61}\text{P}_{0.39}$ of $a=5.984\text{\AA}$. This compares quite well with the experimental value of 5.985\AA obtained by Tietjen et al.⁹

From the results of Oswald¹² the variation of band gap with x is plotted in Fig. 2.1. The experimental results from optical measurements on samples used in this study are also plotted and show a strong correlation to Oswald's results. The temperature variation for $\text{InAs}_{0.61}\text{P}_{0.39}$, obtained from an interpolation of Oswald's data, is shown in Fig. 2.2 for temperatures up to 300K.

2.2 Scattering Processes

In any semiconductor, the charge carriers (i.e. electrons and holes), at temperatures above absolute zero, may be scattered by a number of different mechanisms. These mechanisms normally have their dominance in certain temperature regimes but in some cases two or more may be interacting simultaneously. In a polar semiconductor, such as $\text{InAs}_{1-x}\text{P}_x$, the most important scattering mechanisms which limit the mobility of the charge carriers are polar optical phonon scattering, ionized impurity scattering, neutral impurity scattering, and electron-electron collisions.

In the following sections the theoretical effects of these scattering mechanisms on the transport properties of $\text{InAs}_{1-x}\text{P}_x$ will be considered. For most of the calculations presented here only the theory pertinent to $\text{InAs}_{0.61}\text{P}_{0.39}$ will be shown since the greater portion of the samples studied in this work were of that composition. Comparisons of the theory to experimental data will be made later when the results are presented in Chapter IV and V.

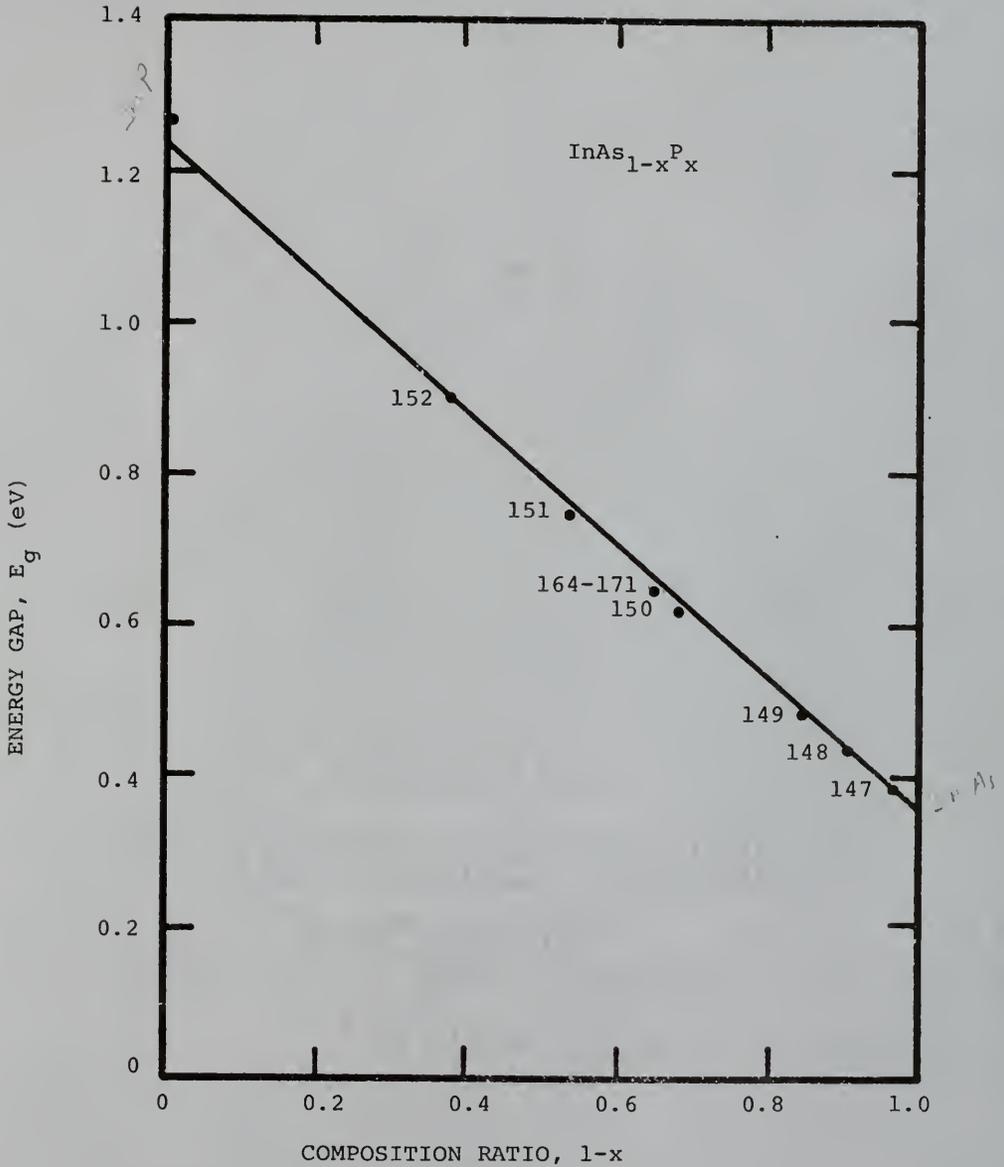


FIGURE 2.1 VARIATION OF ENERGY BAND GAP WITH COMPOSITION

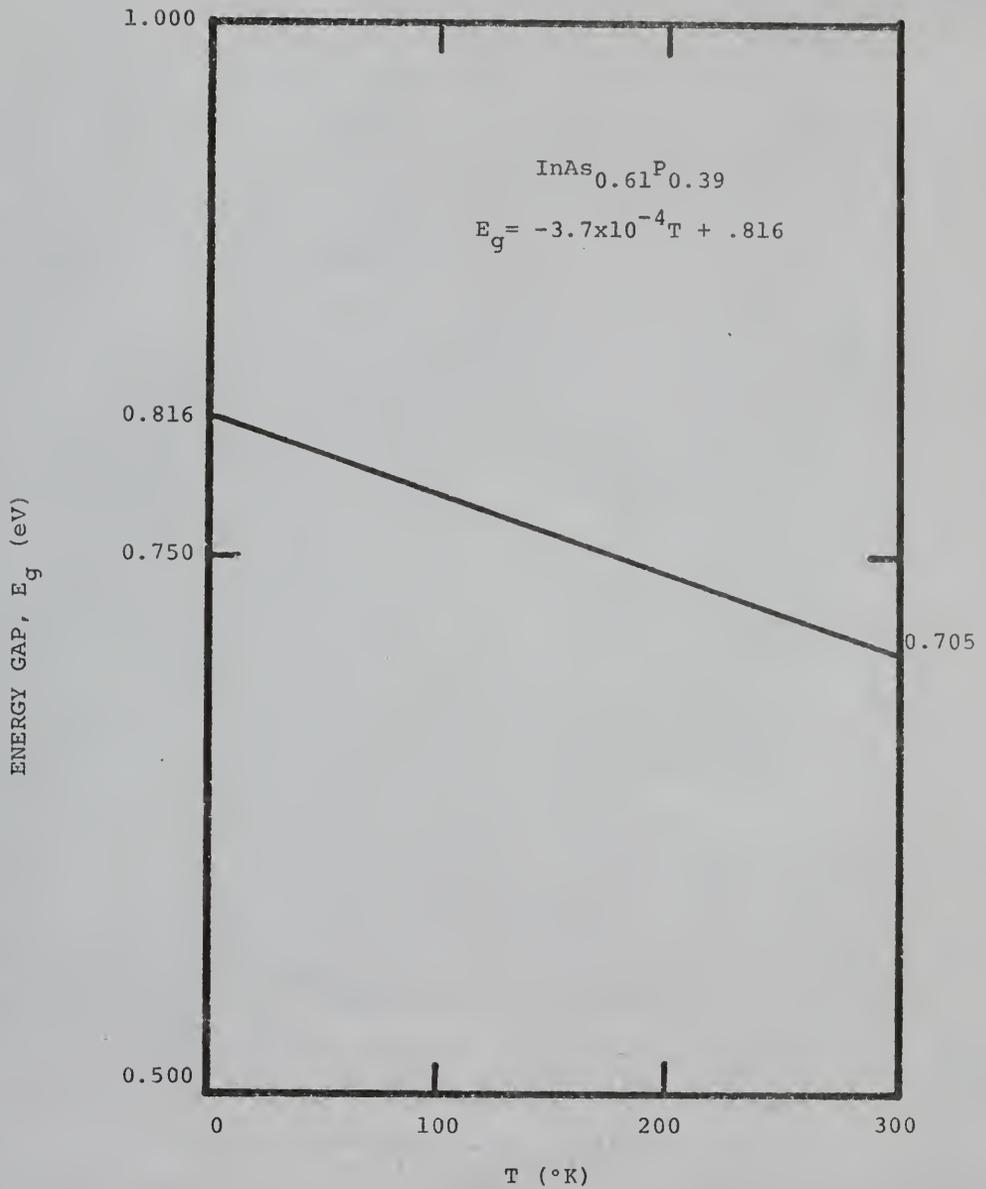


FIGURE 2.2 VARIATION OF ENERGY BAND GAP WITH TEMPERATURE

2.2a Optical Phonon Scattering

The effects of optical phonons in a compound semiconductor are twofold and their strength is dependent upon the nature of the bonding between the atoms. In a crystal dominated by ionic bonds, the opposing motion of ions of opposite charge produce large polarization fields with which electrons strongly interact. However, a less mentioned effect becomes more important in semiconductors with covalent bonding. This process is similar to acoustic phonon scattering in that an electron upon encountering an optical phonon sees the vibrating atoms out of their normal position in the crystal. The crystal potential is altered by this change in position and the electron is deflected from its original course. Unfortunately, the strength of this perturbation is not known and in the theoretical analysis it must be included as an unknown value. Ziman¹⁴ has shown that at high temperatures the mobility limited by this process is quite similar in form to the mobility equation derived from acoustical phonon scattering. The importance of this distinction between the two modes of scattering attributed to optical phonon scattering lies in the fact that the bonding in III-V compounds is neither totally covalent or totally ionic but falls somewhere in between those limits. The bonding scheme is certainly even more confused by the fact that this study deals with the ternary compound, $\text{InAs}_{1-x}\text{P}_x$. As an approximation, however, the contribution from polarization is considered dominant and therefore only

polar optical phonon scattering will be presented here.

Analysis of electron scattering due to polar interaction is complicated by the fact that the approximation of a relaxation time is only valid when the energy emitted or absorbed by an electron in a collision is small compared to the initial energy of the electron. This is true when the condition

$$(\theta_D/T)^2 \ll 1 \quad (2.1)$$

is satisfied. This, as will be seen shortly, is certainly not the case for $\text{InAs}_{1-x}\text{P}_x$ at room temperature or below.

The first correct treatment of this problem was done by Howarth and Sondheimer¹⁵ and although some authors^{16,17} have modified their theory to account for special cases, it is generally in close agreement with experimental data. From the results of their complex mathematical treatment, the mobility due to polar optical scattering may be written as

$$\mu_0 = 3.54 \times 10^{40} \left(\frac{e}{e^*} \right)^2 \left(\frac{m_0}{m^*} \right)^{3/2} MvT^{1/2} \theta_D F \left(\frac{\theta_D}{T} \right) \left[\exp \left(\frac{\theta_D}{T} \right) - 1 \right] \quad (2.2)$$

where e^* is the effective charge, m^* is the effective mass, and v is the volume of the unit cell. The term M is the reduced mass of the atoms given by

$$M = \frac{M_1 M_2}{M_1 + M_2} \quad (2.3)$$

For the case of $\text{InAs}_{1-x}\text{P}_x$, the M_2 was taken to be a linear interpolation between the mass of an arsenic atom and the mass of a phosphorus atom. The function $F \left(\frac{\theta_D}{T} \right)$ is a slowly

varying function which decreases from unity at high temperatures to a minimum of 0.6 when $\theta_D=T$, and then increases steadily with $\frac{\theta_D}{T}$. A graph of this function is shown in Fig. 2.3. The Debye temperature, θ_D , is characteristic of the material and is relatively constant at room temperatures but decreases with decreasing temperature. The values for these parameters are listed in Table 2.1 for InAs, InP, and InAs_{0.61}P_{0.39}. The Debye temperature for InAs_{0.61}P_{0.39} is shown in Fig. 2.4 from a linear interpolation of curves given for InAs and InP by Willardson and Beer.¹⁸ Equation 2.2 is plotted versus inverse absolute temperature in Fig. 2.5 for InAs, InP, and InAs_{0.61}P_{0.39}. It is useful to note that the theoretical mobility due to polar optical scattering shown in Fig. 2.5 may be closely approximated by a power function in this temperature region. For the three compositions shown the following temperature dependences result:

InAs	$\mu=a_1T^{-2.20}$
InAs _{0.61} P _{0.39}	$\mu=a_2T^{-2.28}$
InP	$\mu=a_3T^{-2.42}$

These are necessarily the strongest dependences allowable in this region. Any other scattering mechanisms interacting with polar optical phonons will decrease the mobility and decrease its temperature dependence as will become evident when ionized impurity scattering is considered.

2.2b Ionized Impurity Scattering

Scattering of electrons by ionized impurity centers is in general more effective than phonon scattering, because

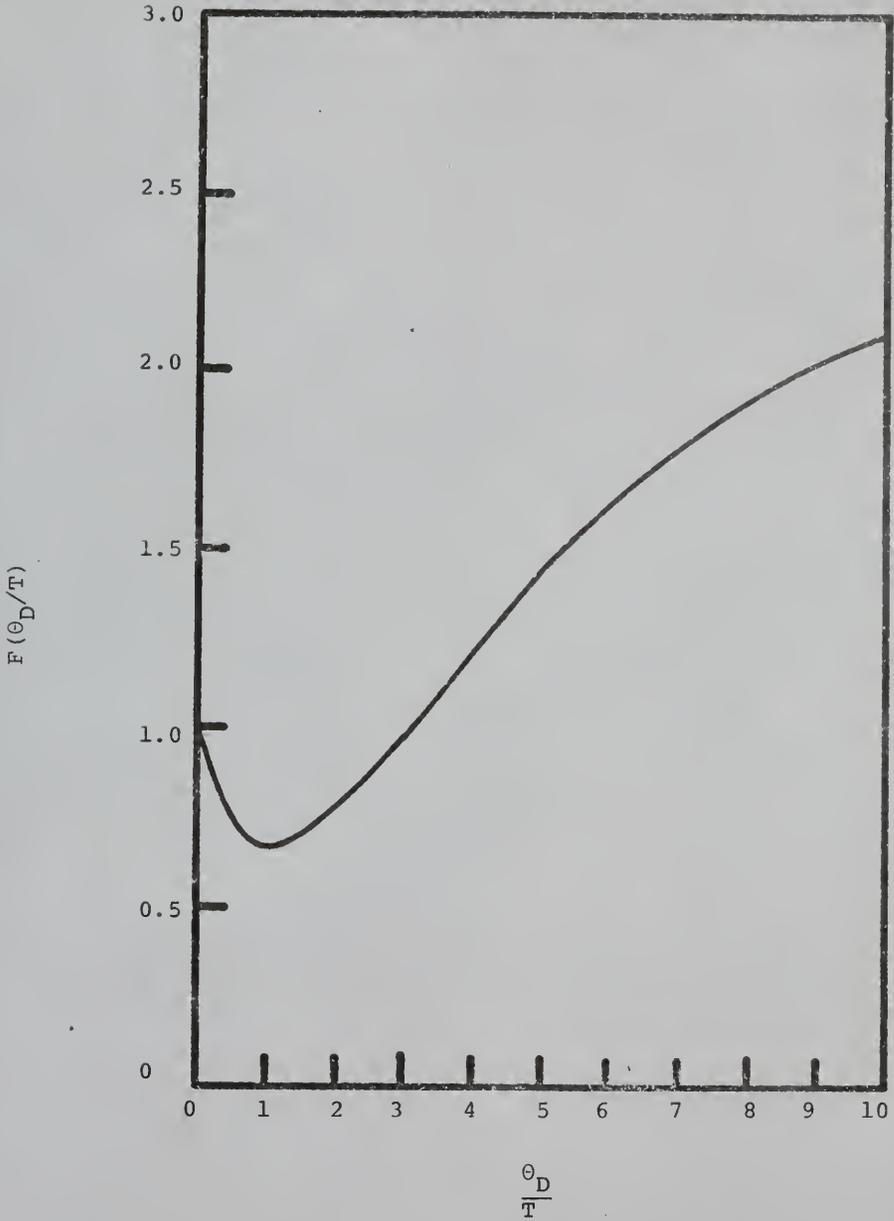
FIGURE 2.3 VARIATION OF THE FUNCTION $F(\theta_D/T)$

TABLE 2.1
 PARAMETERS FOR $\text{InAs}_{1-x}\text{P}_x$

	InAs	$\text{InAs}_{0.61}\text{P}_{0.39}$	InP
$\frac{e^*}{e}$	0.22	0.2278	0.24
$\frac{m^*}{m_0}$	0.02	0.0408	0.073
V	$2.217 \times 10^{-22} \text{ cm}^3$	$2.143 \times 10^{-22} \text{ cm}^3$	$2.020 \times 10^{-22} \text{ cm}^3$
M	$7.527 \times 10^{-23} \text{ g}$	$6.375 \times 10^{-23} \text{ g}$	$4.050 \times 10^{-23} \text{ g}$
κ	11.5	11.26	10.9

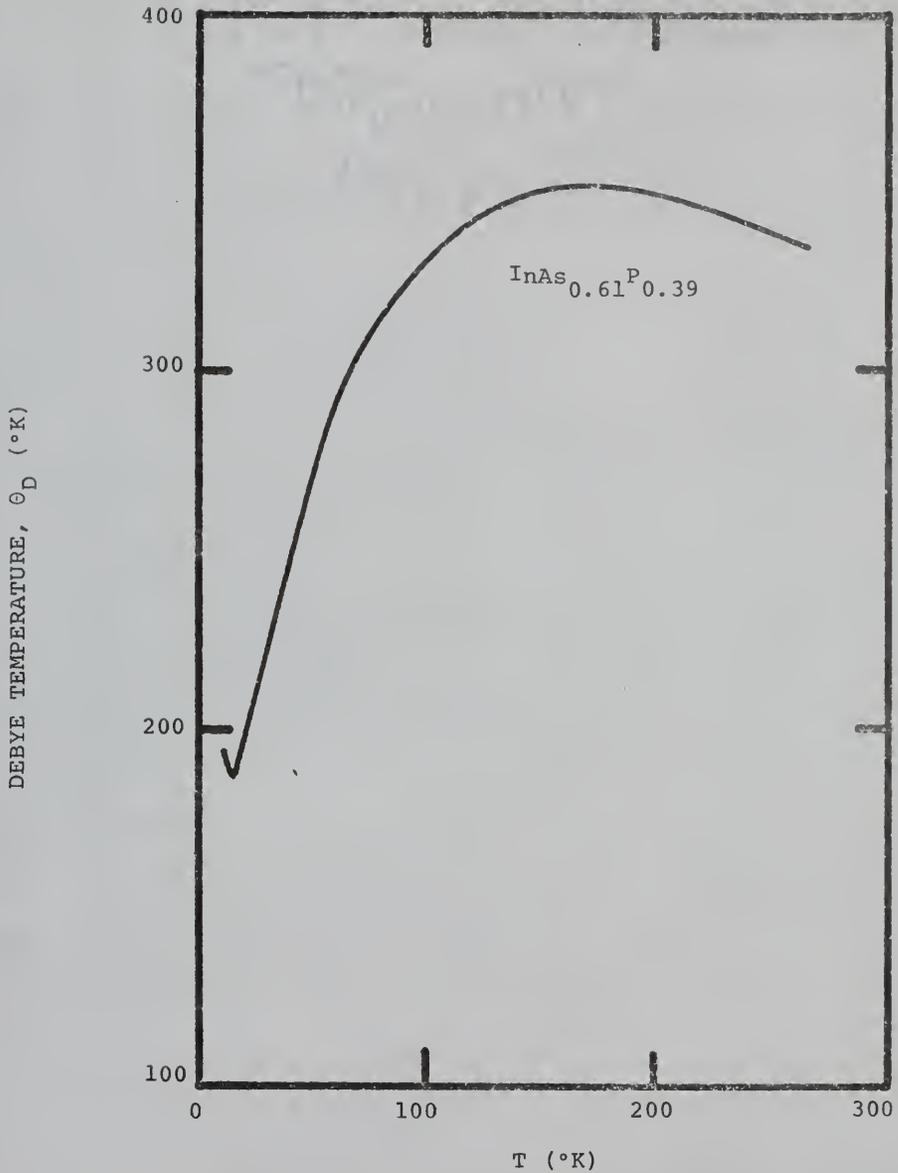


FIGURE 2.4 VARIATION OF DEBYE TEMPERATURE WITH ABSOLUTE TEMPERATURE

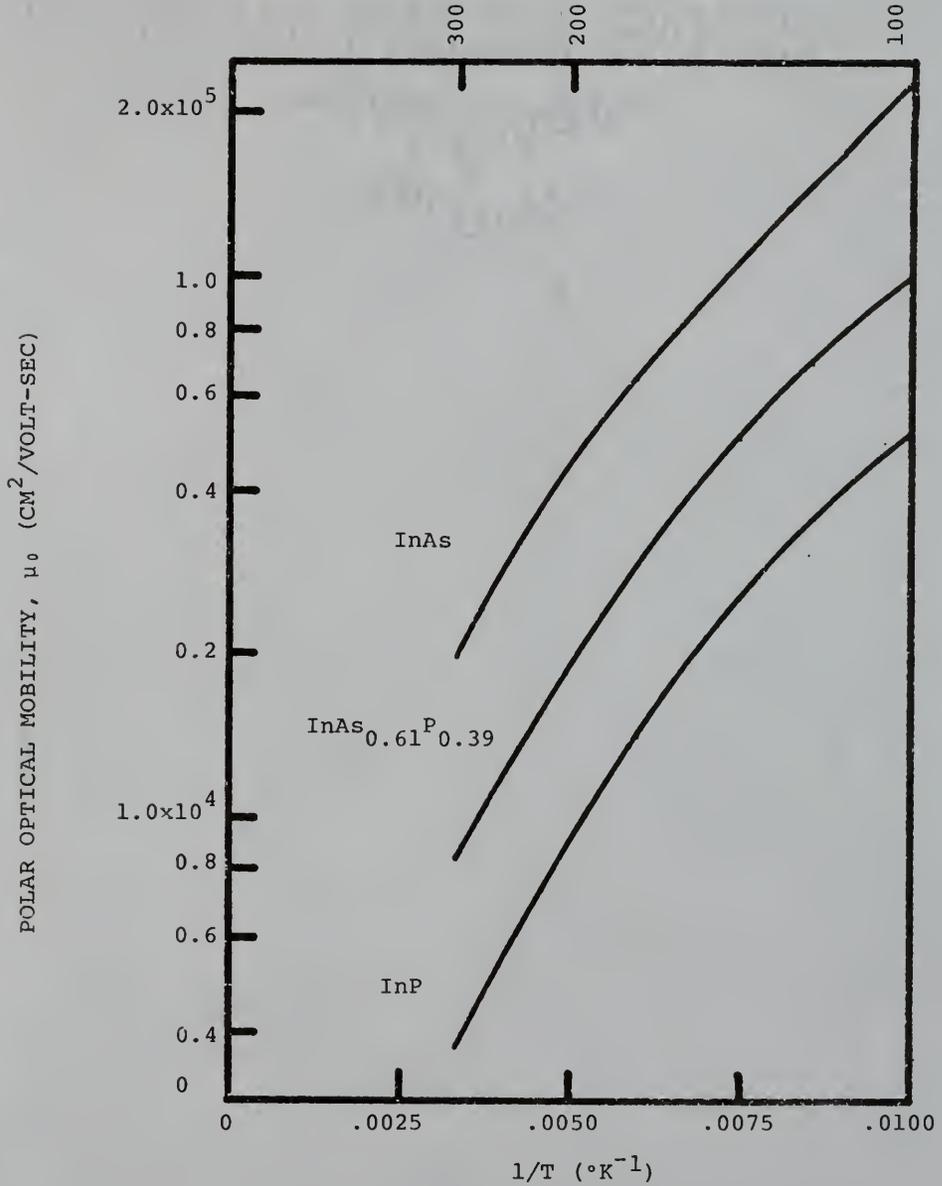


FIGURE 2.5 MOBILITY LIMITED BY POLAR OPTICAL PHONON SCATTERING

of the electric charge associated with each impurity. The perturbing potential is normally assumed to be equal to the charge difference between the valence of the impurity atom and the crystal atom which it replaced. Thus an electron will interact with this perturbing potential and be scattered by the Coulomb field.

Conwell and Weisskopf¹⁹ treated scattering due to ionized impurities in an essentially classical manner. Each ion was assumed to scatter independently of each other but with its scattering strength truncated in the calculations at a distance equal to half the average distance between the ionized impurities. This assumption is somewhat justified by the screening effect of conduction electrons on the impurities. The result of their analysis gives a mobility limit due to ionized impurities in the form

$$\mu_i = \frac{2^{7/2}}{\pi^{3/2}} \frac{\kappa^2 (kT)^{3/2}}{m^{*1/2} e^3 N_i} \frac{1}{\ln[1 + (3\kappa kT/e^2 N_i^{1/3})^2]} \quad (2.4)$$

where κ is the effective dielectric constant, m^* is the effective mass and N_i is the concentration of ionized impurities.

A quantum-mechanical approach by Brooks²⁰ takes into account the effects of screening by the conduction electrons. The results of this treatment give a mobility which is identical to that of Conwell and Weisskopf except for an alteration in the logarithmic term.

$$\mu_i = \frac{2^{7/2} \kappa^2 (kT)^{3/2}}{\pi^{3/2} m^{*1/2} e^3 N_i f(b)} \quad (2.5)$$

$$f(b) = \ln(1+b) - \frac{b}{1+b} \quad (2.6)$$

$$b = \frac{24\pi\kappa m^* k^2 T^2}{nh^2 e^2} \quad (2.7)$$

In Eqn. 2.7, n is the concentration of conduction electrons.

These two forms for the mobility due to ionized impurity scattering, though derived from somewhat different principles, have basically the same form and for temperatures between 300 and 78K have been shown²¹ to give almost identical numerical results for germanium. This close correspondence between the two equations was verified for the ternary semiconductor, $\text{InAs}_{1-x}\text{P}_x$, presented in this work. In most experimental semiconductor work, especially with silicon or germanium, the Brooks-Herring formula, Eqn. 2.5, is used to describe the region of mobility controlled by ionized impurities. However, due to the closeness of the results of the Conwell-Weisskopf formula and in light of some assumptions to be presented later, Eqn. 2.4 will be used here to describe this scattering process.

The Conwell-Weisskopf formula may be expressed in practical units as

$$\mu_i = 3.286 \times 10^{15} \frac{\kappa^2 T^{3/2}}{m^{*1/2} N_i} \frac{1}{\ln[1 + (1.795 \times 10^3 \frac{kT}{N_i^{1/3}})]^2} \quad (2.8)$$

where N_i is expressed in cm^{-3} . Equation 2.8 was combined

with the mobility due to polar optical phonon scattering, Eqn. 2.2, using the relation²²

$$\mu_T^{-1} = \mu_0^{-1} + \mu_i^{-1} \quad (2.9)$$

The results of this combination for $\text{InAs}_{0.61}\text{P}_{0.39}$ are shown in Fig. 2.6 for varying concentrations of ionized impurities N_i . From these curves it may be seen that as the ionized impurity concentration increases the maximum of the mobility curves shift to higher temperatures. Also the initial slopes of the curves at 300K decrease with increasing impurity concentration. As was indicated in the discussion of optical phonon scattering, this portion of the curve dominated by optical phonons may be approximated by the equation

$$\mu = aT^{-\beta} \quad (2.10)$$

The power of temperature dependence, β , is then shown in Fig. 2.7 as a function of the ionized impurity concentration. This curve will serve later as a useful indicator of the impurity content of the samples studied by calculating the temperature power dependence of the experimental data at 300K and comparing that to Fig. 2.7.

2.2c Neutral Impurity Scattering

A third important source of electron scattering is due to the effects of neutral impurities. This type of scattering is most effective at low temperatures where most semiconductors exhibit only a small degree of ionization. It

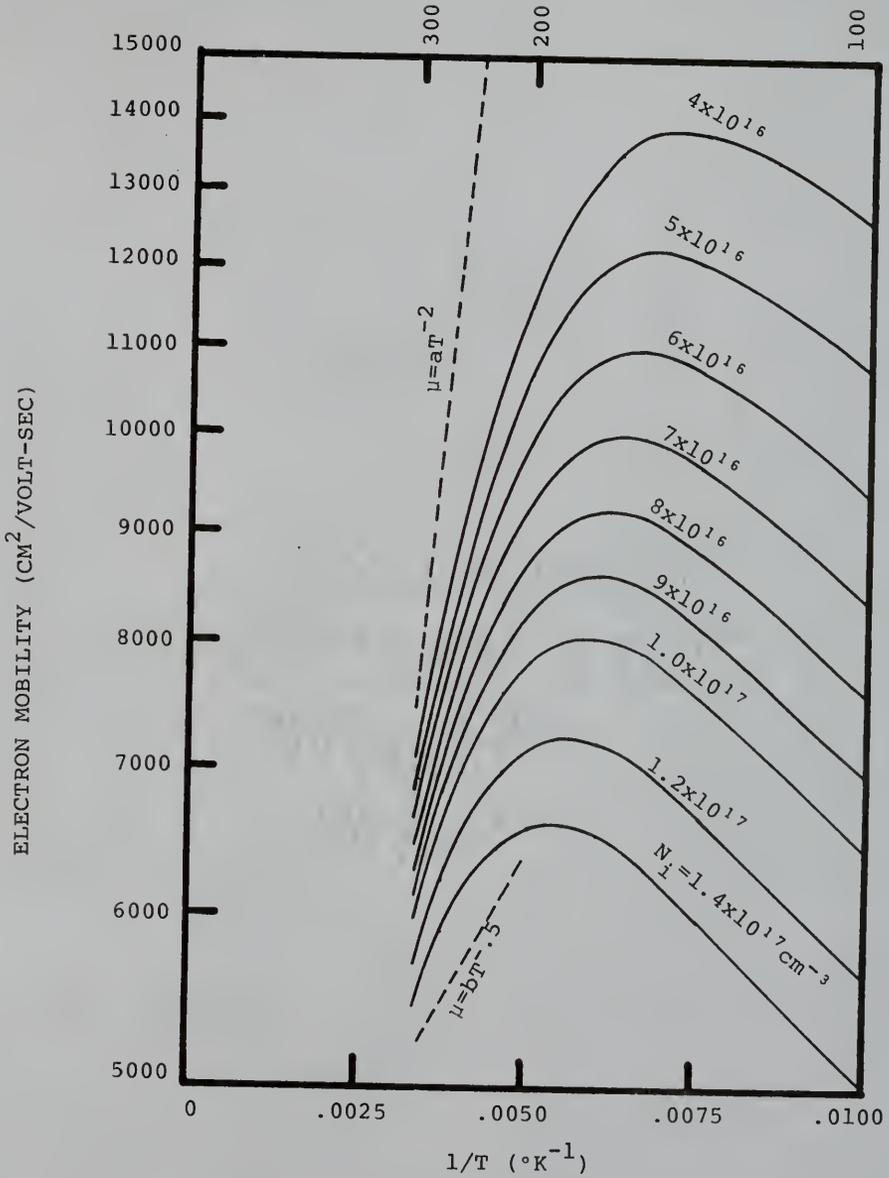


FIGURE 2.6 COMBINED MOBILITY LIMITS DUE TO POLAR OPTICAL PHONON AND IONIZED IMPURITY SCATTERING FOR InAs_{0.61}P_{0.39}

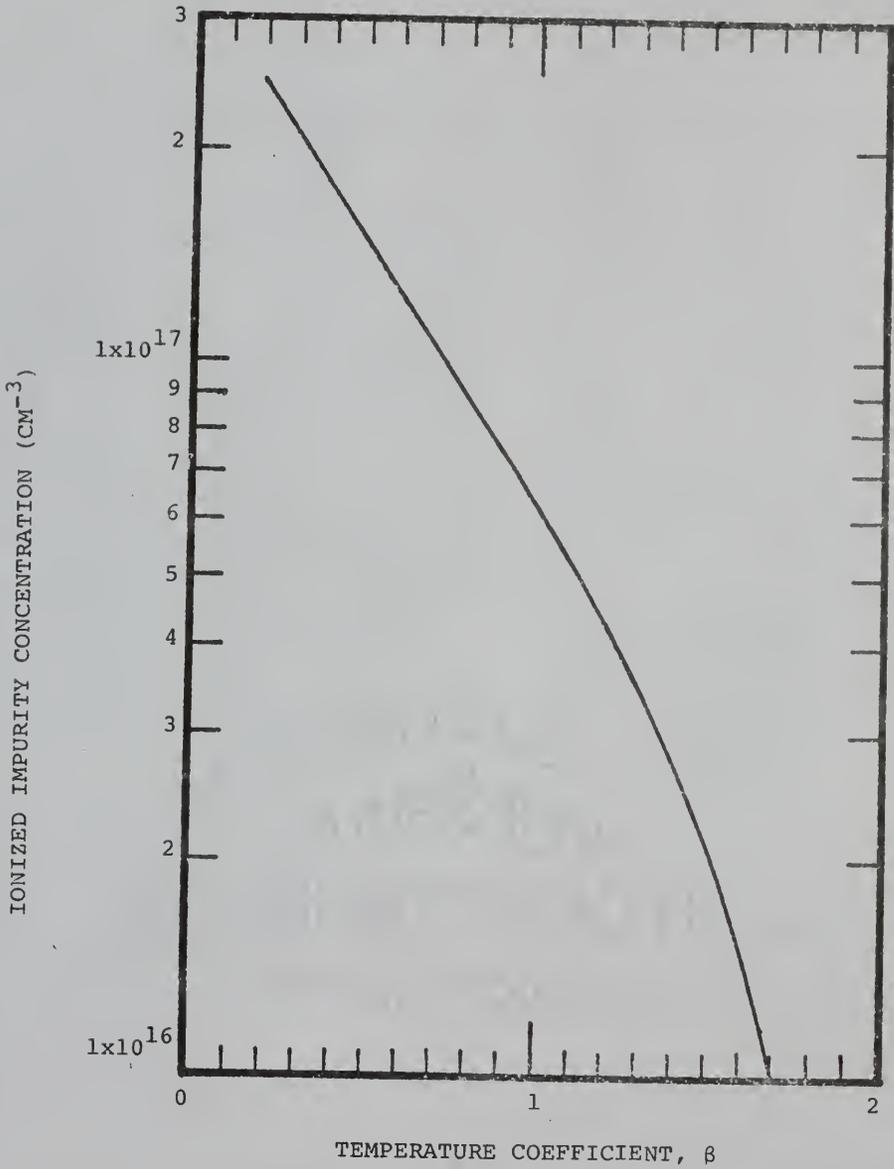


FIGURE 2.7 VARIATION OF TEMPERATURE COEFFICIENT, β , WITH IONIZED IMPURITY CONCENTRATION

may be comparable to scattering due to ionized impurities up to temperatures of around 100K.²³ Erginsoy²⁴ derived a theoretical model for this type of scattering by approximating an unionized donor or acceptor atom with a hydrogen atom. From this model, a mobility was derived which was temperature independent.

$$\mu_{ne} = \frac{1}{20} \frac{m^*e^3}{N_n \kappa h^3} \quad (2.11)$$

However, experimentally this temperature independence is not generally seen.²⁵ Erginsoy's theory was modified by Sclar²⁶ by including the possibility of bound states in the electron-hydrogen impurity scattering problem. His results were temperature dependent and the mobility from this theory may be expressed as

$$\mu_n = 0.82\mu_{ne} \left[2/3 \left(\frac{\kappa T}{E_n} \right)^{1/2} + 1/3 \left(\frac{E_n}{\kappa T} \right)^{1/2} \right] \quad (2.12)$$

where μ_{ne} is given by Eqn. 2.11 and E_n is

$$E_n = 0.71 \left(\frac{m^*}{\kappa^2} \right) eV \quad (2.13)$$

For the case of $\text{InAs}_{0.61}\text{P}_{0.39}$, Eqn. 2.12 may be written as

$$\mu_n = (4.266 \times 10^{13} / N_n) \left[0.4095T^{1/2} + 0.5427/T^{1/2} \right] \quad (2.14)$$

The mobility computed from Eqn. 2.14 is shown in Fig. 2.8 as a function of inverse absolute temperature for different

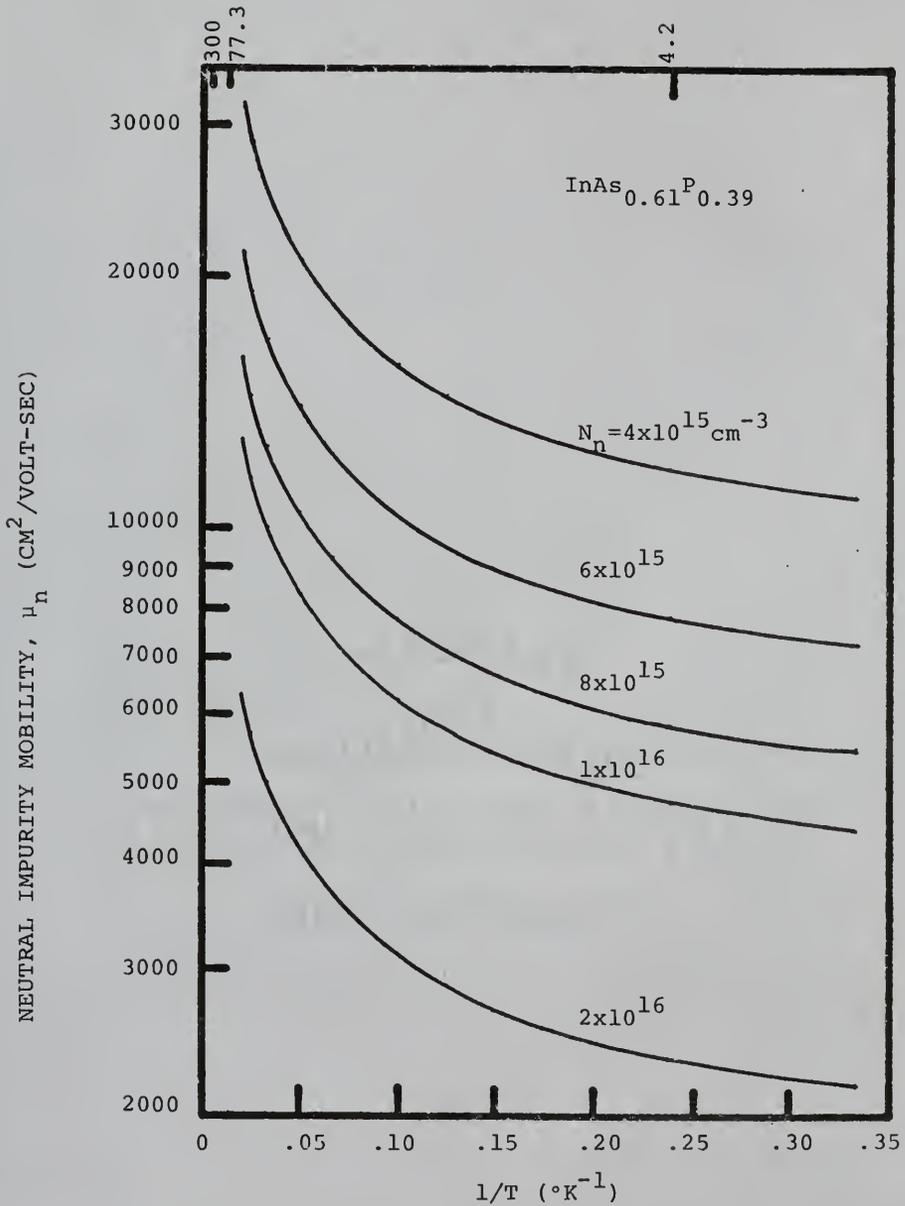


FIGURE 2.8 MOBILITY LIMITED BY NEUTRAL IMPURITY SCATTERING FOR $\text{InAs}_{0.61}\text{P}_{0.39}$

neutral impurity concentrations.

The mobility equations derived from polar optical scattering (Eqn. 2.2), ionized impurity scattering (Eqn. 3.8), and neutral impurity scattering (Eqn. 2.14) were combined in a manner similar to Eqn. 2.9. The results for a constant neutral impurity content of $1 \times 10^{16} \text{ cm}^{-3}$ and varying ionized impurity content are shown in Fig. 2.9. If these are the three dominant scattering mechanisms and if the assumptions involved with each of their derivations are not too rash, then these theoretical curves should be indicative of what might be expected experimentally for $\text{InAs}_{0.61}\text{P}_{0.39}$.

2.2d Electron-Electron Collisions

There are many other sources of electron scattering which tend to further limit and vary the shape of the mobility curves. These will not, however, be considered in this discussion since their effects are considered small or negligible in $\text{InAs}_{1-x}\text{P}_x$. One important source of scattering, though, should be presented at least in a qualitative fashion. This is the interaction of conduction electrons with other conduction electrons which will serve to increase the effectiveness of energy-dependent scattering mechanisms such as ionized impurity scattering.

The effect of electron-electron collisions may be understood by considering an electron current density distributed initially over a certain energy range. Upon encountering an energy-dependent scattering mechanism, such as an ionized

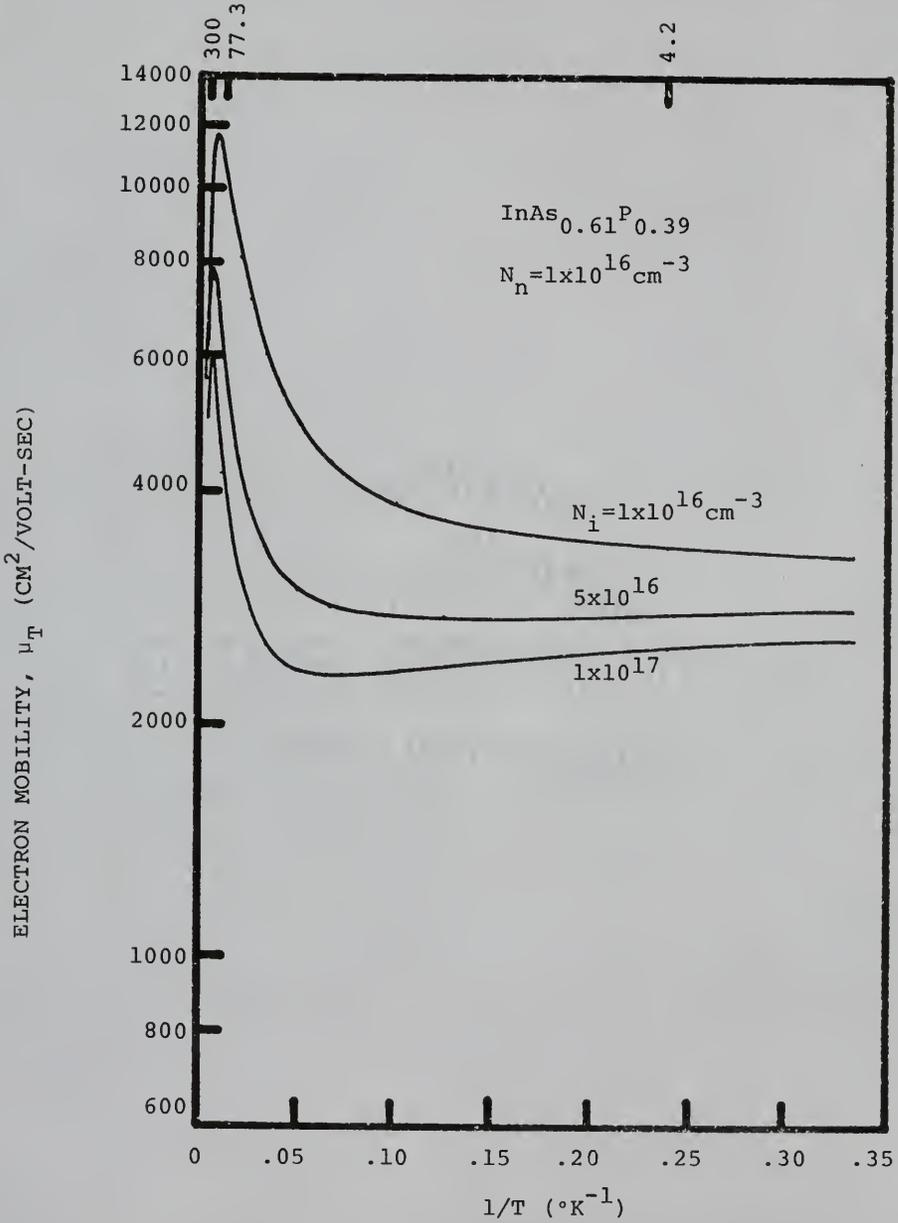


FIGURE 2.9 COMBINED THEORETICAL MOBILITIES
 FOR $\text{InAs}_{0.61}\text{P}_{0.39}$

impurity, those electrons of lower energy, thus lower velocity, will be affected more than the electrons of higher energy. Thus the momentum transfer to the mechanism will be due mostly to lower energy electrons resulting in a non-uniform energy distribution among the electrons. Electron-electron collisions will not in themselves result in a change in the total momentum but will serve to redistribute that momentum, within the electron cloud, to the lower energy electrons. This results in a more efficient mechanism for momentum transfer to the scatterers and thus a lower mobility. The effect of electron-electron collisions is then dependent upon the degree to which the scattering mechanism is energy dependent. Its greatest effect is with ionized impurity scattering and has been shown²⁷ to have a possible effect of reducing the mobility from this source by a factor of 0.6, although this is not normally realized. In the case of $\text{InAs}_{1-x}\text{P}_x$, electron-electron collisions would tend to reduce the maximum peaks of the mobility curves shown in Fig. 2.9.

2.3 Band Conduction

In a semiconductor, electrons needed for conduction may be obtained from two sources. In the case of intrinsic conduction, electrons are excited into the conduction band from the valence band. In the case of extrinsic conduction, electrons are excited from donor levels into the conduction band. Three cases will be considered here. First, the possibility of

intrinsic conduction will be considered briefly. Second, the effects of donor levels with compensating acceptor levels will be shown. Last, the consequences of high donor concentration and the formation of an impurity band will be discussed.

2.3a Intrinsic Conduction

Intrinsic conduction is a property of an ideally pure semiconductor or of the case when the electrons or holes excited from the impurity levels are negligible compared to n_i , the concentration of electrons excited from the valence band into the conduction band. In an ideally pure semiconductor at absolute zero the valence band is completely filled and the conduction band, separated from the valence band by an energy gap, E_g , is completely empty. As the temperature is raised the electrons may gain enough thermal energy to break their bonds and be excited into the conduction band. The result is electrons which are free to propagate in the conduction band and corresponding holes which are capable of conduction within the valence band. It may be shown that the number of carriers in either band may be expressed as a function of absolute temperature by the relation²⁸

$$n_i = 2(2\pi kT/h^2)^{3/2} (m_e^* m_h^*)^{3/4} \exp(-E_g/2kT) \quad (2.15)$$

In realistic crystals, the conduction electron concentration is dominated by intrinsic conductors when either E_g is small

or at high temperatures because of the exponential term in Eqn. 2.15. The effect of intrinsic conduction on $\text{InAs}_{0.61}\text{P}_{0.39}$, with an energy gap of 0.705eV at room temperature, may be seen by substitution of the appropriate values into Eqn. 2.15.

$$n_i = 4.827 \times 10^{15} T^{3/2} (m_e^* m_n^*)^{3/4} \exp\left(\frac{3.7 \times 10^{-4} T - .816}{2kT}\right) \quad (2.16)$$

The density of intrinsic carriers for $\text{InAs}_{0.61}\text{P}_{0.39}$ and also for InAs and InP is shown in Fig. 2.10 where it is seen that for temperatures below room temperature this density is very low especially as the content of phosphorus increases.

2.3b Conduction Due to Compensated Donors

In practical semiconductors, unless extreme caution is taken in their growth and purification, the conduction electrons are excited from donor states rather than from the top of the valence band. Typically there are numerous types of impurity atoms creating states within the forbidden energy gap between the valence and conduction bands. For simplicity, however, only a single shallow donor level and a single deep-lying acceptor level will be considered here. An idealized diagram of the energy states characterizing this condition is shown in Fig. 2.11. It is assumed that the donor density, N_d , is greater than the acceptor density, N_a .

At temperatures somewhat below the onset of intrinsic ionization, it is reasonable to assume that all states in the valence band are filled and all acceptor levels are also

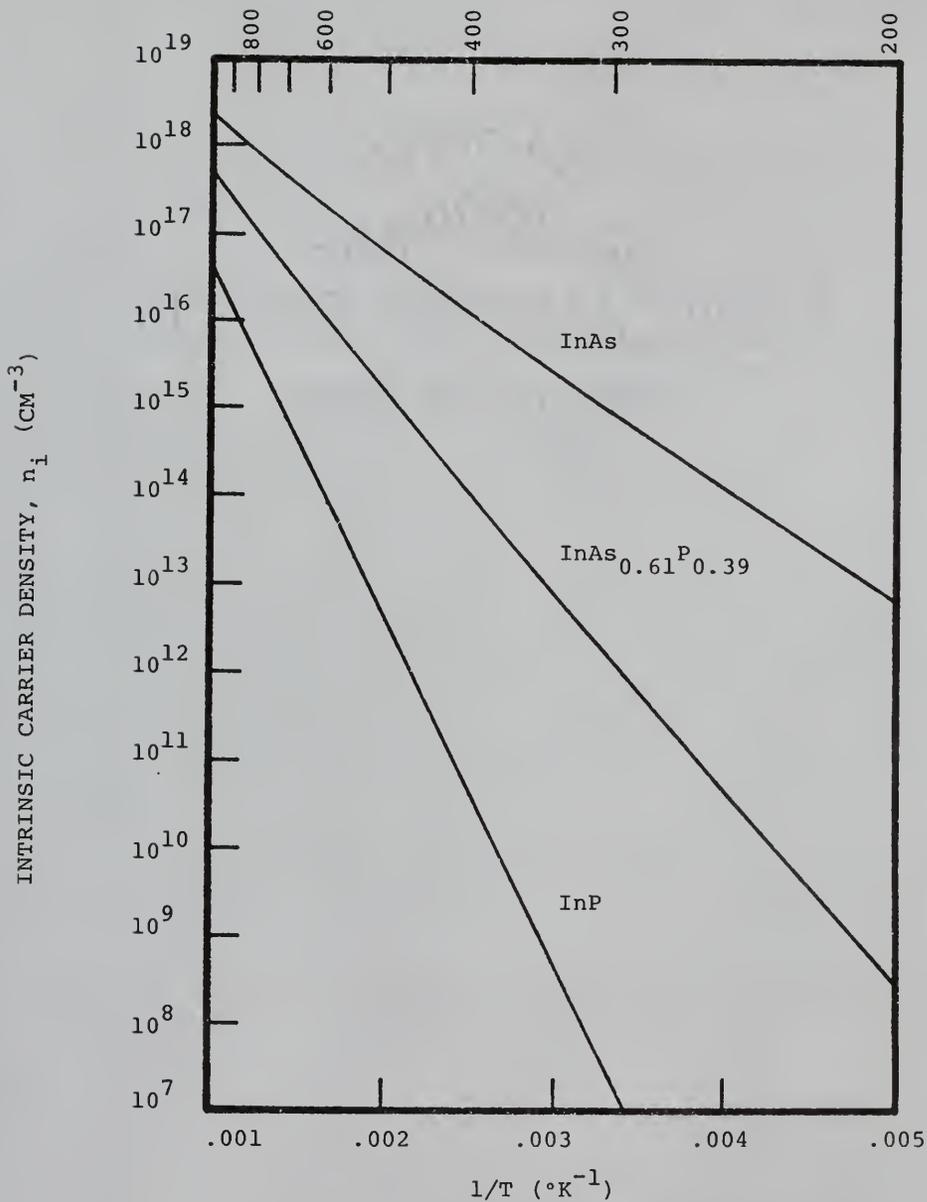


FIGURE 2.10 INTRINSIC CARRIER DENSITY WITH INVERSE ABSOLUTE TEMPERATURE

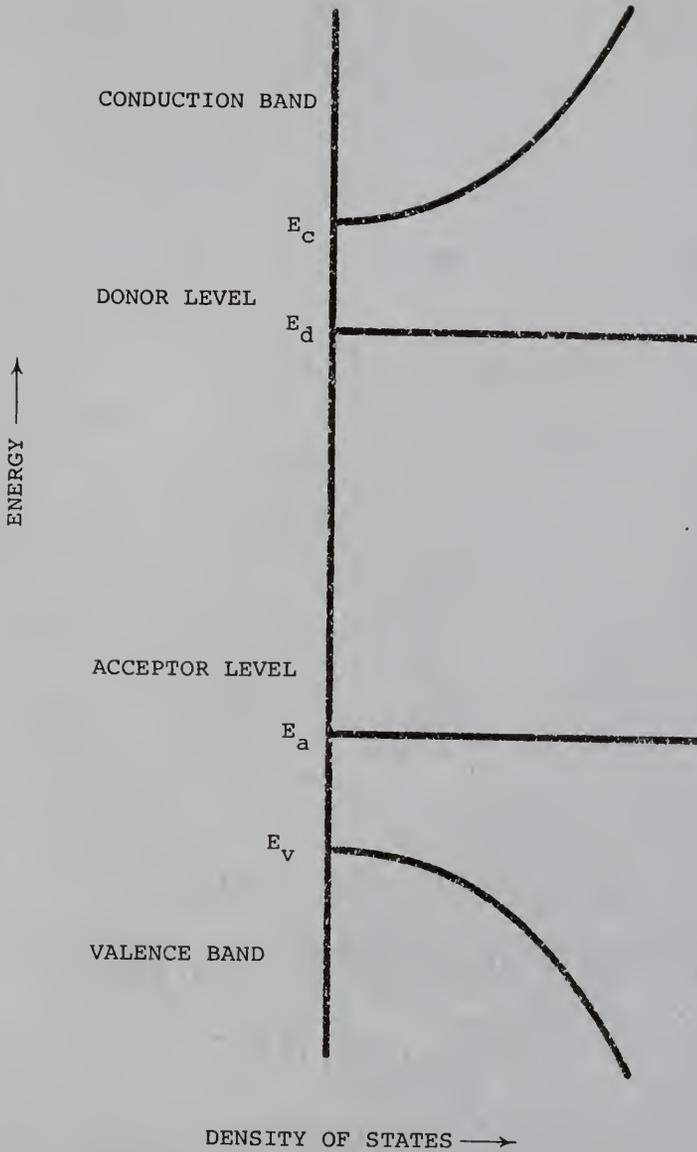


FIGURE 2.11 IDEALIZED DENSITY OF STATES DIAGRAM

filled (ionized). The electrons needed to fill these acceptor states necessarily are drawn from the donor impurities. The donor level is then said to be "compensated" since this leaves only $N_d - N_a$ electrons available to be excited into the conduction band. The conduction electron concentration may be written as

$$n_c = N_d - N_d^0 - N_a \quad (2.17)$$

where N_d^0 is the number of unionized or neutral donors. This is given by

$$N_d^0 = \frac{N_d}{1 + g \exp\left(\frac{E_d - E_f}{kT}\right)} \quad (2.18)$$

where g is the degeneracy factor for the donor level. The number of ionized donors may be found from Eqn. 2.18 and the relation

$$N_d^+ = N_d - N_d^0 \quad (2.19)$$

with the result

$$N_d^+ = \frac{N_d}{1 + g^{-1} \exp\left(\frac{E_d - E_f}{-kT}\right)} \quad (2.20)$$

Now assuming that the Fermi level is at least a few kT beneath the conduction band, the conduction electron density may be expressed using Boltzmann statistics as

$$n_c = N_c \exp \left(\frac{-E_c - E_f}{kT} \right) \quad (2.21)$$

where N_c is the effective density of conduction states.

$$N_c = 2(2\pi m^* kT/h^2)^{3/2} \quad (2.22)$$

$$N_c = 4.827 \times 10^{15} (m^*)^{3/2} T^{3/2} \quad (2.23)$$

$$N_c = 3.978 \times 10^{13} T^{3/2} \text{ for InAs}_{0.61}\text{P}_{0.39} \quad (2.24)$$

Equations 2.20 and 2.21 may then be manipulated²⁹ to obtain

$$\frac{n_c N_d^+}{N_d - N_d^+} = \frac{n_c (n_c + N_e)}{N_d - N_a - n_c} = g N_c \exp \left(\frac{-E_c - E_d}{kT} \right) \quad (2.25)$$

Milnes³⁰ has shown that this may be manipulated into a useful expression for the conduction electron density in terms of N_a , N_d and T .

$$n_c = \frac{2(N_d - N_a)}{\psi + \left[\psi^2 + \frac{4(N_d - N_a)}{gN_c} \exp \left(\frac{E_c - E_d}{kT} \right)^{1/2} \right]} \quad (2.26)$$

$$\psi = 1 + \frac{N_a}{gN_c} \exp \left(\frac{E_c - E_d}{kT} \right) \quad (2.27)$$

For low compensation ($N_a \sim 0$) n_c reduces to

$$n_c = \frac{2N_d}{1 + \left[1 + (4N_d/gN_c) \exp \left(\frac{E_c - E_d}{kT} \right)^{1/2} \right]} \quad (2.28)$$

For high compensation

$$n_c \approx \frac{N_d - N_a}{\psi} \quad (2.29)$$

Equation 2.26 is plotted in Fig. 2.12 for a donor density of $5 \times 10^{16} \text{cm}^{-3}$ with varying amounts of compensation from a deep acceptor level. The effective density of states is from Eqn. 2.24 and the donors are considered to lie at 4.28meV beneath the conduction band edge with a degeneracy of $g=2$. From the curves it is seen that the slopes are nearly exponential, especially below room temperature, and the slopes increase with increasing compensation. It may be shown that increasing the donor concentration will also result in an increase of the slopes.

2.3c Conduction in the Impurity Levels

The discussion to this point has dealt with electrons excited from either the valence band or from donor states into the conduction band where the continuum of empty energy states permits conduction within the semiconductor. It has been shown that for temperatures below 300K the main source of electrons is from the donor impurities. The results of Eqn. 2.26 shown in Fig. 2.12 indicate that as the temperature decreases there is an exponential decrease of carriers in the conduction band which would imply that at very low temperatures few electrons would be available for conduction and both the resistivity and Hall coefficient would become infinitely large near absolute zero. Experimental evidence, however, does not

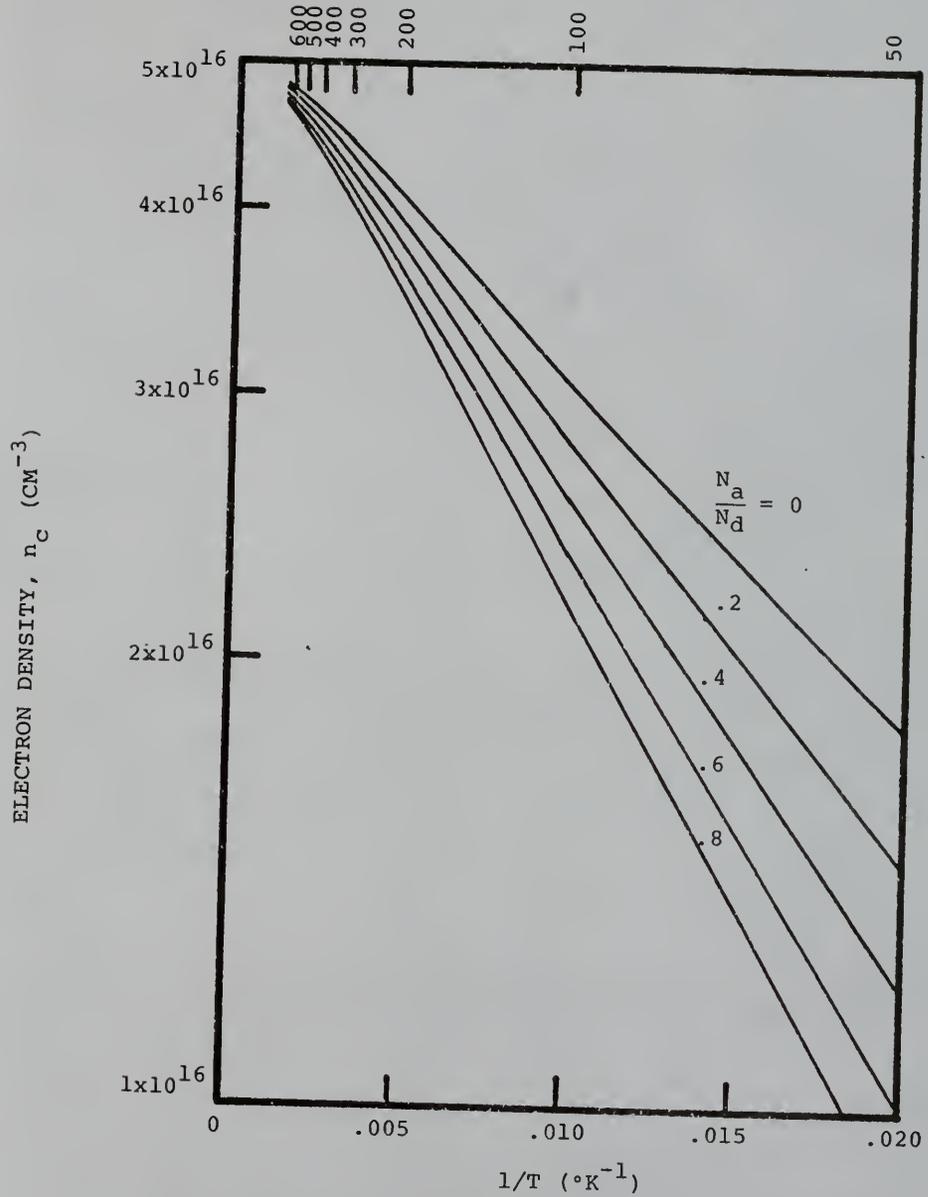


FIGURE 2.12 COMPENSATION EFFECT ON CONDUCTION BAND ELECTRONS

always support these predictions. Several investigators^{31,32,33} have found that in some samples as the temperature decreases there is an initial decrease in carrier concentration but at some low temperature the carrier concentration begins to rise until it approaches a constant level at the lowest temperatures.

The basic assumption of the carrier statistics presented in Section 2.3b was that the donors were thought to lie at a single energy level implying that the impurities are completely localized states. As the concentration of donor impurities increase, i.e. the average distance between impurity ions decreases, the wave functions of the impurities begin to overlap and the donor states lose their localized nature. Baltensperger³⁴ has determined the energy band formation for impurities assumed to be in a regular periodic lattice structure. The results of his calculations were presented by Conwell³⁵ as a function of r_s/a_h^* where r_s is the distance between impurities:

$$r_s = \left(\frac{3}{4\pi N_i} \right)^{1/3} \quad (2.30)$$

and a_h^* is the first Bohr orbit for an electron of mass m^* :

$$a_h^* = \frac{0.53\kappa}{m^*} \text{ \AA} \quad (2.31)$$

which for $\text{InAs}_{0.61}\text{P}_{0.39}$ is $a_h^* = 146.3\text{\AA}$. The results for the energy levels versus impurity spacing are shown in Fig. 2.13 with a lower abscissa scale added to show corresponding impurity

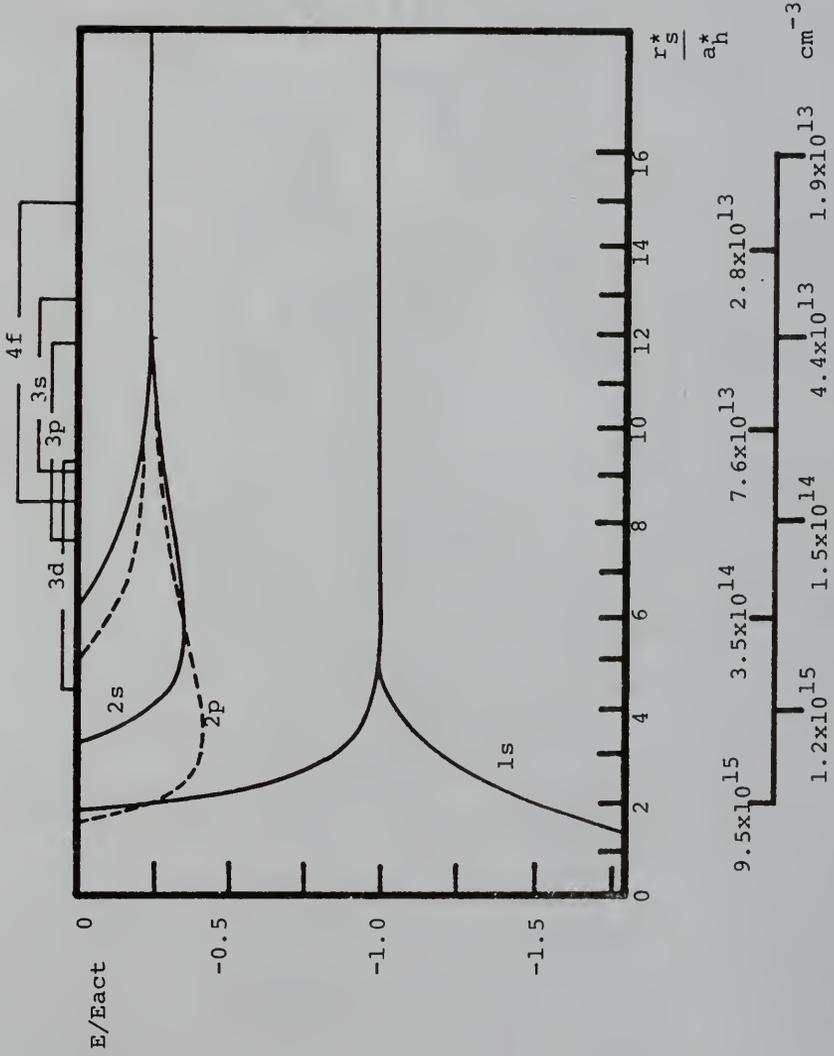


FIGURE 2.13 BALTENSPIERGER'S RESULTS FOR ENERGY LEVELS OF IMPURITIES

concentrations for $\text{InAs}_{0.61}\text{P}_{0.39}$. At large r_s there is a complete set of discrete energy levels. As the distance decreases, successively lower excited levels overlap and form bands. At $r_s \sim 5a_n^*$ the ground state begins to spread resulting in the impurity band.

The term 'band' has been used quite freely and although somewhat descriptive of the actual physical situation, it is somewhat misleading. The implication from the term and the foregoing discussion is that the impurity atoms enter the lattice in a regular periodic fashion. This is not justifiable. In fact, it is the randomness of the impurity atoms that has been one of the major barriers to the development of a working theory to describe this phenomenon. The result of this random nature is a band centered about the single state impurity level E_d . The distribution of states about this level is usually considered to be gaussian with long tails to both low and high energies.^{36,37} A band diagram descriptive of the results of an impurity band formation is given in Fig. 2.14. The perturbation (band tail) of the conduction band edge is also a result of the impurities in that they are a disruption to the periodicity of the original crystal structure. The acceptor levels are also portrayed in a gaussian fashion, but this is inconsequential if those levels are considered deep.

Now that an argument has been established for an impurity band it is essential that it contain empty states to account for conduction within that band. Certainly the presence of

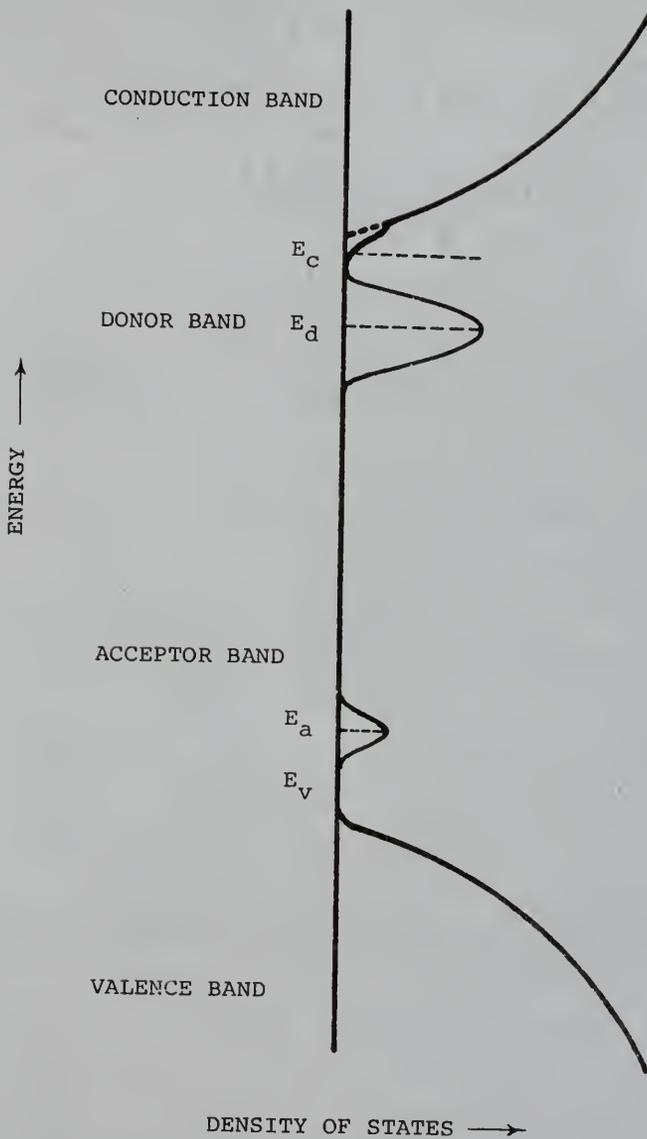


FIGURE 2.14 REALISTIC DENSITY OF STATES DIAGRAM

acceptor states will compensate some of the donors but a more basic argument may be made stemming from the difference between a set of discrete levels and a band. In a localized energy state there are two possible ways for an electron to occupy it due to spin degeneracy. This was taken into account in Eqn. 2.26 when the degeneracy factor $g=2$ was used. With localized states when one spin state is occupied the other state may not be. However, when a band is formed the states are no longer associated with individual atoms so that it may not be known if both spin states of an individual atom are filled or not. Thus in the donor band this results in $2N_d$ states available for occupancy. At absolute zero then, with all the acceptor states filled from the donor levels, there are $N_d + N_a$ empty states in the donor band in which electrons may easily move.

The result of conduction within the donor band has certain consequences. The total number of electrons available for conduction is now constant at $N_d - N_a$. At high temperatures these are all in the conduction band and at absolute zero they are all in the donor band. In the intermediate temperature range, conduction occurs in both bands. The total conductivity is given by³⁸

$$\sigma = n_c e \mu_c + n_d e \mu_d \quad (2.32)$$

and assuming that Hall coefficient expression for intrinsic

conduction may be adapted for this case

$$R_h = \frac{r}{e} \frac{n_c \mu_c^2 + n_d \mu_d^2}{(n_c \mu_c + n_d \mu_d)^2} \quad (2.33)$$

The total carrier concentration is

$$n_t = n_c + n_d = N_d - N_a \quad (2.34)$$

A maximum in the Hall coefficient occurs when

$$n_c \mu_c = n_d \mu_d \quad (2.35)$$

If the mobility in both the conduction band and donor band are considered to have the same temperature dependence, that is

$$b = \frac{\mu_c}{\mu_d} = \text{constant} \quad (2.36)$$

then the relationship for $R_{h_{\max}}$ may be derived as

$$\frac{R_{h_{\max}}}{R_{h_{\text{exh}}}} = \frac{(b+1)^2}{4b} \quad (2.37)$$

$R_{h_{\text{exh}}}$ is the Hall coefficient in the exhaustion region and the scattering coefficient is assumed to be unity at all temperatures. It may also be shown³⁹ from these assumptions that

$$\frac{R_h}{R_{h_{\text{exh}}}} = \frac{(x+b^2)(x+1)}{(x+b)^2} \quad (2.38)$$

where

$$x = \frac{n_d}{n_c} \quad (2.39)$$

The two relations of Eqns. 2.37 and 2.38 may be solved and from experimental data the concentrations of electrons in the two bands may be found, at least to an approximate degree.

CHAPTER III
EXPERIMENTAL PROCEDURES

3.1 Epitaxial Growth

The epitaxial samples used for this research were grown by Dr. John K. Kennedy⁴⁰ using a hydride system similar to Tietjen's. A diagram of the vapor system used to grow the epitaxial samples is shown in Fig. 3.1. Hydrogen is used as the carrier gas and is divided equally between the HCl and the arsine (AsH_3) and phosphine (PH_3) mixture. The total hydrogen flow rate controls the rate of growth and is thus used as a variable for four sets of samples investigated. As the HCl passes over the indium boat it transports the indium in the form of a chloride into the reaction zone where it mixes with the arsine and phosphine. The high temperature of the reaction zone (950°C) causes the decomposition of the hydrides into their respective elements with a by-product of hydrogen. The deposition is then completed on the substrate at a lower temperature ($650\text{--}675^\circ\text{C}$) in the deposition zone. This growth method allows the ratio of As to P to be adjusted and maintained accurately from sample to sample and might also be useful for composition grading during a run.

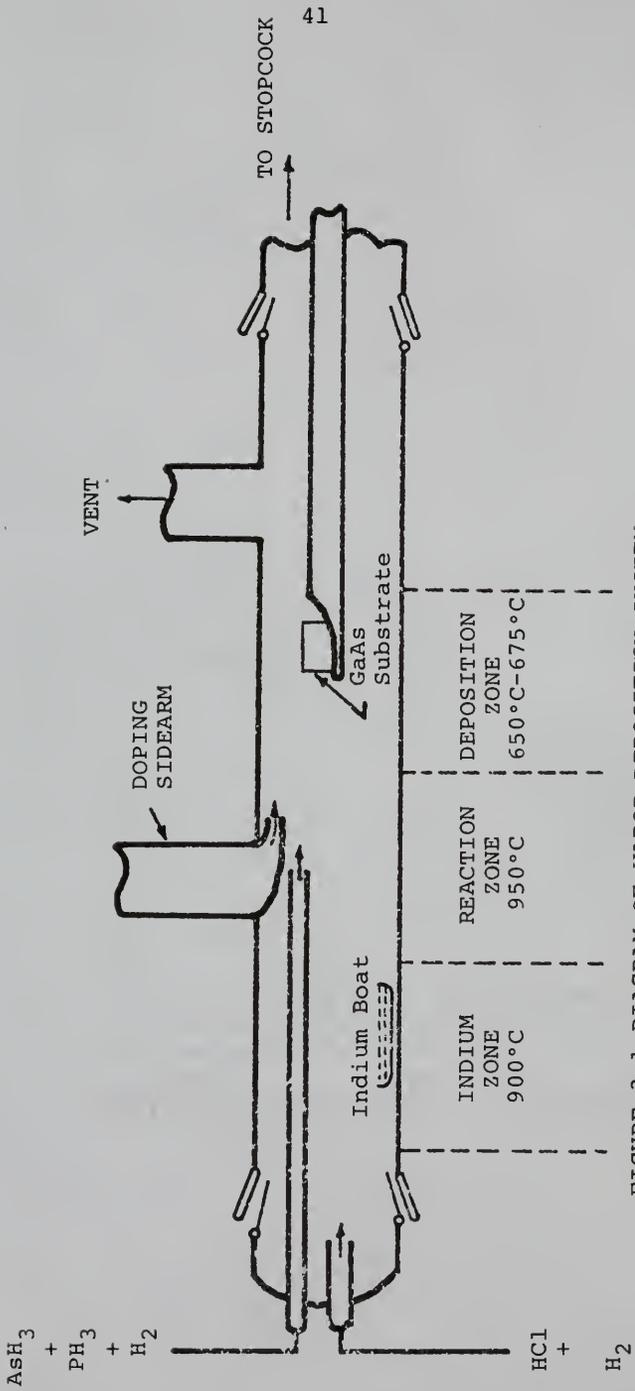


FIGURE 3.1 DIAGRAM OF VAPOR DEPOSITION SYSTEM.

The substrates used were Cr doped, semi-insulating GaAs ($\rho > 10^6$ ohm-cm) oriented $5^\circ \pm 0.5^\circ$ off the [001] axis toward the [110] direction. One face was chemically polished to a mirror finish and the other mechanically lapped. In preparation for deposition, each substrate was degreased in trichloroethane and etched for 30~45 minutes in Caro's acid (H_2SO_5) using an inclined, rotating Teflon beaker. The substrates were rinsed in baths of deionized water and methanol, then blown dry with filtered helium. After this cleaning procedure they were placed directly into the deposition furnace.

Five sets of samples were grown and investigated. The first set, samples 147-152, were grown at the same hydrogen flow rate but with varying As to P ratio. The other four sets were all of the same composition, $InAs_{0.61}P_{0.39}$, but the hydrogen flow rate was varied within each set and deposition time was varied from set to set resulting in different epitaxial thicknesses. Thus this research investigated changing composition, changing hydrogen flow rate, and changing epitaxial thicknesses. A list of the samples with their compositional and growth parameters is given in Table 3.1.

3.2 Sample Preparation

The epitaxial samples as received from Dr. Kennedy were approximately 1x2 centimeters with epitaxial deposits on both the front and back surfaces. The samples were scribed using a Kulicke and Soffa Model 750 Scriber on the back surface and cleaved to obtain two .5x.5 centimeter samples from

TABLE 3.1 GROWTH PARAMETERS AND EPITAXIAL THICKNESSES FOR $\text{InAs}_{1-x}\text{P}_x$

	<u>Sample</u>	<u>Flow Rate (CM³/MIN)</u>	<u>X</u>	<u>t (μm)</u>
Group I	172	1780	.392	4.27
	173	1530	.392	4.11
	174	1280	.392	4.08
	175	910	.392	3.70
	176	730	.392	2.86
	177	570	.392	2.35
	178	515	.392	2.67
				(avg. = 3.73)
Group II	164	1780	.392	13.23
	168	1530	.392	10.96
	166	1280	.392	10.91
	169	910	.392	8.62
	167	730	.392	7.24
	170	570	.392	6.50
	171	515	.392	5.33
			(avg. = 8.97)	
Group III	153	1780	.392	23.28
	154	1530	.392	19.26
	155	1280	.392	27.46
	156	910	.392	22.17
	157	730	.392	18.68
	159	515	.392	20.62
			(avg. = 21.91)	
Group IV	196	3070	.392	108.75
	197	2430	.392	114.67
	181	1780	.392	106.08
	186	1530	.392	102.50
			(avg. = 108.00)	
Group V	147	2100	.034	8.87
	148	2100	.100	9.09
	149	2100	.200	11.30
	150	2100	.392	34.28
	151	2100	.624	35.90
	152	2100	.774	46.36
			(avg. = 24.30)	

the center. Excess pieces were used for compositional analysis using an electron microprobe. The epitaxial layer thickness of the sample used was measured using an optical microscope equipped with a micrometer eyepiece. Each side of the sample was measured in several places and the results averaged. These results are given in Table 3.1.

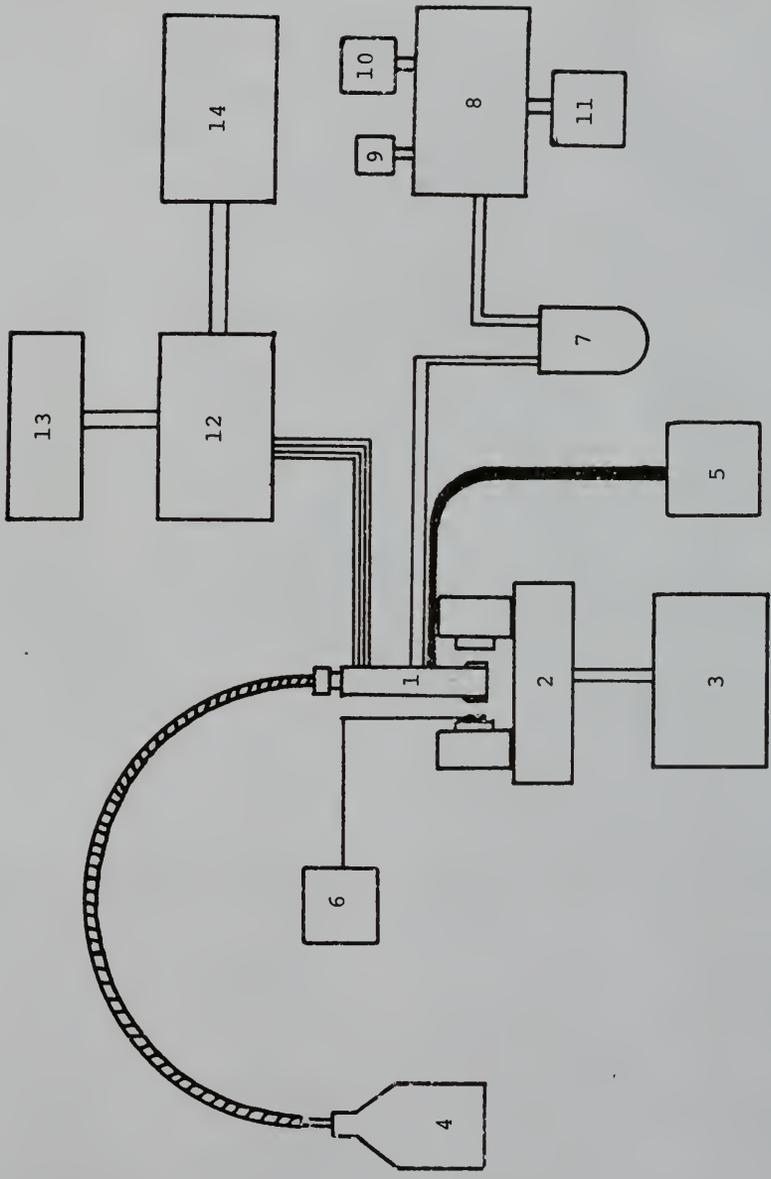
In preparation for mounting conducting leads, each sample was first cleaned in baths of trichloroethylene, acetone, methanol, then finally deionized water. The sample was then soldered with indium onto an Al_2O_3 substrate to provide thermal conduction to the cryostat. Electrical connection was obtained by soldering thin wires, using pure indium, to each corner of the sample. The solder connections were typically 0.2 mm in diameter and each was tested for ohmicity. The other ends of the leads were soldered onto the Al_2O_3 substrate at which point leads from the cryostat were joined. With this arrangement the sample could be inserted and removed from the equipment without disturbing the ohmic contacts on the sample.

3.3 Experimental Apparatus

The experimental arrangement used for most measurements, Fig. 3.2, incorporated a Heli-Tran Model LT-3-110 to attain temperatures continuously variable between 3K to 300K with a normal $\pm 0.1\text{K}$ stability in the lower range. Temperature readings were made using a chromel versus gold with 0.07 atomic percent iron thermocouple read by a Honeywell Model 2783 six-dial potentiometer. Both the thermocouple junction and the

FIGURE 3.2 - Experimental Setup for Measuring Resistivity and Hall Effect

- 1) Heli-Tran Model LT-3-110 cold tip
- 2) Varian V-3706 6-inch electromagnet
- 3) Varian sweep power supply
- 4) Liquid helium dewar
- 5) Vacuum pump
- 6) Bell Model 620 gaussmeter
- 7) Deionized ice bath
- 8) Honeywell Model 2783 potentiometer
- 9) Standard cell
- 10) Six-volt current source
- 11) Hewlett-Packard Model 725A DC Micro Volt-Ammeter
- 12) Control panel
- 13) Electronic Measurements Model C633 Constant Current Power Supply
- 14) Cimron Model 6653A Digital Multimeter



sample were mounted on a copper heat sink in the cryotip - the thermocouple with GE 7031 varnish and the sample with Cry-Con grease.

A uniform magnetic field was provided by a Varian V-3703 electromagnet with six-inch pole pieces. Fields up to 6 kilogauss in strength and as low as 10 gauss were used for Hall coefficient and magnetoresistance measurements. The magnetic field was monitored by a Bell 620 gaussmeter.

The thin epitaxial samples were especially suited for measurement using the standard Van der Pauw⁴¹ technique. The four leads from each corner of the sample were connected to a switching control panel which provided the necessary interchange of current and voltage leads and also current reversal. In addition, the magnetic field was reversed during each set of measurements to average out any inhomogeneities in the magnetic field.

An Electronic Measurements C633 constant current supply was used to provide a current of 0.5 milliamperes through the sample. This low current was used to eliminate possible heating effects but yet produce voltages large enough to be read accurately. The voltage across the samples was read by a Cimron 6653A digital multimeter with a resolution of one micro-volt.

CHAPTER IV

EXPERIMENTAL RESULTS OF $\text{InAs}_{0.61}\text{P}_{0.39}$

4.1 Sample Description

Four sets of samples were grown using the methods described in Chapter III with the arsine to phosphine ratio adjusted so as to give 0.61 As and 0.39 P. The deposition time was varied from set to set to obtain different epitaxial layer thicknesses. For samples of Group I (172-178) the average thickness was $3.4 \mu\text{m}$, for Group II (164-171) the average was $9.0 \mu\text{m}$, for Group III (153-159) the average was $21.9 \mu\text{m}$, and for Group IV (196-186) the average was $108.0 \mu\text{m}$.

Within each set, the thickness of each sample was somewhat dependent upon the flow rate as shown in Fig. 4.1 for the first three sets. It might be appropriate at this point to note that the thicknesses, as given in Table 3.1, are averages of numerous measurements made on each sample and that some samples, especially the thicker ones, were not of uniform thickness. The thicker samples also showed a greater density of visible surface defects in the form of hillocks. It is difficult to estimate to what extent these problems affected the reliability of the experimental results.

The alloy composition was verified using an electron microprobe. The results of this analysis showed significant

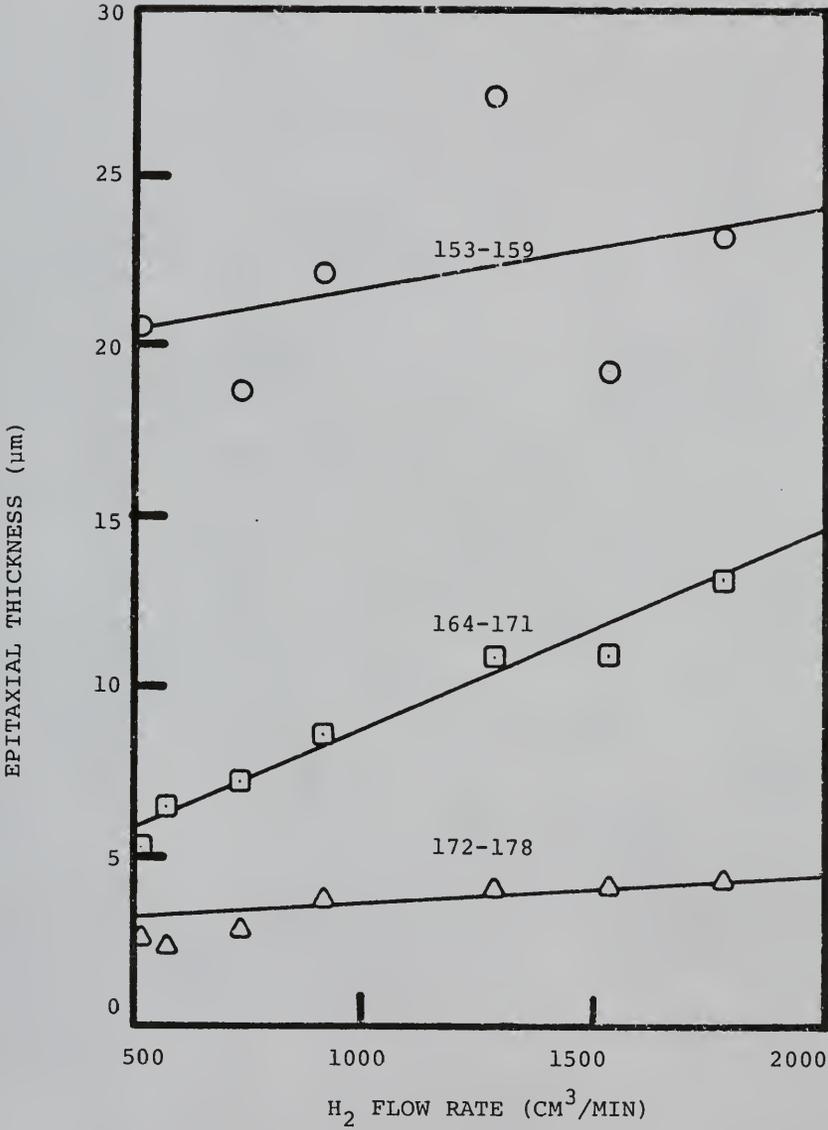


FIGURE 4.1 EPITAXIAL THICKNESS VARIATION WITH HYDROGEN FLOW RATE

scatter as illustrated in Fig. 4.2. However, the average of all samples gives a composition of $\text{InAs}_{.616}\text{P}_{.384}$ which is close to the value prescribed for these samples.

4.2 Resistivity Data

Resistivity measurements were made on samples of each group over the temperature range from 4.2K to 300K. Some samples of Groups I and IV were measured only from liquid nitrogen temperatures to room temperature in an effort to conserve liquid helium. The results of these measurements are graphed versus inverse absolute temperature in Figs. 4.3-4.7.

The resistivity curves show, in general, three regions of interest. At the highest temperatures most curves, especially those of the thick samples in Groups III and IV, show an exponential decrease with decreasing temperature until approximately 100K which is expected from the normal band conduction process. After reaching a minimum, the resistivity increases exponentially with decreasing temperature in the second region of interest. At approximately 20K, the resistivity begins to saturate and varies linearly with temperature down to the lowest temperatures measured. This linear variation is shown more clearly for samples of each group in Figs. 4.8-4.11. The resistivity curves for these samples are similar to those found for other semiconductors such as $\text{Ge}^{42,43}$ and $\text{InSb}^{44,45}$.

The resistivity in the two low temperature regions below the resistivity minimum may be approximated by the equation

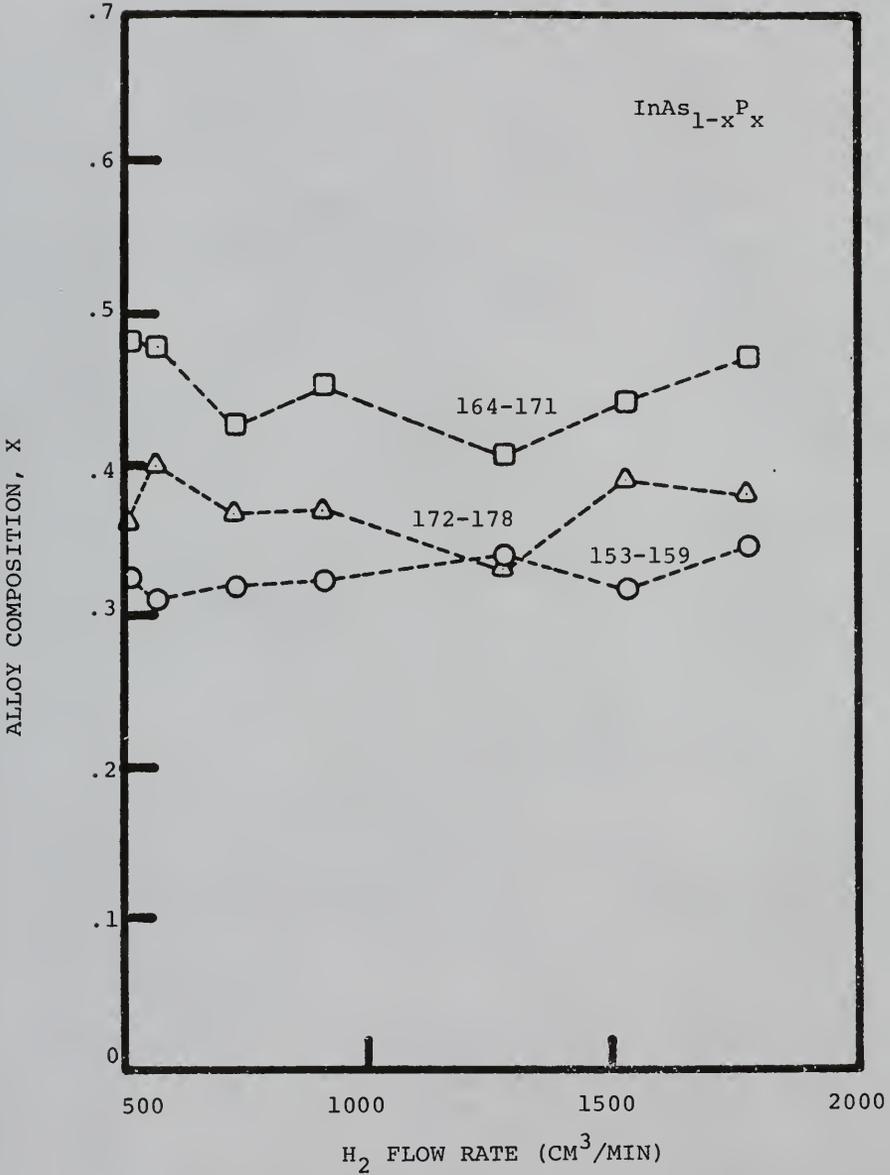


FIGURE 4.2 ALLOY COMPOSITION FOR THREE SETS OF SAMPLES

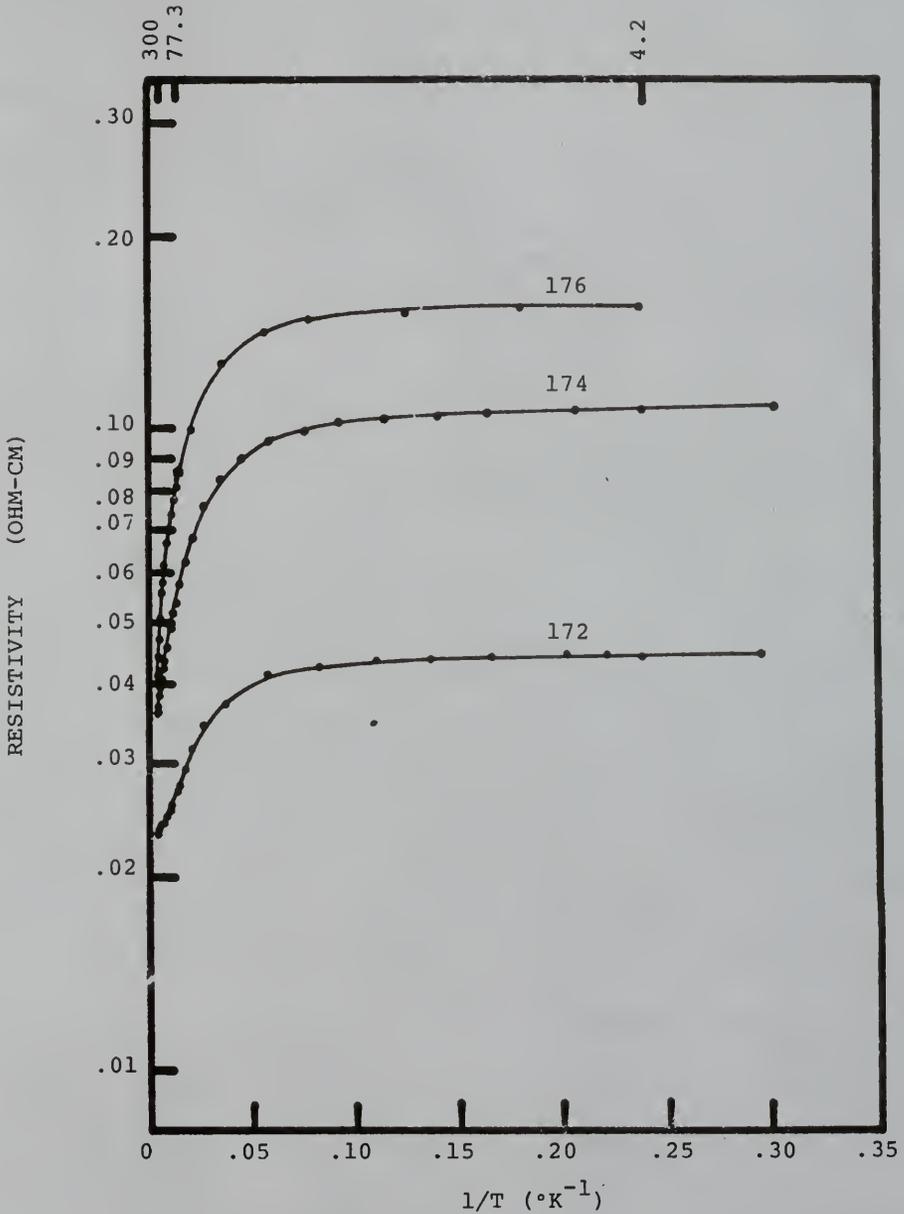


FIGURE 4.3 RESISTIVITY OF SAMPLES 172, 174, 176
VERSUS INVERSE TEMPERATURE

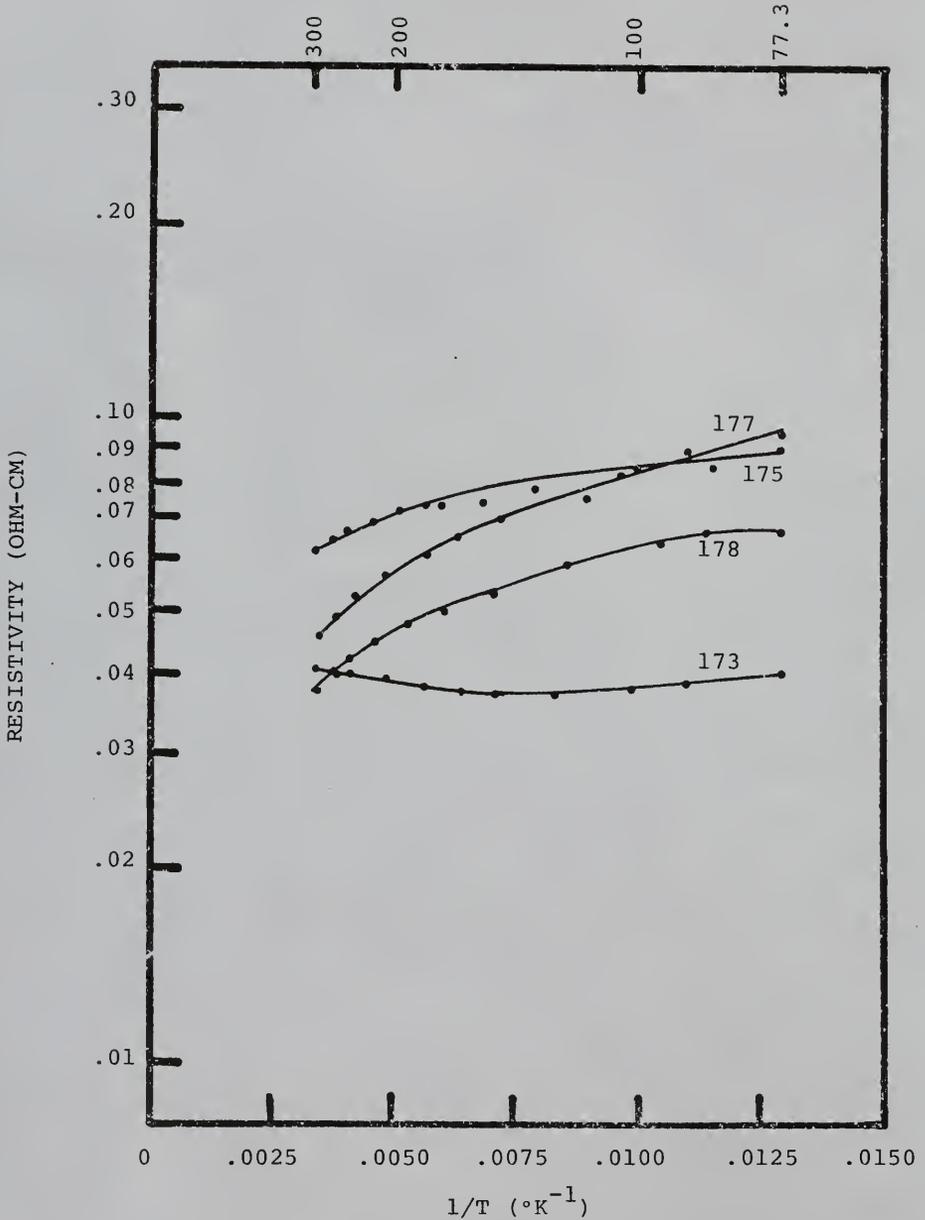


FIGURE 4.4 RESISTIVITY OF SAMPLES 173, 175, 177, 178, VERSUS INVERSE TEMPERATURE

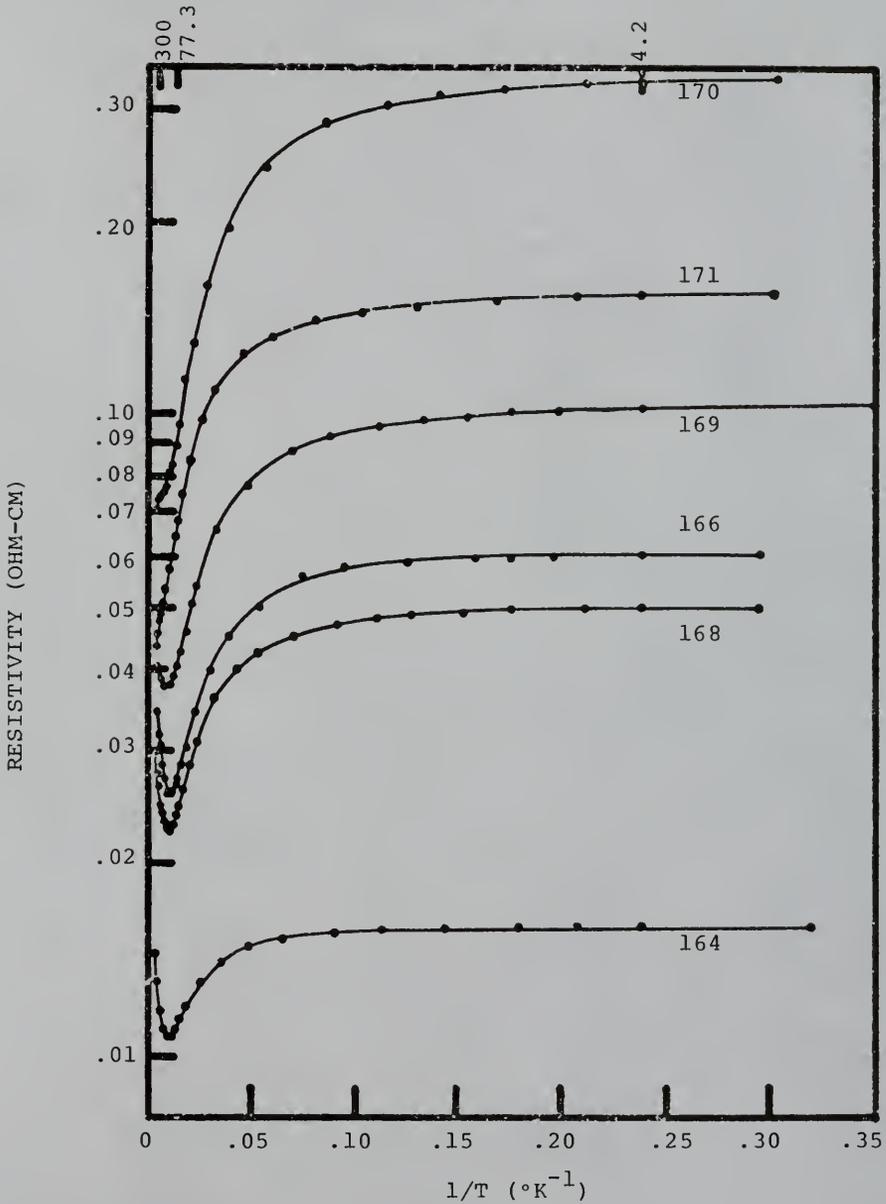


FIGURE 4.5 RESISTIVITY OF SAMPLES 164-171
VERSUS INVERSE TEMPERATURE

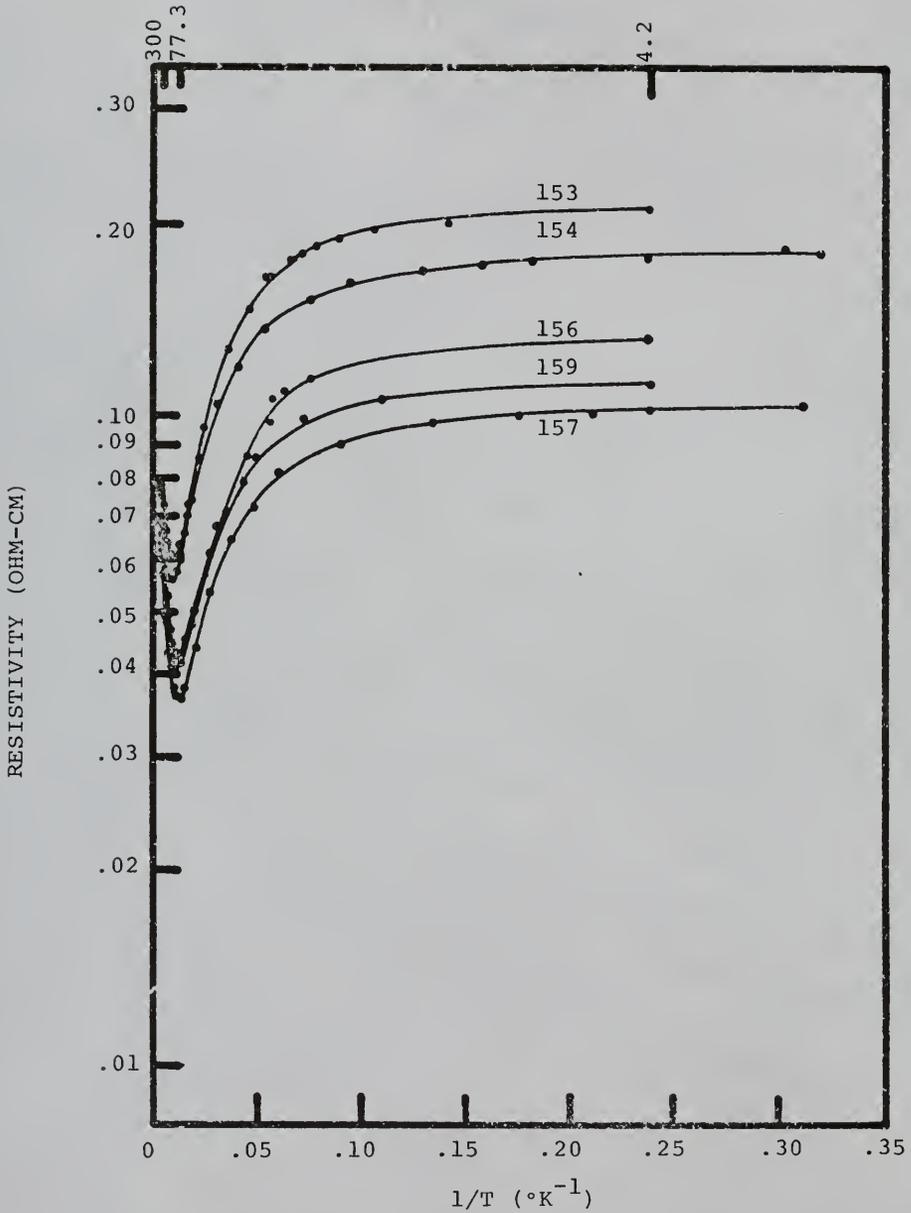


FIGURE 4.6 RESISTIVITY OF SAMPLES 153-159
VERSUS INVERSE TEMPERATURE

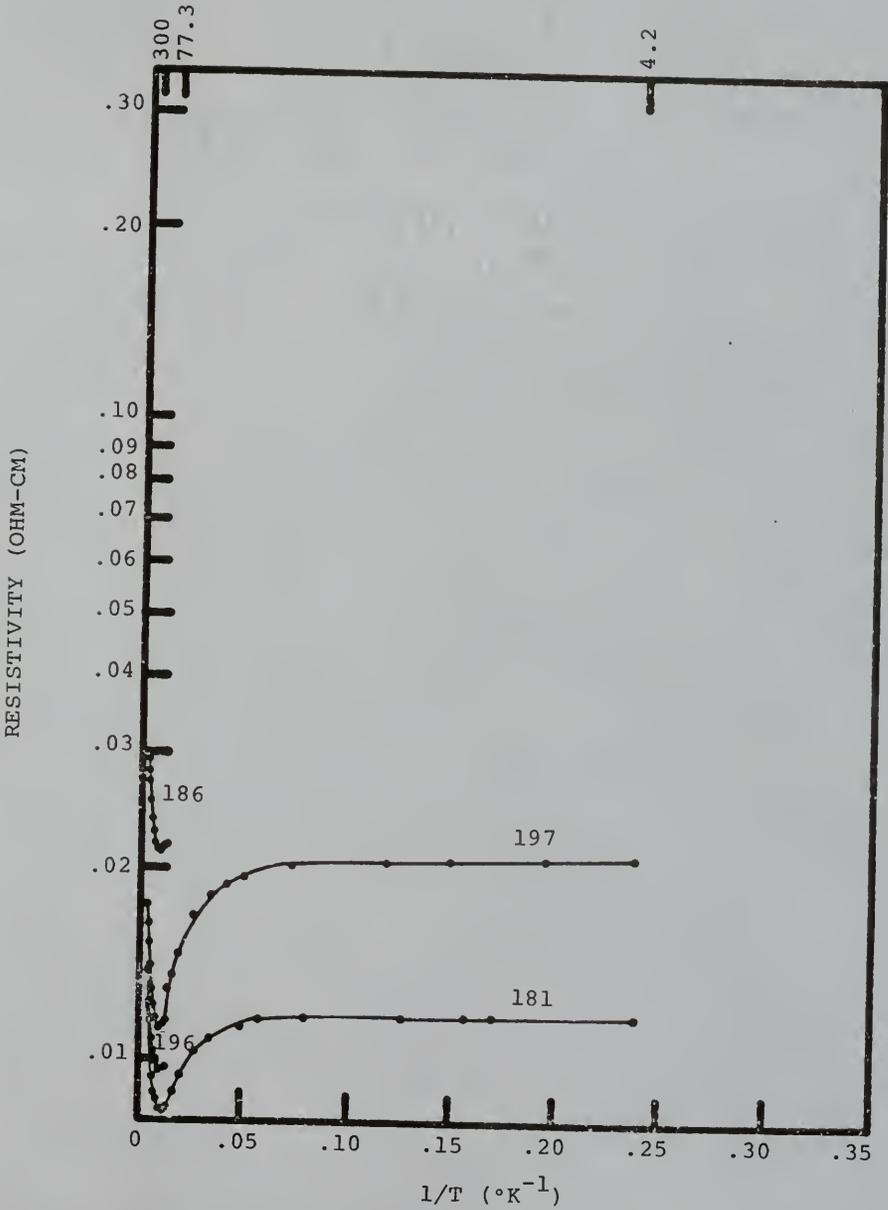


FIGURE 4.7 RESISTIVITY OF SAMPLES 196-186
VERSUS INVERSE TEMPERATURE

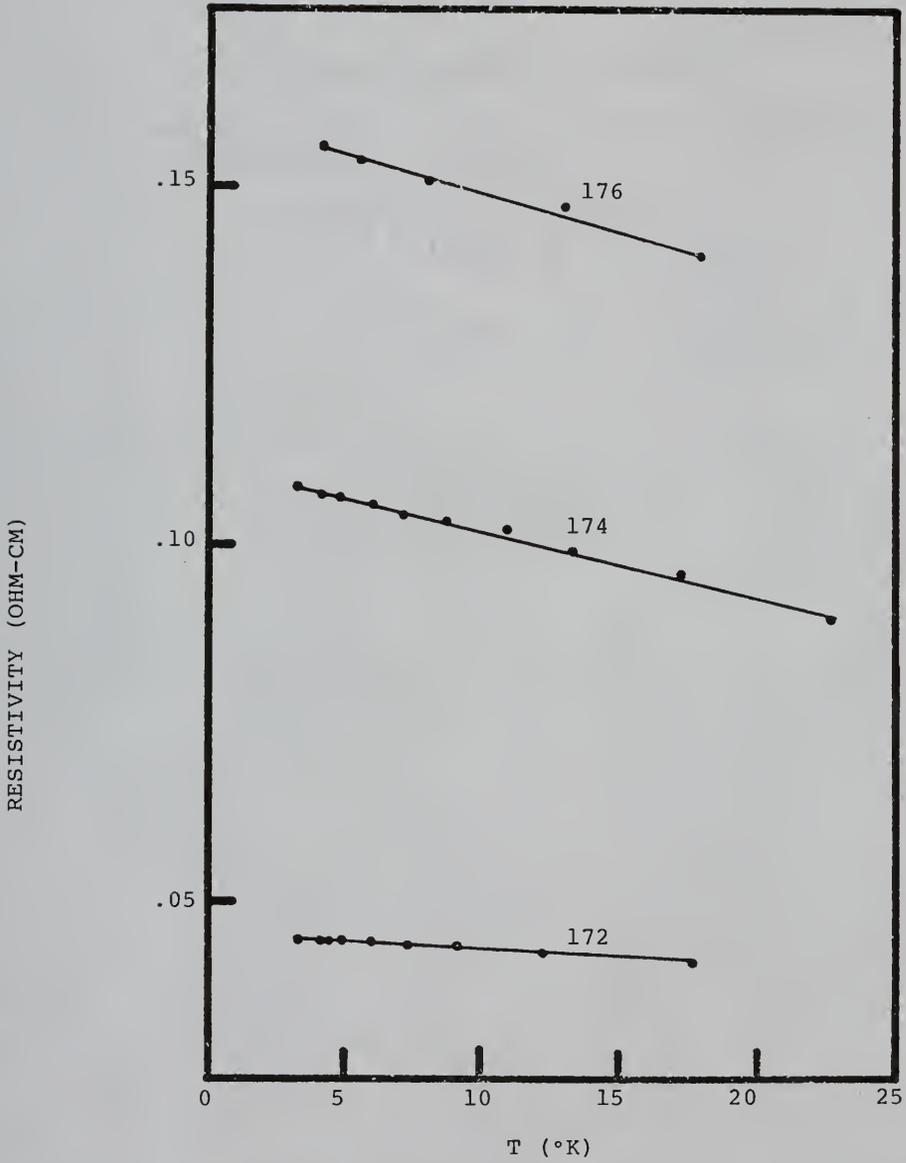


FIGURE 4.8 LINEAR VARIATION OF RESISTIVITY FOR SAMPLES 172, 174, 176

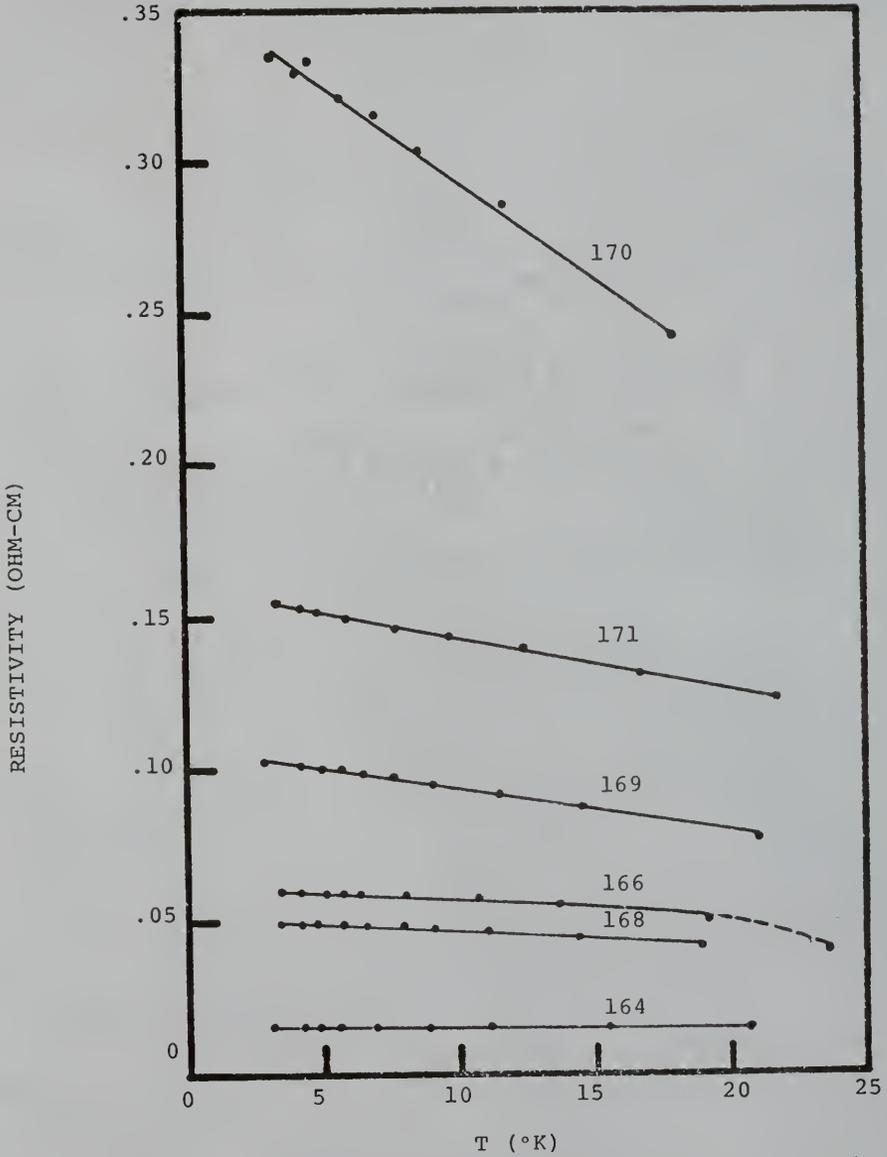


FIGURE 4.9 LINEAR VARIATION OF RESISTIVITY FOR SAMPLES 164-171

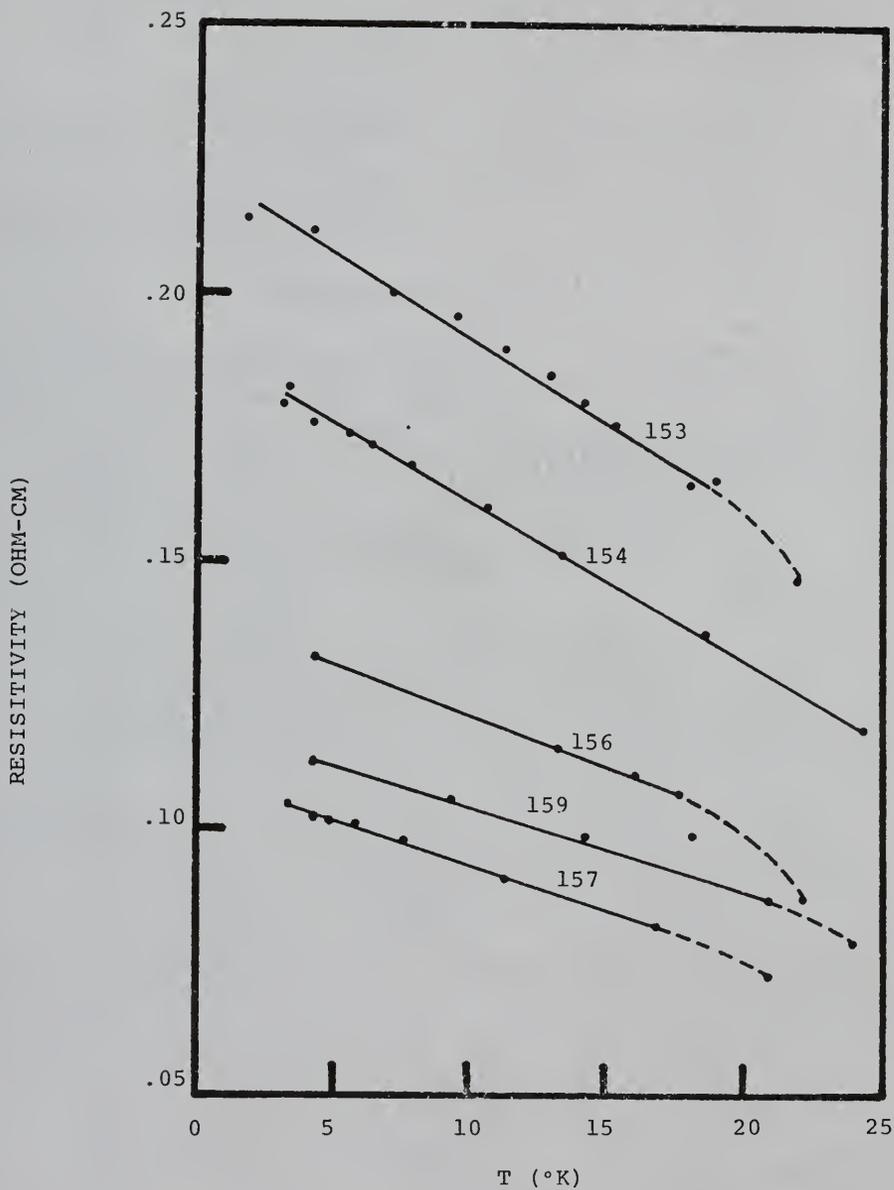


FIGURE 4.10 LINEAR VARIATION OF RESISTIVITY FOR SAMPLES 153-159

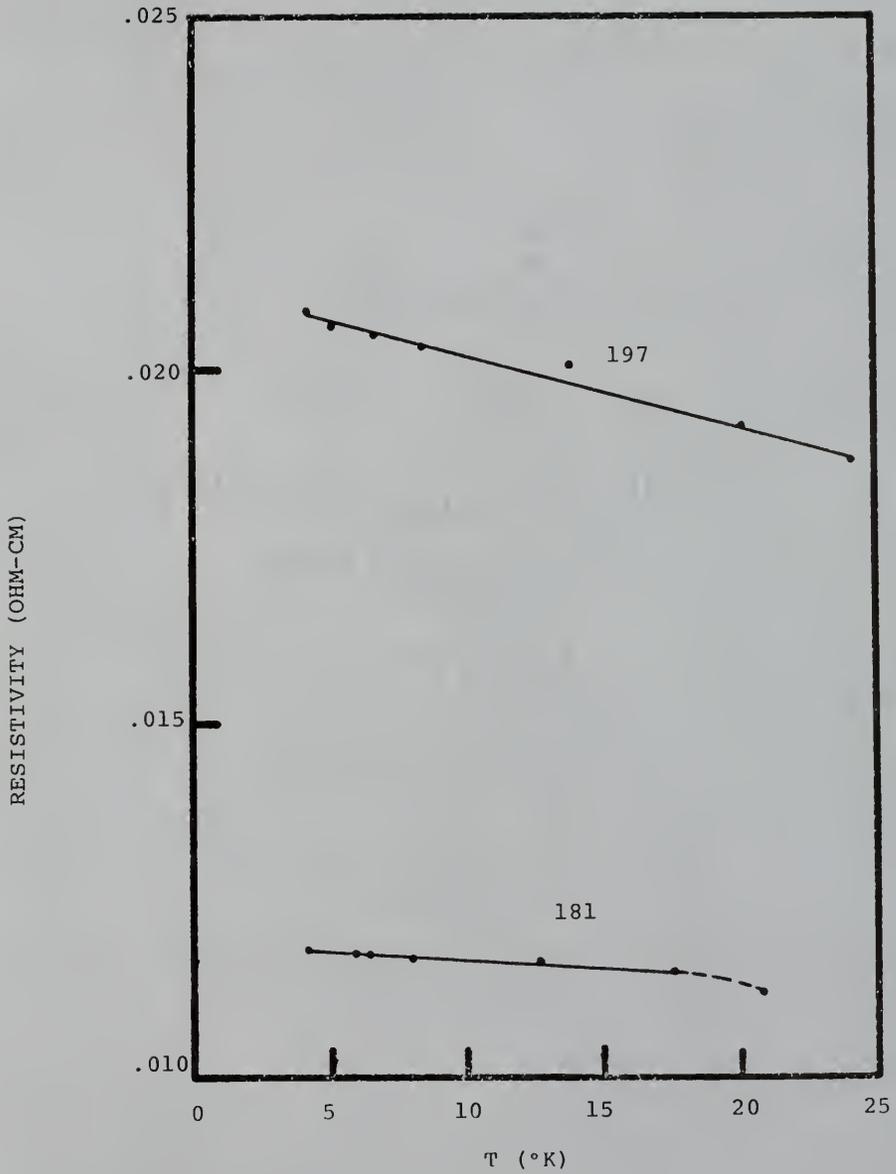


FIGURE 4.11 LINEAR VARIATION OF RESISTIVITY FOR SAMPLES 181, 197

$$\rho^{-1} = C_2 \exp(-E_2/kT) + C_3T + C_4 \quad (4.1)$$

where the first term represents the exponential increase and the other two terms describe the slow linear increase at the lowest temperatures. This equation was fitted to the resistivity data using a least squares approximation to determine the parameters C_2 , C_3 , C_4 and the conductivity activation energy, E_2 . The results of these calculations are listed in Table 4.1. Of special interest are the results for E_2 . These are plotted in Fig. 4.12 against the hydrogen flow rate. For the thin samples the activation energy shows a sharp increase with decreasing flow rate. As the epitaxial thickness increases, the activation energy changes its dependence until, for the thick samples, it shows a decrease with decreasing flow rate. This is further borne out by the results for the 100 μm samples (197 and 181) which were not plotted.

One other point of interest is the movement of the resistivity minimum with changes in thickness. For the thinnest samples (172-178), this minimum occurs at a temperature higher than 300K which was the upper limit of our equipment. The 9 μm samples (164-171) showed, on an average, a minimum at about 170K. The other two groups (153-159 and 196-186) both showed minimums at around 100K. This might be attributed to the effects of a transition layer between the GaAs substrate and the $\text{InAs}_{1-x}\text{P}_x$ epilayer. If the interface layer is of the order of a micron it would significantly affect the characteristics of the 3 μm samples, but become less significant as

TABLE 4.1 CONDUCTIVITY PARAMETERS

$$\rho(T)^{-1} = C_2 \exp(-E_2/kT) + C_3T + C_4 \quad (T < 100K)$$

<u>Sample</u>	<u>Flow Rate</u>	<u>C₂</u>	<u>E₂ (meV)</u>	<u>C₃</u>	<u>C₄</u>
172	1780	45.8	1.48	.125	21.93
173	1530	31.7	1.62		
174	1280	30.2	3.16	.084	8.99
175	910	17.9	3.40		
176	730	30.1	7.01	.049	6.22
177	570	37.5	13.70		
178	515	48.1	14.70		
164	1780	109.1	1.26	.380	81.87
168	1530	58.7	2.19	.341	24.97
166	1280	53.7	2.36	.279	20.69
169	910	35.7	2.47	.239	11.95
170	570	18.5	3.47	.122	3.42
171	515	26.9	3.63	.119	8.16
153	1780	25.0	3.13	.147	5.52
154	1530	26.1	3.04	.176	6.70
155	1280	33.1	2.04	.237	12.56
156	910	30.9	1.85	.180	9.31
157	730	39.4	2.46	.305	11.59
159	515	29.7	1.72	.213	10.76
197	2430	107.0	2.01	.236	47.15
181	1780	155.0	1.73	.151	84.11

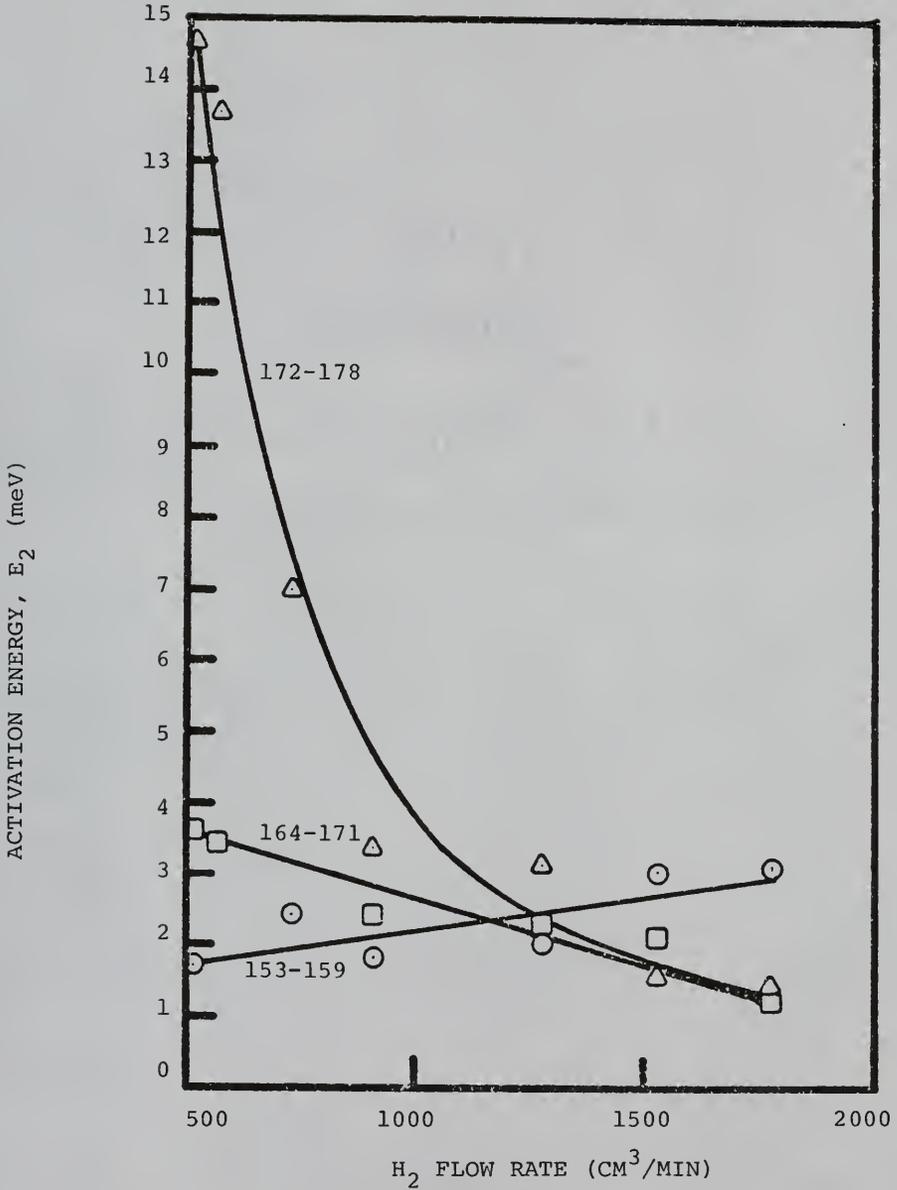


FIGURE 4.12 VARIATION OF ACTIVATION ENERGY, E_2 , WITH FLOW RATE

the thickness of the epilayer increases.

4.3 Hall Coefficient and Carrier Concentration

The Hall coefficient, R_h , was measured for each of these four groups of samples as both a function of temperature and as a function of magnetic field strength. The temperature variations are plotted versus inverse absolute temperature in Figs. 4.13-4.17 from 4.2K to 300K. The magnetic field strength used was 5 kilogauss which is not quite the high field limit but should introduce little error since the field dependence was slight except at temperatures around 60K.

The temperature dependence of the Hall coefficient shows a sharp increase with decreasing temperature from 300K to about 60K which may be attributed to normal band conduction. However, at $T \sim 60K$ a maximum is reached and the Hall coefficient begins to decrease until approximately $T=20K$ at which point the Hall coefficient becomes relatively constant. For each sample the low temperature value is very close to the value of the Hall coefficient at 300K.

This type of behavior may be explained by the concept of a donor band presented in Section 2.3c. From Eqn. 2.33 the limits for high temperature may be seen by assuming all available donor electrons are ionized into the conduction band. Thus $n_c = N_d - N_a$ and $n_d = 0$. The Hall coefficient is then

$$R_h = \frac{r_1}{en_c} \quad (\text{high temp}) \quad (4.2)$$

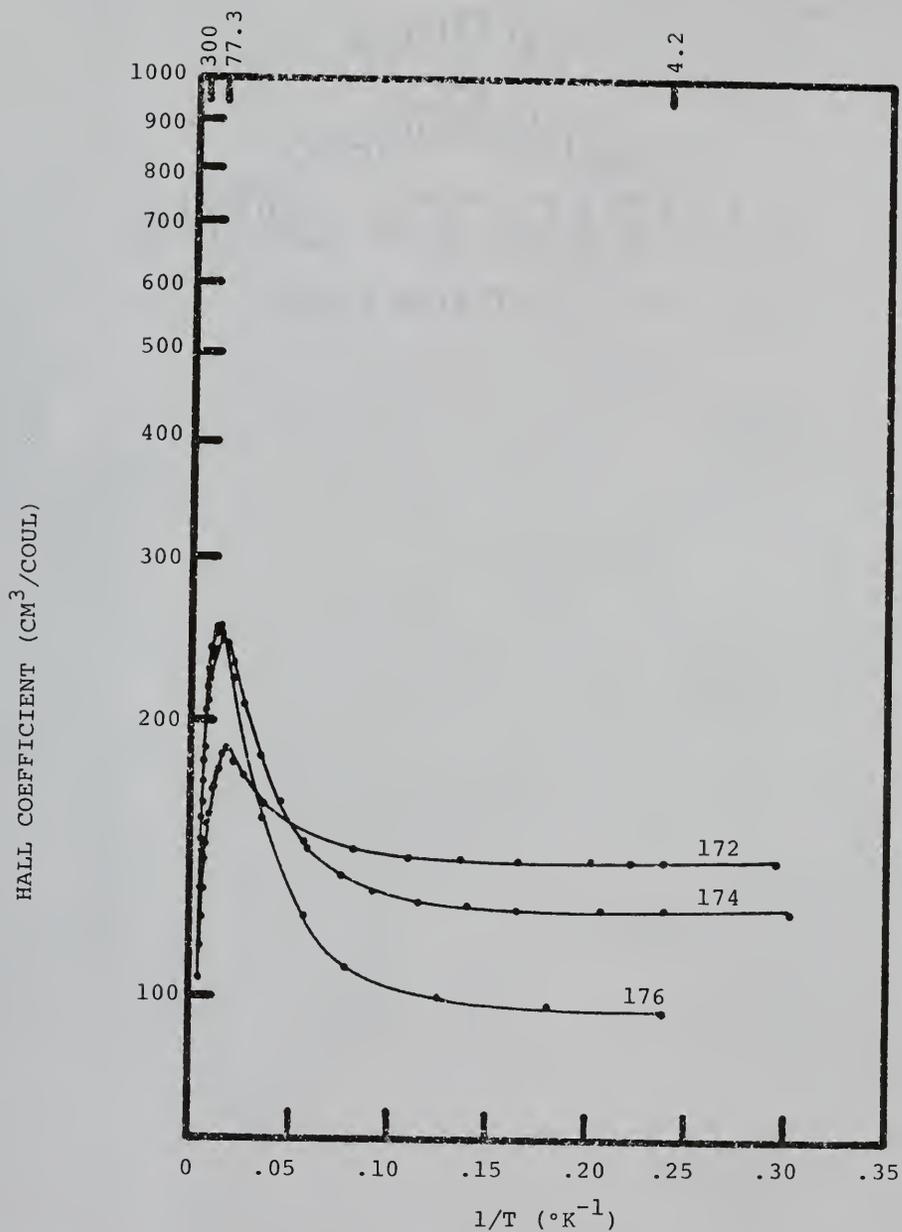


FIGURE 4.13 HALL COEFFICIENT OF SAMPLES
172, 174, 176

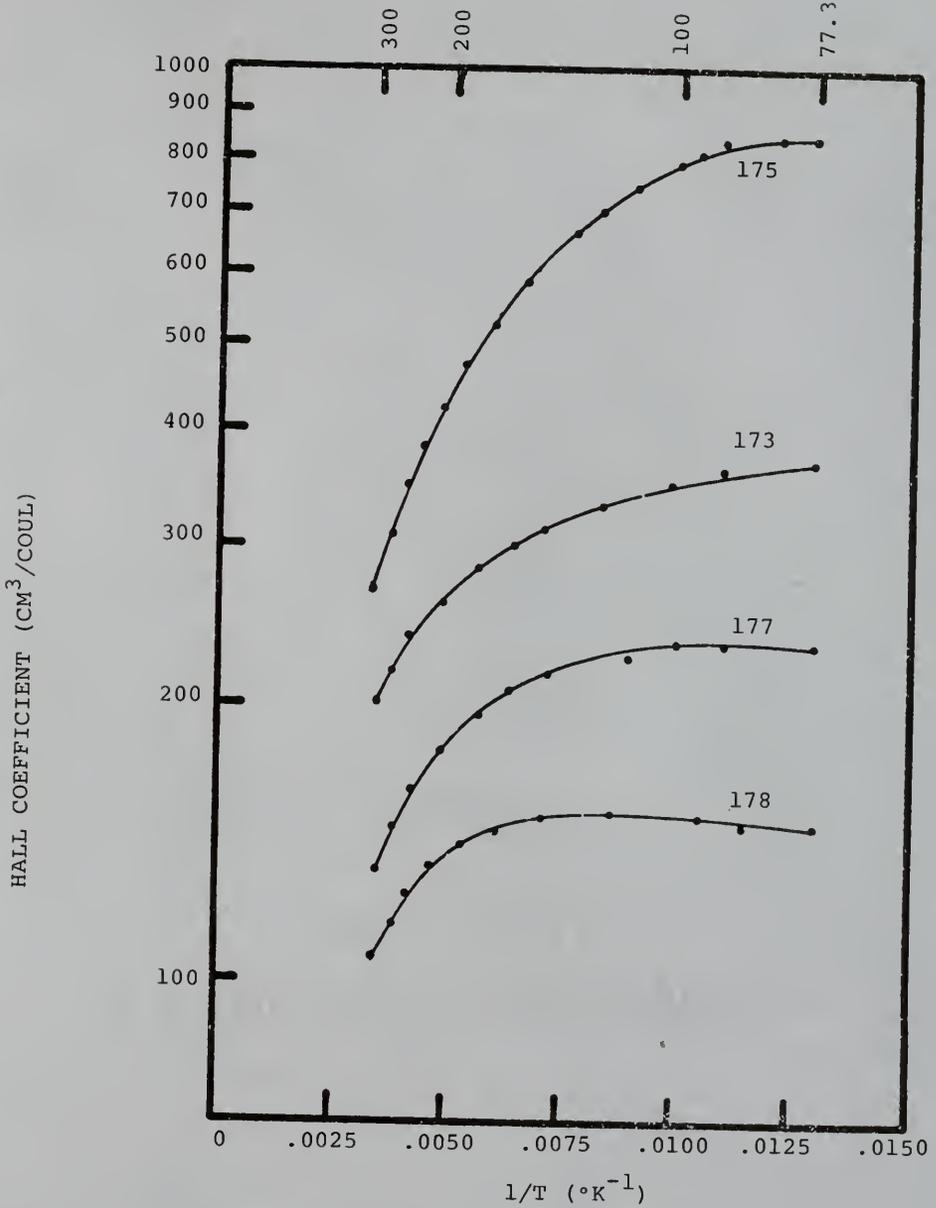


FIGURE 4.14 HALL COEFFICIENT OF SAMPLES
173, 175, 177, 178

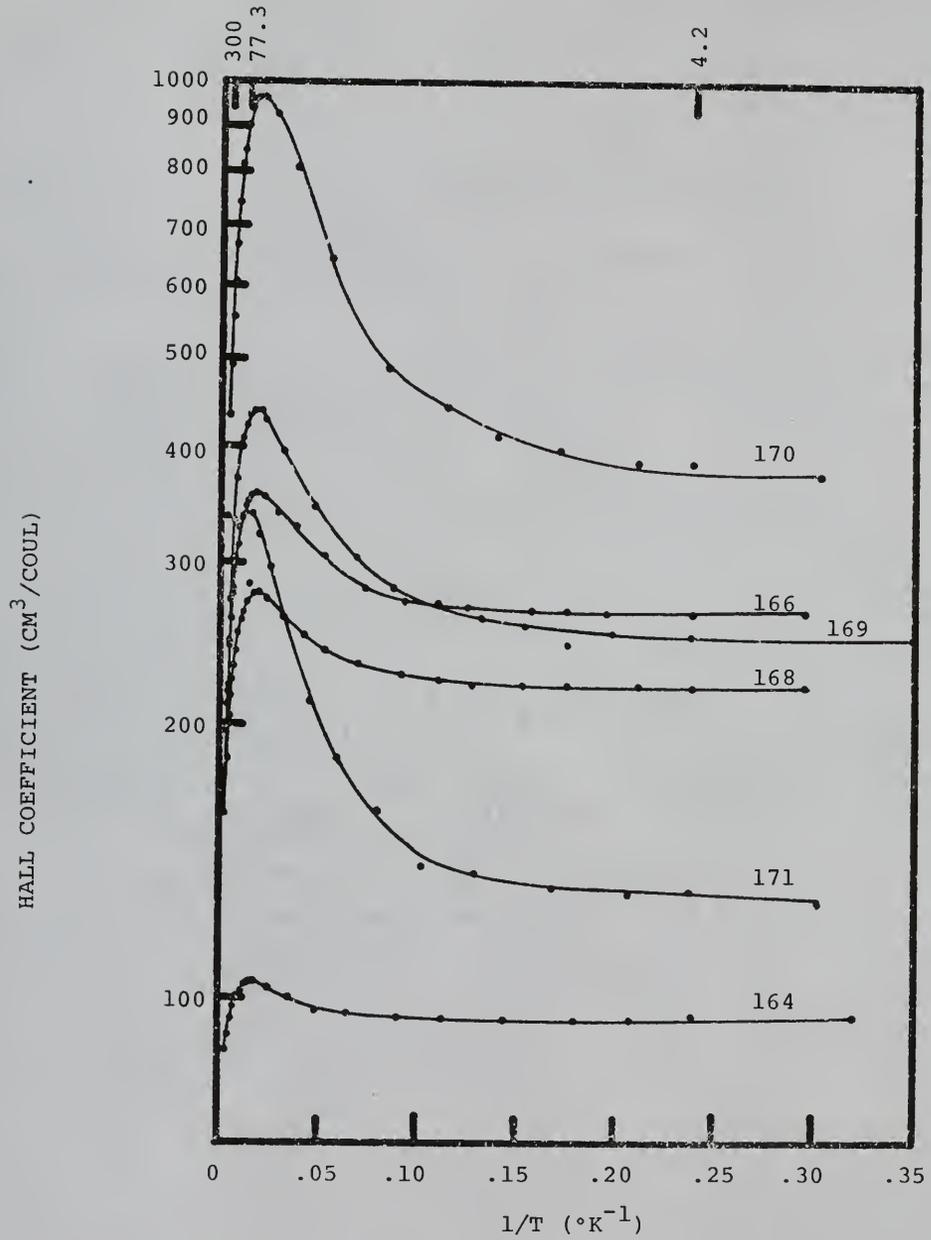


FIGURE 4.15 HALL COEFFICIENT OF SAMPLES
164-171

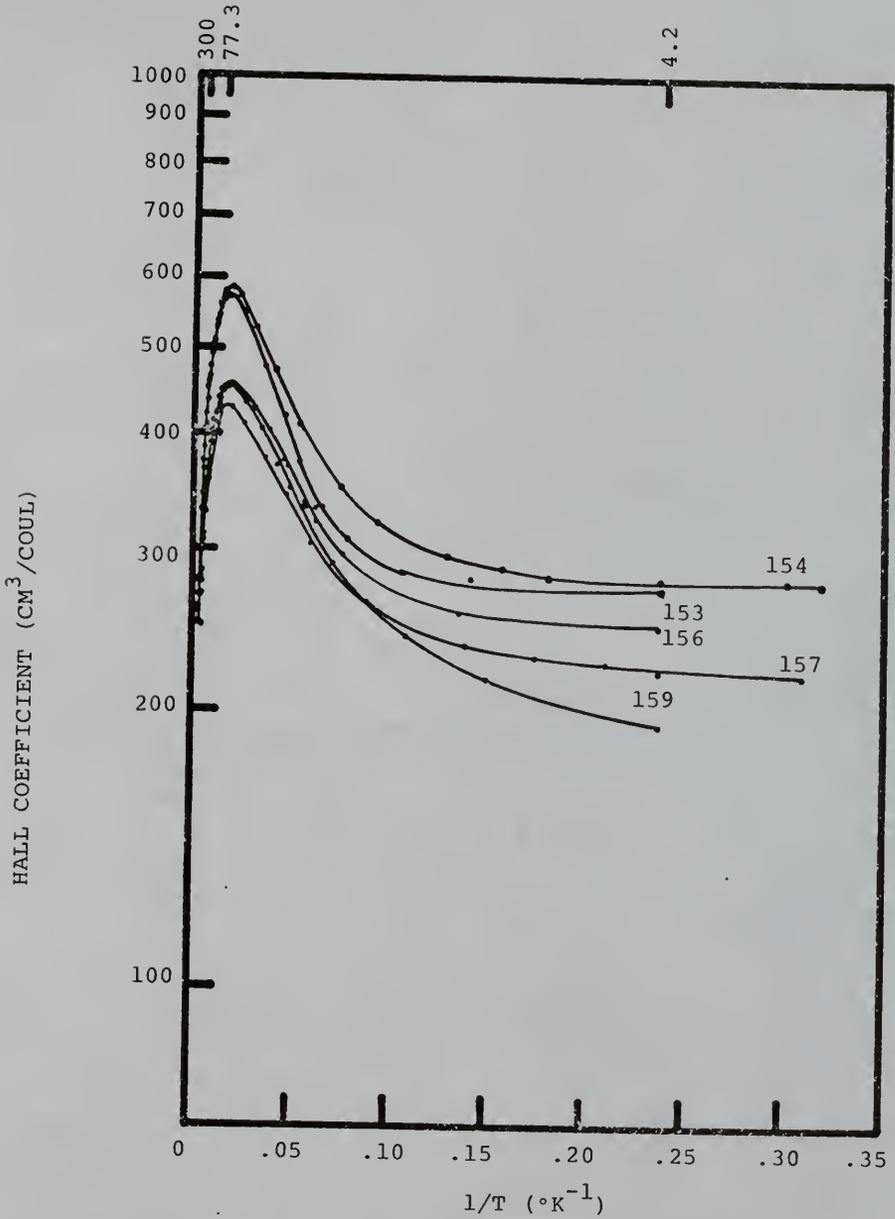


FIGURE 4.16 HALL COEFFICIENT OF SAMPLES
153-159

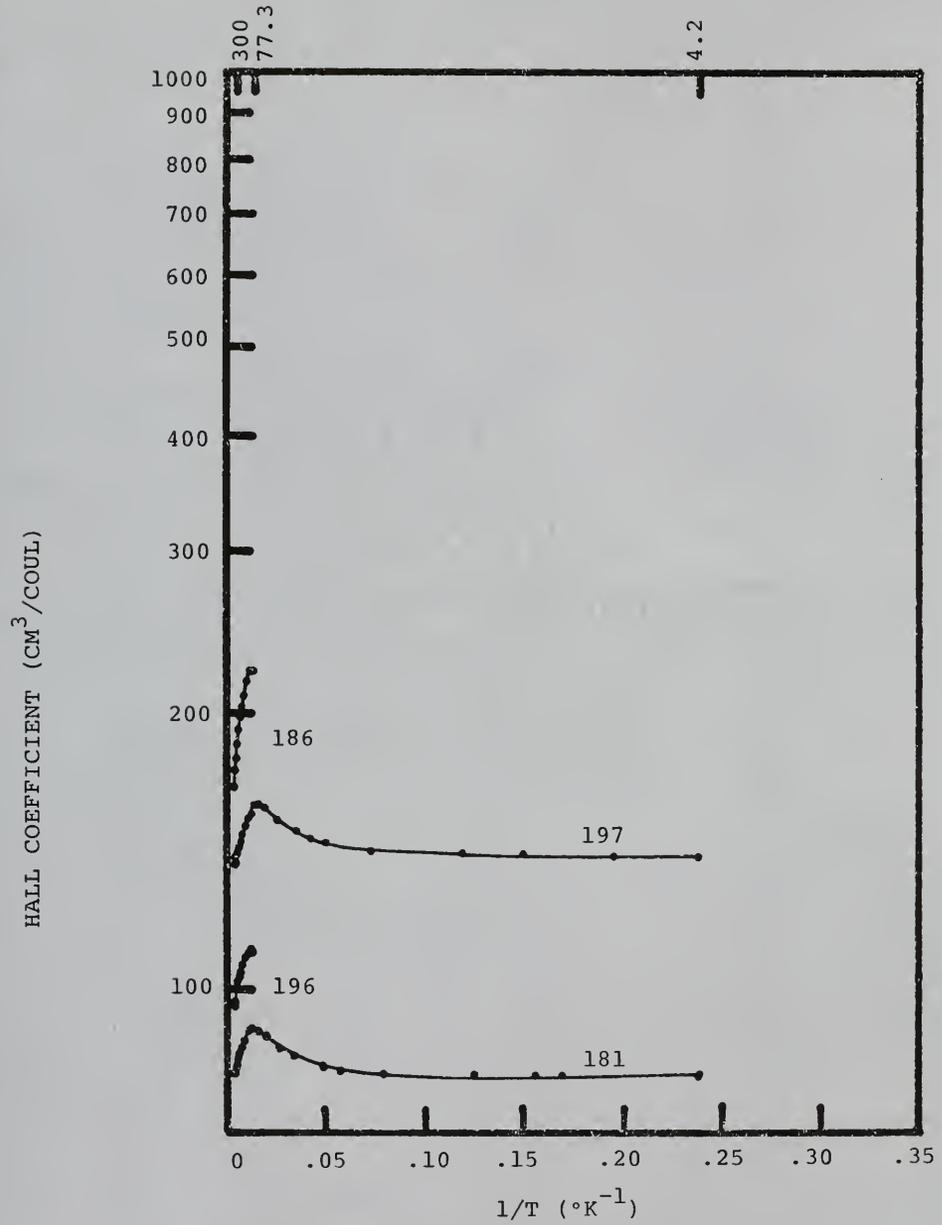


FIGURE 4.17 HALL COEFFICIENT OF SAMPLES
196-186

At low temperatures all the excited electrons have dropped back into the donor band so that $n_c=0$ and $n_d=N_d-N_a$.

$$R_h = \frac{r}{en_d} \quad (\text{low temp}) \quad (4.3)$$

Eqs. 4.2 and 4.3 are identical except for the scattering factor which might be assumed to be unity in each case without causing much error. The Hall coefficients at both high and low temperatures should then be equal and given by

$$R_h = \frac{1}{e(N_d-N_a)} \quad (4.4)$$

The free electron concentration was calculated from the single band equation:

$$n_h = \frac{r}{eR_h} \quad (4.5)$$

Here again the scattering factor r was assumed to be unity. From experimental data for these samples the Hall coefficient showed little dependence on the magnetic field strength. The greatest error introduced by assuming $r=1$ should be less than about 10 percent and only in the intermediate temperature range. The results from Eqn. 4.5 are shown in Figs. 4.18 to 4.22 for $\text{InAs}_{0.61}\text{P}_{0.39}$. These curves show that all the samples had rather high impurity content especially since there was no intentional doping involved in the growth process. Only two samples (170 and 175) fell into the 10^{15}cm^{-3} concen-

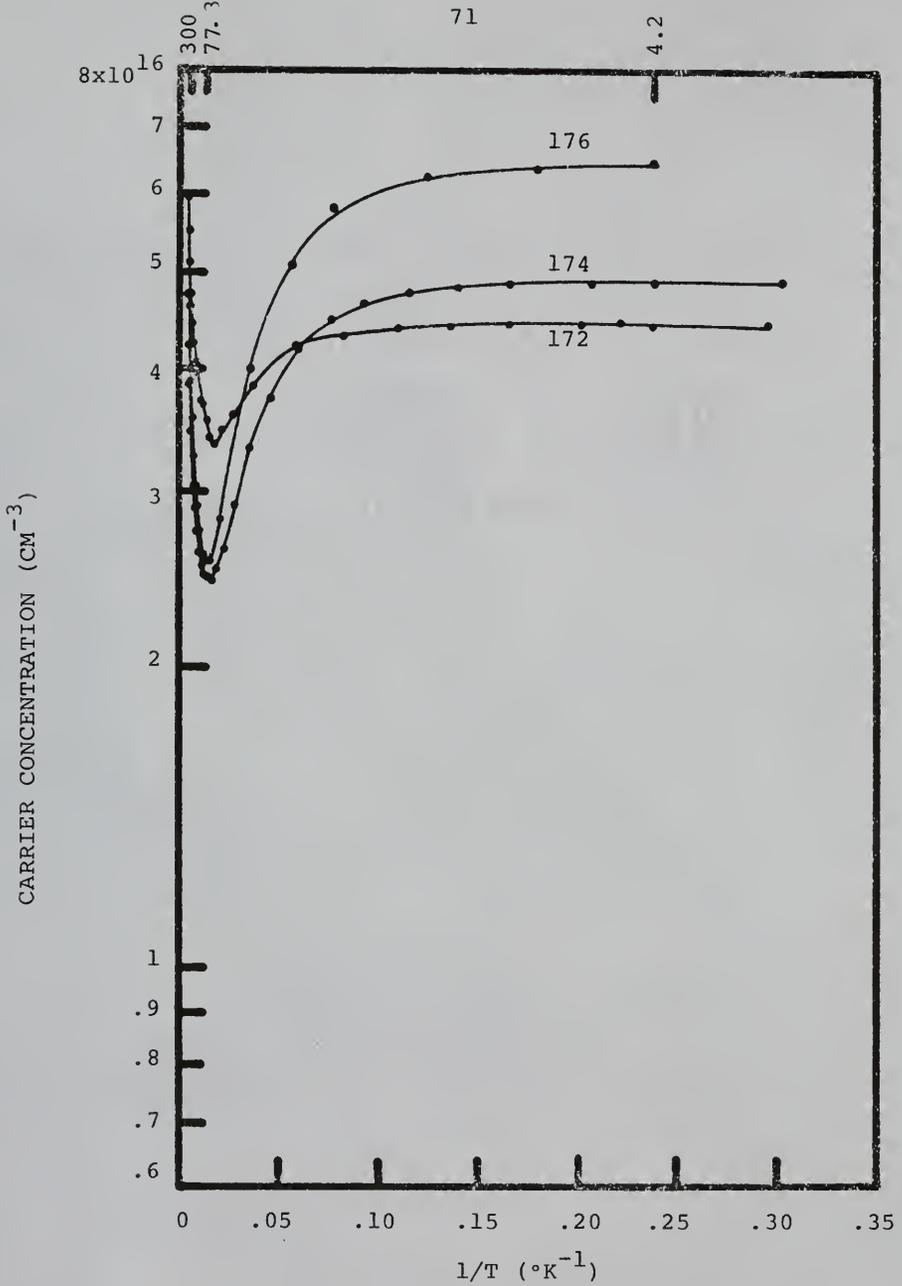


FIGURE 4.18 CARRIER CONCENTRATION OF SAMPLES 172, 174, 176

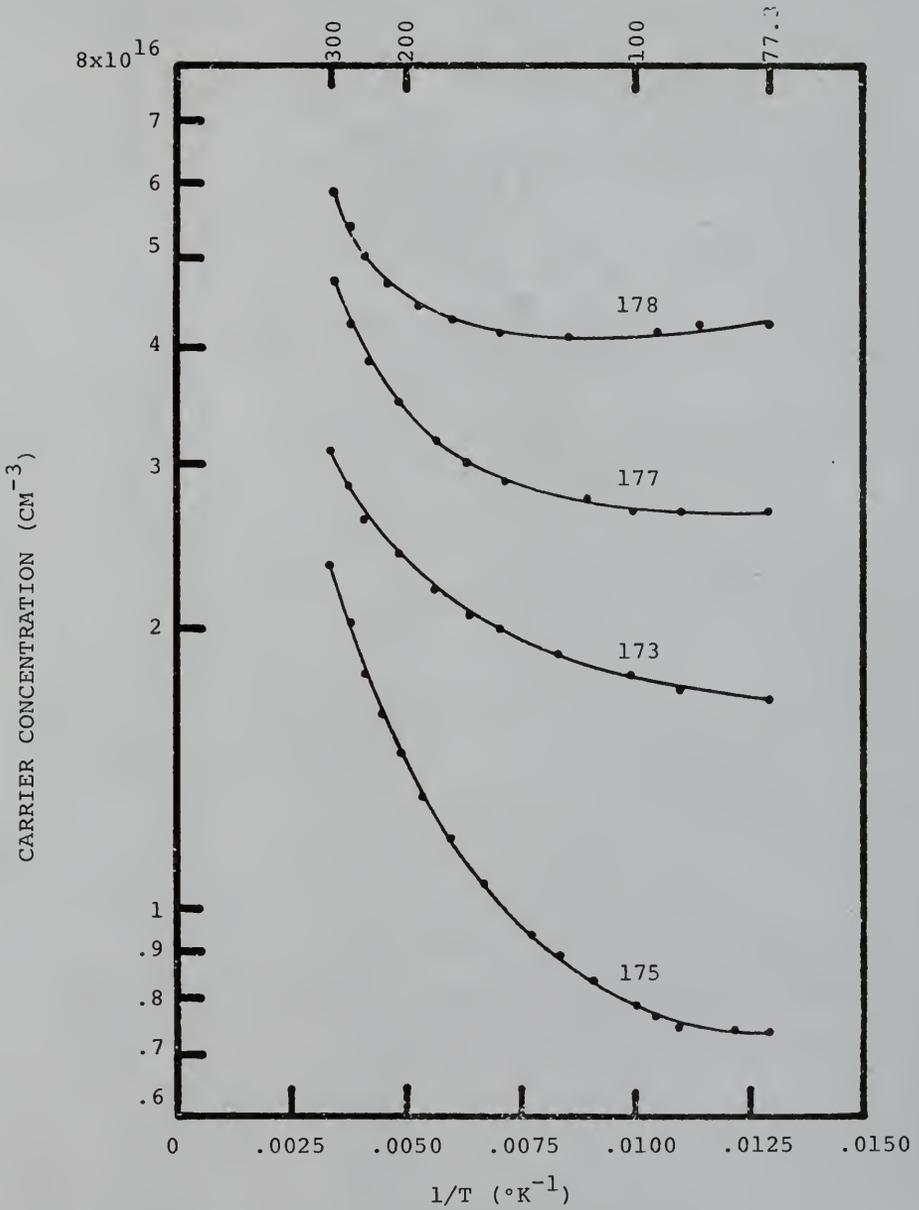


FIGURE 4.19 CARRIER CONCENTRATION OF SAMPLES
173, 175, 177, 178

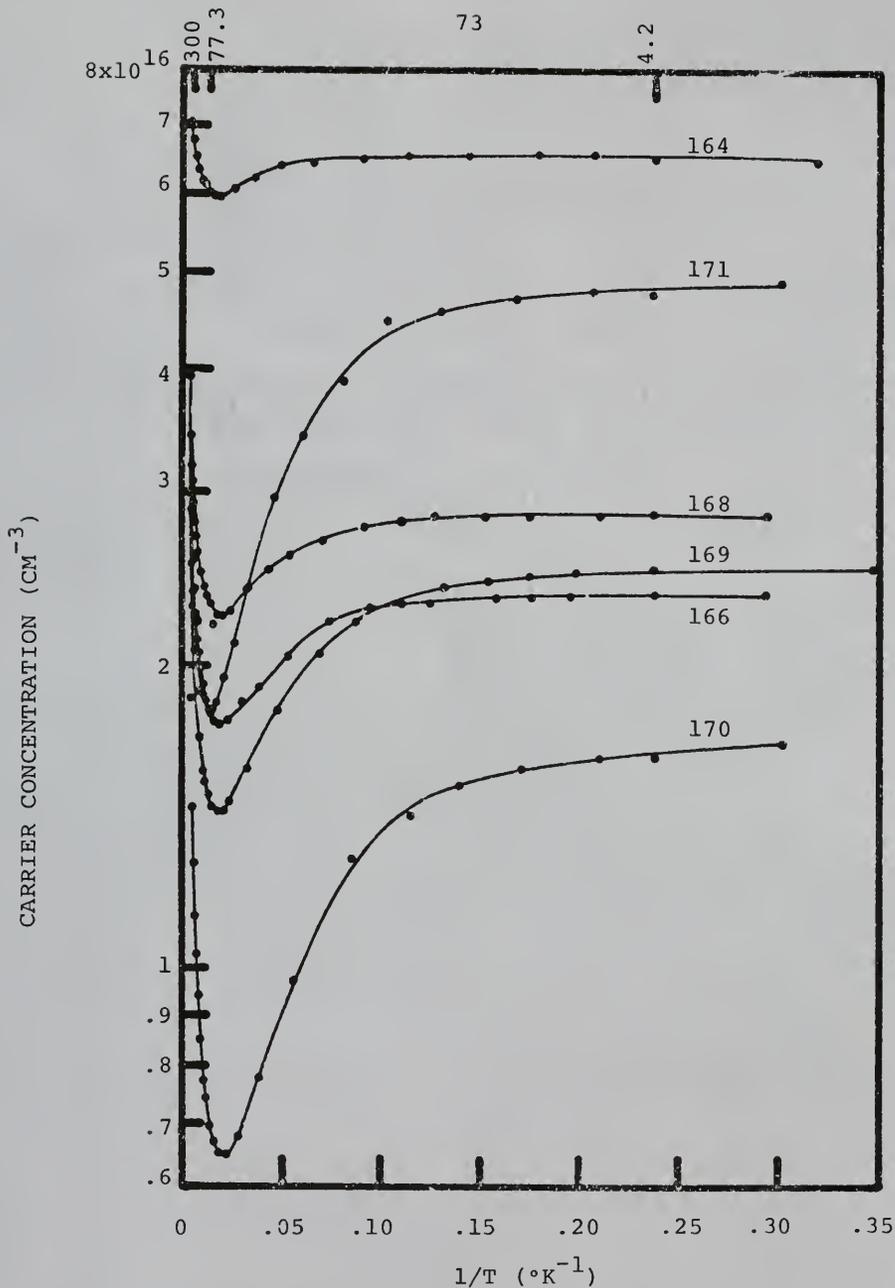


FIGURE 4.20 CARRIER CONCENTRATION OF SAMPLES
164-171

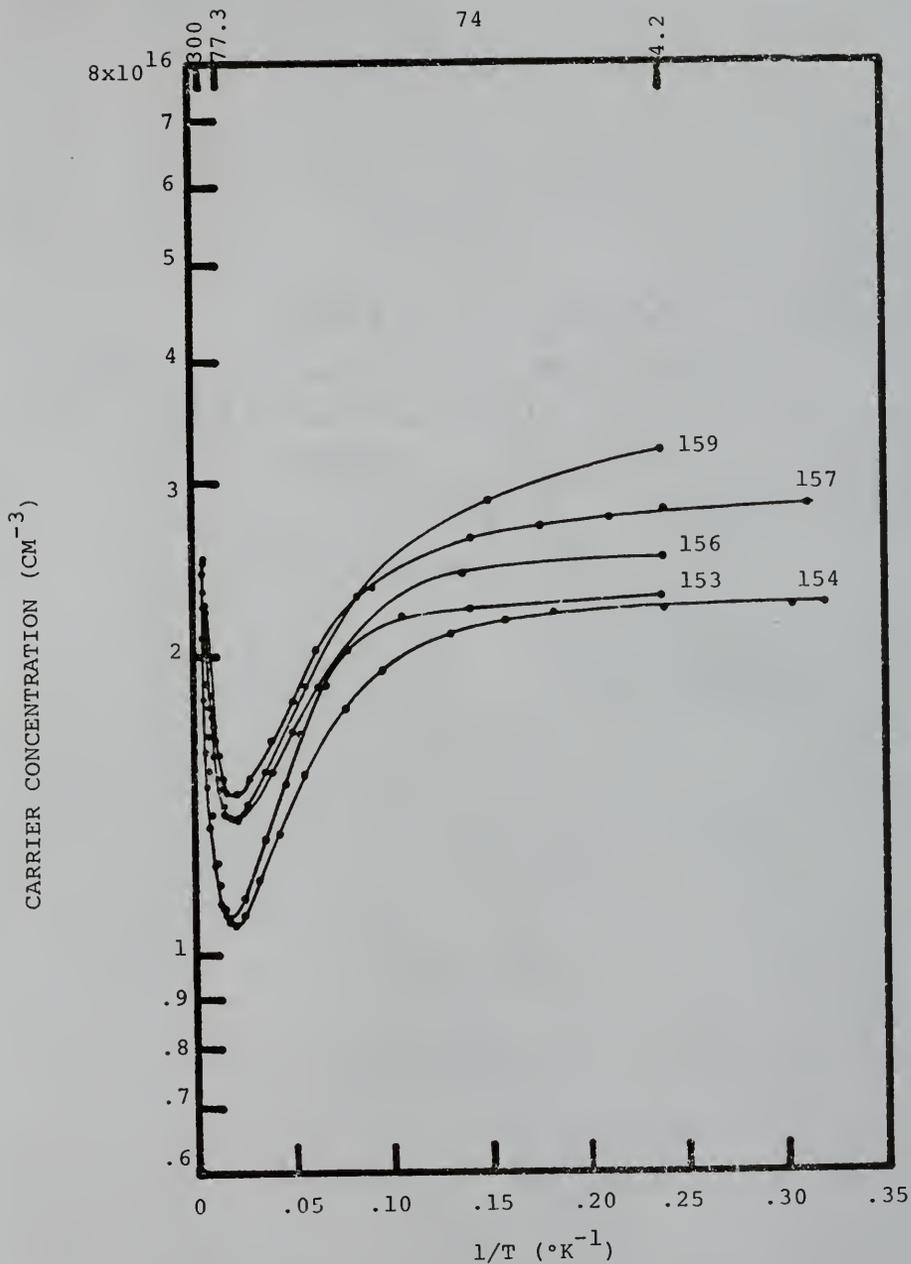


FIGURE 4.21 CARRIER CONCENTRATION OF SAMPLES 153-159

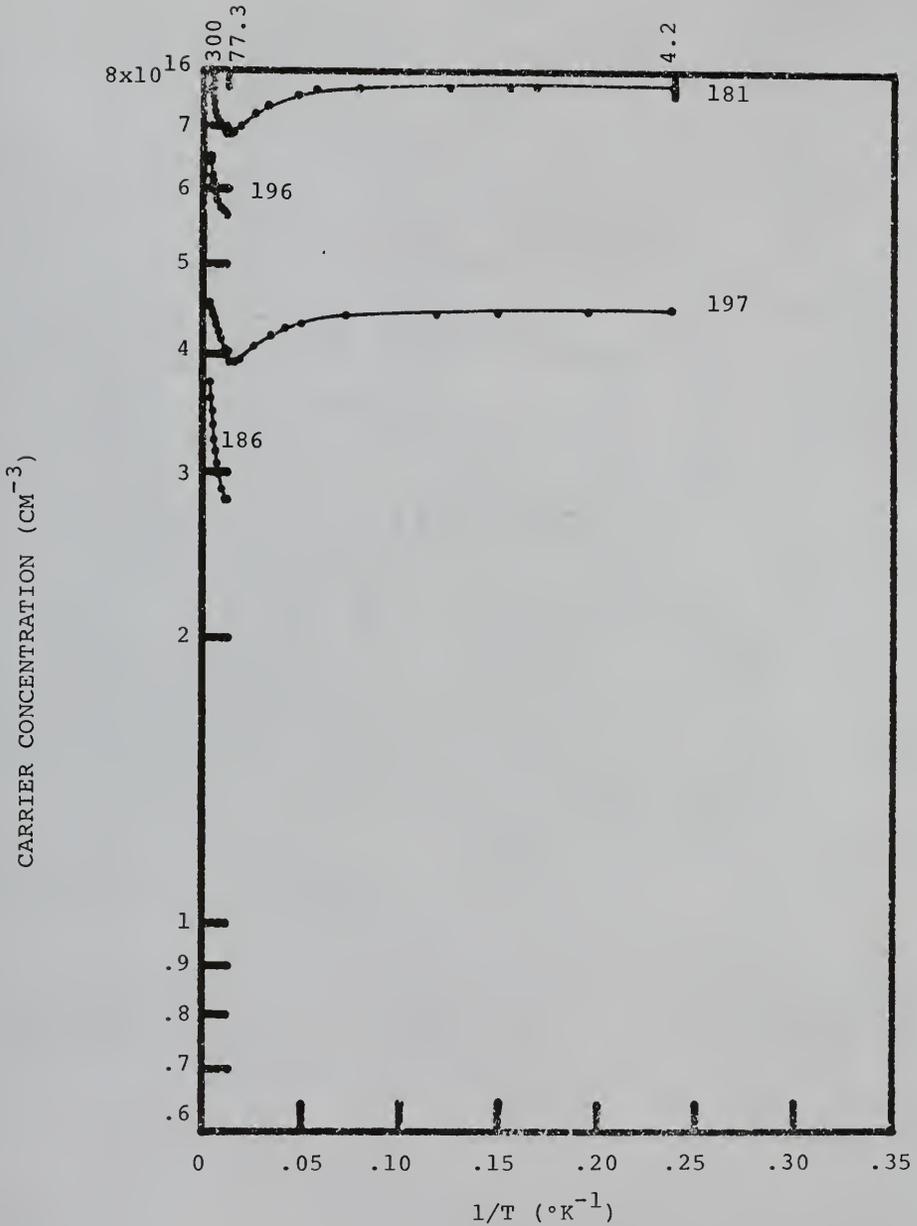


FIGURE 4.22 CARRIER CONCENTRATION OF SAMPLES
196-186

tration range and then only at their minimum points.

The curves in Figs. 4.18-4.22 are, of course, showing the effects of electrons in both the conduction and impurity bands. The actual electron concentrations must be derived from a more rigorous equation such as Eqn. 2.33. This was done for each of the samples by using Eqn. 2.37 to first determine b , the ratio of the mobility in the conduction band to the mobility in the donor band. The result for b was then used in Eqn. 2.38 to determine x , the ratio of free donor electrons to free conduction electrons. This analysis provided the variation of conduction electrons and donor electrons with temperature and the results are illustrated in Figs. 4.23 to 4.26 for a sample from each group (172, 164, 153 and 181) along with n_h from Eqn. 4.5.

The results from this method show both the exponential decrease of the conduction band electrons with temperature and the constant concentration of electrons ($N_d - N_a$) in the donor band at low temperatures. A different analysis of similar curves from GaAs samples was made by Berg.⁴⁶ The approach involved curve fitting to provide the best scattering factor, r . The results were extremely similar to those obtained here for $\text{InAs}_{0.61}\text{P}_{0.39}$ by this approximate method.

The importance of separating the concentration of electrons from each band is that the temperature variation of the conduction band electrons may now be seen. The exponential decrease is clearly evident in Figs. 4.23 to 4.26 and was

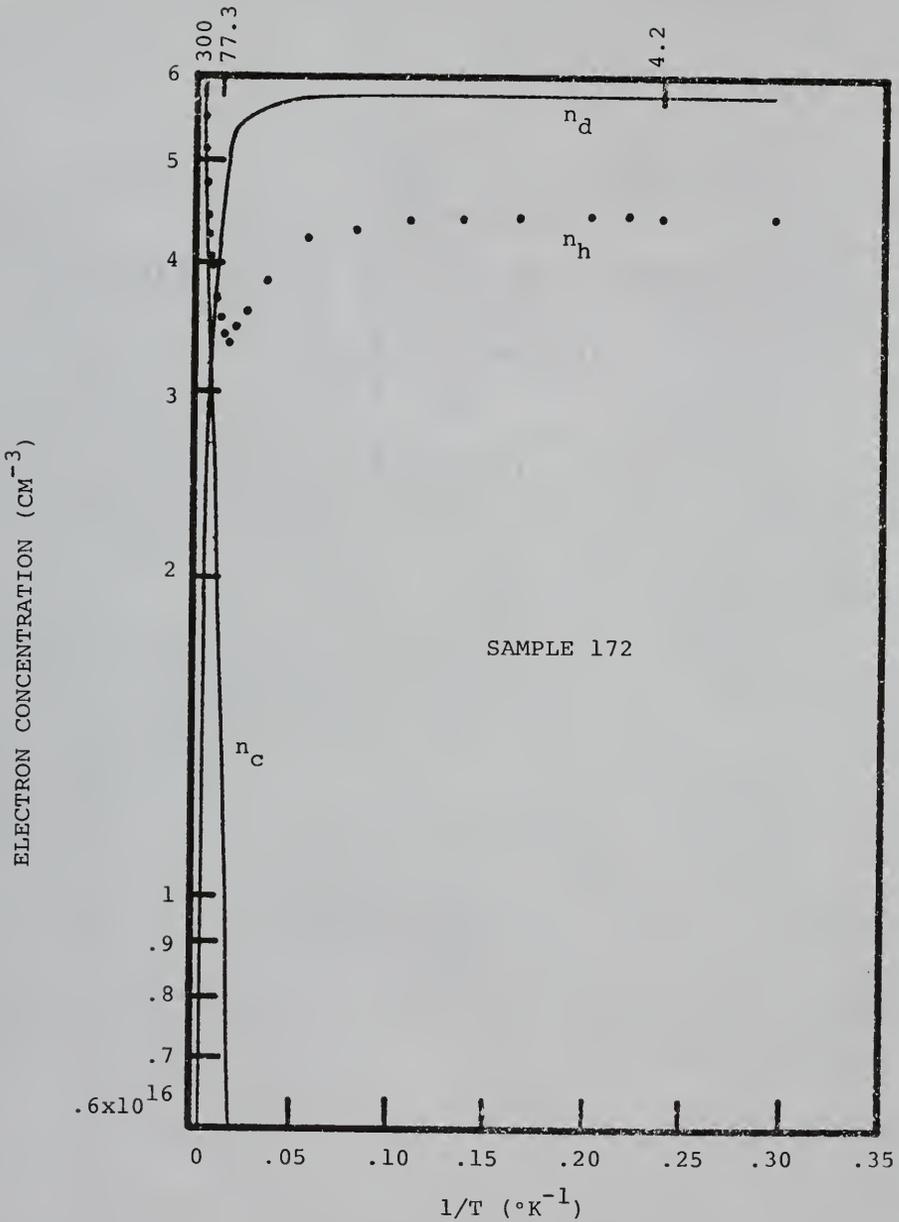


FIGURE 4.23 ELECTRON CONCENTRATION IN THE CONDUCTION AND DONOR BANDS FOR SAMPLE 172

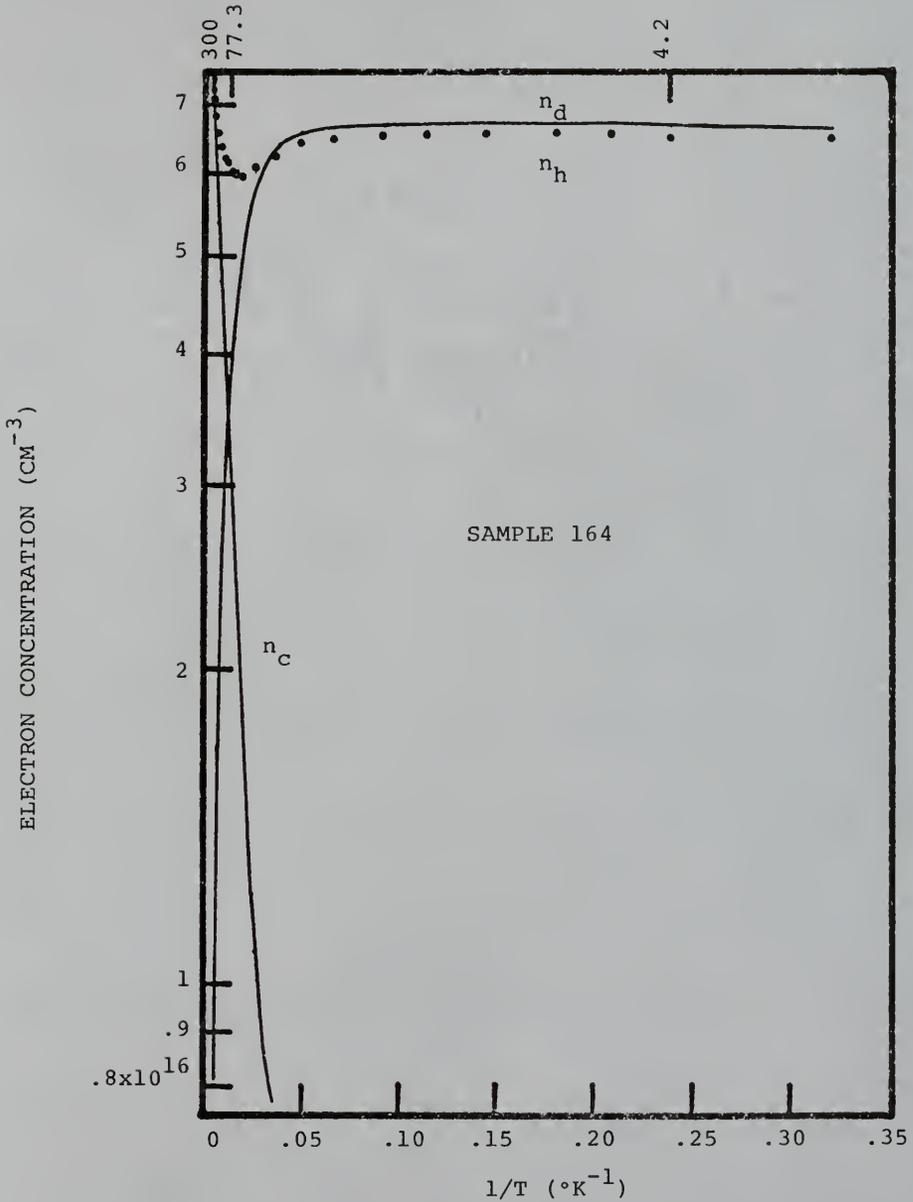


FIGURE 4.24 ELECTRON CONCENTRATION IN THE CONDUCTION AND DONOR BANDS FOR SAMPLE 164

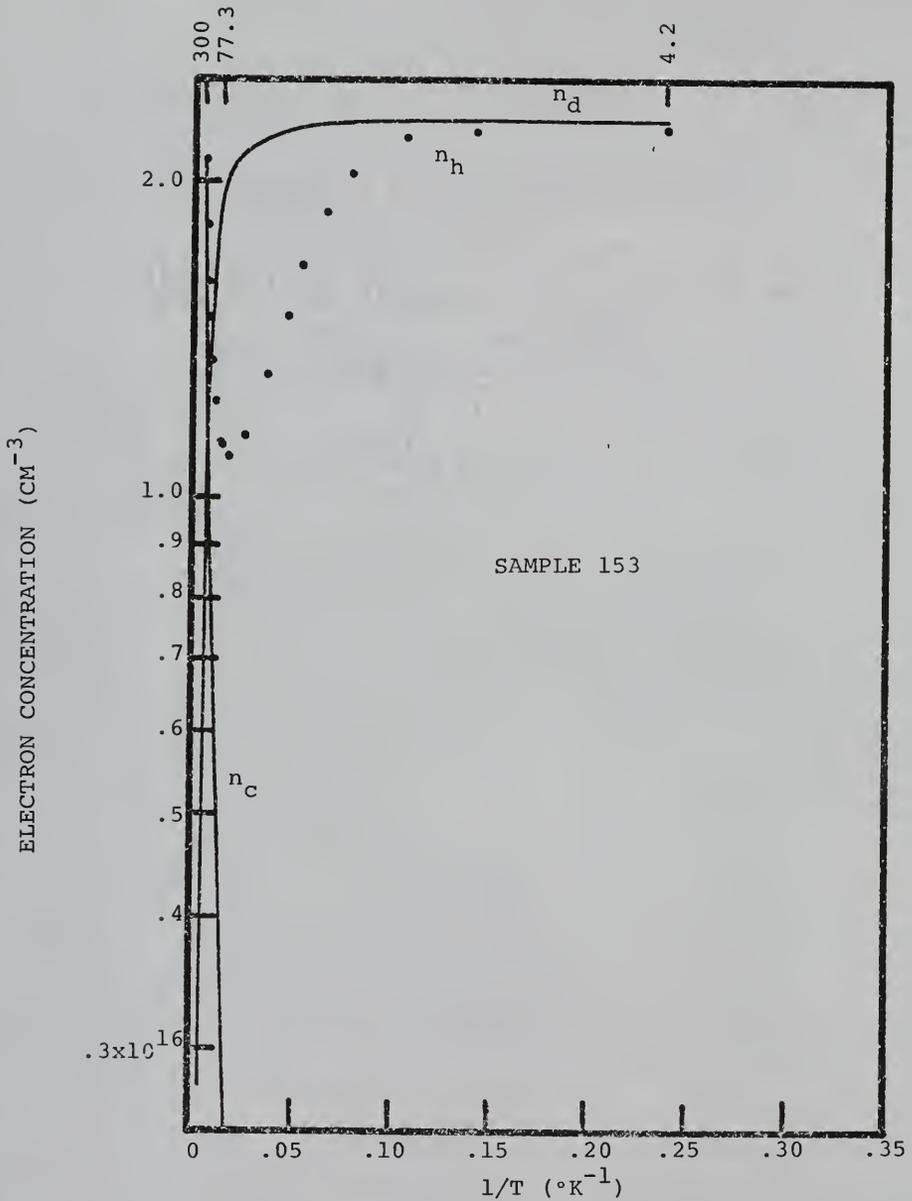


FIGURE 4.25 ELECTRON CONCENTRATION IN THE CONDUCTION AND DONOR BANDS FOR SAMPLE 153

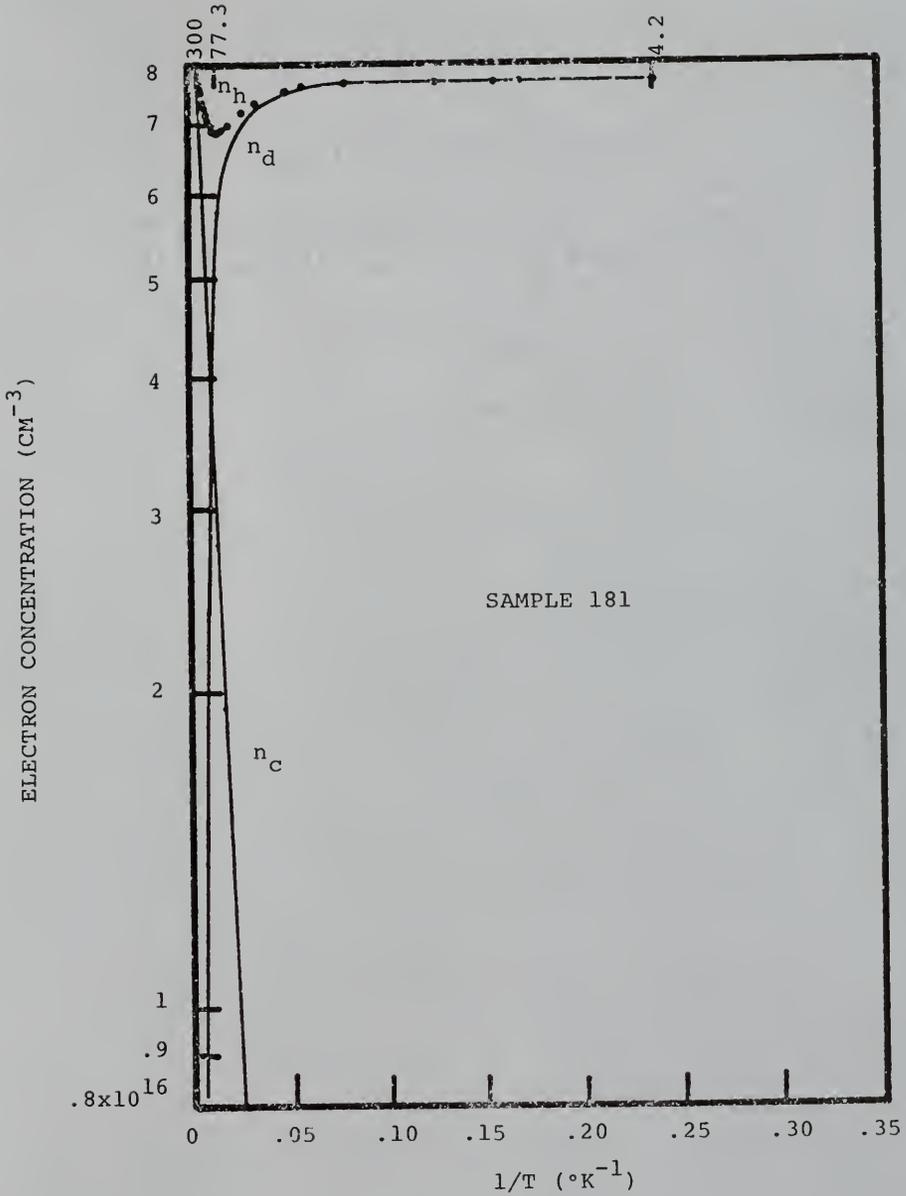


FIGURE 4.26 ELECTRON CONCENTRATION IN THE CONDUCTION AND DONOR BANDS FOR SAMPLE 181

fitted by least squares to an exponential of the form

$$n_C = A_C \exp (-E_{C_1}/kT) \quad (4.6)$$

The results for A_C and E_{C_1} obtained by this method are listed in Table 4.2 along with b , the mobility ratio. It should be noted that samples 173, 175, 177, 178, 196 and 186 were only measured from 77.3 to 300K. Because of their incomplete curves the analysis is only an approximation. The values for E_{C_1} show definite trends and are plotted in Fig. 4.27 for the first three groups of samples. For the 3 μm (172-178) and 9 μm (164-171) samples there is an almost linear decrease of E_{C_1} with increasing flow rate. For the 22 μm (153-159) samples the value of E_{C_1} increases with increasing flow rate. Similar type trends were observed in the analysis of resistivity (Fig. 4.12). Again the sample characteristics seemed to be governed by not only the hydrogen flow rate but also the epitaxial thickness. The interpretation of these trends in E_{C_1} is not so clear cut as indicated by Section 2.3b. The exponential dependence of the conduction electrons is described by Eqn. 2.26. The slopes of the curves generated from this equation (Fig. 2.12) are varied by changes in the total impurity level and by changes in the compensation ratio. Thus an increase in E_{C_1} indicates an increase in the impurities, an increase in the compensation, or some combination of these two.

TABLE 4.2

	$\underline{b}(\mu_C/\mu_d)$	\underline{A}_C	\underline{E}_{C_1} (meV)
172	4.94	9.74	14.76
173*	5.18	5.72	17.83
174	5.82	8.77	19.37
175*	10.57	5.45	24.67
176	8.42	10.26	24.45
177*	4.90	11.95	25.31
178*	3.48	15.45	26.74
164	2.39	8.76	6.90
168	4.04	4.17	8.62
166	4.37	3.81	10.59
169	6.31	4.20	12.59
170	9.49	2.65	15.06
171	8.72	5.52	15.99
153	6.31	4.43	20.95
154	6.31	4.33	18.68
155	5.74	5.92	16.69
156	5.14	4.09	14.71
157	5.63	3.80	13.71
159	7.36	3.58	13.61
196*	2.20	8.98	9.62
197	2.23	5.70	6.00
181	2.01	10.81	8.49
186*	3.04	5.94	12.85

*indicates analysis from incomplete data

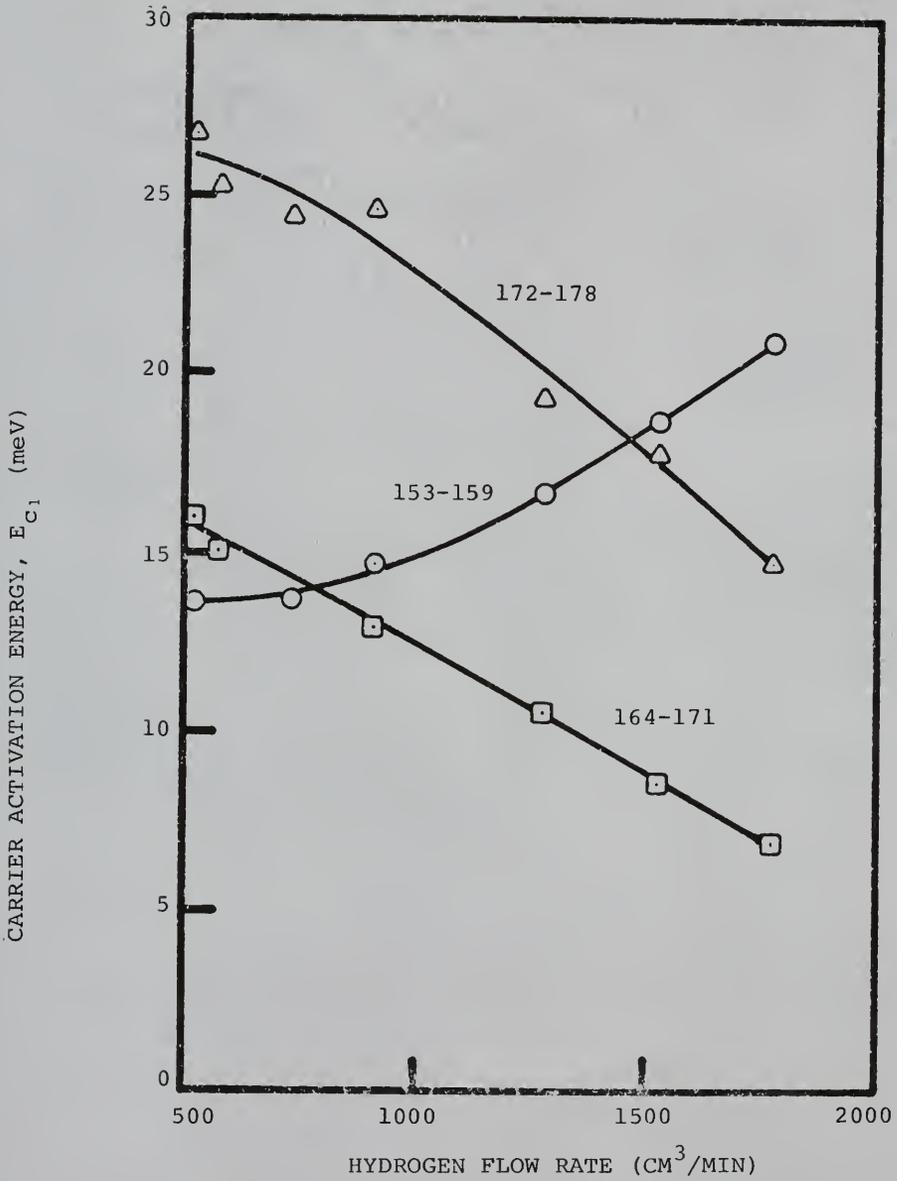


FIGURE 4.27 CARRIER ACTIVATION ENERGY, E_{c1} , VERSUS HYDROGEN FLOW RATE

4.4 Mobility

The mobility of electrons in $\text{InAs}_{0.61}\text{P}_{0.39}$ may be calculated from the resistivity and Hall coefficient data by the following relation

$$\mu_h = \frac{R_h}{\rho} \quad (4.7)$$

This is called the Hall mobility. The actual drift mobility may be found by dividing μ_h by the scattering factor r . Since r is assumed to be unity for all temperatures the two mobilities are assumed equal for convenience. The experimental curves derived by using Eqn. 4.7 are shown in Figs. 4.28 to 4.32 plotted against inverse absolute temperature. The curves show a sharp initial increase with decreasing temperature until a peak is reached at approximately 100K. The mobility then falls exponentially until around 20K. For temperatures below 20K the mobility becomes almost constant. These curves are seen to compare well with Fig. 2.9 which is the theoretical mobility derived from a combination of polar optical phonon, ionized impurity, and neutral impurity scattering. The agreement indicates these three scattering mechanisms are dominant in the epitaxial layers.

The high temperature portion of the mobility curves may be best approximated by a power equation such as

$$\mu = aT^{-\beta} \quad (4.8)$$

A least squares fit of the mobility data from 300 to 200K

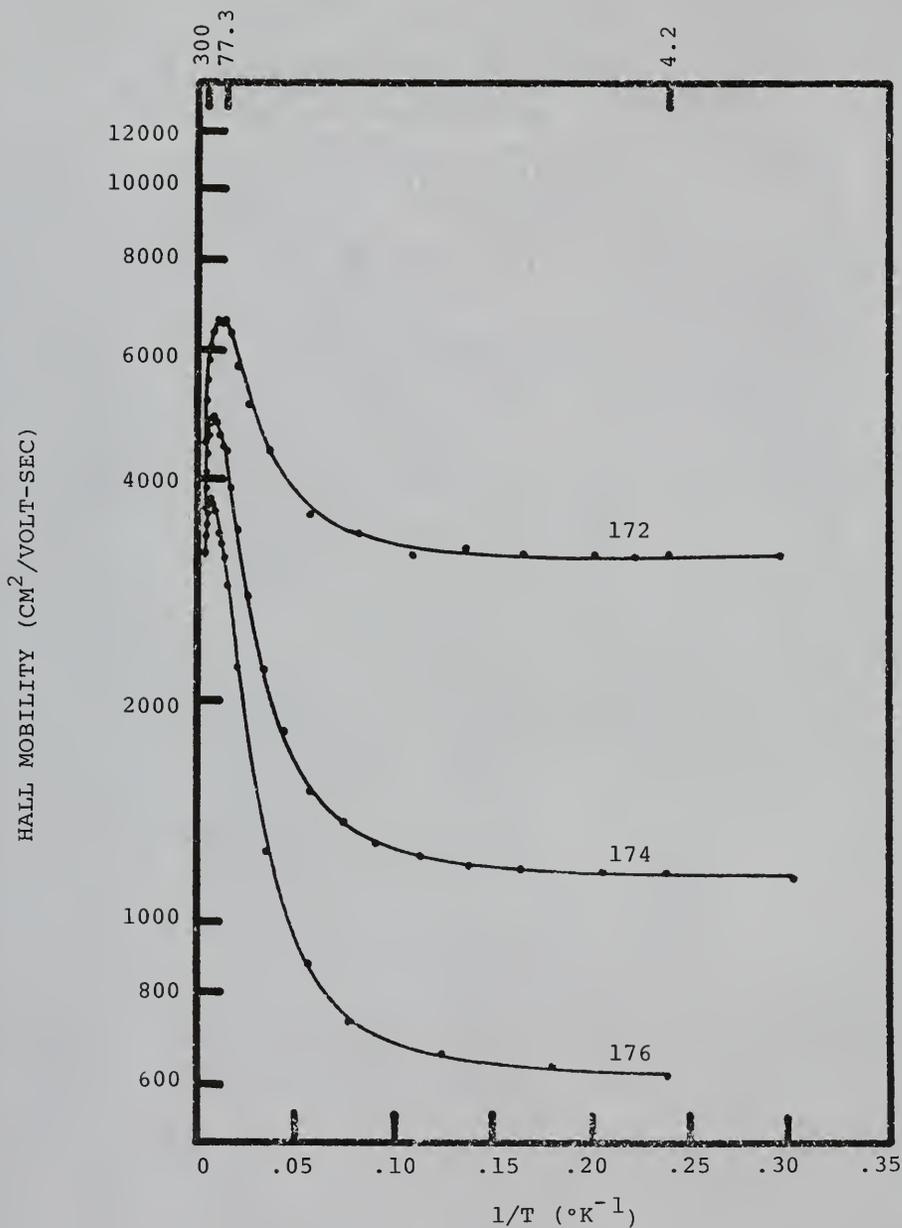


FIGURE 4.28 HALL MOBILITY OF SAMPLES 172, 174, 176

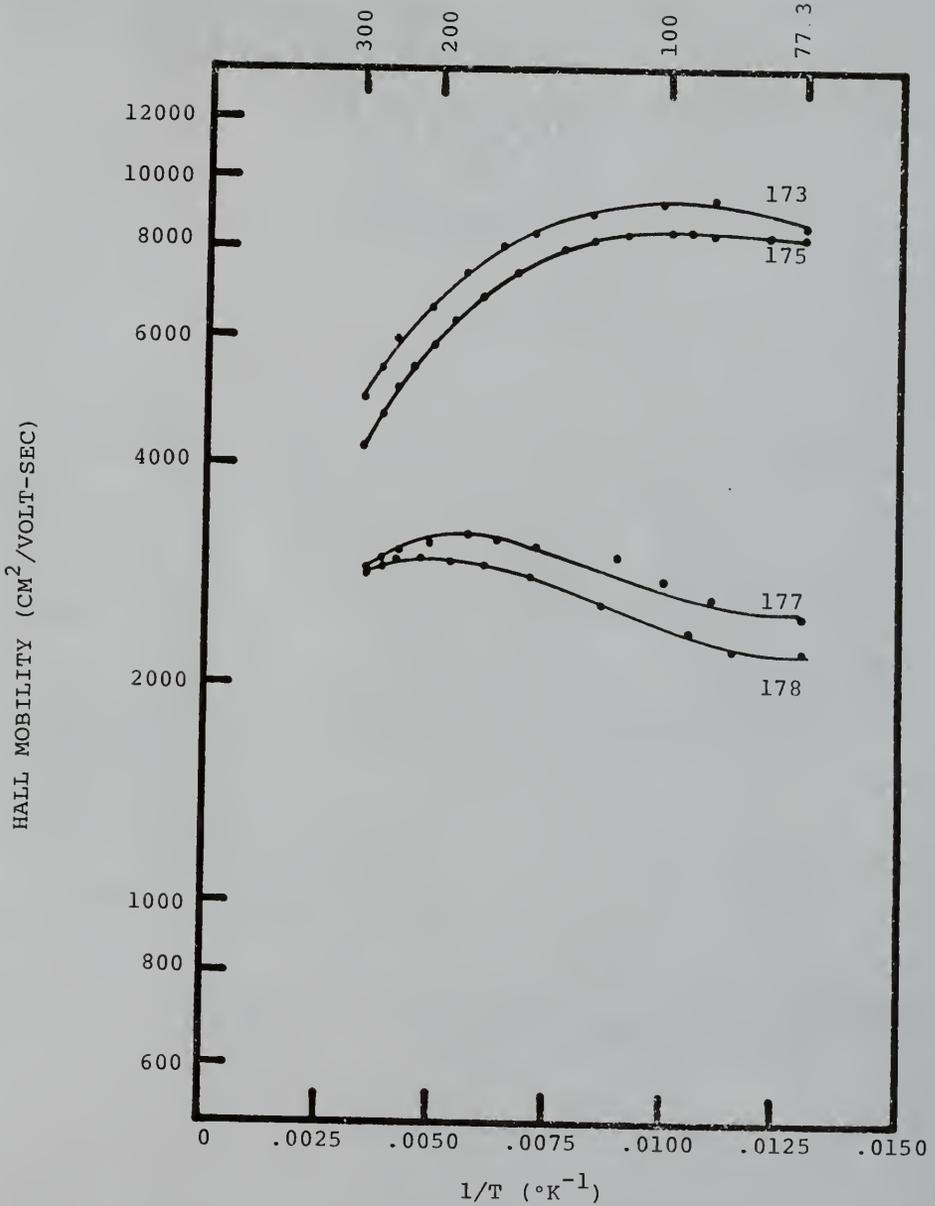


FIGURE 4.29 HALL MOBILITY OF SAMPLES 173, 175, 177, 178

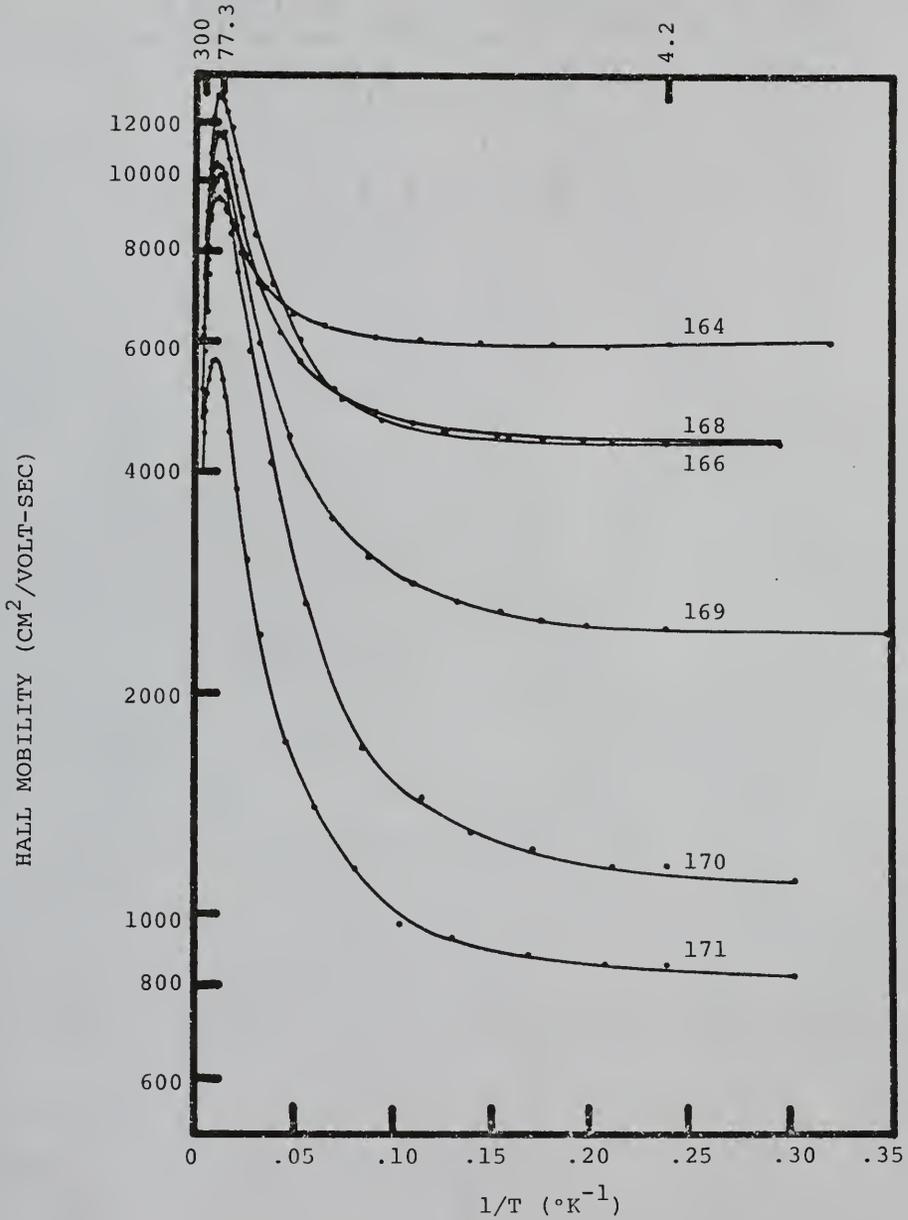


FIGURE 4.30 HALL MOBILITY OF SAMPLES 164-171

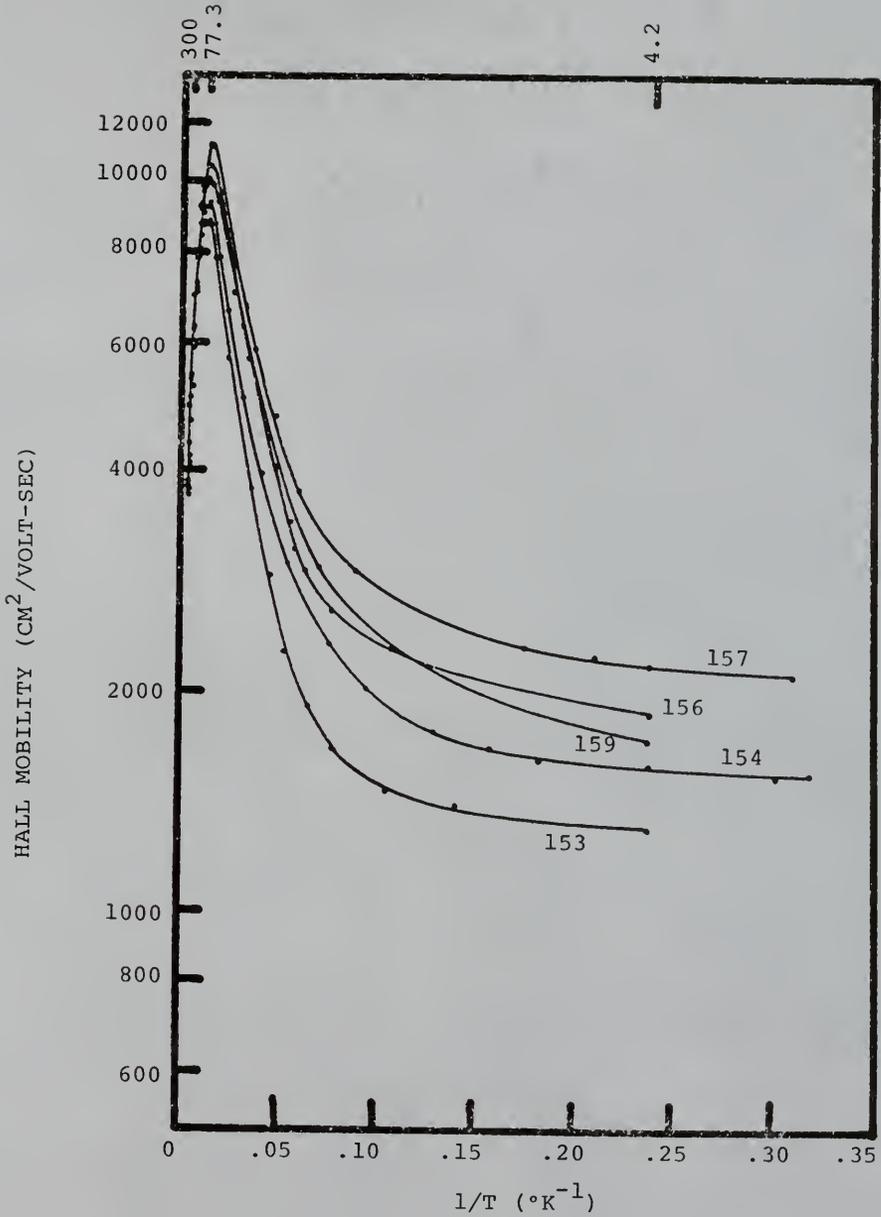


FIGURE 4.31 HALL MOBILITY OF SAMPLES 153-159

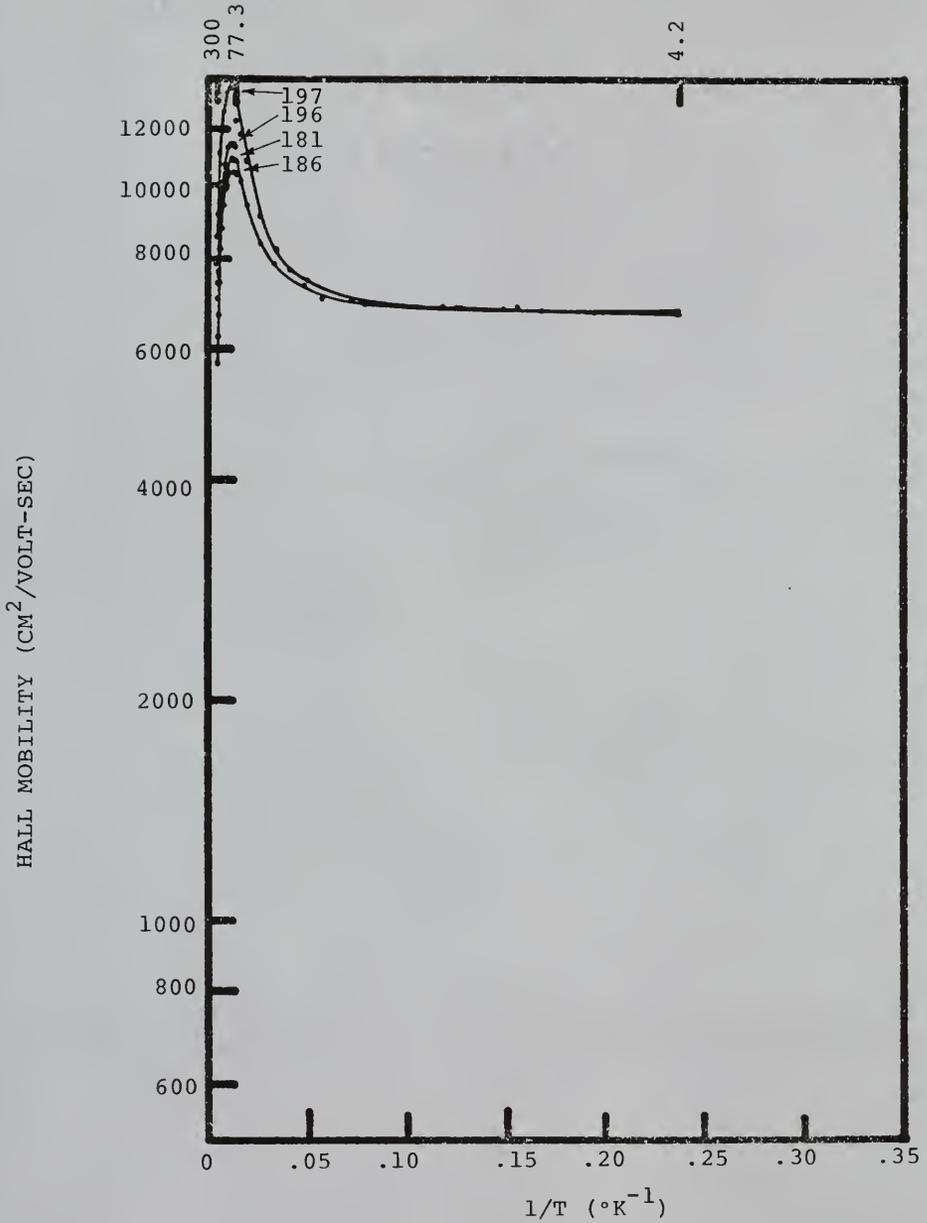


FIGURE 4.32 HALL MOBILITY OF SAMPLES 196-186

was made for each sample to determine the parameters α and β . From the theoretical dependence of β on the impurity concentration, N_i (shown in Fig. 2.7), the values for total impurities contained in each sample could be found. Because of the approximations, it should be emphasized again that the value obtained will also be only approximate. With the relations

$$N_i = N_d + N_a \quad (4.9)$$

$$n_{\max} = N_d - N_a \quad (4.10)$$

the concentration of donor and acceptor impurities could be found. A list of the values derived from this analysis of the mobility curves is contained in Table 4.3.

Some general trends in these results should be noted and compared to the results from the carrier concentration analysis. The total impurity concentration and donor compensation in samples 172-178 show an increase with decreasing flow rates. This is directly correlated to the increase of E_{C1} with decreasing flow rate in Fig. 4.27. The samples 164-171 show a similar increase in compensation but some scatter in the impurity concentration. The samples 153-159 show both a decreasing impurity concentration and a decreasing compensation level with decreasing flow rate which corresponds also to the decrease in E_{C1} with decreasing flow rate. The last set (196-186) shows too much scatter to see definite trends.

TABLE 4.3

	α	β	$\frac{N_i(\text{cm}^{-3})}{10^{16}}$	$\frac{N_d(\text{cm}^{-3})}{10^{16}}$	$\frac{N_d(\text{cm}^{-3})}{3.34 \times 10^{16}}$	$\frac{N_a}{N_d}$
172	1.31x10 ⁵	.59	12.65x10 ¹⁶	9.31x10 ¹⁶	3.34x10 ¹⁶	.36
173	5.15	.82	8.65	5.88	2.77	.47
174	.71	.52	13.40	9.14	4.26	.47
175	51.60	1.25	3.80	3.07	.73	.24
176	.23	.35	19.11	12.79	6.32	.49
177	.16	.30	20.56	12.65	7.92	.63
178	.12	.25	22.35	14.12	8.24	.58
164	1.37	.55	13.74	10.41	3.33	.32
168	5.41	.79	9.00	6.21	2.79	.45
166	8.64	.86	7.91	5.40	2.51	.47
169	5.53	.82	8.49	5.74	2.75	.48
170	8.48	.91	7.40	4.63	2.77	.60
171	.94	.55	13.30	9.09	4.21	.46
153	8.48	.95	5.91	4.10	1.81	.44
154	8.10	.92	6.27	4.26	2.01	.47
155	4.39	.83	7.38	5.59	1.79	.32
156	18.90	1.09	5.05	3.78	1.27	.33
157	17.60	1.07	5.15	4.00	1.15	.29
159	16.50	1.07	5.15	4.19	.96	.23
196	3.01	.66	11.17	8.78	2.39	.27
197	3.97	.69	10.60	7.58	3.02	.10
181	2.76	.65	11.25	9.49	1.76	.19
186	6.25	.83	8.44	6.10	2.34	.38

CHAPTER V

EXPERIMENTAL RESULTS OF $\text{InAs}_{1-x}\text{P}_x$

5.1 Sample Description

A fifth set of samples were grown using the methods described in Chapter III with the arsine to phosphine ratio varied so as to produce samples of varying composition. These samples (147-152) were grown at a constant hydrogen flow rate of $2100 \text{ cm}^3/\text{min}$ on semi-insulating GaAs substrates. Though the deposition time for each sample was held constant, the resultant epitaxial thicknesses were seen to be strongly dependent on the composition. A plot of this experimental variation from Table 3.1 is shown in Fig. 5.1 where it is seen that the growth of phosphorus-rich layers is strongly favored. From the results of $\text{InAs}_{0.61}\text{P}_{0.39}$, it would be expected that this thickness variation would affect the transport characteristics of these samples due to the interface states.

Another noticeable physical variation was the quality of the surfaces of the epitaxial layers. The surfaces definitely degenerated as the phosphorus content increased. The surfaces of the arsenic rich samples (147, 148) could be characterized as dull but yet smooth. As the phosphorus content increased the surfaces tended to become more shiny

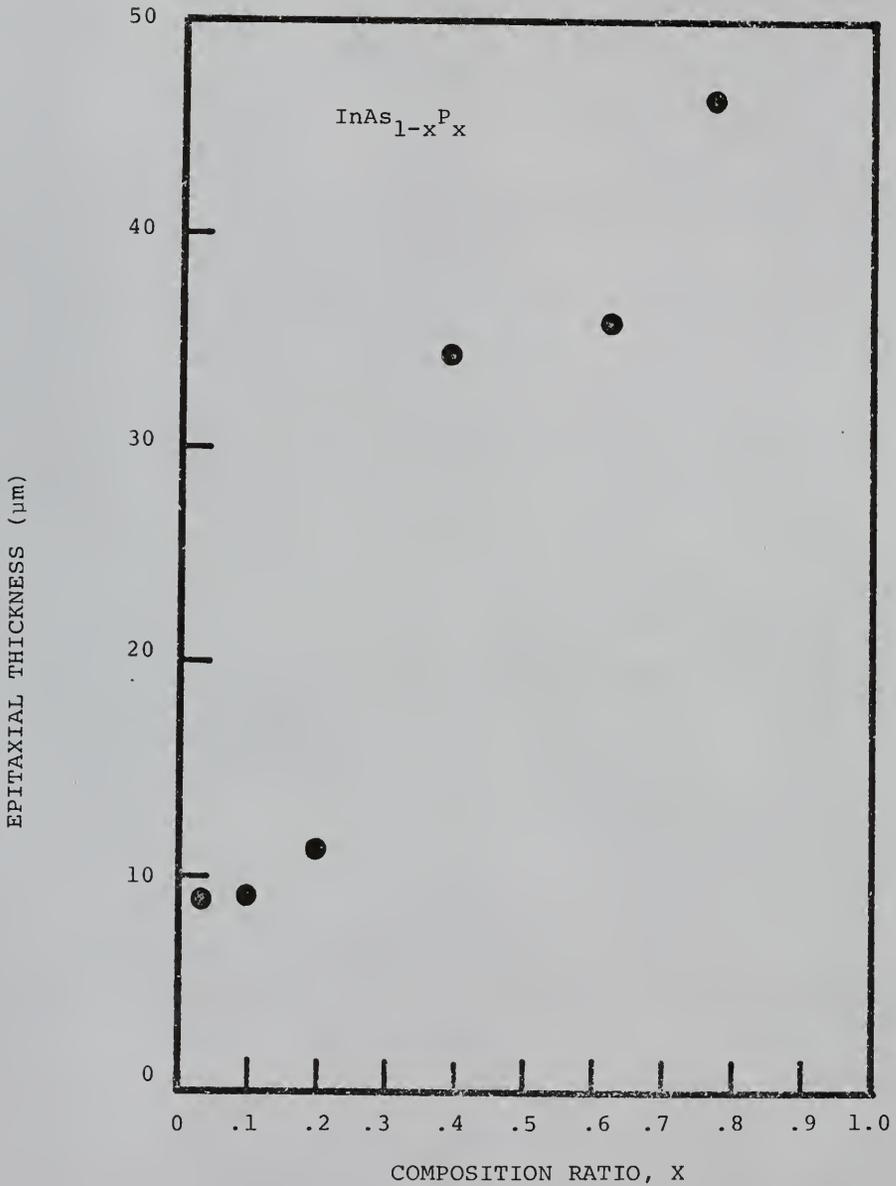


FIGURE 5.1 VARIATION OF EPITAXIAL THICKNESS WITH ALLOY COMPOSITION

but were plagued by large surface irregularities (hillocks).

5.2 Resistivity Data

Resistivity measurements were made on the samples of Group V over the temperature range from 4.2K to 300K. The results of these measurements are shown in Fig. 5.2 as functions of inverse absolute temperature. The results show an increase of resistivity from 0.15 ohm-cm for sample 147 to 0.1 ohm-cm for sample 152 at room temperature. As functions of inverse temperature, the curves decrease exponentially from 300K to 200K, reach a minimum at approximately 80K, then increase exponentially until 20K where they saturate and show a slight linear dependence with decreasing temperature.

The resistivity in the low temperature region below 80K may be approximate by the equation

$$\rho^{-1} = C_2 \exp(-E_2/kT) + C_3T + C_4 \quad (5.1)$$

A least squares fit was used to determine the constants C_2 , C_3 , C_4 and the conductivity activation energy E_2 . The results of this fit are listed in Table 5.1 and a plot of the activation energy E_2 is shown in Fig. 5.3 as a function of the alloy composition.

5.3 Hall Coefficient and Carrier Concentration

The Hall coefficient was measured for this set of samples at a magnetic field strength of 5 kilogauss over

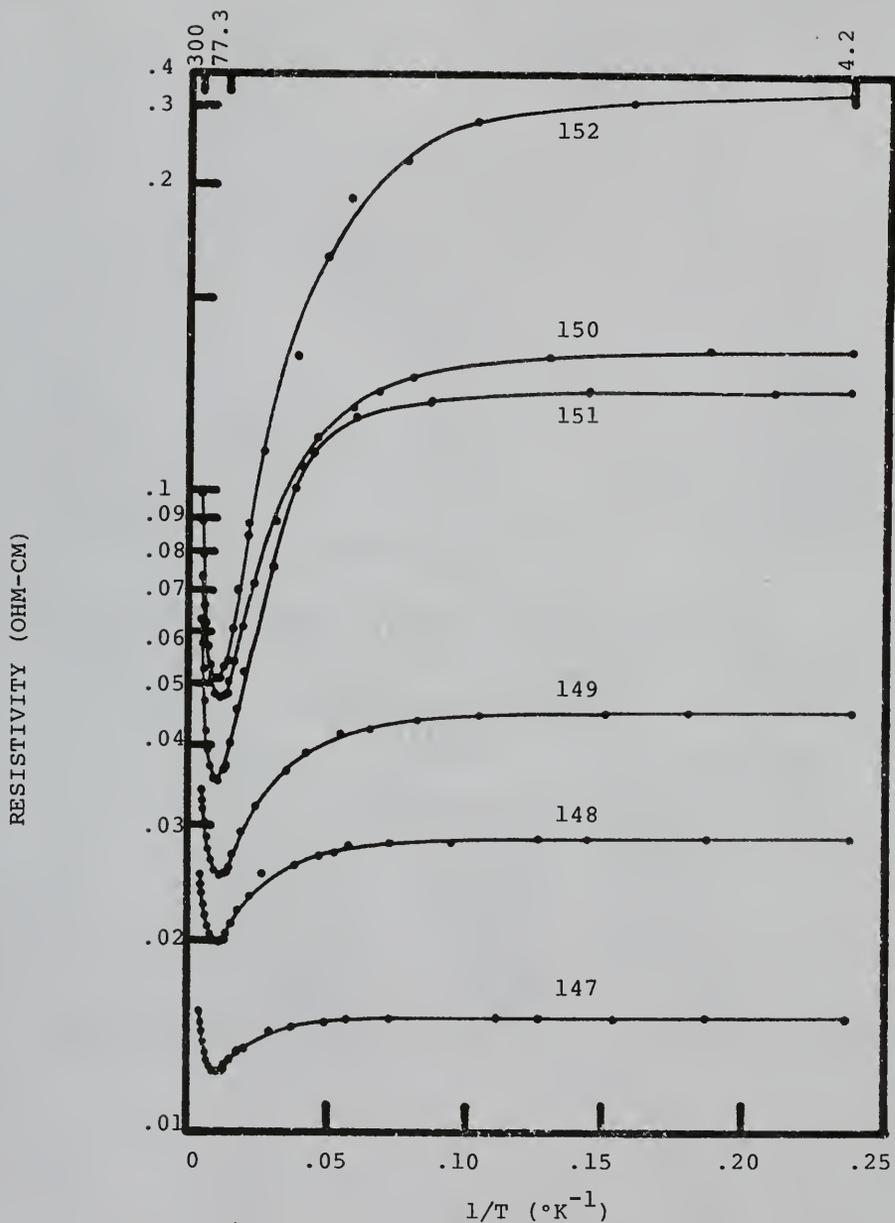


FIGURE 5.2 RESISTIVITY OF SAMPLES 147-152
WITH INVERSE TEMPERATURE

TABLE 5.1

CONDUCTIVITY PARAMETERS

$$\rho(T)^{-1} = C_2 \exp(-E_2/kT) + C_3T + C_4 \quad (T < 80K)$$

<u>SAMPLE</u>	<u>X</u>	<u>C₂</u>	<u>E₂ (meV)</u>	<u>C₃</u>	<u>C₄</u>
147	.034	86.9	0.68	.077	65.31
148	.100	60.9	1.46	.090	33.97
149	.200	52.7	2.36	.092	21.44
150	.392	34.8	3.59	.107	5.42
151	.624	54.5	4.82	.057	6.62
152	.774	38.8	5.10	.084	1.93

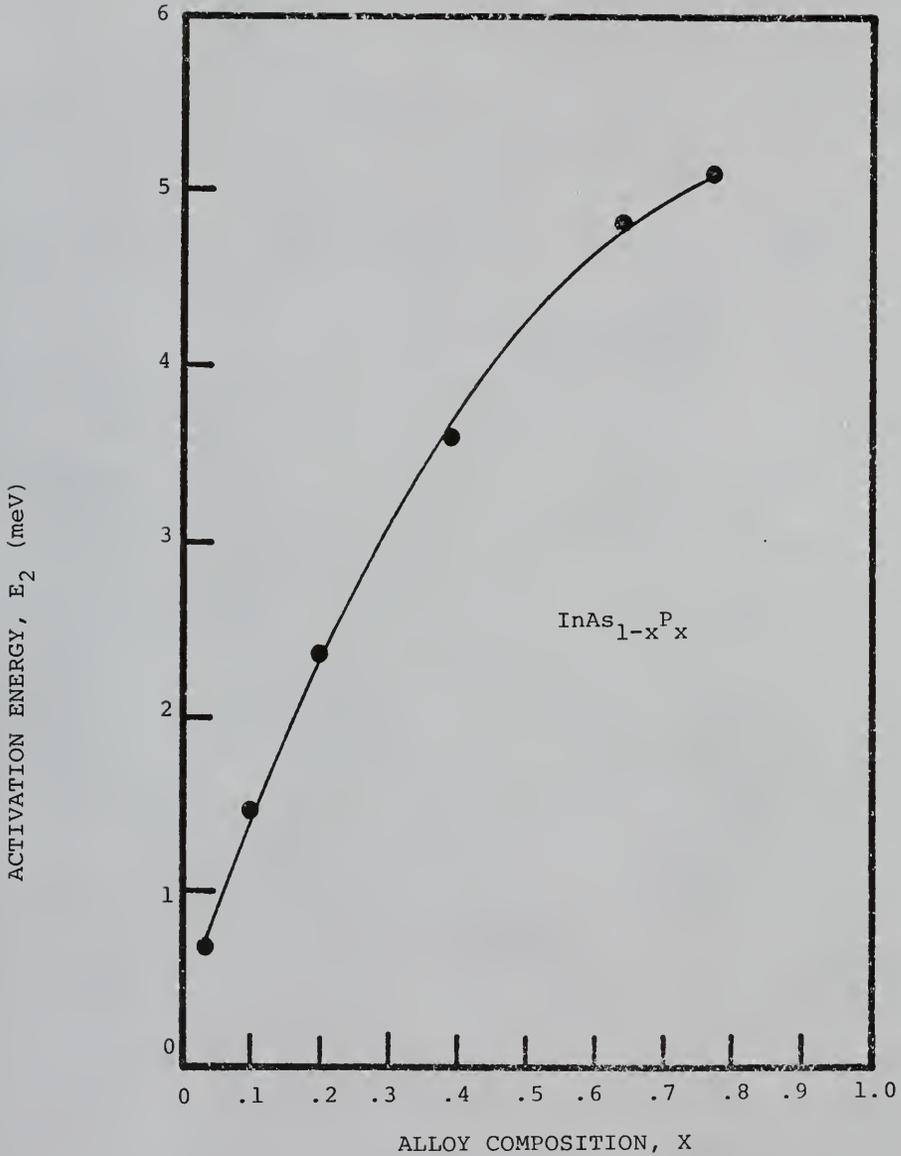


FIGURE 5.3 VARIATION OF ACTIVATION ENERGY, E_2 , WITH ALLOY COMPOSITION

the temperature range from 4.2K to 300K. The temperature dependence of this set are shown in Fig. 5.4 where it is seen that the curves show an overall increase as the percentage of phosphorus increases within the epilayer. Of particular interest is the shift of the Hall maximum as a function of composition. The maximum occurs at about 115K for sample 147 and decreases to approximately 38K for sample 152. A Hall maximum occurring at high temperatures indicates in general an increase in the impurity content as indicated in Section 2.3c. The temperatures for the Hall maximum of each sample are given in Table 5.2.

The free electron concentration was calculated from the Hall coefficient using the relation

$$n_h = \frac{1}{eR_h} \quad (5.2)$$

The results, Fig. 5.5, show that the concentrations were between about $1 \times 10^{16} \text{ cm}^{-3}$ to $5 \times 10^{16} \text{ cm}^{-3}$ for all samples. The concentration increased as the samples became more arsenic rich. Using the analysis shown in Section 2.3c, the electron concentrations in both the donor and conduction bands. The exponential decrease of carriers in the conduction band was fitted to the equation

$$n_c = A_c \exp (-E_{c_1}/kT) \quad (5.3)$$

The values of the mobility ratio, $b = \mu_c/\mu_d$, the coefficient

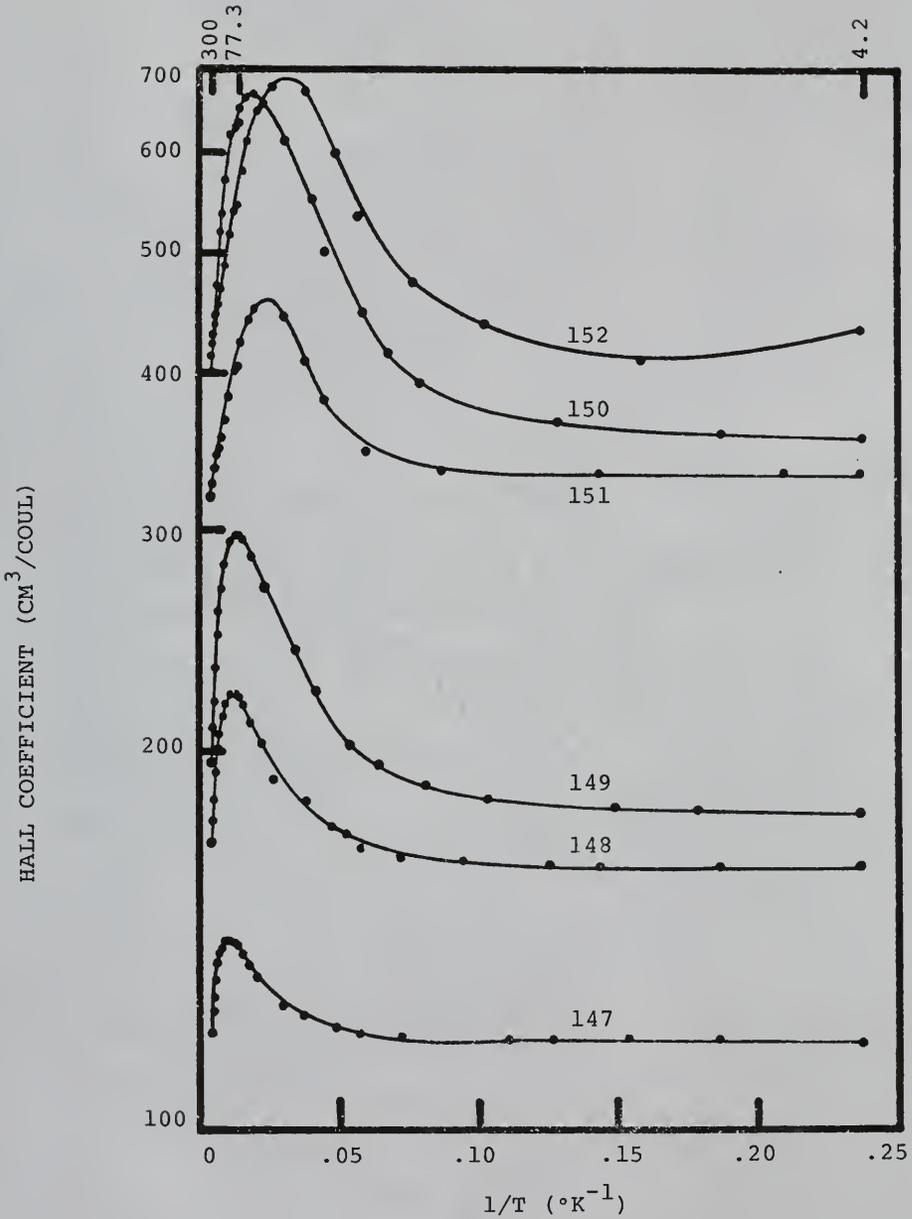


FIGURE 5.4 HALL COEFFICIENT OF SAMPLES 147-152 WITH INVERSE TEMPERATURE

TABLE 5.2

<u>SAMPLE</u>	$T_{R_{\max}}$	$b(\mu_c/\mu_d)$	A_c	E_{c_1} (meV)
147	115K	2.45	11.54	21.6
148	90K	3.23	7.85	20.9
149	73K	4.47	6.27	20.0
150	57K	5.39	2.50	14.5
151	52K	3.39	2.44	5.9
152	38K	4.35	1.82	5.1

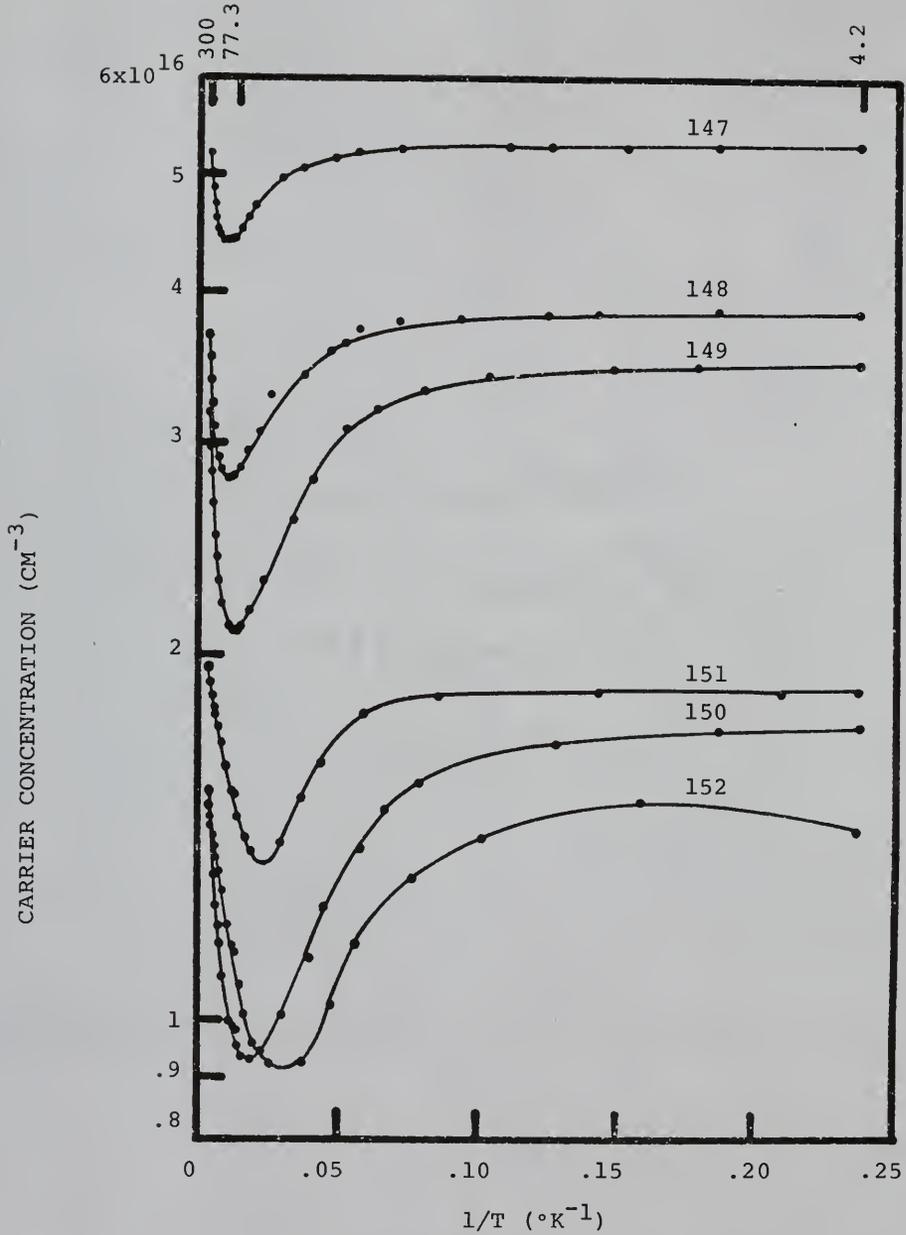


FIGURE 5.5 CARRIER CONCENTRATION OF SAMPLES 147-152 WITH INVERSE TEMPERATURE

A_{C_1} , and the activation energy, E_{C_1} , are also given in Table 5.2. In Fig. 5.6, E_{C_1} is plotted as a function of alloy composition. As was discussed previously, an increase in E_{C_1} may be indicative of increased impurity content, increased compensation, or a combination of these two. The high values of E_{C_1} for the sample 147-149 are most likely a result of their decreased thickness where interface states might be a more dominant factor in controlling the transport properties.

5.4 Mobility

The electron mobility for Group V samples was calculated using the relation

$$\mu_h = \frac{R_h}{\rho} \quad (5.4)$$

The results, Fig. 5.7, show mobilities as high as 13,000 $\text{cm}^2/\text{volt-sec}$ for sample 150 at 77K. Because of the low effective mass for InAs, it would be expected that the mobility of the arsenic-rich samples would be quite high. The mobilities at 300K are plotted against alloy composition in Fig. 5.8. A theoretical curve for that temperature, derived from Ehrenreich,²² is also shown. Ehrenreich's curve is based on polar optical scattering and ionized impurity scattering (Conwell-Weisskopf formula¹⁹) using $N_i = 5 \times 10^{16} \text{cm}^{-3}$. The fit for large x is acceptable but there is an obvious departure from the theory for samples 147-149.

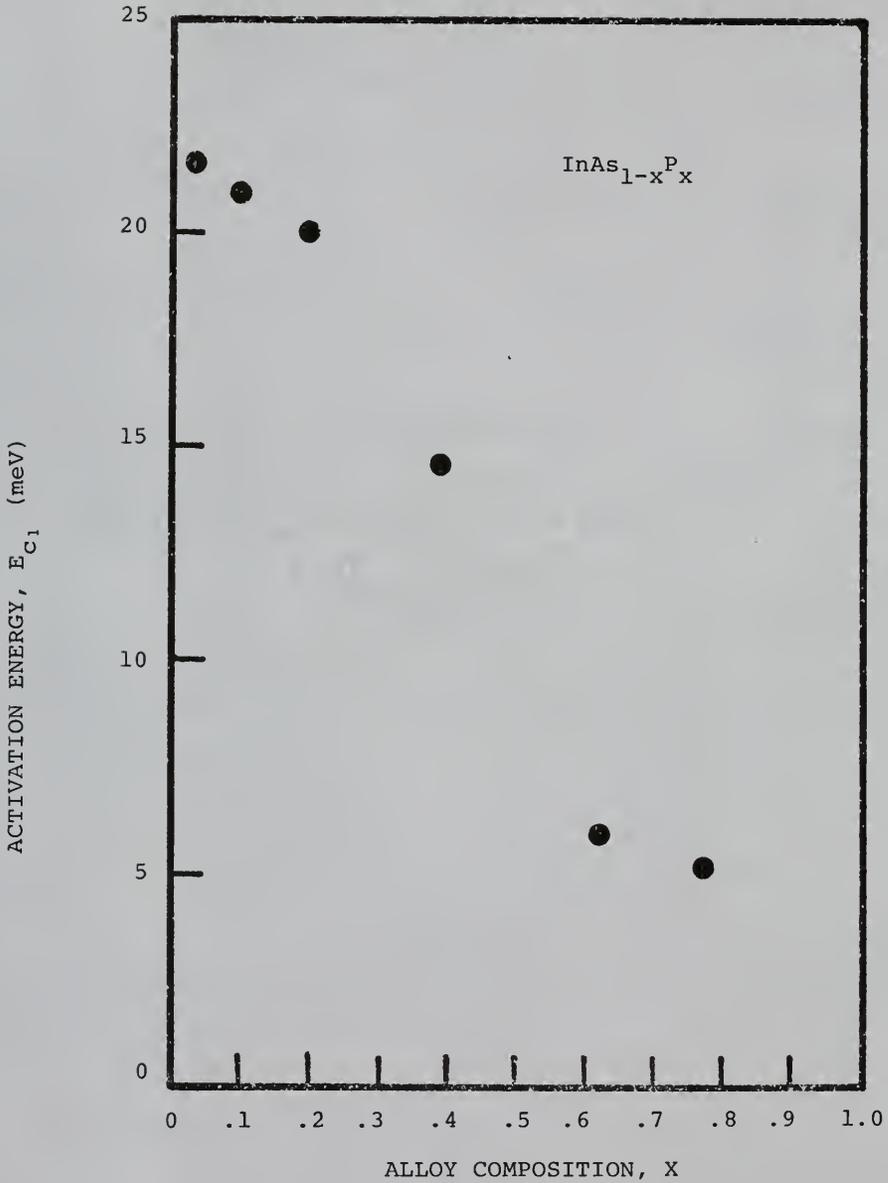


FIGURE 5.6 VARIATION OF ACTIVATION ENERGY, E_{C1} , WITH ALLOY COMPOSITION

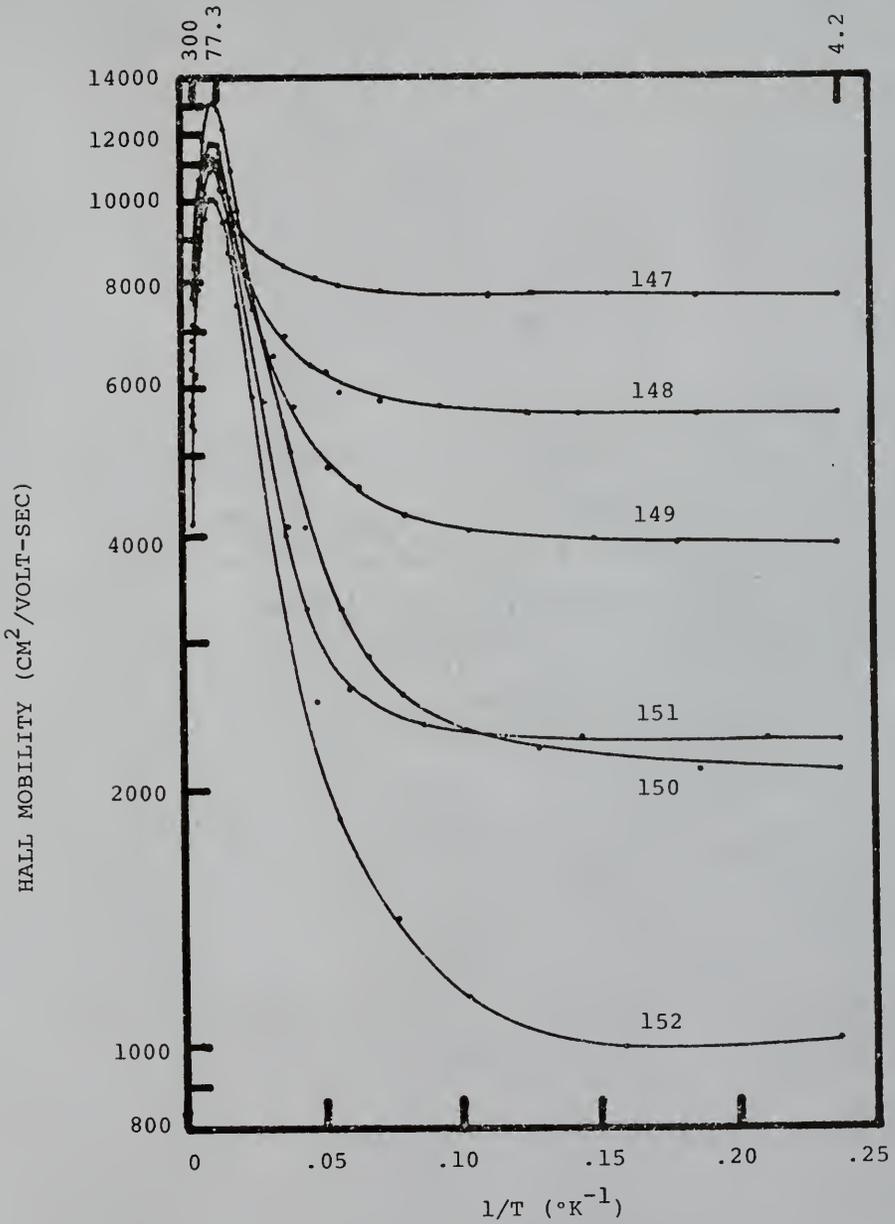


FIGURE 5.7 HALL MOBILITY OF SAMPLES 147-152
WITH INVERSE TEMPERATURE

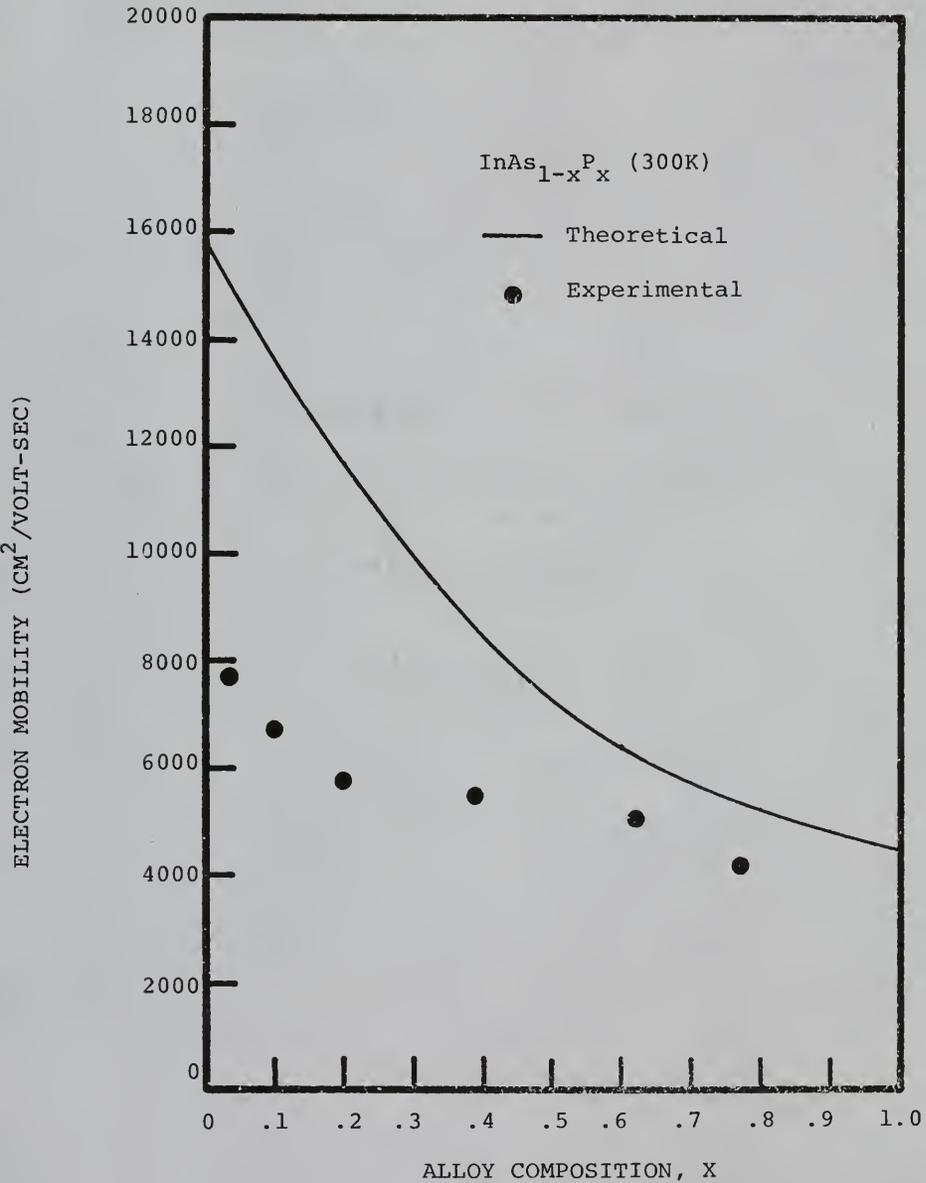


FIGURE 5.8 COMPARISON OF HALL MOBILITY TO THEORETICAL MOBILITY AT 300K

This might be explained by an increase in N_i due to either lattice mismatch or the interface states.

The high temperature portion of the mobility curves (200K-300K) was fitted by least squares to the power equation

$$\mu = aT^{-\beta} \quad (5.5)$$

The results for a and β in Table 5.3 show an increase in both parameters as the phosphorus content increases. The β values are well below those given in Section 2.2a for polar optical phonon scattering, indicating that ionized impurity scattering is quite effective in these samples even at room temperature.

TABLE 5.3

$$\mu = aT^{-\beta} \quad (200-300K)$$

<u>SAMPLE</u>	<u>a</u>	<u>β</u>
147	2.55×10^5	.615
148	3.68	.705
149	8.04	.868
150	12.01	.950
151	13.83	.988
152	29.09	1.152

CHAPTER VI
CONCLUSIONS

There are several conclusions which may be drawn from the experimental results of electron transport in both $\text{InAs}_{0.61}\text{P}_{0.39}$ (Chapter IV) and $\text{InAs}_{1-x}\text{P}_x$ (Chapter V). A comparison of the theoretical and experimental results shows that the mobility may be adequately described by the interactions of optical phonon, ionized impurity, and neutral impurity scattering over the whole temperature region studied. It is suggested that any further or similar work should include regions of higher temperature for two reasons. First, the true effect of polar optical phonon scattering could be seen more easily and thus extracted from the experimental mobility at lower temperatures. This would result in a more accurate knowledge of the effects of ionized impurity scattering. Second, higher temperatures would push the carrier concentration well into the exhaustion range where a more accurate figure for $N_d - N_a$ could be obtained. The basic problem with higher temperatures is that of electrical contacts to the samples. Spring-type contacts to small indium dots on the sample could be a possible solution. Metals with higher melting temperatures than indium could be tried for direct wire connections.

All samples investigated were seen to have a high concentration of impurities which formed a band centered at the donor level, capable of conduction at even the lowest temperatures. The mobility within this band was calculated to be much smaller than the mobility in the conduction band, typically by a factor of 0.2. The compensation of the donor impurities by acceptor states was also evidence with values of N_a/N_d ranging from 0.19 to 0.63. The impurity and compensation levels were governed by two factors - the hydrogen flow rate during the epitaxial growth and the thickness of the epitaxial layers. For the thinner groups of samples the impurity compensation levels increased as the thickness decreased. This effect may be attributed to the interface states due to the lattice mismatch between GaAs and $\text{InAs}_{1-x}\text{P}_x$. A calculation for $\text{InAs}_{0.61}\text{P}_{0.39}$ shows that these states would, under ideal conditions, be at least $6.7 \times 10^{12} \text{cm}^{-2}$. If they are distributed over, for example, a $1 \mu\text{m}$ transition layer there would be $6.7 \times 10^{16} \text{cm}^{-3}$ ionized states in addition to all other impurities. In a $3 \mu\text{m}$ sample this would definitely affect the carrier concentration and mobility. Evidence of this effect is clearly seen in sample 172-178 and in the $\text{InAs}_{1-x}\text{P}_x$ sample (147-152) where the arsenic-rich epilayers fall short of their expected mobility at 300K. The effect of flow rate variation is more clearly seen in the thicker samples (153-159) where decreasing the flow rate decreases

both the concentration of impurities and the compensation level. The thickest samples (196-186) however were plagued by nonuniform epilayer thicknesses and large surface irregularities.

It is suggested that future research on $\text{InAs}_{1-x}\text{P}_x$ epitaxial layers should be directed toward decreasing the interface states. This might be accomplished by using different substrates or variations in the substrate orientation. The hydride growth system is easily adapted to composition grading which might also tend to reduce interfacial states.

The results of this research indicate a definite need for better and more controlled growth procedures. The hydride system would seem to be quite useful if these problems could be overcome. However, in spite of the high impurity content, the $\text{InAs}_{1-x}\text{P}_x$ samples still maintained high mobility levels which is one of their most enhancing features. It is hoped that this work will stimulate more research into the $\text{InAs}_{1-x}\text{P}_x$ system, especially in respect to device applications.

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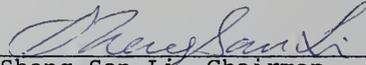
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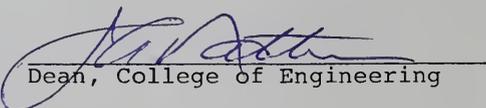
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