

Some Band Structure Investigations
on Semiconducting Arsenides

by

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TO MY PARENTS

STATEMENT OF ORIGINALITY

To the best of the author's knowledge, the following parts of the present work are original:

(1) The investigation of the (000) and $\langle 111 \rangle$ conduction bands of InAs by using heavily-doped samples; the study of the variation of the (000) and $\langle 111 \rangle$ conduction band parameters of InAs with doping; the method of determining the band parameters in the analysis of the Hall effect and magnetoresistance data [Equations (II-36)-(II-42), Section II-314],

(2) The method of determining the cyclotron effective mass of electrons and the Dingle temperature by curve fitting the experimental data of magnetoresistance oscillation amplitude [Equations (II-72)-(II-77), Section II-3154],

(3) The study of the structure of electoreflectance spectrum with various biasing voltages, electrolytes and carrier concentrations of InAs samples (Section III-44), (Thompson made the initial measurements),

(4) The confirmation of the parabolic variation of the $\Lambda_{3v}-\Lambda_{1c}$ interband transition energies with composition for the InAs-GaAs alloys by electoreflectance measurements (Section III-53), [This work was concurrent with, and independent from, the work of Williams and Rehn (68W1, 69W1)],

(5) The determination of interband transition energies of five II-IV-As₂ compounds and two (2InAs)-(II-IV-As₂) alloys by reflectance and modulated reflectance methods (Section IV-4).

ABSTRACT

Low-temperature Hall effect and magnetoresistance and room-temperature electroreflectance, infrared absorption and thermoelectric power measurements have been made on In_2Se_3 - and In_2Te_3 -doped InAs samples, to investigate the (000) and $\langle 111 \rangle$ conduction bands and the effect of heavy doping on the separation of these two conduction band minima of this compound.

A study of the structure of the electroreflectance spectra of InAs has been made under various experimental conditions. The work was extended to study the E_1 ($\Lambda_{3v}-\Lambda_{1c}$) interband transition energies for the InAs - GaAs alloys, and to correlate the reflectance and modulated reflectance peaks of two (2InAs)-(II-IV-As₂) alloys and five II-IV-As₂ compounds.

Harland's (65H1) oscillatory magnetoresistance data on n-type GaSb have also been analyzed.

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CHAPTER I

INTRODUCTION AND ENERGY-BAND CONCEPTS

1. INTRODUCTION

Research in semiconductor physics, as well as in other fields of physical science, involves two major factors: materials and methods. The combinations of these two factors can provide great varieties of projects to be shared by a large number of researchers. Some researchers prefer to develop or use a particular method, theoretical and/or experimental, to study certain properties of different materials, while some prefer to use a number of methods to study various aspects of a particular material or class of materials. The title of this thesis indicates that the author is more inclined to the latter approach.

Semiconductor research was started in the 1940's on group IV elements germanium and silicon. Later, investigations by Welker (52W1) indicated that III-V compounds are also semiconductors with properties close to group IV materials, their isoelectronic analogs. The growing importance of III-V compounds since 1952 can be reflected by the increasing number of publications on these materials, including those concerning the development of experimental techniques in producing good quality crystals and in precise measurements of various physical properties, and those concerning the development of theoretical tools in analyzing and interpreting experimental results.

Besides the III-V compounds, the field of semiconductor research has also covered other materials, since the search for new materials has always been a stimulating topic. One approach is to prepare new compounds. In addition to binary compounds, such as II-VI, IV-VI, $\text{II}_3\text{-V}_2$, $\text{III}_2\text{-VI}_3$, etc., studies have also been extended to ternary compounds, such as $\text{I-IV}_2\text{-V}_3$, II-IV-V_2 , etc. These ternary compounds are derived from the III-V compounds with the considerations of isoelectronic analogy. These materials evidently provided great varieties of semiconducting properties for investigations. A somewhat different approach is to form alloys from two semiconducting elements or compounds. This is motivated by the purpose to obtain materials with varying semiconducting properties. Examples are the mixed III-V alloys, in which the most investigated ones are pseudo-binary systems with a common group III or group V element, such as InAs-InSb, InAs-GaAs, etc.

One of the major investigations in semiconductor research is the study of energy band structures of materials. (The concept of "energy bands" will be illustrated in the following sections). The methods in band structure investigations are so diverse that each one is concerned only with a certain aspect of the problem. In order to obtain a more complete picture, the correlation of results on various aspects of the band structures of the materials is required. The aim of the work as presented in this thesis is to provide and correlate various experimental information on some semiconducting arsenides,

including InAs and II-IV-V₂ compounds, and alloys containing InAs as one of the constituent compounds, e.g. InAs-GaAs, 2InAs-CdSnAs₂, and 2InAs-ZnSnAs₂. The experimental methods include Hall effect, magnetoresistance, infrared absorption, thermoelectric power (on InAs), and reflectance work (on all materials concerned).

2. BASIC BAND THEORY OF SOLIDS

The calculation of electronic wave functions and energy levels in a solid would be extremely complicated unless a number of approximations were made. A basic approximation is to treat the problem as a one-electron case. The electron is considered as belonging to the crystalline lattice as a whole rather than to a particular atom, and hence the field as experienced by the electron is that due to the periodic arrangement of the nuclei in the lattice plus that due to the charge distribution of other electrons. Thus the problem is reduced to a case of electronic motion in a periodic potential $V(\vec{r})$. The Schrödinger equation is

$$[\vec{p}^2/2m_e + V(\vec{r})] \psi_{\vec{k}}(\vec{r}) = E_{\vec{k}} \psi_{\vec{k}}(\vec{r}) \quad (\text{I-1})$$

when the effect of spin-orbit coupling of the electron is not included. Here $\vec{p}$ is the momentum operator, m_e the free electron mass, $\psi_{\vec{k}}$ the wave function of the electron with wave vector $\vec{k}$ (the eigenfunction), and $E_{\vec{k}}$ the corresponding energy (the eigenvalue). By using Bloch's theorem (28B1),

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) \exp(i\vec{k} \cdot \vec{r}) \quad (\text{I-2})$$

where $u_{\vec{k}}(\vec{r})$ is a function with periodicity of the lattice.

The essential features of the results obtainable from equations (I-1) and (I-2) may be illustrated by a simple one-dimensional model of periodic array of square-well potential as presented by Kronig and Penney (30K1). In this simple case, the

Schödinger equation can be solved analytically, and the boundary conditions of the wave functions give rise to the dependence of E on k . The result indicates that:

(1) The energy spectrum of electrons consists of a number of allowed energy bands separated by forbidden regions.

(2) The discontinuities in the E versus k curve occur at the boundaries of the Brillouin zones of this one-dimensional lattice, i.e. $k = \pm n\pi/a$, a being the primitive translation vector of the lattice and $n = 1, 2, 3, \dots$ indicating the boundaries of the first, second, third, $\dots$ Brillouin zones.

(3) Within a given energy band, $E(k)$ is periodic in k , i.e. $E(k) = E(k + 2\pi n/a)$.

Therefore the energy spectrum can be represented by the $E(k)$ relation within the first Brillouin zone, i.e. with the reduced wave vector in the range $-\pi/a \leq k \leq \pi/a$, and such a representation of $E(k)$ is called the band structure of the material.

Although the square-well potential is only a very crude approximation, the ideas as deduced from such a model are quite valid for a realistic three-dimensional case. The energy spectrum of electrons in a solid also consists of allowed and forbidden energy bands, and the discontinuities and periodicities of the $E(\vec{k})$ relation are determined by the boundaries of the Brillouin zones in various directions of $\vec{k}$. In order to construct the Brillouin zones, a knowledge of the crystal structure of the material is required. With a given crystal

structure, the primitive translation vectors $\vec{t}_1, \vec{t}_2, \vec{t}_3$ of the lattice can be selected, and then the primitive translation vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ of the reciprocal lattice can be constructed by using the definition

$$\vec{b}_i = 2\pi \cdot \frac{\vec{t}_j \times \vec{t}_k}{\vec{t}_i \cdot (\vec{t}_j \times \vec{t}_k)} \quad (I-3)$$

i, j, k being cyclic permutation of 1, 2, 3. The boundaries of the Brillouin zones are determined by the planes bisecting the vectors from the origin to all points of the reciprocal lattice. The first Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice, i.e. the figure bounded by those planes which are nearest to the origin.

The band structure of a solid, which involves the dependence of E on a vectorial quantity $\vec{k}$, is usually represented by the contour graph of constant-energy surfaces, or E versus $\vec{k}$ graph along certain directions of $\vec{k}$. The choice of suitable directions is determined from symmetry considerations by using group theory. The present investigation is only concerned with III-V and II-IV-V₂ materials, and hence the crystal structures and band structure characteristics of these materials will be considered in the following sections.

3. CRYSTAL STRUCTURES OF III-V AND II-IV-V₂ COMPOUNDS

From isoelectronic considerations, III-V compounds are the closest analogs of group IV elements, while II-IV-V₂ compounds are the closest analogs of III-V compounds. Therefore the crystal structures of these three types of materials can be expected to be very similar. It is well established that the group IV semiconductors germanium and silicon crystallize in diamond structure, i.e. two interpenetrating f.c.c. sublattices of identical atoms displaced by a vector $\frac{a}{4}(\vec{i}+\vec{j}+\vec{k})$, a being the lattice parameter of the cube and $\vec{i}$, $\vec{j}$, $\vec{k}$ the three orthogonal unit vectors. With such a configuration of lattice points, each atom is surrounded by four nearest neighbors. III-V compounds crystallize in zincblende structure, which is different from diamond structure in such a way that one of the f.c.c. sublattices is occupied by III, while the other sublattice by V. Hence, each atom is surrounded by four atoms of the other group, and consequently the lattice shows a lower symmetry.

In each II-IV-V₂ compound, one of the interpenetrating f.c.c. sublattices is occupied by V, while the other sublattice shared by II and IV. If the II and IV atoms are randomly distributed in the sublattice, the structure of the compound remains as zincblende. However, if these II and IV atoms are ordered, as shown in Figure I-1, the symmetry of the lattice is lowered further, and such a configuration is called chalcopyrite structure. Here the unit cell becomes tetragonal with lattice

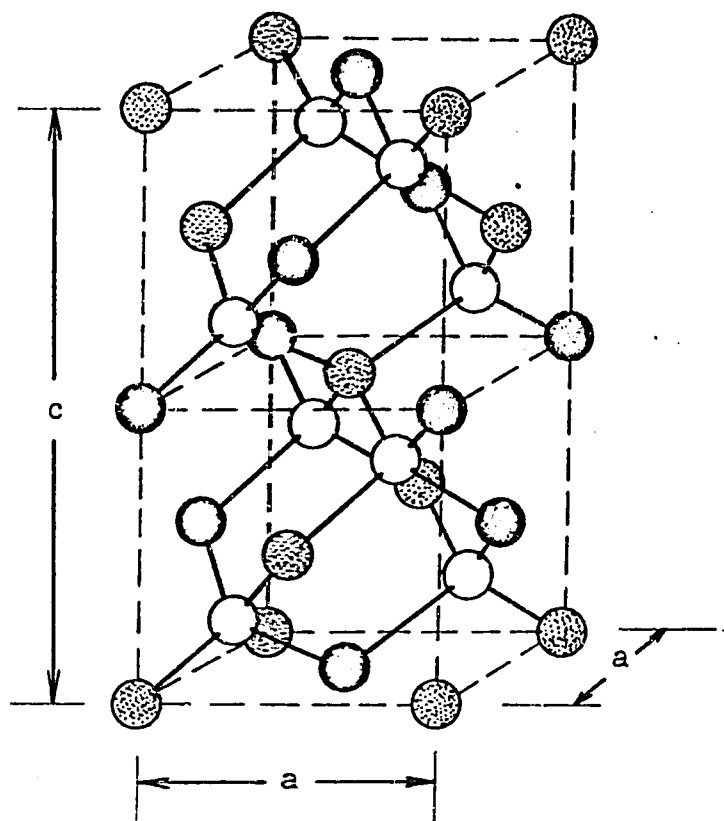


Figure I-1 Unit cell of II-IV-V_2 compound with chalcopyrite structure. $\odot$: II, $\bullet$: IV, $\circ$: V.

parameters a , a , c . In addition to the ordering of II and IV atoms, the tetragonal axis contracts slightly, i.e. $1.8 < c/a < 2.0$, with the exception of ZnSnAs_2 and ZnSnP_2 in which $c/a = 2.0$ (Borshchevskii et al 67B4). All existing II-IV-V₂ compounds (II: Cd, Zn; IV: Sn, Ge, Si; V: As, P) crystallize in zincblende modifications immediately upon solidification from their molten state, and assume chalcopyrite structure at certain temperatures below their melting points. However, their high temperature modifications can also be obtained by fast cooling of the materials from their molten state, and in some cases an amorphous state of the materials is obtained upon quenching, e.g. CdGeAs_2 and CdGeP_2 (Goryunova et al 65G2, Vaipolin et al 67V2).

4. BAND STRUCTURE CHARACTERISTICS OF III-V AND II-IV-V₂ COMPOUNDS

For the study of band structures of a solid, a knowledge of the shape of its Brillouin zones is required. The construction of the first Brillouin zone of the diamond and zincblende lattices has been given in standard texts (e.g. Brillouin 46B1, Kittel 53K1). The primitive translation vectors in both cases can be selected as

$$\begin{aligned}\vec{t}_1 &= \frac{a}{2} (\vec{i} + \vec{j}) \\ \vec{t}_2 &= \frac{a}{2} (\vec{j} + \vec{k}) \\ \vec{t}_3 &= \frac{a}{2} (\vec{i} + \vec{k})\end{aligned}\tag{I-4}$$

a being the lattice parameter. The primitive translation vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$ in its reciprocal lattice are constructed according to relation (I-3), and then the vectors $\vec{k}$ of the reciprocal lattice are given by

$$\begin{aligned}\vec{k} &= f\vec{b}_1 + g\vec{b}_2 + h\vec{b}_3 \\ &= \frac{2\pi}{a} [(f-g+h)\vec{i} + (f+g-h)\vec{j} + (-f+g+h)\vec{k}]\end{aligned}\tag{I-5}$$

f, g, h being integers. The boundaries of the first Brillouin zone, as represented by the Wigner-Seitz cell, form a truncated octahedron in $\vec{k}$ -space (Figure I-2), and are represented by

$$\begin{aligned}k_x, k_y, k_z &= \pm 2\pi/a \\ \pm k_x \pm k_y \pm k_z &= \pm 3\pi/a\end{aligned}\tag{I-6}$$

In a chalcopyrite unit cell with lattice parameters

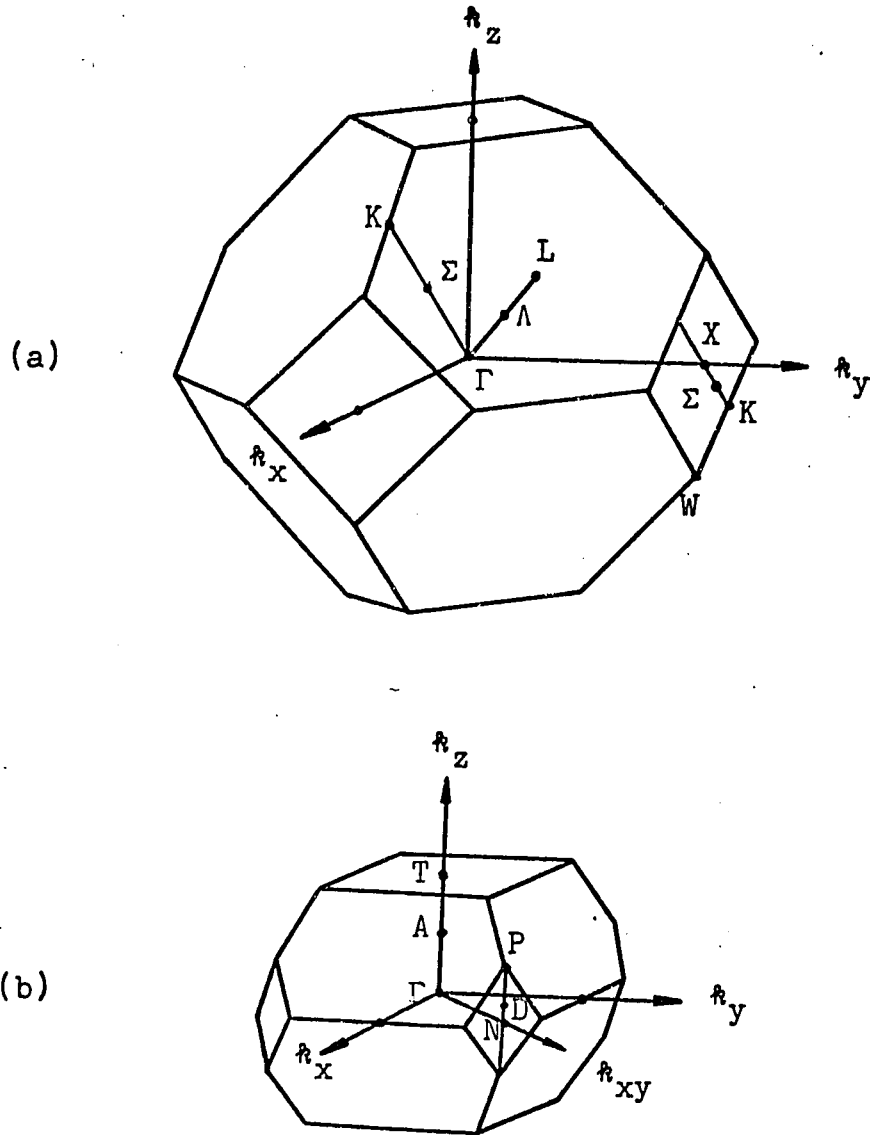


Figure I-2 First Brillouin zone of (a) zincblende lattice, (b) chalcopyrite lattice.

a, a, c, the primitive translation vectors can be chosen as

$$\begin{aligned}\vec{t}_1 &= \frac{1}{2} (a\vec{i} + a\vec{j} - c\vec{k}) \\ \vec{t}_2 &= \frac{1}{2} (-a\vec{i} + a\vec{j} + c\vec{k}) \\ \vec{t}_3 &= \frac{1}{2} (a\vec{i} - a\vec{j} + c\vec{k})\end{aligned}\tag{I-7}$$

Then the vectors in its reciprocal lattice are

$$\begin{aligned}\vec{K} &= f\vec{b}_1 + g\vec{b}_2 + h\vec{b}_3 \\ &= \frac{2\pi}{a} [(f+h)\vec{i} + (f+g)\vec{j} + \frac{a}{c} (g+h)\vec{k}]\end{aligned}\tag{I-8}$$

f, g, h being integers. Hence the first Brillouin zone, as represented by the Wigner-Seitz cell, is determined by the 14 planes (Figure I-2):

$$\begin{aligned}K_z &= \pm 2\pi/c \\ K_x \pm K_y &= \pm 2\pi/a \\ K_x \pm \frac{a}{c} K_z &= \pm \frac{\pi}{a} (1 + a^2/c^2) \\ K_y \pm \frac{a}{c} K_z &= \pm \frac{\pi}{a} (1 + a^2/c^2)\end{aligned}\tag{I-9}$$

In Figure I-2, the notations of the symmetry points and directions of the first Brillouin zones of the zincblende and chalcopyrite lattices follow the well established conventions.

The boundaries of the second Brillouin zone of the chalcopyrite lattice is determined by the planes bisecting the next 14 shortest non-zero $\vec{K}$'s of equation (I-8). With the approximation $c = 2a$, these boundaries are also given by equations (I-6). Therefore the correspondence between some symmetry points of the Brillouin zones of the two structures

can be established. This is seen on the sections of the two embedded zones on the k_y-k_z plane and on the $k_{xy}-k_z$ plane as shown in Figure I-3. The correspondence is:

Zincblende		Chalcopyrite
Γ	$\longleftrightarrow$	Γ
W	$\longleftrightarrow$	Γ
L	$\longleftrightarrow$	N
X (0,0,2 π /a)	$\longleftrightarrow$	Γ
X (0,2 π /a,0)	$\longleftrightarrow$	T
X (2 π /a,0,0)	$\longleftrightarrow$	T

From the above considerations (similarities in crystal structures, Brillouin zones, etc.,) it is expected that some correspondence between the band structure characteristics of III-V and II-IV-V₂ compounds can also be established.

The band structure calculations are formidable problems in the field of semiconductor research. Since the full development of this is beyond the scope of the present work, only some general ideas are presented here. The approach by symmetry consideration of the crystal structure using group theory can give a qualitative idea of the band structure, such as the degeneracy of various energy bands in the vicinity of some symmetry points or along certain symmetry directions. For materials with diamond or zincblende structure, the important ones are Γ , L, X, and K points, and Λ , Δ , and Σ directions. The symmetry studies on zincblende materials can be represented by the work of Parmenter (55P2) and Dresselhaus (55D1). With the

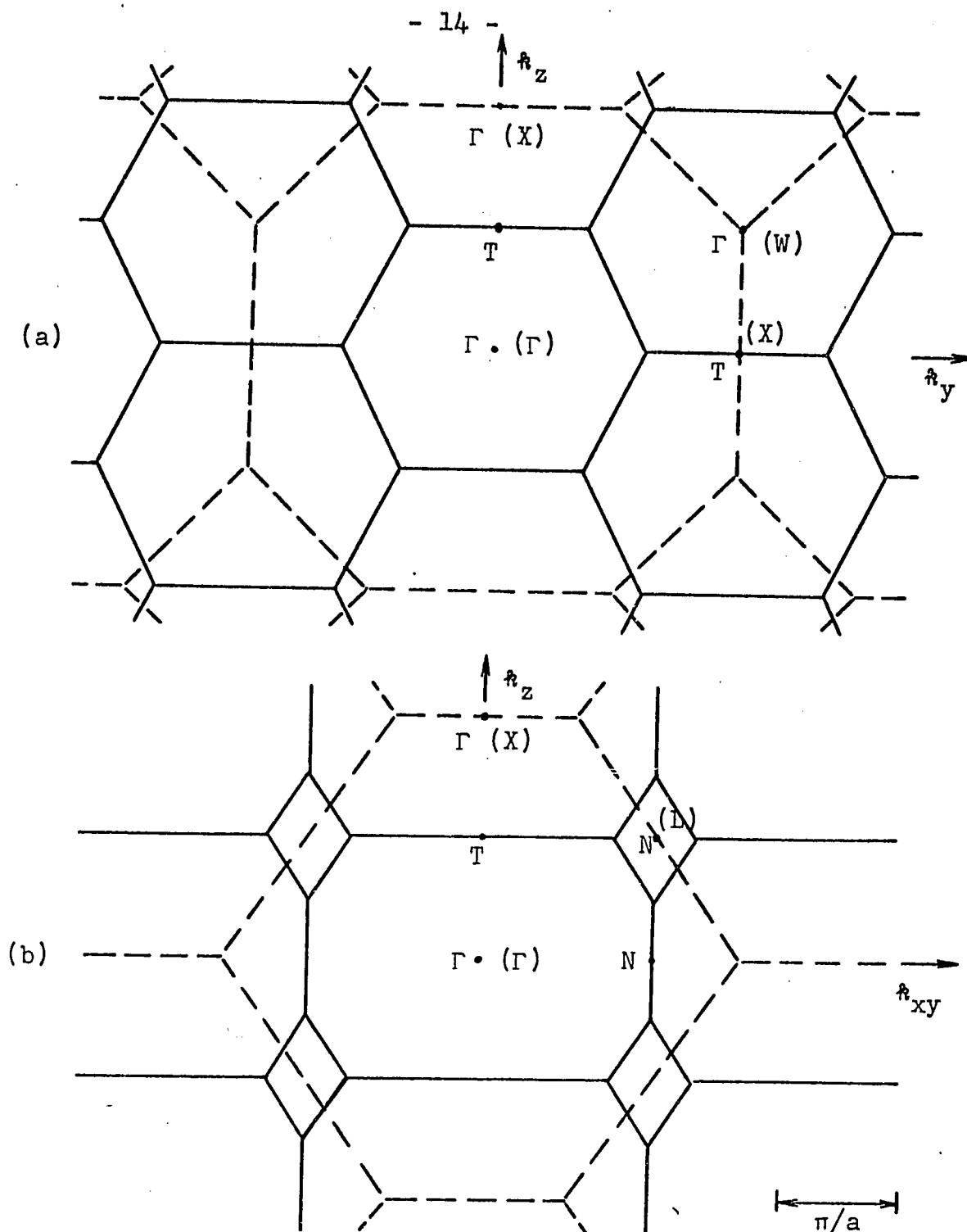


Figure I-3 Sections of the first Brillouin zones of the chalcopyrite (—) and zincblende (----) lattices. (a) k_y - k_z section, (b) k_{xy} - k_z section. Symbols of symmetry points of zincblende shown in brackets.

information obtained from symmetry considerations, further calculations of the band structure can be carried out by some quantum-mechanical approaches. The model presented by Kane (56K1, 57K1) in the band calculations of germanium and InSb with the $\vec{k} \cdot \vec{p}$ perturbation approach is quite accurate for analyzing the energy bands in the vicinity of a symmetry point. A different approach, as developed by Phillips (58P1), is the pseudopotential method for a complete zone analysis. This approach aims only at a good overall fit, and consequently the calculations at certain symmetry points may be less accurate. More recent development of the empirical pseudopotential method by Brust (64B2) and Cohen and Bergstresser (66C8) has reached better accuracy in the band calculations. The $\vec{k} \cdot \vec{p}$ approach by Cardona's group (66C3, 66C4, 66P3) has extended the band calculations over the full zone rather than calculations in the vicinity of symmetry points.

The band structure of a typical III-V compound, as summarized from the above investigations, is shown in Figure I-4. Here the band structure of germanium is included for comparison. The subscripts v and c indicate valence band and conduction band, respectively. Here the removal of degeneracy in various symmetry points and directions due to the effect of spin-orbit coupling is readily seen. The marked differences between the band structures of the two cases only occur between Γ and X along the Δ direction. The degeneracies of the energy levels X_{1c} , X_{4v} and Δ_{5v} (near X) of the group IV materials are removed

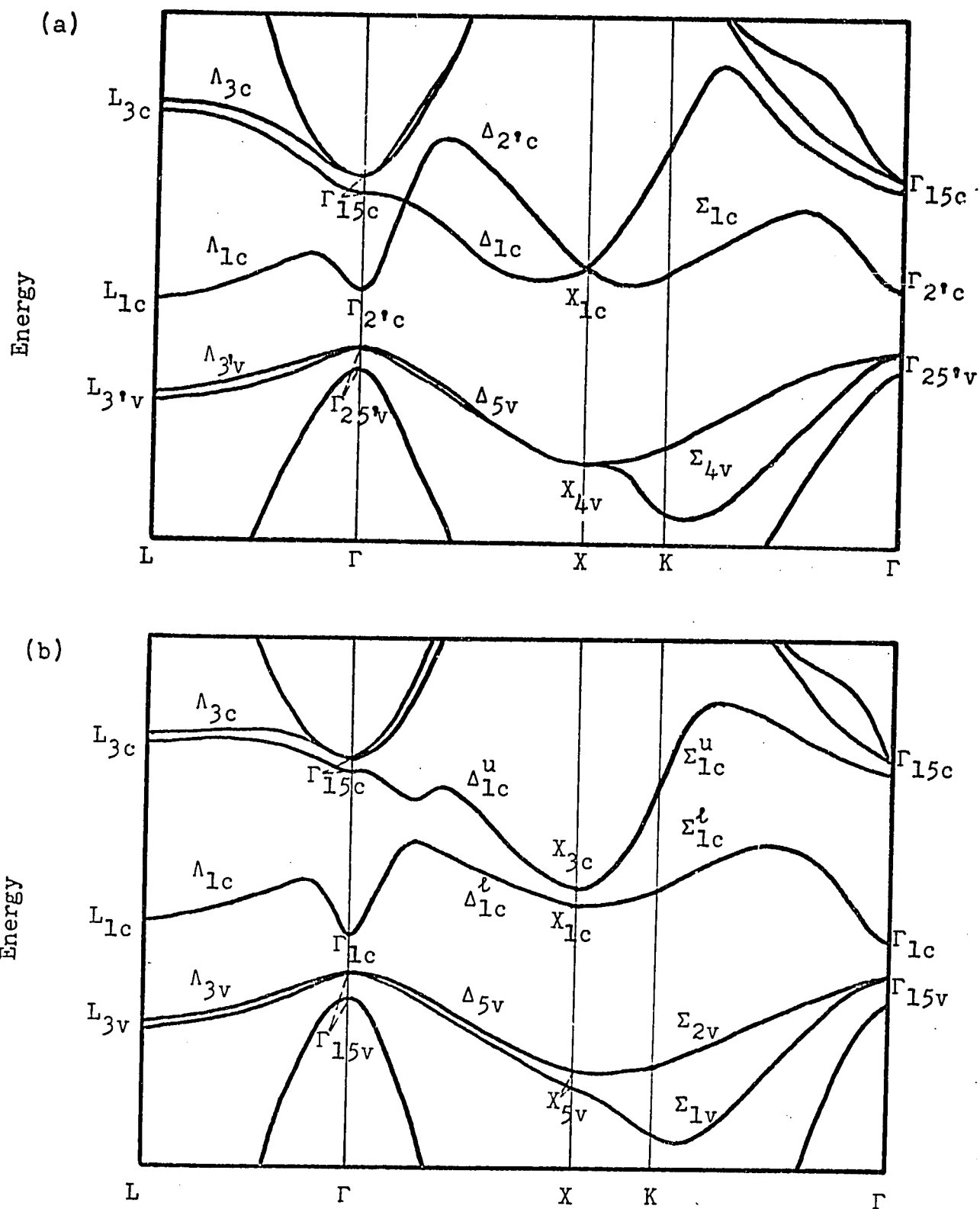


Figure I-4 Band structure of (a) germanium, (b) a typical III-V compound.

in the case of III-V where the levels are labeled X_{3c} , X_{1c} , X_{5v} and Δ_{5v} . Furthermore, the cross-over of the Δ_{1c} and Δ_{2c} bands of the former does not occur in the band structure of the latter where the two bands are labeled Δ_{1c}^u and Δ_{1c}^l . Here only a qualitative picture of the band structure of the III-V materials is presented, since the relative positions of the levels are different for individual compounds. The lowest conduction band minimum can be situated either at Γ point (such as InSb, InAs, InP, GaSb and GaAs) or along Δ direction (such as AlSb, AlAs and GaP).

The band structures of the chalcopyrite materials are more complicated. The theoretical investigations of Sandrock and Treusch (64Sl), Lietz and Rössler (64Ll), Gashimzade (63Gl), and Chaldyshev's group (60Cl, 62Cl, 63C2, 64Cl, 66Kl, 68G2, 68Kl, 68P3) have included the following features:

(1) The symmetry considerations have indicated double degeneracy at points $\Gamma(0,0,0)$, $T(0,0,2\pi/c)$, $N(\pi/a,\pi/a,0)$ and $P(\pi/a,\pi/a,\pi/c)$, and on the lines $A(0,0,k)$ and $D(\pi/a,\pi/a,k)$ without considering the spin-orbit interaction. This interaction usually removes the degeneracy and leads to splitting of the bands. However, the degeneracy is not removed at T.

(2) The valence band structure of the chalcopyrite lattice is very similar to that of zincblende in which the highest valence band maximum is situated at Γ . As a result of the reduction in symmetry in the chalcopyrite structure, the highest valence band at Γ splits off, the magnitude of the

splitting, ΔE_k , being the order of hundredths of an eV, much smaller than the spin-orbit splitting Δ_0 .

(3) The conduction band structure of the chalcopyrite lattice is more complex, but has features similar to its nearest isoelectronic analogs. The lowest conduction band minimum of CdSnAs_2 , CdGeAs_2 , ZnSnAs_2 , ZnGeAs_2 and ZnSnP_2 lies at Γ . The lowest conduction band minimum of ZnSiAs_2 , CdSiP_2 , ZnGeP_2 and ZnSiP_2 lies along the Δ direction in the Brillouin zone of zincblende, and therefore corresponds to the levels in the vicinity of Γ and T of chalcopyrite. The relative positions of Γ and T minima determine the fundamental band gap of these materials to be direct or indirect.

With the above considerations, the band structure characteristics of zincblende and chalcopyrite lattices in the vicinity of Γ are very similar, as shown in Figure I-5. Here m_n^* , m_{p1}^* , m_{p2}^* , m_{p3}^* indicate the effective mass of electrons and holes in various bands. The concept of effective mass has been given in the standard texts (e.g. Kittel 53K1, Smith 59S1, Madelung 64M1). The effective masses of carriers in a semiconductor are very closely related to its band structure, and this can be visualized from the following examples (for spherical constant-energy surfaces):

Band curvature effective mass of a state of energy E,

$$m^* = \hbar^2 / (\nabla_{\mathbf{k}}^2 E) \quad (\text{I-10})$$

Cyclotron effective mass of a state of energy E,

$$m^* = \hbar^2 / (\nabla_{\mathbf{k}} E) \quad (\text{I-11})$$

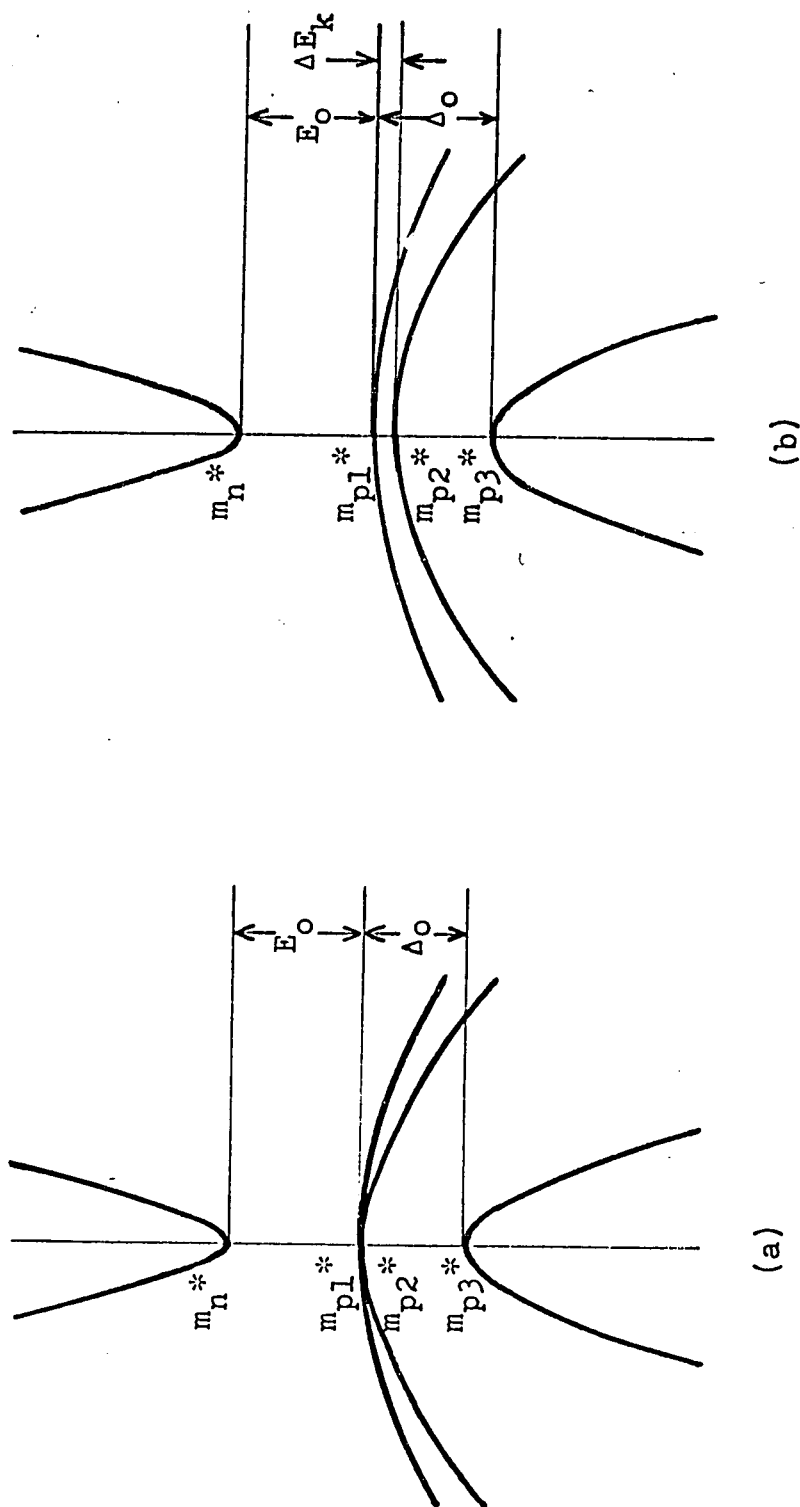


Figure I-5 Band structure in the vicinity of Γ point: (a) zincblende lattice, (b) chalcopyrite lattice.

Density-of-states effective mass,

$$m^* = \frac{\hbar^3}{2E_F} \left(\frac{3n}{8\pi} \right)^{2/3} \quad (I-12)$$

where $\hbar$ is Planck's constant divided by 2π , the subscript F indicates the value to be evaluated at the Fermi level, and n is the carrier concentration.

5. BAND STRUCTURE CHARACTERISTICS OF ALLOY SEMICONDUCTORS

The alloys formed from two semiconducting compounds are usually semiconductors. In this work, the alloys considered are pseudo-binary systems, including a mixed III-V, and two (III-V)-(II-IV-V₂) systems with a common group V element As, i.e. InAs-GaAs, 2InAs-CdSnAs₂, and 2InAs-ZnSnAs₂. (These can also be written as In_{1-x}Ga_xAs, In_{2(1-x)}Cd_xSn_xAs₂, and In_{2(1-x)}Zn_xSn_xAs₂ with x indicating the mol. percentage of one of the constituent compounds in each case.) In these systems, complete solid solutions exist throughout the alloy range. However in producing the alloys, care must be taken to obtain single-phase equilibrium condition, otherwise the results of measurements would be ambiguous and misleading.

No information has been reported thus far on band structure calculations of alloys with two constituent compounds of different crystal structures. However, in the case that the constituent compounds are of same crystal structure, a general theory concerning the band structures of the alloys is available.

In an alloy system, for instance In_{1-x}Ga_xAs, one of the f.c.c. sublattices is occupied by the common element As, while the other f.c.c. sublattice is occupied by In and Ga with random distribution. Hence in such a disordered lattice, the potential $V(\vec{r})$ as experienced by an electron is given by the sum of two parts: $V_{\text{per}}(\vec{r})$, the periodic part, and $V_{\text{aper}}(\vec{r})$, the aperiodic part. Nordheim (31N1) first introduced the concept

of the virtual crystal model in which V_{per} is taken as the average of all the possible allowed random configurations of the alloyed atoms, and hence V_{aper} represents the difference between the actual value V and V_{per} . The potential V_{per} , so defined, can be taken to vary linearly with the alloy composition x , and then band parameters, such as the energy separation E between bands at a given point in $\vec{k}$ -space can be expected to vary smoothly with x . Although in early investigations, Muto (38M1) and Parmenter (55P1) suggested a linear variation of E with x due to the potential V_{per} , recent band structure calculations by Van Vechten and Bergstresser (69V2) on various III-V alloy systems indicate that the E versus x relation deduced from V_{per} in these cases is in fact parabolic. The effect of the aperiodic part V_{aper} , as obtained from second-order perturbation analysis by Parmenter (55P1), results in blurring of the band edge and movement from the value of the virtual crystal model, and consequently contributes to further deviation from linearity in the E versus x relation. The net effect of such deviations can be represented by a term proportional to $x(1-x)$ (Cardona 63C1). Then the E versus x relation can be expressed as

$$E = (\alpha + \beta x) + \gamma x (1 - x) \quad (\text{I-13})$$

where α , β , γ are constants. Here the constant γ indicates the magnitude of the deviation due to the contributions from the virtual crystal and from the effect of disorder of the alloy lattice.

CHAPTER II

CONDUCTION BAND OF InAs

1. INTRODUCTION AND REVIEW OF THE LITERATURE

Band structure investigations on the direct band-gap compound InAs have been reported in a number of publications, the majority of which are related to the (000) conduction and valence bands. The band structure information about the (000) bands of this compound is summarized in Table II-1. Band structure parameters of the whole class of III-V compounds are given in the book by Madelung (64M1) and will not be reproduced here.

Energy-band separations and effective masses of carriers are two important parameters in the band structure of a semiconductor. The doping dependence of these parameters of InAs has also been reported by various authors, e.g. the variation of the optical energy gap with electron concentration (Stern and Dixon 59S4, Stern 60S1, Dixon and Ellis 61D1), and the variation of the electron effective mass with electron concentration (Spitzer and Fan 57S2, Stern 57S3, Cardona 61C3, Gashimzade and Kesamanly 61G1, Zhumakulov 66Z1). The varying electron effective mass evidently indicates the non-parabolicity of the (000) conduction band, i.e. E is not proportional to k^2 .

As for the studies involving conduction bands above the (000) minimum, reflectance work on this compound (e.g. reflectance: Lukeš and Schmidt 62L2, Greenaway and Cardona 62G4; electro-

Table II-1 Summary of band structure parameters of the (000) bands of InAs.

Energy # parameter, effective mass	Temperature (°K)	Value	Reference##
E_o	300	0.35 eV	OA(60D1)
	4	0.425 eV	OA(61D1)
dE_o/dT (Temperature coefficient)	>300	-3.3×10^{-4} eV/°K	OA(58M1)
	80-300	-2.8×10^{-4} eV/°K	OA(61D1)
	<80	small than -2.8×10^{-4} eV/°K	OA(61D1)
dE_o/dP (Pressure coefficient)	300	8.5×10^{-6} eV/Kg.cm ⁻² (P<2000 Kg.cm ⁻²)	OA(58T1)
		4.8×10^{-6} eV/Kg.cm ⁻² (P<20000 Kg.cm ⁻²)	OA(61E1)
Δ_o		0.43 eV	OA(57S4, 58M1, 60D1)
m_n^*/m_e	300	0.027	FR(61C3)
	80	0.026	FR(61P1)
		0.023	CR(61P1)
	1.5-300	0.020	HR(57S1)
	<20	0.020	SD(58S1)
	Helium temp.	0.018	SD(58F2)
m_{p1}^*/m_e	500-800	0.33	HR(56W1)
	300	0.4	OA(57S4, 60D1)
	0	0.41	OA(58M1)
m_{p2}^*/m_e	0	0.025	OA(58M1)
m_{p3}^*/m_e	0	0.083	OA(58M1)

Meaning of symbols given in Figure I-5, Section I-4.

Meaning of the abbreviations: CR - Cyclotron resonance,
FR - Faraday rotation, HR - Hall effect and resistivity,
OA - Optical absorption, SD - Shubnikov-de Haas effect.

reflectance: Cardona et al 67C1; thermoreflectance: Matatagui et al 68M1) has given some energy separations between conduction and valence bands at certain positions in $\vec{k}$ -space. The band structure calculation of this compound by Cohen and Bergstresser (66C8) with the pseudopotential approach has indicated that the $\langle 111 \rangle$ and $\langle 100 \rangle$ conduction band minimum are about 1.0 and 1.6 eV respectively above the (000) minimum. Since the pseudopotential method only aims at a good overall fit of the band structure, energy values of some local points may be less accurate. However it has clearly indicated the relative positions of various levels.

Besides reflectance work, experimental investigations designed to obtain information about the conduction bands above the fundamental (000) minimum usually require high carrier concentrations in the material in order that electrons are also present in the higher band, e.g. the $\langle 111 \rangle$ band in this case. Heavy doping of InAs with selenium or tellurium gives very high electron concentrations up to 10^{19} - 10^{20} cm⁻³ (10^{25} - 10^{26} m⁻³). Likewise, when InAs is alloyed with In₂Se₃ (Woolley and Keating 61W3), with In₂Te₃ (Woolley et al 61W4), or with cross substitutionally derived compounds, for example In₂SnTe (Woolley et al 65W2), because of non-stoichiometry at low concentrations of the chalcogenides, the effect is the same as that obtained by doping with selenium or tellurium. As the number of donor atoms increases, the Hall coefficient drops rapidly to a minimum and then levels out or increases slightly. This suggests that the

electrons from the donor atoms enter the $\langle 111 \rangle$ band after filling up the available states in the (000) band. This suggestion is supported by optical absorption measurements on such materials by the above authors. The effective optical energy-gap is about 1.0 eV at room temperature while appreciable numbers of electrons enter the $\langle 111 \rangle$ minima. Thus, with an intrinsic band gap of 0.35 eV, this would indicate a separation of the (000) and $\langle 111 \rangle$ minima of about 0.65 eV.

Up to the present time, the information about the $\langle 111 \rangle$ conduction band of InAs is still very fragmentary. Therefore the aim of this part of the research project is to gain a deeper insight into the two lowest conduction band minima by using heavily-doped materials. In order to analyze the experimental results of the present work, such as the magnetoresistance studies, certain $(E, \mathbf{k})$ relation for the (000) conduction band is required. It has been mentioned in Section I-4 (abbreviation of "Section 4 of Chapter I") that the $\vec{\mathbf{k}} \cdot \vec{\mathbf{p}}$ perturbation method presented by Kane (56K1, 57K1) is quite accurate for analyzing the energy bands in the vicinity of a symmetry point. Thus the development of such $(E, \mathbf{k})$ relation according to Kane's theory will be outlined in the following section.

2. KANE MODEL

The first step in the $\vec{k} \cdot \vec{p}$ approach is to consider the Schrödinger equation for an electron in the periodic potential $V(\vec{r})$ with inclusion of the effect of spin-orbit coupling:

$$\left[H_0 + \frac{\hbar}{4m_e c^2} (\vec{\nabla} V \times \vec{p}) \cdot \vec{\sigma} \right] \psi_{\vec{k}}(\vec{r}) = E_{\vec{k}} \psi_{\vec{k}}(\vec{r}) \quad (\text{II-1})$$

$$\text{where } H_0 = \frac{\vec{p}^2}{2m_e} + V(\vec{r}) \quad (\text{II-2})$$

$\vec{\sigma}$ is the spin operator, c the velocity of light, and other symbols are identical to those in equation (I-1). The wave functions $\psi_{\vec{k}}(\vec{r})$ are written in terms of the periodic functions $u_{\vec{k}}(\vec{r})$ by using equation (I-2), and then equation (II-1) becomes

$$(H_0 + H') u_{\vec{k}}(\vec{r}) = \left(E_{\vec{k}} - \frac{\hbar^2 k^2}{2m_e} \right) u_{\vec{k}}(\vec{r}) \quad (\text{II-3})$$

where the Hamiltonian H' represents the perturbed terms involving $\vec{k} \cdot \vec{p}$, $(\vec{\nabla} V \times \vec{p}) \cdot \vec{\sigma}$, and $(\vec{\nabla} V \times \vec{k}) \cdot \vec{\sigma}$. In order to expand the wave functions of the perturbed problem in terms of those of the unperturbed problem, Kane uses two s-functions and six p-functions as basis functions. Therefore in the calculation, only one conduction band and three valence bands are included. This is only an approximation, since the contributions from higher bands are not considered. The calculation leads to an 8×8 secular determinant. In order that the number of parameters involved in the determinant can be reduced to a minimum, these eight

basis functions are derived by using symmetry properties of the crystal structure. For the zincblende structure, the only parameters remaining are E_0 , Δ_0 , and P . Here E_0 and Δ_0 are the energy gap and the splitting of the valence band due to spin-orbit interaction of the electron, respectively, as shown in Figure I-5, and P is a momentum matrix element. The secular determinant then reduces to the following equation:

$$\begin{aligned} & (E + E_0 - a\hbar^2) [(E - a\hbar^2) (E + E_0 - a\hbar^2) \cdot \\ & \cdot (E + E_0 + \Delta_0 - a\hbar^2) - a\hbar^2 P^2 (E + E_0 + \frac{2}{3}\Delta_0 - a\hbar^2)] \\ & = 0 \end{aligned} \quad (\text{II-4})$$

where $a = \hbar^2/2m_e$. There are four roots of this equation at $\hbar = 0$: $E = 0$, $-E_0$, $-E_0$, and $-(E_0 + \Delta_0)$, which indicate the locations of these four bands at (000) in $\vec{k}$ -space.

It must be realized that in the derivation of equation (II-4), the effect of lattice vibrations is not considered. Such effect can be neglected only at low temperatures. Therefore at higher temperatures, instead of the parameter E_0 representing the measured band gap, a parameter E_0^* must be used (Ehrenreich 57El). E_0^* is called the "effective-mass band-gap" which represents the separation between the conduction band minimum and the valence band maximum at (000) when only lattice dilatation effects are considered.

In the present work, equation (II-4) is quite capable of representing the $(E, \hbar)$ relation of the (000) conduction band of the materials under investigation, by using appropriate values

of E_0 (or E_0^*), Δ_0 , and P^2 . Thus further development based on this equation will not be given here.

3. HALL EFFECT AND TRANSVERSE MAGNETORESISTANCE

31. THEORY AND METHODS OF ANALYSIS

311. GENERAL CONSIDERATIONS

The theories of Hall effect and magnetoresistance have been reviewed by Jan (57J1), Smith (59S1), Weiss (66W1), Becker (66B4), and Roth and Argyres (66R1). The purpose of Section II-31 is to present a method for analyzing the low-temperature Hall effect and magnetoresistance data on In_2Se_3 - and In_2Te_3 -doped InAs samples in this work. In the following two sections (II-312 and 313), the existing information about electronic conductions in isotropic band and anisotropic band relevant to this work is collected. The ideas obtained from the one-conduction-band model, as concerning Hall coefficient R , conductivity σ , resistivity ρ , and magnetoresistivity $\Delta\rho$, then lead to the development of the model for two-band conduction (Section II-314).

Chambers (52C1) has derived the expressions of R and ρ ($=1/\sigma$) for two-band conduction in terms of these parameters due to the individual bands. The magnetic field (B) dependence of both R and ρ of this model takes the form

$$(a + bB^2) / (f + gB^2),$$

a , b , f , and g being constants. Harland (65H1, 66H1) has used this model to analyze Hall effect and magnetoresistance data on tellurium-doped GaSb samples. In Harland's work, the expressions for R and ρ are expanded in power series of B , up to terms in B^2 and B^4 , respectively, and a curve-fitting

method is used to obtain coefficients of the power series and hence values of R and ρ (and σ) of the individual bands. In the present work, an analytic method for analyzing the experimental data on heavily-doped InAs samples is developed. As will be seen later in this chapter, the present method is found to be capable of analyzing the experimental data for two-band conduction. This method has also been used by Aubin (69A1) in the magnetoresistance work on heavily-doped InSb.

In Section II-315, the methods for analyzing the effect of magnetoresistance oscillations (Shubnikov-de Haas effect) are also included for the completeness of the presentation of the theories of magnetoresistance. Although this effect is not observed on the InAs samples used in this work due to low mobilities of the carriers, the methods are applied to analyze Harland's oscillatory magnetoresistance data on n-type GaSb (65H1) (Appendix).

312. CONDUCTION IN AN ISOTROPIC BAND

In the presence of crossed electric and magnetic fields $\vec{E}$ and $\vec{B}$, the equation of motion of an electron in a solid is of the form

$$m^* \vec{v} = -e (\vec{E} + \vec{v} \times \vec{B}) \quad (\text{II-5})$$

In a conduction band with spherical constant-energy surfaces, the electron effective mass m^* is isotropic, i.e. independent of the direction of motion of the electron. When the magnetic field $\vec{B}$ is along the z-direction, the solution of equation (II-5) is

$$v_x + i v_y = \frac{e}{m^*} (e_x + i e_y) \left[\frac{1 - \exp(i\omega t)}{i\omega} \right] \quad (\text{II-6})$$

where $\omega = eB/m^*$, defined as the cyclotron frequency, and m^* the cyclotron effective mass, which may also be written as m_c^* .

The electrons in the crystal undergo collisions in the conduction process. The probability that an electron has not made a collision at time t after the previous collision is $\exp(-t/\tau)$, where τ is defined as the relaxation time or mean time between collisions. Then the average electron velocity takes the form

$$\bar{v}_x + i \bar{v}_y = \frac{1}{\tau} \int_0^\infty (v_x + i v_y) \exp(-\frac{t}{\tau}) dt \quad (\text{II-7})$$

which gives

$$\begin{aligned} \bar{v}_x &= -\frac{e}{m^*} \left[\left(\frac{\tau}{1 + \omega^2 \tau^2} \right) e_x - \left(\frac{\omega \tau^2}{1 + \omega^2 \tau^2} \right) e_y \right] \\ \bar{v}_y &= -\frac{e}{m^*} \left[\left(\frac{\tau}{1 + \omega^2 \tau^2} \right) e_y - \left(\frac{\omega \tau^2}{1 + \omega^2 \tau^2} \right) e_x \right] \end{aligned} \quad (\text{II-8})$$

The above expressions are not strictly valid, since they are derived under the assumption that τ is a constant. When τ is energy dependent, the expected average of the right side of equation (II-8) with respect to energy E must be taken. For a quantity Z averaged over the energy states, the relation is (Zawadzki 62Z1)

$$\langle Z \rangle = \frac{\int_0^{\infty} (-\partial f_0 / \partial E) Z \hbar^3 dE}{\int_0^{\infty} (-\partial f_0 / \partial E) \hbar^3 dE} \quad (\text{II-9})$$

where f_0 is the Fermi-Dirac distribution function and $\hbar$ the wave vector. Then the current densities J_x and J_y , defined as $-ne\bar{v}_x$ and $-ne\bar{v}_y$ respectively (n being the electron concentration) are

$$\begin{aligned} J_x &= A e_x - D e_y \\ J_y &= A e_y + D e_x \end{aligned} \quad (\text{II-10})$$

where

$$\begin{aligned} A &= ne^2 \left\langle \frac{\tau}{m^* (1 + \omega^2 \tau^2)} \right\rangle \\ D &= ne^2 \left\langle \frac{\omega \tau^2}{m^* (1 + \omega^2 \tau^2)} \right\rangle \end{aligned} \quad (\text{II-11})$$

When there is no transverse current, i.e. $J_y = 0$, the Hall coefficient R and the conductivity σ (or resistivity ρ) are given by

$$R = \frac{e_y}{J_x B} = - \frac{D}{(A^2 + D^2) B} \quad (\text{II-12})$$

$$\sigma = 1/\rho = (A^2 + D^2) / A \quad (\text{II-13})$$

Then A and D can also be expressed in terms of R, σ , and B as

$$\begin{aligned} A &= \frac{\sigma}{1 + \sigma^2 B^2 R^2} \\ D &= \frac{\sigma^2 B R}{1 + \sigma^2 B^2 R^2} \end{aligned} \quad (\text{II-14})$$

The above expressions (II-10) - (II-14) will be used in the derivation of the model for two-band conduction (Section II-314). As for the calculation of R and σ (or ρ) due to one-band conduction, the $(E, \hbar)$ and $(m^*, \hbar)$ relations are involved in the expectation values in equations (II-11). Upon expanding $\tau/[m^*(1+\omega^2\tau^2)]$ and $\omega\tau^2/[m^*(1+\omega^2\tau^2)]$ in power series up to quadratic terms of B,

$$\begin{aligned} A &= ne^2 [\langle \tau/m^* \rangle - e^2 B^2 \langle (\tau/m^*)^3 \rangle] \\ D &= ne^3 B \langle (\tau/m^*)^2 \rangle \end{aligned} \quad (\text{II-15})$$

By substituting this into equation (II-12) and (II-13), the Hall coefficient R, zero-field conductivity σ^0 , and conductivity σ become

$$R = -\frac{1}{ne} \langle (\tau/m^*)^2 \rangle / \langle \tau/m^* \rangle^2 \quad (\text{II-16})$$

$$\sigma^0 = ne^2 \langle \tau/m^* \rangle \quad (\text{II-17})$$

$$\sigma = ne^2 \{ \langle \tau/m^* \rangle + e^2 B^2 [\frac{\langle (\tau/m^*)^2 \rangle^2 - \langle (\tau/m^*)^3 \rangle \langle \tau/m^* \rangle}{\langle \tau/m^* \rangle}] \}$$

The magnetoresistivity is

$$\Delta\rho = \rho - \rho^0 = \frac{1}{\sigma} - \frac{1}{\sigma^0} \quad (\text{II-18})$$

ρ^0 being the zero-field resistivity. Hence

$$\Delta\rho/\rho^0 = W (R\sigma^0 B)^2 \quad (\text{II-19})$$

$$\text{where } W = \frac{\langle (\tau/m^*)^3 \rangle \langle \tau/m^* \rangle}{\langle (\tau/m^*)^2 \rangle} - 1 \quad (\text{II-20})$$

It is quite evident that equations (II-19) and (II-20) imply that $W = 0$ when τ/m^* is energy independent. Such an ideal case of energy independent τ/m^* does not represent an actual situation in the conduction process in a non-degenerate material. However, in a highly degenerate material in which the Fermi level is well above the conduction band minimum, the tailing of energy distribution of the electrons, effectively $4kT$ (k being the Boltzmann constant), is practically insignificant especially at helium temperature. This can be easily seen, since even a Fermi level of 0.005 eV is greater than $13kT$ at $T = 4.2^\circ\text{K}$ ($kT = 3.62 \times 10^{-4}$ eV). Hence the electrons taking part in the conduction process are those in the immediate vicinity of the Fermi level, and then the assumption of energy independent τ/m^* in a small energy range is reasonably valid.

313. CONDUCTION IN AN ANISOTROPIC BAND

The method given in the preceding section can be generalized to an anisotropic band. In this case, instead of an isotropic effective mass m^* , the effective mass components along three principal directions m_1^* , m_2^* , m_3^* must be considered. After obtaining the expressions for $\bar{v}_x$ and $\bar{v}_y$ equivalent to equations (II-8), the three effective mass components m_1^* , m_2^* and m_3^* are permuted in order to account for the contributions from all equivalent ellipsoids along different directions. When the constant-energy surfaces are in the form of ellipsoids of revolution as in the case of the $\langle 111 \rangle$ or $\langle 100 \rangle$ conduction band, the effective mass is reduced to the longitudinal and transverse components m_L^* and m_T^* only. The Hall coefficient R is obtained from $R = \epsilon_y / (J_x B)$, as before, by imposing the condition $J_y = 0$. The result is

$$R = - \frac{1}{ne} \cdot \frac{\langle (\tau/m_T^*)^2 \rangle}{\langle \tau/m_T^* \rangle^2} \cdot \frac{3K_1 (K_1 + 2)}{(2K_1 + 1)^2} \quad (\text{II-21})$$

where $K_1 = m_L^*/m_T^*$. This equation has been shown to hold for any crystal with cubic symmetry (Smith 59S1). When $K_1 = 1$, this reduces to the form obtained for the isotropic band given in equation (II-16).

The full theory of magnetoresistance of a semiconductor with electrons present in an anisotropic band is very complicated. Here, the relevant results from theoretical investigations as

reviewed by Smith (59S1) will be given. Pearson and Suhl (51P1) have derived the crystal-orientation dependence of magneto-resistivity

$$\Delta\rho/\rho^0 = [b + c(il+jm+kn) + d(i^2l^2+j^2m^2+k^2n^2)]B^2 \quad (\text{II-22})$$

where i, j, k and l, m, n are the direction cosines giving the directions of the current flow and the magnetic field respectively. The coefficients b, c , and d depend on the directions of the axes of the ellipsoids of revolution and may be expressed in terms of K_1 . For symmetrical arrangement of the ellipsoids along the $\langle 111 \rangle$ axes in $\vec{k}$ -space, the coefficients are given by

$$\begin{aligned} b = -c &= \left[\frac{(2K_1+1)^2(1+W_1)}{3K_1(K_1+2)} - 1 \right] R_1^2 \sigma_1^2 \\ d &= \left[\frac{2(K_1-1)^2(2K_1+1)(1+W_1)}{3K_1(K_1+2)} \right] R_1^2 \sigma_1^2 \end{aligned} \quad (\text{II-23})$$

where the subscript 1 indicates the $\langle 111 \rangle$ conduction band.

As has been mentioned in the preceding section, W represents variable degeneracy of the electrons in the conduction band. For a highly degenerate material in which electrons are also present in the $\langle 111 \rangle$ conduction band, a Fermi level of 0.005 eV above the $\langle 111 \rangle$ minimum is quite sufficient to make the tailing of the energy distribution of electrons insignificant at helium temperature. Hence, the assumption that $W_1 = 0$ is reasonably valid. Then the magnetoresistivity due to the

anisotropy of the $\langle 111 \rangle$ band is

$$\Delta \rho_1 / \rho_1^0 = H_1 (R_1 \sigma_1 B)^2 \quad (\text{II-24})$$

$$\text{where } H_1 = \frac{(K_1 - 1)^2}{3K_1(K_1 + 2)} [1 - (il + jm + kn)^2 + (i^2 l^2 + j^2 m^2 + k^2 n^2) \cdot \frac{2(2K_1 + 1)}{(K_1 + 2)}] \quad (\text{II-25})$$

314. TWO-BAND CONDUCTION

When there are two types of carriers in the crystal, as in the case of heavily-doped InAs where electrons are present in the (000) and $\langle 111 \rangle$ conduction bands, the current density is simply an algebraic sum of the contributions from these two types of carriers in the form as

$$\begin{aligned} J_x &= (A_0 + A_1) \varepsilon_x - (D_0 + D_1) \varepsilon_y \\ J_y &= (A_0 + A_1) \varepsilon_y + (D_0 + D_1) \varepsilon_x \end{aligned} \quad (\text{II-26})$$

where A_0 , D_0 and A_1 , D_1 are given in expressions (II-11) with appropriate effective mass and relaxation time, m_0^* , τ_0 and m_1^* , τ_1 respectively. Relations (II-14) are still of the form

$$\begin{aligned} A_i &= \frac{\sigma_i}{1 + \sigma_i^2 B^2 R_i^2} \\ D_i &= \frac{\sigma_i^2 B R_i}{1 + \sigma_i^2 B^2 R_i^2} \end{aligned} \quad \} i = 0, 1 \quad (\text{II-27})$$

where R_0 , R_1 and σ_0 , σ_1 represent the Hall coefficient and conductivity due to electrons in the (000) and $\langle 111 \rangle$ conduction band minima separately. The absence of the transverse current, i.e. $J_y = 0$, gives rise to the following relations analogous to expressions (II-12) and (II-13):

$$R = - \frac{D_0 + D_1}{[(A_0 + A_1)^2 + (D_0 + D_1)^2] B} \quad (\text{II-28})$$

$$\sigma = \frac{(A_0 + A_1)^2 + (D_0 + D_1)^2}{A_0 + A_1} \quad (\text{II-29})$$

upon substituting for A_0 , A_1 , D_0 and D_1 from relations (II-27), the expressions for Hall coefficient R and resistivity ρ of the material are:

$$R = \frac{(R_0 \sigma_0^2 + R_1 \sigma_1^2) + \sigma_0^2 \sigma_1^2 R_0 R_1 (R_0 + R_1) B^2}{(\sigma_0 + \sigma_1)^2 + \sigma_0^2 \sigma_1^2 (R_0 + R_1)^2 B^2} \quad (\text{II-30})$$

$$\rho = 1/\sigma = \frac{(\sigma_0 + \sigma_1) + \sigma_0 \sigma_1 (R_0^2 \sigma_0 + R_1^2 \sigma_1) B^2}{(\sigma_0 + \sigma_1)^2 + \sigma_0^2 \sigma_1^2 (R_0 + R_1)^2 B^2} \quad (\text{II-31})$$

These relations have been obtained by Chambers (52C1) and shown to be valid for energy dependent τ in the electron scattering process.

Since R , ρ (or σ) and B are measurable quantities, their correlations are to be used in the determination of R_0 , R_1 , σ_0 and σ_1 . The method of curve-fitting $R(B)$ and $\rho(B)$ to solve for these four constants from equations (II-30) and (II-31) would be quite tedious. As has been mentioned in Section II-311, Harland (65H1) has used the method of series expansion by retaining the first few terms of lower power of B . Notwithstanding that this approximation has reduced the accuracy of the analysis to some extent, a curve fitting method involving iterative processes still has to be used to solve for the coefficients of the expansions and ultimately the

constants R_0 , R_1 , σ_0 and σ_1 . It is therefore more practical to solve for these constants in terms of the measurable quantities directly. The present approach involves the use of the zero-field Hall coefficient R^0 and resistivity ρ^0 (or conductivity σ^0) which are deduced from equations (II-30) and (II-31) by setting $B = 0$,

$$R^0 = \frac{R_0 \sigma_0^2 + R_1 \sigma_1^2}{(\sigma_0 + \sigma_1)^2} \quad (\text{II-32})$$

$$1/\rho^0 = \sigma^0 = \sigma_0 + \sigma_1 \quad (\text{II-33})$$

Then the magnetoresistivity is

$$\begin{aligned} \Delta\rho &= \rho - \rho^0 \\ &= \frac{\sigma_0 \sigma_1 (\sigma_0 R_0 - \sigma_1 R_1)^2 B^2}{\sigma^0 [\sigma^0{}^2 + \sigma_0^2 \sigma_1^2 (R_0 + R_1)^2 B^2]} \end{aligned} \quad (\text{II-34})$$

Upon eliminating R_1 and σ_1 from equation (II-34) by using relations (II-32) and (II-33), the magnetic field dependence of $\Delta\rho$ has the form:

$$\Delta\rho = \frac{\sigma^0 \sigma_0 (\sigma^0 - \sigma_0) (R^0 \sigma^0 - R_0 \sigma_0)^2}{B^{-2} \sigma^0{}^2 (\sigma^0 - \sigma_0)^2 + \sigma_0^2 (R_0 \sigma^0{}^2 - 2R_0 \sigma^0 \sigma_0 + R_0 \sigma_0^2)^2} \quad (\text{II-35})$$

which can further be simplified as

$$\rho^0 / \Delta\rho = s B^{-2} + u \quad (\text{II-36})$$

where

$$s = \frac{\sigma^0 - \sigma_0}{\sigma_0 (R^0 \sigma^0 - R_0 \sigma_0)^2} \quad (\text{II-37})$$

$$u = \frac{\sigma_0 [R^0 \sigma^0 + R_0 (\sigma^0 - 2\sigma_0)]^2}{(\sigma^0 - \sigma_0)(R^0 \sigma^0 - R_0 \sigma_0)^2} \quad (\text{II-38})$$

Therefore the magnetoresistance data can be expressed conveniently in the straight line graph of $\rho^0/\Delta\rho$ versus B^{-2} according to equation (II-36), and s and u represent the slope and intercept respectively from the graph. Hence, the constants σ_0 and R_0 can be expressed in terms of σ^0 , R^0 , s and u from equations (II-37) and (II-38),

$$\sigma_0 = \frac{\sigma^0}{2} \left[1 + \sqrt{\frac{(\sqrt{u} + R^0 \sigma^0 \sqrt{s})^2}{4 + (\sqrt{u} + R^0 \sigma^0 \sqrt{s})^2}} \right] \quad (\text{II-39})$$

$$R_0 = \frac{1}{\sigma_0} \left[R^0 \sigma^0 - \sqrt{\frac{\sigma^0 - \sigma_0}{s \sigma_0}} \right] \quad (\text{II-40})$$

When expressed in terms of known quantities σ_0 , σ^0 , R_0 and R^0 from equations (II-32) and (II-33), σ_1 and R_1 can be written as

$$\sigma_1 = \sigma^0 - \sigma_0 \quad (\text{II-41})$$

$$R_1 = \frac{R^0 \sigma^0{}^2 - R_0 \sigma_0{}^2}{(\sigma^0 - \sigma_0)^2} \quad (\text{II-42})$$

The next step is to deduce the carrier concentrations n_0 , n_1 and the mobilities μ_0 , μ_1 of the electrons in the two bands. As has been indicated in preceding sections, the

carrier concentration is determined by the Hall coefficient, variable degeneracy of the carriers and the anisotropy of the band. The general form according to equation (II-21) is

$$n_i = - \frac{r_i F_i}{R_i e} \quad i = 0, 1 \quad (\text{II-43})$$

where

$$\left. \begin{aligned} r_i &= \frac{\langle (\tau_i / m_{Ti}^*)^2 \rangle}{\langle \tau_i / m_{Ti}^* \rangle^2} \\ F_i &= \frac{3K_i (K_i + 2)}{(2K_i + 1)^2} \\ K_i &= m_{Li}^* / m_{Ti}^* \end{aligned} \right\} \quad (\text{II-44})$$

In the present work, the materials are completely degenerate, and hence $r_0 = r_1 = 1$, while the (000) minimum has spherical constant-energy surfaces, $K_0 = 1$, and then $F_0 = 1$. Thus

$$\begin{aligned} n_0 &= - 1/(R_0 e) \\ n_1 &= - F_1/(R_1 e) \end{aligned} \quad (\text{II-45})$$

The mobility is given by

$$\mu_i = \sigma_i / (n_i e) \quad i = 0, 1 \quad (\text{II-46})$$

Therefore the magnetoresistance data effectively determine the quantities n_0 , n_1/F_1 , μ_0 and $\mu_1 F_1$, and consequently the variations of these quantities with y , the atomic percentage of selenium or tellurium in the samples.

315. MAGNETORESISTANCE OSCILLATIONS (SHUBNIKOV-DE HAAS EFFECT)

3151. INTRODUCTION

Oscillations in the magnetoresistance of bismuth crystals were first observed by Shubnikov and de Haas (30S1). This phenomenon was then referred to as Shubnikov-de Haas effect. The reviews on the experimental evidence and the theoretical treatments of this and some related oscillatory effects in transport properties of metals and semiconductors have been given by Kahn and Frederikse (59K1), Adams and Keyes (62A1) and Roth and Argyres (66R1).

This effect is the consequence of the quantization of the motion of electrons in the plane perpendicular to the magnetic field. The conduction band then splits into Landau-level sub-bands with spacing of the adjacent minima by an energy of $\hbar\omega$, ω being the cyclotron frequency,

$$\omega = e B / m_c^* \quad (\text{II-47})$$

Here m_c^* represents the cyclotron effective mass which is defined as (Ziman 64Z1):

$$m_c^* = \hbar^2 k / \nabla_k E \quad (\text{II-48})$$

As for highly degenerate materials, this is evaluated at the Fermi level, i.e. $E = E_F$ and $k = k_F$. The n th level is $(n + 1/2) \hbar\omega$ in energy above the zero-field conduction band minimum. The density of states approaches high values at the bottom of all Landau-level sub-band minima. The gradual

variation of the magnetic field gives rise to the passage of the successive Landau levels through the Fermi energy. Therefore the Fermi level "experiences" oscillatory variation of the density of states, and consequently, the oscillatory behavior of various physical properties is expected (such as magnetoresistance, Hall coefficient, etc.)

The experimental data of oscillatory magnetoresistance consist of two parts: the period and the amplitude of the oscillations, from which values of electron concentration n_0 , cyclotron effective mass of the electrons m_c^* , and the Dingle temperature T' (to be explained later) of the specimen can be deduced. In the following, methods for analyzing this oscillatory phenomenon are collected. A method for analyzing the amplitude of the oscillations is also developed in the present work. The application of this on tellurium-doped GaSb will be given in the Appendix.

3152. CONDITIONS FOR THE OSCILLATORY BEHAVIOR

As has been mentioned in the review articles by the above authors (59K1, 62A1, 66R1), the oscillatory phenomena occur under the following conditions:

(1) The energy separation $\hbar\omega$ of the Landau levels must be distinct, such that

$$(\hbar\omega) (\tau) \gg \hbar$$

or $\omega\tau \gg 1$

(II-49)

according to Heisenberg's uncertainty principle. Here, τ is the relaxation time. This relation can also be written as

$$\mu B \gg 1 \quad (\text{II-50})$$

μ being the mobility of the electrons. Here, μ is in $\text{m}^2/\text{V}.\text{sec}$ and B in W/m^2 . This requires a high mobility of the electrons in the material at a reasonable magnetic field intensity B .

(2) The carriers must remain degenerate at low temperatures, and the zero-field Fermi energy must exceed the separation of the Landau levels, i.e.

$$E_F > \hbar\omega \quad (\text{II-51})$$

This sets an upper limit of the magnetic field.

(3) The temperature must be low enough such that the spacing of the Landau levels exceeds the thermal broadening, i.e.

$$\hbar\omega > kT \quad (\text{II-52})$$

k being the Boltzmann constant.

3153. PERIOD OF OSCILLATIONS

As the results of gradual variation of the magnetic field, the ladder of Landau levels passes through the Fermi energy, and at each passage,

$$E_F = (n + 1/2) \hbar\omega \quad n = 0, 1, 2, 3, \dots$$

$$\text{or } \frac{1}{B} = \left(n + \frac{1}{2} \right) \frac{e \hbar}{E_F m_c^*} \quad (\text{II-53})$$

The oscillations of magnetoresistance are therefore periodic in $1/B$. The period of oscillations, which is the separation of the adjacent $1/B$ values for the n th and $(n+1)$ th Landau levels, is given by

$$\Delta \left(\frac{1}{B} \right) = \frac{e \hbar}{E_F m_c^*} \quad (\text{II-54})$$

Hence the information obtainable from the experimental value of the period of oscillations is the product $E_F m_c^*$, which is closely related to the electron concentration n_0 in the conducting solid through the following equation (Kahn and Frederikse 59K1, Harland 65H1):

$$n_0 = \frac{(2E_F m_c^*)^{3/2}}{3\pi^2 \hbar^3} \left[1 - \frac{3\pi^{1/2}}{4} \left(\frac{kT}{E_F} \right)^{3/2} \sum_{M=1}^{\infty} \frac{(-1)^{M+1}}{M^{1/2}} \cdot \frac{\cos\left(\frac{2\pi M E_F}{\hbar \omega} + \frac{\pi}{4}\right)}{\sinh\left(\frac{2\pi^2 M kT}{\hbar \omega}\right)} \right] \quad (\text{II-55})$$

This equation is derived under the condition $E_F \gg \hbar \omega$, which is reasonably valid for highly degenerate materials. Here, the relation between n_0 and $E_F m_c^*$ may be approximated by the non-oscillating part of the above equation:

$$n_0 \approx \frac{(2 E_F m_c^*)^{3/2}}{3 \pi^2 \hbar^3} \quad (\text{II-56})$$

Then n_0 can be expressed in terms of the period of magneto-

resistance oscillations:

$$n_0 = \frac{1}{3\pi^2} \left[\frac{2e}{\hbar \Delta(1/B)_{\text{period}}} \right]^{3/2} \quad (\text{II-57})$$

A slightly different approach using the extremal cross-section S of the Fermi surface perpendicular to the magnetic field also yields the same result. It has been shown by Ziman (60Z1), by considering the quantization of electronic motion in the plane perpendicular to the magnetic field, that

$$\Delta(1/B)_{\text{period}} = \frac{2\pi e}{\hbar S} \quad (\text{II-58})$$

When the constant-energy surface is spherical and the carriers are highly degenerate (Smith et al 59S2),

$$\begin{aligned} S &= \pi k_F^2 \\ &= \pi (3\pi^2 n_0)^{2/3} \end{aligned} \quad (\text{II-59})$$

Then from the above two equations,

$$n_0 = \frac{1}{3\pi^2} \left[\frac{2e}{\hbar \Delta(1/B)_{\text{period}}} \right]^{3/2} \quad (\text{II-60})$$

which is identical to equation (II-57). This result has been shown to be reasonably valid through experimental investigations. Hall effect and magnetoresistance results on tellurium-doped GaSb samples by Harland (65H1) have indicated that the electron concentrations n_0 in the materials as deduced from $\Delta(1/B)_{\text{period}}$

are quite compatible with the values obtained from the model of two-band conduction.

3154. AMPLITUDE OF OSCILLATIONS

The quantum-mechanical treatments by Lifshits and Kosevich (58L1), Argyres (58A1) and Adams and Holstein (59A2) have given similar expressions for the oscillatory part of the longitudinal and transverse magnetoresistance. For a material with spherical constant-energy surfaces, the oscillatory term in the transverse magnetoresistance can be written as

$$\frac{\Delta \rho_{osc}}{\rho^0} = \frac{5\sqrt{2} \pi^2 kT}{(\hbar \omega E_F)^{\frac{3}{2}}} \cdot \sum_{M=1}^{\infty} \frac{(-1)^M M^{\frac{1}{2}} \exp(-\frac{2\pi M}{\omega \tau})}{\sinh(\frac{2\pi^2 M kT}{\hbar \omega})} \cos(\frac{2\pi M E_F}{\hbar \omega} - \frac{\pi}{4}) \quad (II-61)$$

when collision broadening is taken into account. Here, ρ^0 is the zero-field resistivity, and τ is the collision broadening cut-off time. The argument of the exponential term $-2\pi M/(\omega \tau)$ can be written as $-2\pi^2 M k T' / (\hbar \omega)$. Here,

$$T' = \frac{\hbar}{\pi k \tau} \quad (II-62)$$

is defined as the collision broadening temperature (or Dingle temperature), and in a limited temperature range, say $2.0^\circ K \leq T \leq 4.2^\circ K$, T' can be taken as a constant for each specimen.

The above expression for $\Delta \rho_{osc} / \rho^0$ has been used by

Cuff et al (61C5) in the investigations on PbTe, and Yep and Becker (66Y1) on GaSb. The higher harmonic terms ($M > 1$) are neglected in both cases. Retaining only the term $M = 1$, the amplitude of the oscillations $\Delta\rho_A$ can be simplified to

$$\Delta\rho_A(T, B) = \frac{5/2 \pi^2 \rho^2 kT \left(\frac{m_c^*}{e\hbar E_F B} \right)^{\frac{1}{2}}}{\exp\left(\frac{2\pi^2 k m_c^* T}{e\hbar B} \right) \sinh\left(\frac{2\pi^2 k m_c^* T}{e\hbar B} \right)} \quad (\text{II-63})$$

At a constant intensity of the field B , the temperature dependence of $\Delta\rho_A$ is in a relatively simple form:

$$\Delta\rho_A(T) \propto T / \sinh\left(\frac{2\pi^2 k m_c^* T}{e\hbar B} \right) \quad (\text{II-64})$$

Therefore the ratio of the oscillation amplitudes of constant B at two temperatures T_1 and T_2 is expressed as:

$$\frac{\Delta\rho_A(T_1)}{\Delta\rho_A(T_2)} = \frac{T_1 \sinh\left(\frac{2\pi^2 k m_c^* T_2}{e\hbar B} \right)}{T_2 \sinh\left(\frac{2\pi^2 k m_c^* T_1}{e\hbar B} \right)} \quad (\text{II-65})$$

From this relation, the cyclotron effective mass m_c^* of the electrons can be calculated.

The Dingle temperature T' can also be deduced from equation (II-63) by keeping the temperature T constant. Then,

$$[\Delta\rho_A(B)] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 k m_c^* T}{e\hbar B} \right) \propto \exp\left(- \frac{2\pi^2 k m_c^* T'}{e\hbar B} \right) \quad (\text{II-66})$$

From the linear relation of $\ln\{[\Delta\rho_A(B)]B^{\frac{1}{2}}\sinh(\frac{2\pi^2 k m_c^* T}{e\hbar B})\}$ with B^{-1} , T' can be obtained from the slope with a known value of m_c^* , which is obtainable from equation (II-65).

A different approach in analyzing the $\Delta\rho_A(T,B)$ data is by rearranging expression (II-66) as

$$\Delta\rho_A(B) \propto \frac{1}{B^{\frac{1}{2}} \sinh(\frac{2\pi^2 k m_c^* T}{e\hbar B}) \exp(\frac{2\pi^2 k m_c^* T'}{e\hbar B})} \quad (\text{II-67})$$

This expression may be approximated to the form

$$\Delta\rho_A(B) = \frac{a_1}{B^{\frac{1}{2}} \sinh(\frac{c}{B})} \quad (\text{II-68})$$

$$\text{or} \quad \Delta\rho_A(B) = a_2 B^{-\frac{1}{2}} \exp(-\frac{c}{B}) \quad (\text{II-69})$$

$$\text{where} \quad c = \frac{2\pi^2 k m_c^*}{e\hbar} (T + T') \quad (\text{II-70})$$

and a_1 and a_2 are the proportionality constants. The relation in the form of equation (II-69) has been used by some authors (Zilberman 55Z1, Frederikse and Holsler 58F2). Besides these, a more simplified form

$$\Delta\rho_A(B) = a_2 \exp(-\frac{c}{B}) \quad (\text{II-71})$$

has also been used (Sladek 58S1). Here, the omission of the term $B^{-\frac{1}{2}}$ does not seem to be theoretically justified. Some authors even used the term $B^{\frac{1}{2}}$ (Reynolds et al 54R1, Hyman and Siklossy 65H2) or $B^{2.4}$ (Overton and Berlincourt 55O1) in

treating various oscillatory phenomena, including magneto-resistance, Hall coefficient and susceptibility. Therefore at a fixed temperature T , an expression which is more general than equations (II-68) and (II-69) may be used:

$$\Delta\rho_A(B) = \frac{a}{B^b \sinh(\frac{c}{B})} \quad (\text{II-72})$$

where a and b are constants, and c is also defined by equation (II-70).

An apparent reason that the above authors preferred to use some approximated forms of $\Delta\rho_A(B)$ rather than the general form given in equation (II-72) must be attributed to difficulties encountered in the manipulation of this equation, which involves a hyperbolic sine function and three unknown parameters a , b and c . In the present work, a method is developed for fitting experimental data of $\Delta\rho_A(B)$ to determine the constants a , b and c from equation (II-72). The relation between c and T as given by equation (II-70) is linear, and hence the cyclotron effective mass m_c^* and the Dingle temperature T' can be obtained from the slope and intercept of the c versus T graph. This least-square fitting method is presented in the following.

Equation (II-72) can be rewritten as

$$\ln(\Delta\rho_A) = \ln a - b \ln B - \ln \sinh \frac{c}{B} \quad (\text{II-73})$$

With a set of data of $(\Delta\rho_{Ai}, B_i)$, a total of N pairs in number,

the sum of the squares of deviations is

$$S = \sum_{i=1}^N (\ln \Delta \rho_{Ai} - \ln a + b \ln B_i + \ln \sinh c/B_i) \quad (\text{II-74})$$

The derivatives $\partial S/\partial a = 0$, $\partial S/\partial b = 0$ and $\partial S/\partial c = 0$ give three simultaneous equations for a , b and c . The first two equations are further simplified to give a and b separately in terms of c :

$$\begin{aligned} \ln a = & \left\{ \sum_i (\ln \Delta \rho_{Ai}) \sum_i (\ln B_i)^2 \right. \\ & - \sum_i (\ln B_i) \sum_i [(\ln \Delta \rho_{Ai}) (\ln B_i)] \\ & + \sum_i (\ln B_i)^2 \sum_i (\ln \sinh c/B_i) \\ & \left. - \sum_i (\ln B_i) \sum_i [(\ln B_i) (\ln \sinh c/B_i)] \right\} \cdot \\ & \cdot \{ N \sum_i (\ln B_i)^2 - [\sum_i (\ln B_i)]^2 \}^{-1} \quad (\text{II-75}) \end{aligned}$$

$$\begin{aligned} b = & \left\{ \sum_i (\ln \Delta \rho_{Ai}) \sum_i (\ln B_i) \right. \\ & - N \sum_i [(\ln \Delta \rho_{Ai}) (\ln B_i)] \\ & + \sum_i (\ln B_i) \sum_i (\ln \sinh c/B_i) \\ & \left. - N \sum_i [(\ln B_i) (\ln \sinh c/B_i)] \right\} \cdot \\ & \cdot \{ N \sum_i (\ln B_i)^2 - [\sum_i (\ln B_i)]^2 \}^{-1} \quad (\text{II-76}) \end{aligned}$$

The third equation $\partial S/\partial c = 0$ gives

$$\sum_i \frac{\ln \Delta \rho_{Ai} - \ln a + b \ln B_i + \ln \sinh \epsilon/B_i}{B_i \tanh \epsilon/B_i} = 0 \quad (\text{II-77})$$

Upon substituting the expressions of $\ln a$ and b into equation (II-77), the value of ϵ can then be calculated through an iterative process. Thus from expressions (II-75) and (II-76), values of a and b can also be obtained.

Through the linear variation of ϵ with T , values of m_c^* of the samples can be deduced. These values can be compared with the calculated ones based on the Kane model (Section II-2). Such calculation is considered in the following section.

3155. CALCULATION OF ELECTRON EFFECTIVE MASS BASED ON THE KANE MODEL

When the Kane model is assumed, the $(E, \hbar k)$ relation takes the form as given by equation (II-4):

$$(E - a\hbar^2) (E + E_0 - a\hbar^2) (E + E_0 + \Delta_0 - a\hbar^2) - a\hbar^2 p^2 (E + E_0 + \frac{2}{3}\Delta_0 - a\hbar^2) = 0 \quad (\text{II-78})$$

Here, $a = \hbar^2/2m_e$. For highly degenerate materials in which the Fermi level is well above the (000) conduction band minimum, the cyclotron effective mass m_c^* is the value of $\hbar^2 k / (\nabla_{\hbar k} E)$ evaluated at the Fermi level, as has been mentioned in Section

(II-3151). Hence the expression for m_c^* is easily obtained by differentiating equation (II-78) with respect to $\hbar$. Then by rearranging the terms,

$$\frac{m_c^*}{m_e} = \left\{ 1 + \frac{P^2(E+E_0+\frac{2}{3}\Delta_0-a\hbar^2)}{[3E^2+(4E_0+2\Delta_0-6a\hbar^2)E+E_0(E_0+\Delta_0)-a\hbar^2(4E_0+2\Delta_0+P^2-3a\hbar^2)]} \right\}^{-1} \bigg|_{\substack{\hbar=\hbar_F \\ E=E_F}} \quad (\text{II-79})$$

$\hbar_F$ can also be replaced by the electron concentration n_0 through the following relation (Smith et al 59S2):

$$\hbar_F^2 = (3\pi^2 n_0)^{2/3} \quad (\text{II-80})$$

Hence, the variation of m_c^* with n_0 can be deduced with given values of E_0 , Δ_0 and P^2 . The effective mass at the bottom of the (000) conduction band is

$$\frac{m_o^*}{m_e} = \left[1 + \frac{P^2(E_0+\frac{2}{3}\Delta_0)}{E_0(E_0+\Delta_0)} \right]^{-1} \quad (\text{II-81})$$

as obtained by substituting $E = a\hbar^2 = 0$ in equation (II-79).

32. MATERIALS, EQUIPMENT AND EXPERIMENTAL TECHNIQUE

321. PREPARATION OF SPECIMENS

The specimens used in this work were prepared by alloying InAs with In_2Se_3 and In_2Te_3 . Here the commercial InAs was of electron concentrations 10^{22} - 10^{23} m^{-3} . The compounds In_2Se_3 and In_2Te_3 were synthesized by melting stoichiometric quantities of the 99.999% pure elements in small evacuated, sealed quartz ampoules. The air pressure in the ampoule was about $1\text{-}5 \times 10^{-5} \text{ mm Hg}$ when sealed off. The ingots of $\text{InAs-In}_2\text{Se}_3$ and $\text{InAs-In}_2\text{Te}_3$ alloys were then prepared by direct synthesis of the compounds concerned, and each ingot was centrifuged while cooling to solid form to prevent formation of voids. The alloys investigated here were InAs-rich. The contents of In_2Se_3 and In_2Te_3 in the alloys were only up to 2.6 and 2.3 mol. % respectively.

These ingots in the quartz ampoules were annealed at 800°C for 4 to 6 weeks. Each annealing furnace was constructed by winding a Kanthal resistance wire on a 2' long alumina tube of inner diameter $1\frac{1}{2}$ ". The wire coil was fixed in place by a thin coating of "Kyanex" refractory cement. The tube was mounted in a rectangular aluminum box with square "transite" end plates, and the box was filled with "vermiculite" (insulating material). A Pt vs. Pt+13%Rh thermocouple was inserted into the horizontal furnace tube at the position of the plateau of the temperature profile to monitor the furnace temperature. The hot zone was maintained by a Superior Electric Co. "Powerstat"

and regulated by a Phillips on-off controller which maintained the temperature to within a few degrees C in the vicinity of the thermocouple. The ampoules were placed near the thermocouple for better stability in the annealing temperature.

The complete systems of $\text{InAs-In}_2\text{Se}_3$ and $\text{InAs-In}_2\text{Te}_3$ have been investigated by Woolley and Keating (61W2, 61W3, 61K1) and Woolley et al (61W4, 60P1), and it has been shown that these annealing temperature and time were sufficient to ensure good equilibrium conditions. The resulting material was mechanically good and coarsely polycrystalline. The specimens were cut from the annealed ingot with a 0.008" thick carborundum wheel. Each specimen was cut to give a parallelepiped shape of dimensions approximately $10 \times 2.5 \times 1.5$ mm. The geometry of the specimen was an important factor in the accuracy of the calculation of the Hall coefficient and resistivity. Therefore accurately parallel sides and rectangular cross-section were required. This was achieved by careful lapping of the specimen on a flat glass plate by a lapping block with a mixture of water and silicon carbide grinding powder (Grit 800 or 1000). All four sides were lapped until the specimen cross-section was ~ 2 mm by ~ 0.7 mm. These dimensions were measured at different points along the specimen with a Moore and Wright micrometer. The uniformity of the thickness and width of the specimen treated this way was better than 0.5 %.

After the specimen was etched in Wolsky solution ($7\text{HCl} : 1\text{HNO}_3 : 8\text{CH}_3\text{COOH}$) for a few seconds and rinsed in distilled

water, the electrical contacts were made to the specimen. The contacts included the two end faces for specimen current, one narrow strip (or dot) on one side and two narrow strips (or dots) on the other side for Hall and resistance voltages. Three methods were used:

(1) Electroplating of tin (Harland 65H1, Aubin 69A1).

The specimen was masked with nail polish except for the desired positions for electrical contacts. The specimen, held by self-clasping tweezers, was first etched in Wolsky solution and rinsed in water, and then dipped in a tin plating solution ($1\text{SnCl}_4 : 1\text{HCl} : 20\text{H}_2\text{O}$). With the specimen as the cathode and a platinum wire as the anode, and a current about 1 ma, flowing for half an hour, the five exposed areas were covered with a thin layer of tin. The nail polish was then dissolved by acetone. With this method, the width of the contacts was usually beyond 0.3 mm.

(2) Annealing of tin balls. A graphite jig was designed and built to hold the parallelepiped shape specimen on its flat side, one piece of tin pressing each end of the specimen, and three 9-mil tin balls at their appropriate positions on the narrow sides of the specimen surface. Then the specimen assembly in the graphite jig was annealed at $400\text{--}500^\circ\text{C}$ under helium atmosphere for a few minutes. The width of the point contacts was improved to about 0.1 to 0.2 mm.

(3) Evaporation of indium. The evaporator assembly was a Veeco Model VE-400. The ends of the specimen were indium-

evaporated by wrapping the rest of the specimen with thin metal foil and masking tape. As for the side contacts, the mask was a copper foil through which two parallel slits, $1\frac{1}{2}$ mm long and ~6 mm in separation, had been cut with a razor blade. Therefore when indium evaporated, it condensed on the copper foil and on the specimen through the slits. The specimen was turned over and centered over one of the slits to obtain another thin strip of indium. The specimen was then annealed at 150-200°C for 30 seconds in helium gas at a pressure of 30 mm Hg. The width of the line contacts thus obtained was less than 0.2 mm.

In all cases mentioned above, the contacts were ohmic with contact resistance of 1-5 ohms. The method of indium evaporation was found to be more convenient in operation and therefore was used for most specimens in this work.

The center-to-center separation of the electrical contacts of the specimen was then measured with a traveling microscope. The specimen was mounted on a rectangular shaped glass plate with glyptol cement. Some conducting silver paint was used to connect the indium (or tin) contacts to five no. 32 enamelled copper wires as shown in Figure II-1. These wires were connected to the measuring equipment through shielded cables.

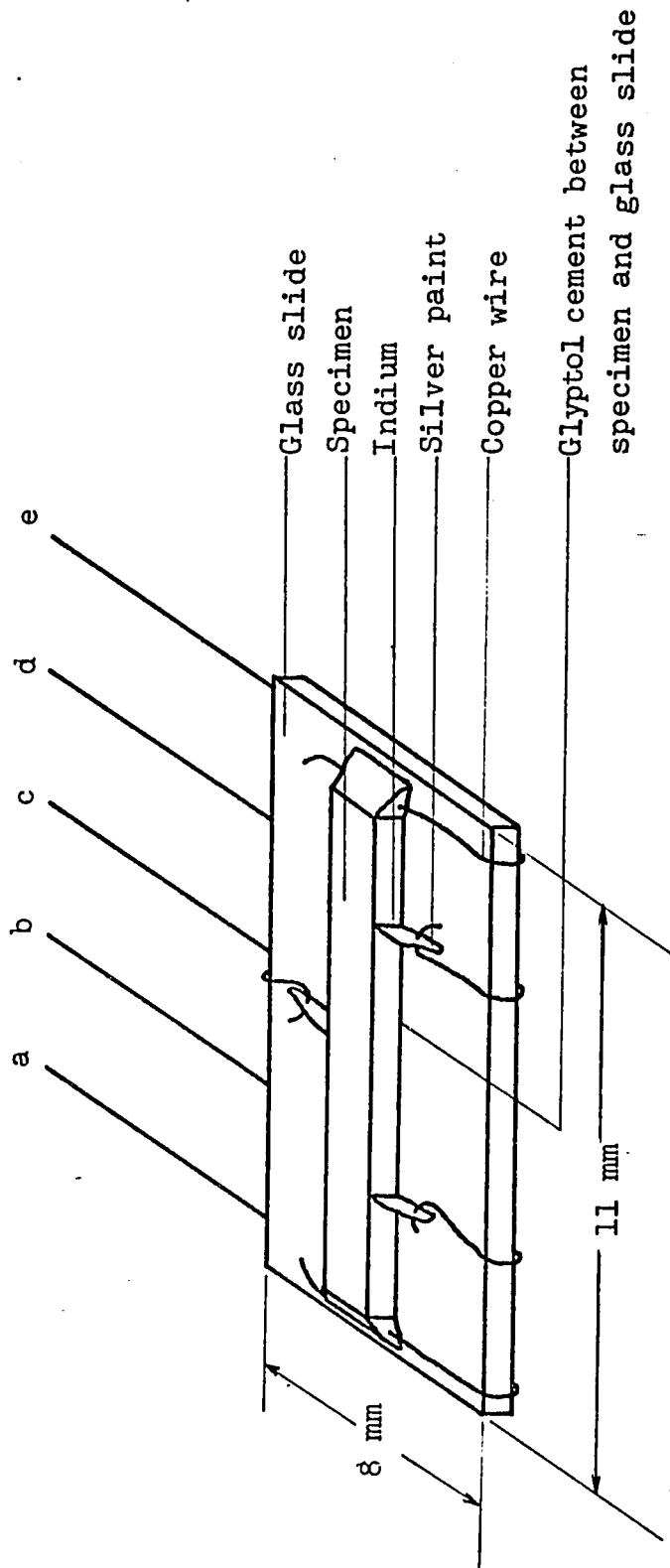


Figure II-1 Mounted specimen for Hall effect and magnetoresistance measurements.

a, e : Current leads

b, d : Resistance probes

c, d : Hall probes

322. EQUIPMENT

3221. METAL CRYOSTAT AND SPECIMEN HOLDER

The metal cryostat used in this work was built at the National Research Council, Ottawa, and was originally designed for use with the Pacific Electric Co. electromagnet with pole separation of $1\frac{1}{2}$ " as described in Harland's thesis (65H1). The original blueprint is reproduced in Figure II-2. The cryostat consisted of:

- (1) an outer vacuum jacket,
- (2) a liquid nitrogen tank in the upper compartment,
- (3) a liquid helium tank in the lower compartment,
- (4) a radiation shield anchored to the upper tank,
- (5) a silver specimen chamber separated from the lower tank by a stainless steel thermal resistance.

The high vacuum was maintained in the system by the continuous operation of an oil diffusion pump. Constant temperature of the specimen was maintained by means of helium exchange gas introduced into the silver specimen chamber. Since the measurements were made at 4.2°K only, the description on heating and temperature regulating systems installed in this cryostat will not be given here.

Some modifications of the cryostat were made:

- (1) The tail of the cryostat was lengthened by about 4" and reduced in diameter to $1\frac{3}{16}$ " in order to fit into the $1\frac{1}{4}$ " pole gap of the electromagnet used in this work. These changes were also made at National Research Council, Ottawa.

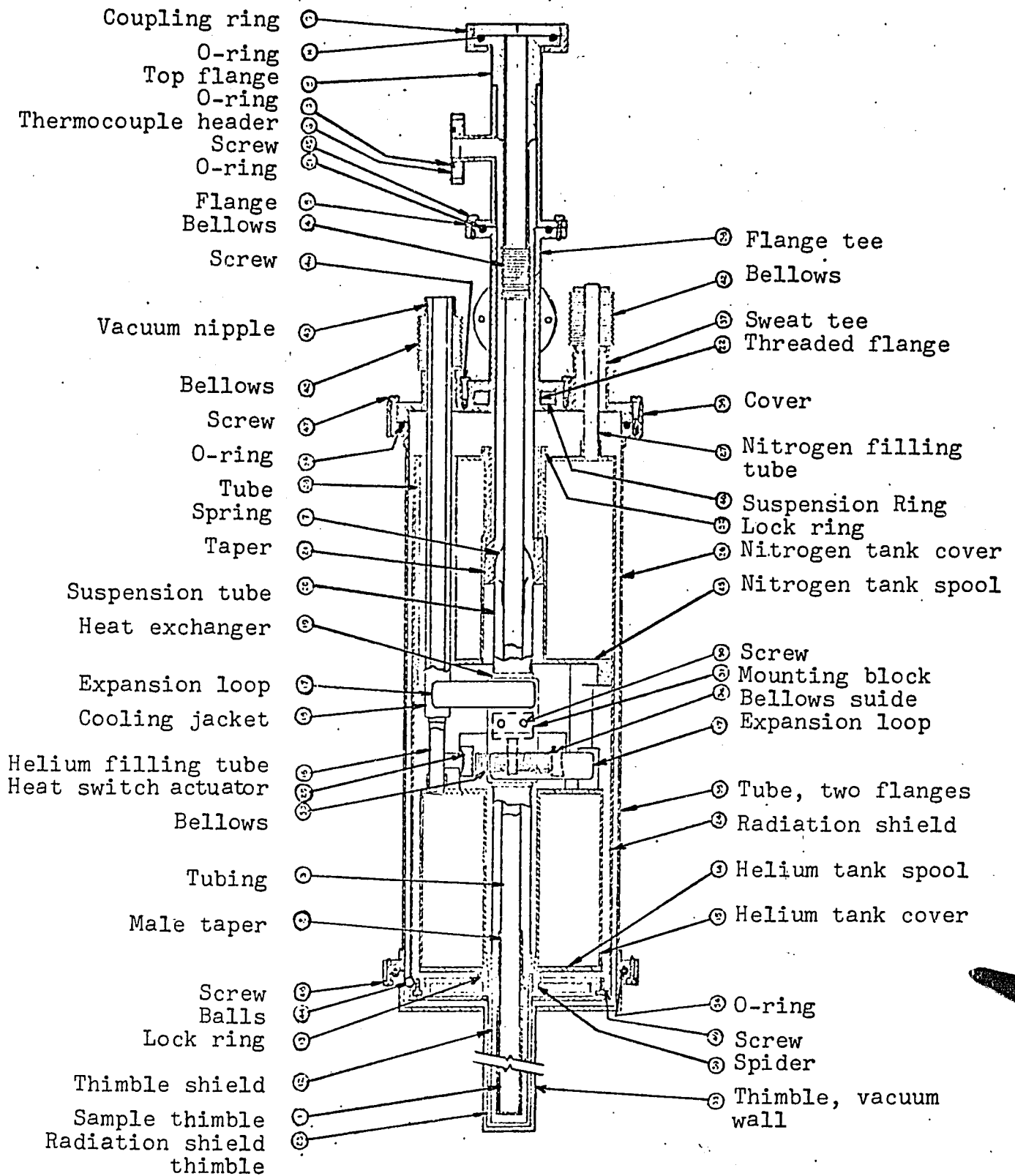


Figure II-2 Metal cryostat.

(2) The cryostat was also equipped with fittings to accomodate the helium recovery system in this laboratory.

The specimen holder assembly was designed to satisfied the following requirements:

(1) Simplicity in specimen alignment with the magnetic field direction.

(2) Minimal thermal leak from room temperature and minimal thermo-emf generation.

(3) Vacuum tight but electrical isolation from the cryostat.

The specimen holder, as shown in Figure II-3, was made of bakelite (an insulating material) and was connected to the cryostat head by means of a thin-wall stainless-steel tube of $\frac{1}{4}$ " diameter. A rotatable vacuum seal on the cryostat head allowed the alignment of the specimen in the magnetic field.

The mounted specimen, as shown in Figure II-1, was clamped on the specimen holder such that the length of the former was perpendicular to the axis of the latter. The five copper wires of the mounted specimen were then soldered to the corresponding copper pins of the specimen holder.

3222. SPECIMEN HOLDER FOR ROOM TEMPERATURE HALL EFFECT MEASUREMENTS

Room temperature Hall measurements are usually suitable to determine the carrier concentration of an extrinsic material

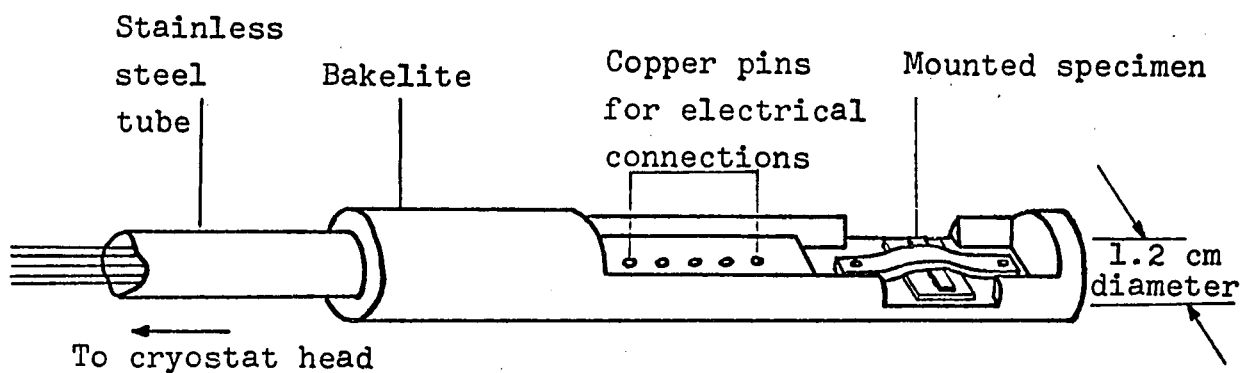


Figure II-3 Specimen holder for Hall effect and magneto-resistance measurements at 4.2°K .

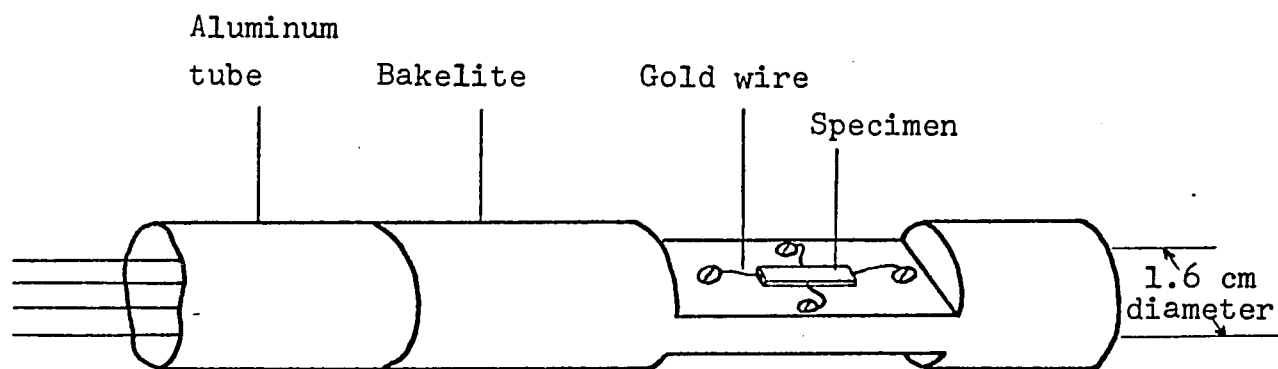


Figure II-4 Specimen holder for room temperature Hall effect measurements.

with carriers in only one band. Therefore a simple specimen holder was constructed for this purpose. It was made of a bakelite block supported by an aluminum tube from the base of the electromagnet. The specimen was mounted on the bakelite block with glyptol cement or a strip of masking tape. The aluminum tube could be rotated to allow for the alignment of the specimen in the magnetic field. The specimen holder with the mounted specimen is shown in Figure II-4. Here only four contact points were used: two along the length of the specimen for the current and two across the width of the specimen for the Hall voltage. Ohmic contacts of <5 ohms were made by spark welding 0.005" diameter gold wires on to the specimen. The four copper wires were connected to the measuring equipment via shielded cables.

3223. MAGNET AND MAGNETIC FIELD CONTROL EQUIPMENT

The measurements were made with a Magnion-Harvey-Wells Model L158 15" electromagnet along with a Model HS-10200 power supply and a Model FFC-4 field regulator. The pole separation was $1\frac{1}{4}$ ". A gaussmeter was mounted on a platform with a micrometer adjustment in order that the rotating-coil field sensing probe could be moved radially in and out of the pole gap with a range of 2". The probe, which was on a common shaft with a permanent magnet generator, was driven at 1800 rpm by a synchronous motor and thus generated a 30 cps voltage, proportional

to the field intensity in its vicinity. A similar constant amplitude voltage, which was produced by the permanent magnet generator, was used as a precision reference voltage in measuring and controlling the magnetic field. The accuracy of the setting of the field was about 5 parts in 10^5 and the stability was 1 part in 10^6 . Over an area of approximately 1 cm^2 in the center of the pole gap where the specimen was situated, the uniformity of the field was about 1 part in 10^5 .

In order that the tail of the cryostat could be fitted in the pole gap, the field sensing probe was placed at $1\frac{1}{5}$ " from the central position of the pole faces. Therefore the magnetic field at the central position, where the specimen was situated, was calibrated against the field at the radial position $1\frac{1}{5}$ " from it. The procedure was as follows:

With the probe in the "outside" position and the operation mode of the field regulator on "Field Set", the dials of the five decade switches were set for a certain field intensity (in the range $0.3000\text{--}3.0000 \text{ W/m}^2$). The ammeter then indicated an increase of current until the field intensity at the sensing probe reached the same value as the setting of the dials. The operation mode was then switched to "Sweep" but the sweeping rate was set to zero so that the current remained constant. The probe was then moved to the "central" position of the pole gap. The probe then sensed a field different from the dialed value, so that the error signal caused the galvanometer needle to deviate from its balanced position. The dials were then reset

to achieve a zero error signal on the galvanometer. This setting on the dials was the field intensity at the "central" position corresponding to the initial setting of the field intensity at the "outside" position of the probe. Then this procedure was repeated for a different initial setting of the dials. The calibration for the fields B_{outside} and B_{central} is shown in Table II-2. The maximum field obtainable at the central position of the pole gap was about 3.2 W/m^2 with the current of 205 amp.

3224. MEASURING EQUIPMENT

The specimen current was supplied by two 12 V lead-acid batteries in parallel and measured by the voltage drop across a 1-ohm standard resistor (Leads and Northrup) with a Rubicon type K potentiometer. The voltage developed between the resistance probes or the Hall probes (Figure II-1) was amplified by an Astrodata Model 120 nanovolt amplifier and then measured with a Hewlett-Packard 3440A digital voltmeter (to which a Model 3443A high gain autorange unit was installed). The gain of this nanovolt amplifier could be varied in 10 steps from 200 to 2 million.

Since relative change in resistance due to the magnetic field was small, the magnetoresistance of the specimen deduced from the direct readings of the variation of the resistance with the magnetic field would be very inaccurate. Due to the asymmetric positions of the Hall probes, the voltage developed

Table II-2 Calibration of magnetic field (W/m^2).

B_{outside}	B_{central}	B_{outside}	B_{central}
3.0000	3.1976	1.5500	1.6934
2.9000	3.1009	1.5000	1.6382
2.8000	3.0043	1.4500	1.5831
2.7000	2.9076	1.4000	1.5281
2.6000	2.8105	1.3500	1.4734
2.5000	2.7126	1.3000	1.4186
2.4000	2.6140	1.2500	1.3640
2.3000	2.5148	1.2000	1.3093
2.2000	2.4146	1.1500	1.2547
2.1000	2.3121	1.1000	1.2001
2.0000	2.2031	1.0500	1.1455
1.9500	2.1451	1.0000	1.0909
1.9000	2.0870	0.9000	0.9818
1.8500	2.0294	0.8000	0.8727
1.8000	1.9723	0.7000	0.7636
1.7500	1.9159	0.6000	0.6545
1.7000	1.8598	0.5000	0.5454
1.6500	1.8041	0.4000	0.4363
1.6000	1.7487	0.3000	0.3272

across them at zero-field was in fact the contribution from the resistance of the specimen. Therefore, a back-off system was used to obtain the "net" magnetoresistance and Hall voltages. The readings of the zero-field resistance and Hall voltages were nulled by opposing to them appropriate voltages supplied by 12 V lead-acid batteries and variable resistors. Hence the change in voltage across these resistance or Hall probes was amplified and then displayed on the digital voltmeter. The circuit diagram is shown in Figure II-5. All wires from the specimen to the measuring and control panel were shielded, and the switch was a double-deck rotary type with silver contacts, in order to minimize various sources of noise and pickup.

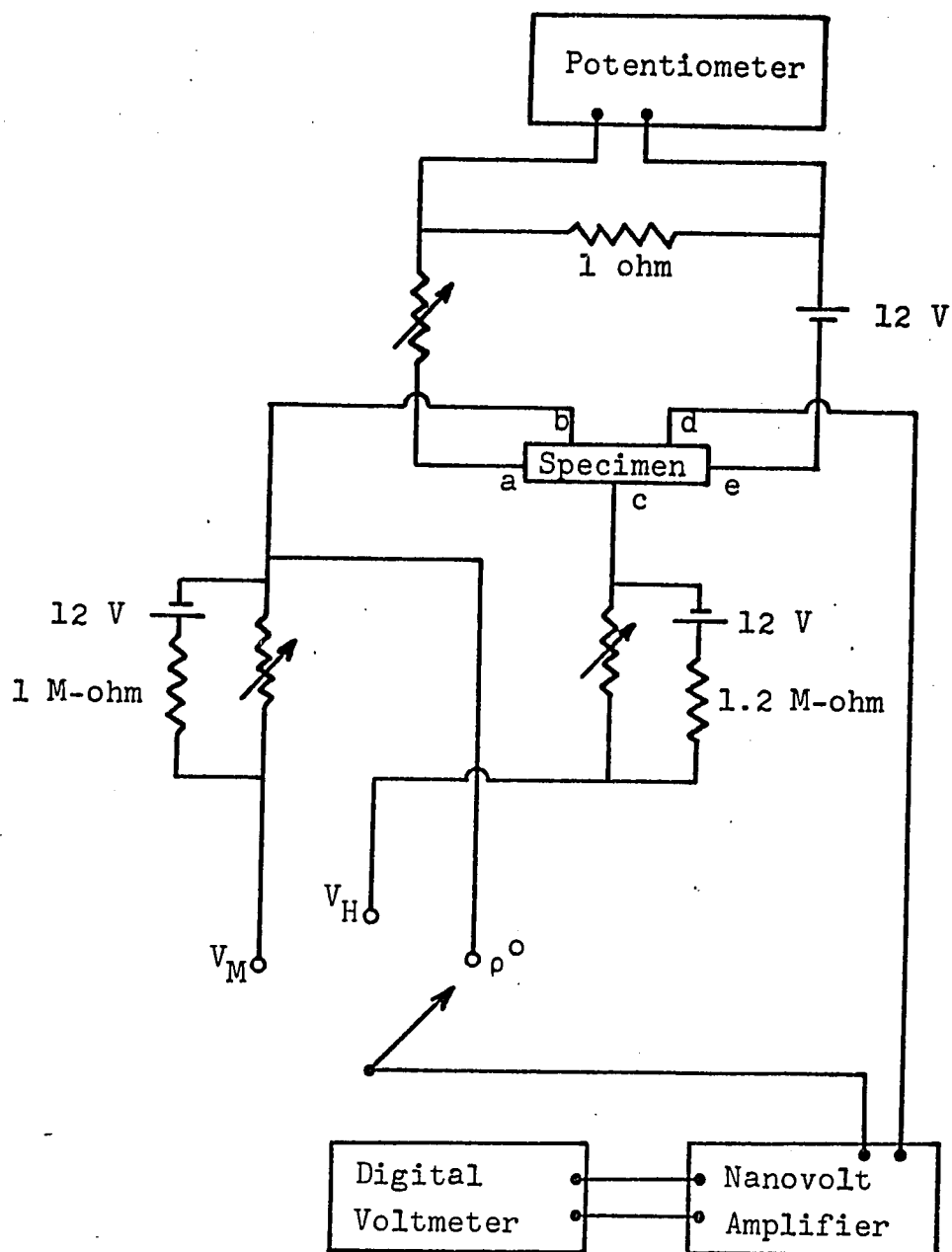


Figure II-5 Circuit for Hall effect and magnetoresistance measurements.

323. PROCEDURE OF MEASUREMENTS

The specimen holder with the mounted specimen was inserted into the cryostat with the long side of the specimen parallel to the faces of the two poles of the electro-magnet. The batteries for specimen current and for back-off voltages were then connected and allowed to stabilize for about 5 hours prior to any measurements. The specimen chamber was evacuated and then filled with helium exchange gas to a pressure of approximately 710 mm Hg. The specimen current was adjusted to a value ~ 100 ma.

For measurements at 4.2°K , the two refrigerant tanks were initially filled with liquid nitrogen. After thermal equilibrium was established between the refrigerant tanks and the specimen chamber, the liquid nitrogen in the lower tank was blown off by pressurized air and then liquid helium was siphoned into this tank.

The magnetic field was turned on in the "forward" direction and set at "zero" intensity. The dials on the decade resistance box coupled with the back-off batteries were adjusted to give nearly null resistance and Hall voltages of the specimen. Then the field was set and regulated at various intensities. The corresponding magnetoresistance and Hall voltages were taken from the digital voltmeter readings. Corrections for these nearly null voltages at zero-field were also made. In the measurements, the field at the position of the field sensing probe was set in the range 0.30 to 3.00 W/m^2 in intervals of

0.05 or 0.10 W/m². The specimen current was also accurately measured with the potentiometer and it varied less than 5 parts in 10⁵ during the measurement.

The process was then repeated with the magnetic field direction reversed. The observed Hall voltage could involve the contribution from the magnetoresistance. Since the Hall voltage reversed with the magnetic field but the magnetoresistance did not, any contribution of the latter to the former would be cancelled by taking the average of the voltages for the two field directions.

Finally, the back-off batteries were disconnected and the zero-field resistance voltage was taken.

33. DATA ANALYSIS AND RESULTS

331. ANALYSIS BASED ON THE TWO-BAND MODEL

The resistivity of the specimen can be calculated from the simple relation

$$\rho^0 = \frac{t w}{l} \cdot \frac{V^0}{I} \quad (\text{II-82})$$

where t = specimen thickness

w = specimen width

l = separation between the two resistance probes on the specimen

V^0 = voltage across the resistance probes in zero magnetic field

I = specimen current

The magnetoresistivity $\Delta\rho$ is therefore given by

$$\Delta\rho = \frac{t w}{l} \cdot \frac{V_M}{I} \quad (\text{II-83})$$

where V_M is the average of the magnetoresistance voltages V_{M+} and V_{M-} with the forward and reversed magnetic field directions.

The Hall voltage V_H was obtained from the average values of the magnitudes of V_{H+} and V_{H-} in both field directions in order to cancel the offset voltage due to the asymmetry of the Hall probes and the voltage due to magnetoresistance. Hall coefficient R can be conveniently written as

$$R = \frac{t V_H}{I B} \quad (\text{II-84})$$

from its definition $R = \epsilon_y / (J_x B)$.

The magnetoresistivity was measured directly from the readings of the 4-figure digital voltmeter with the zero-field resistivity voltage backed-off to zero. Therefore the variation of $\Delta\rho(B)$ was very accurately obtained. A typical example is shown in Figure II-6. However the change of Hall coefficient ΔR due to the magnetic field could not be measured directly with a similar arrangement, and thus the value of ΔR at each field intensity B must be taken from the difference of two separate measurements R and R^0 . Usually the value of R was quite close to that of R^0 , i.e. $(R-R^0)/R^0 \sim$ a few percents at the most, with the field intensity B up to 3.2 W/m^2 . Therefore the value of ΔR at each field intensity, and the variation of $\Delta R(B)$ could not be accurately determined.

In the present investigation, the data were analyzed with the two-band model, and hence only the low-field Hall coefficient was required. The magnetoresistance data were presented as a plot of $\rho^0/\Delta\rho$ versus B^{-2} . As shown in Figures II-7 and II-8, the experimental results on both In_2Se_3 - and In_2Te_3 -doped InAs systems satisfied the linear relation given by equation (II-36). The graph of $\rho^0/\Delta\rho$ versus B^{-2} for each specimen was fitted to a straight line by a least square fit, values of slope s and intercept u were determined, and hence values of σ_0 , σ_1 , R_0 and R_1 calculated from equations (II-39) - (II-42). Consequently, values of n_0 , n_1/F_1 , μ_0 and $\mu_1 F_1$ were obtained from equations (II-45) and (II-46). The

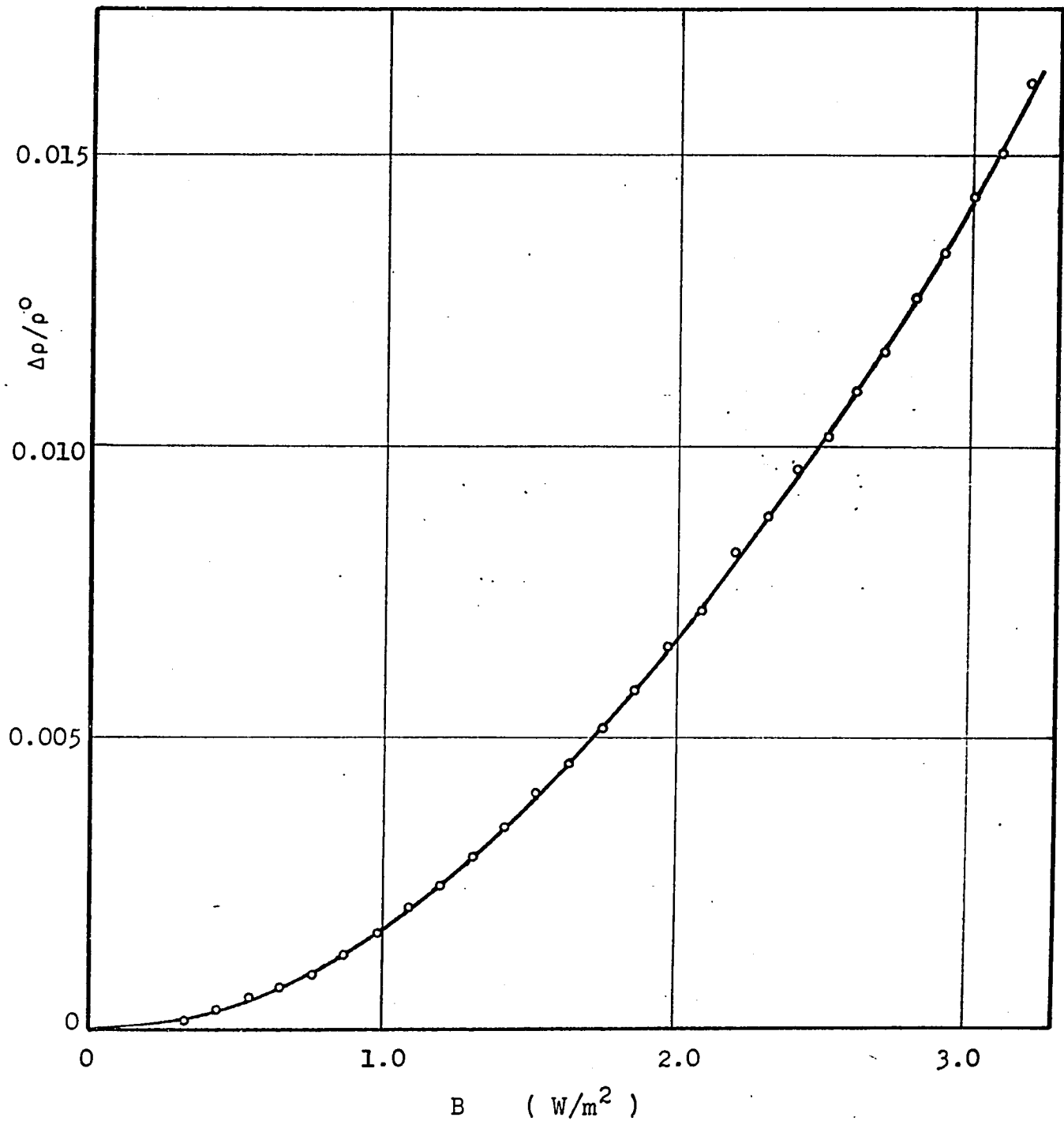


Figure II-6 Variation of magnetoresistivity with magnetic field of a typical specimen, at 4.2°K . (Specimen B3-1).

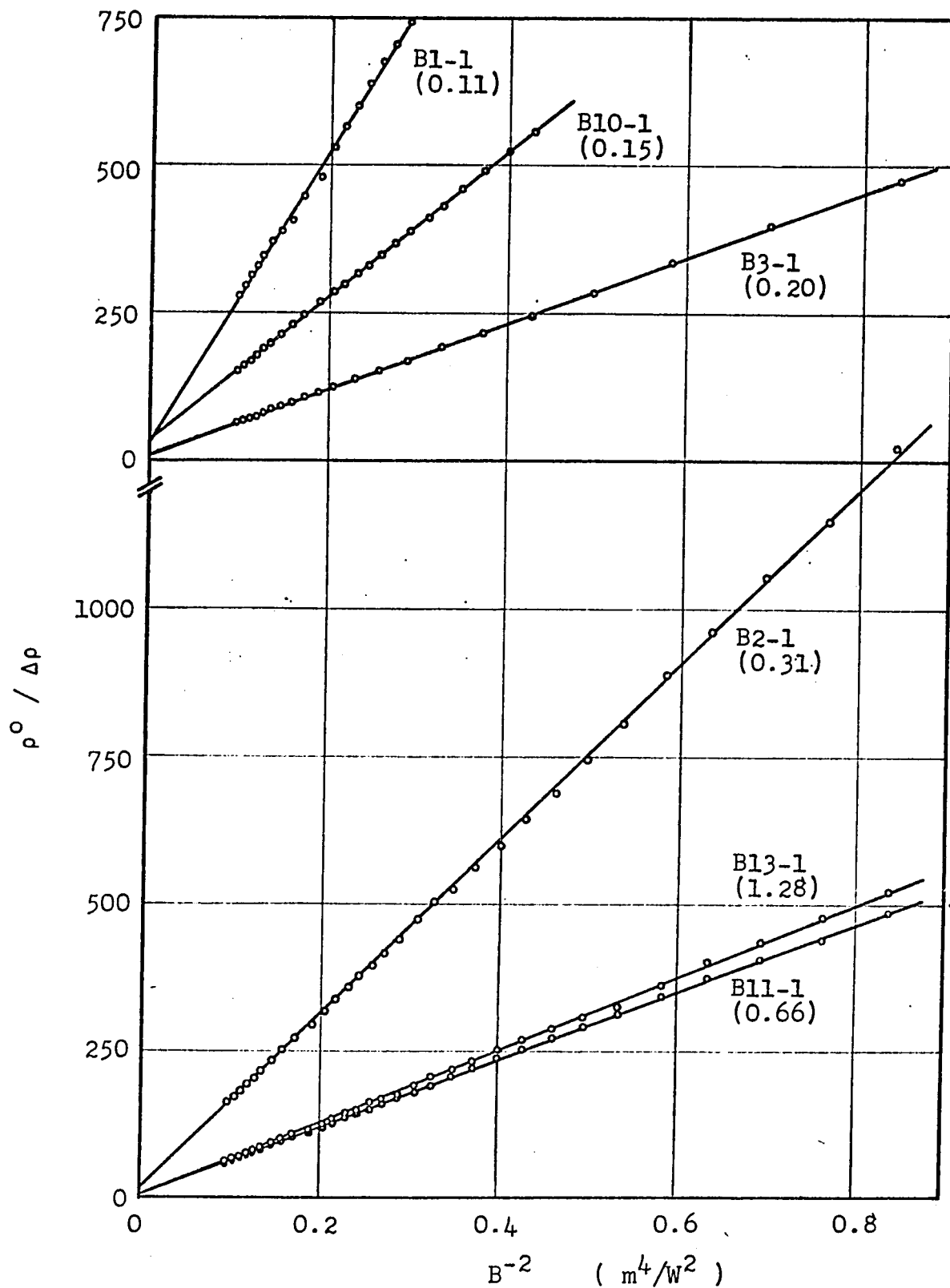


Figure II-7 Variation of $\rho^0 / \Delta\rho$ with B^{-2} at $4.2^\circ K$ for In_2Se_3 -doped InAs specimens. (Value in brackets indicates atomic % selenium in specimen.)

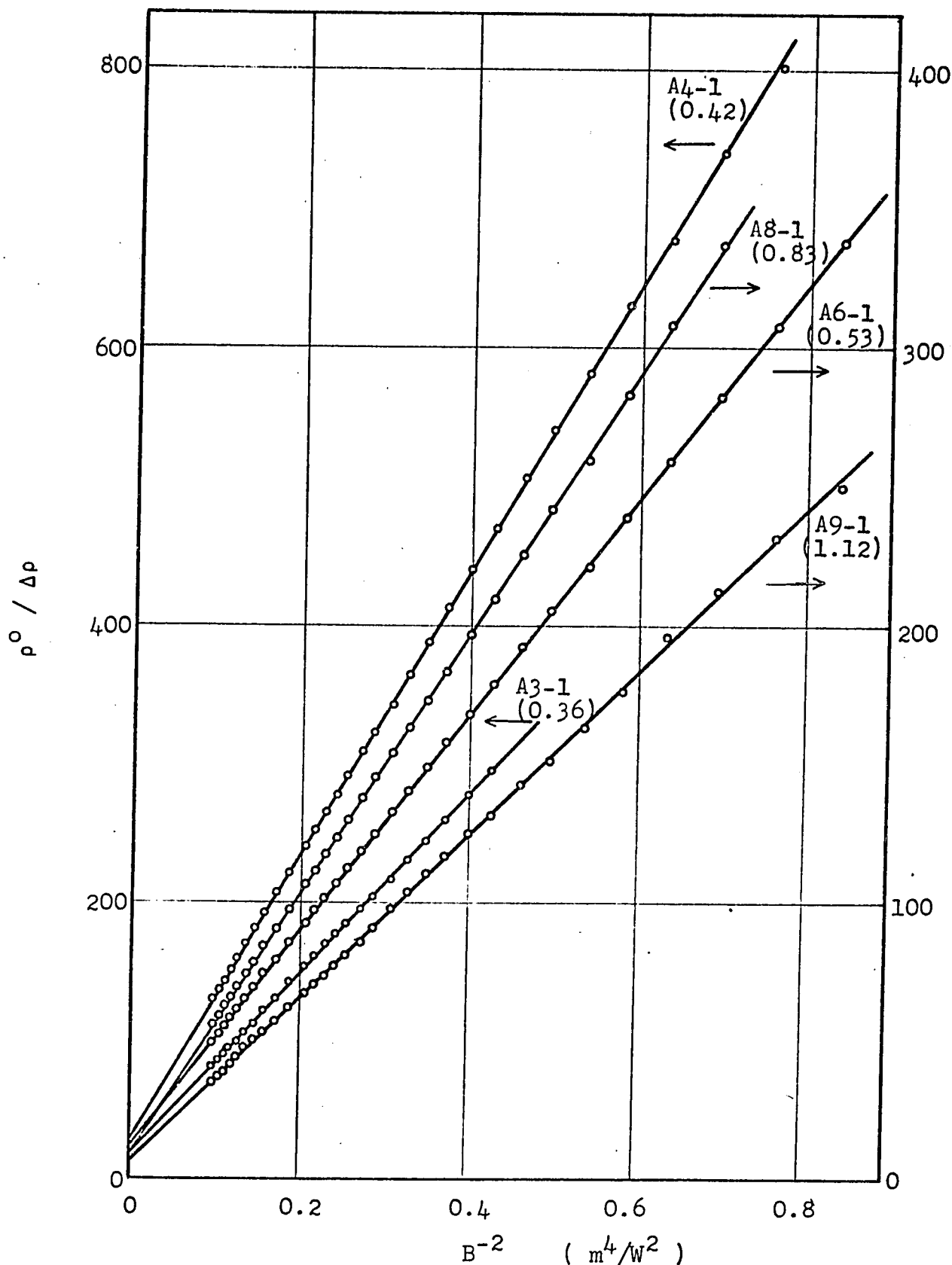


Figure II-8 Variation of $\rho^0 / \Delta\rho$ with B^{-2} at 4.2°K for In_2Te_3 -doped InAs specimens. (Value in brackets indicates atomic % tellurium in specimen.)

results of the analysis are listed in Table II-3.

In order to obtain the variation of carrier concentration over a wider range of impurity content, room temperature Hall measurements were also made on some purer specimens. The results together with those by Pamplin (60Pl) and Keating (61K1) from the consideration of a single band are listed in Table II-4. It is seen that, at the onset of the two-band conduction, the results of the electron concentrations obtained from the single band analysis were in good agreement with the values derived from the two-band model. However, at higher selenium or tellurium percentage, the single band model failed to yield the actual properties of the conduction bands.

Although the value of F_1 was not accurately known, its probable value must be in the range 0.8-0.9, and hence the values of n_1/F_1 and $\mu_1 F_1$ gave a good indication of the variation of n_1 and μ_1 with y . In order to show the form of the variation of n_1 and hence n_0+n_1 with y , a value has been assumed here of $F_1 = 0.82$, the value in the cases of germanium and GaSb (Piller 64Pl). The variation of n_0 , n_1 , n_0+n_1 , μ_0 and $\mu_1 F_1$ with y for both the In_2Se_3 - and In_2Te_3 -doped specimens is shown in Figures II-9 and II-10.

It is seen that as y increases, n_0 rapidly increases initially as the (000) band minimum is filled with electrons from donor selenium or tellurium. As the two-band conduction starts, n_1 increases gradually to high values with increasing y . This indicates that the available states of the $\langle 111 \rangle$ conduction

Table II-3 Results of Hall effect and magnetoresistance measurements on In_2Se_3 - and In_2Te_3 -doped InAs specimens at 4.2°K.

System	Specimen label	y (atom.%)	$-R^0 (10^{-7} \text{ m}^3/\text{Coul})$	$\rho (10^{-6} \text{ ohm.m})$	$\sqrt{s} (\text{W/m}^2)$	$\sqrt{u}$	$n_0 (10^{25} \text{ m}^{-3})$	$n_1/F_1 (10^{25} \text{ m}^{-3})$	$\mu_{O2} (m^2/\text{Vsec})$	$\mu_{L1} (m^2/\text{Vsec})$
In_2Se_3 -doped InAs	B1-1	0.11	1.754	0.729	48.07	7.24	3.332	0.271	0.245	0.146
	B1-2	0.11	1.702	0.754	48.90	7.35	3.359	0.356	0.231	0.145
	B10-1	0.15	1.538	0.720	36.19	4.83	3.563	0.607	0.222	0.125
	B10-2	0.15	1.521	0.730	35.34	5.15	3.393	0.822	0.219	0.135
	B3-1	0.20	1.461	0.763	23.78	2.64	3.307	1.354	0.209	0.093
	B9-1	0.28	1.254	0.939	68.74	8.28	3.273	1.770	0.143	0.111
	B2-1	0.31	1.137	0.901	38.56	3.72	3.663	2.152	0.141	0.082
	B2-2	0.31	1.136	0.897	38.63	3.75	3.686	2.127	0.142	0.082
	B11-1	0.66	1.155	1.126	24.02	1.44	3.151	4.367	0.128	0.035
	B13-1	1.28	1.135	1.302	24.76	1.75	2.394	5.089	0.120	0.038
	B13-2	1.28	1.135	1.290	24.84	1.53	2.715	5.140	0.117	0.032
In_2Te_3 -doped InAs	A11-1	0.12	2.900	0.742			2.153		0.385	
	A3-1	0.36	1.858	0.655	25.57	4.32	2.944	0.526	0.296	0.157
	A4-1	0.42	1.790	0.632	32.08	5.47	3.180	0.380	0.291	0.163
	A6-1	0.53	2.241	0.774	19.70	3.58	2.252	0.677	0.310	0.161
	A8-1	0.83	1.773	0.788	21.63	3.20	2.636	1.126	0.247	0.110
	A8-2	0.83	1.847	0.787	22.02	3.26	2.622	0.981	0.254	0.128
	A9-1	1.12	1.759	0.914	17.15	2.59	1.948	2.069	0.234	0.110

Table II-4 Room temperature results of Hall effect measurements on In_2Se_3 - and In_2Te_3 -doped specimens of the present work, and Keating's (61K1) and Pamplin's (60P1) Hall effect and resistivity results.

System	Specimen Label	y (atom.%)	n_0 (m^{-3})	μ_0 ($\text{m}^2/\text{V}.\text{sec}$)
In_2Se_3 -doped InAs	B85-1	0.002	5.1×10^{23}	
	B84-1	0.005	1.6×10^{24}	
	B86-1	0.009	2.9×10^{24}	
	B21-1	0.012	4.3×10^{24}	
	B21-2	0.012	4.7×10^{24}	
	B4-1	0.018	5.9×10^{24}	
	B4-2	0.018	6.0×10^{24}	
	B20-1	0.032	1.2×10^{25}	
	B6-1	0.048	1.6×10^{25}	
	B18-1	0.052	1.8×10^{25}	
	B17-1	0.115	3.5×10^{25}	
	Keating (61K1)	0.014	5.6×10^{24}	0.445
		0.028	1.2×10^{25}	0.340
		0.055	2.5×10^{25}	0.235
		0.17	4.3×10^{25}	0.190
		0.26	5.8×10^{25}	0.145
		0.26	5.3×10^{25}	0.120
		0.55	5.4×10^{25}	0.086
		1.00	5.9×10^{25}	0.076
In_2Te_3 -doped InAs	A1-1	0.11	1.85×10^{25}	
	A11-1	0.12	2.15×10^{25}	
	A10-1	0.20	3.16×10^{25}	
	Pamplin (60P1)	0.035	3.7×10^{24}	0.97
		0.05	2.4×10^{25}	0.38
		0.1	2.2×10^{25}	0.41
		0.2	2.6×10^{25}	0.40
		0.35	3.1×10^{25}	0.22
		0.38	4.0×10^{25}	0.28
		0.6	4.0×10^{25}	0.25
		1.0	4.0×10^{25}	0.18

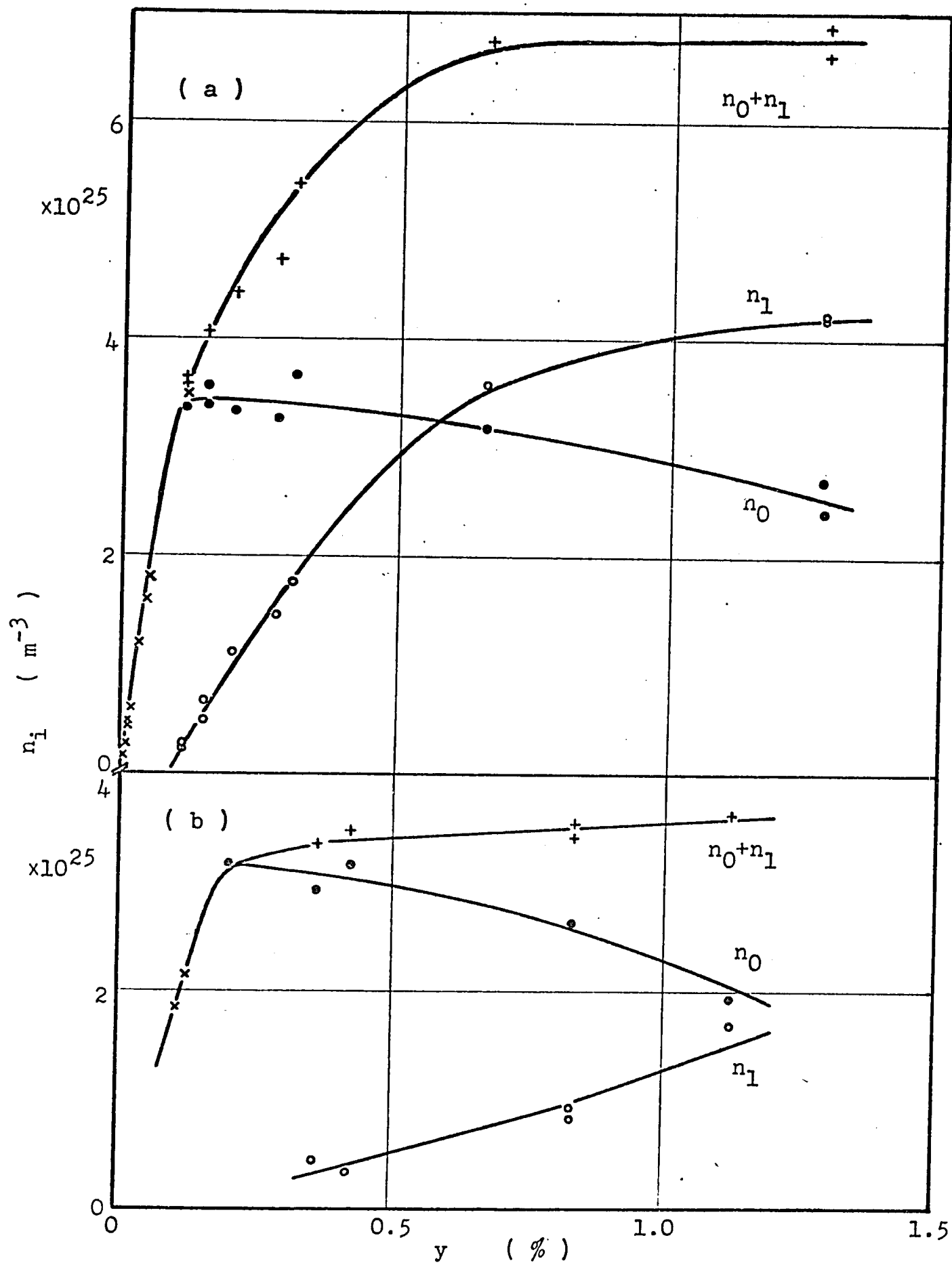


Figure II-9 Variation of electron concentration n_i with atomic % of selenium or tellurium y at $4.2^\circ K$: (a) In_2Se_3 -doped, (b) In_2Te_3 -doped samples. (x: room temperature values.)

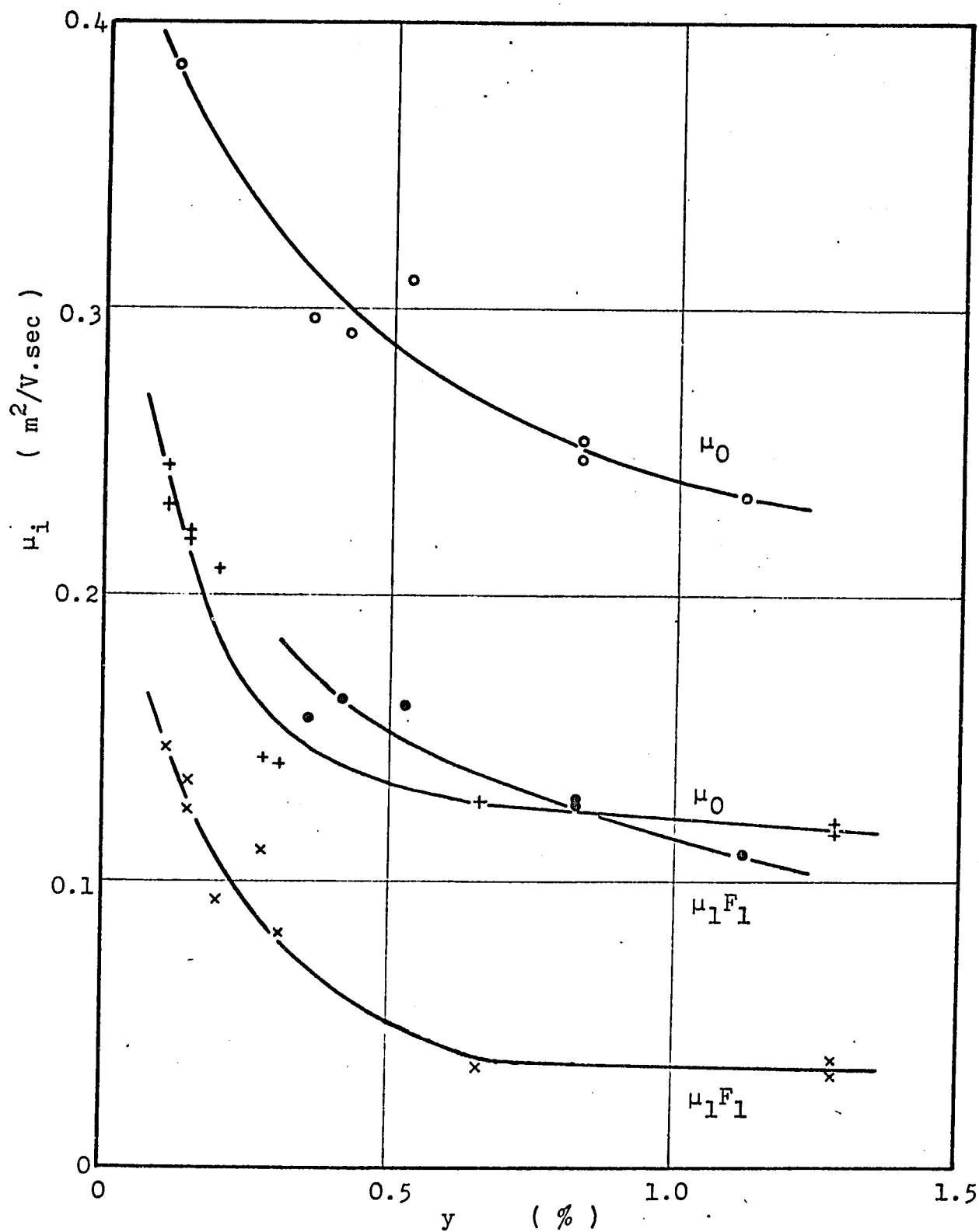


Figure II-10 Variation of mobility μ_i with atomic % of selenium or tellurium y at 4.2°K : + and x, In_2Se_3 -doped; o and •, In_2Te_3 -doped samples.

band minima are gradually filled up with electrons. For a small range of y after the onset of the two-band conduction, n_0 stays fairly constant. However, when $y > 0.3$ atomic %, a noticeable decrease in n_0 is observed. The mobilities of the carriers decrease with increasing y , and this is compatible with the results obtained by Pamplin (60Pl) and Keating (61K1) who considered only one type of carriers. The mobility values measured by these authors are effectively the weighted average of the mobilities of the two types of carriers in the conduction bands. The decrease in mobility can be explained partly by the increasing number of scattering centers and vacancies on lattice sites as y increases.

Due to the high reliability and stability of the magnetic field and the measuring equipment, the accuracy of the Hall effect and magnetoresistance measurements must practically depend on the specimens only, such as the homogeneity of the materials and the geometry of the specimens. The materials were expected to be reasonably homogeneous, since reproducible results were obtainable on different specimens cut from the same ingot, and the variations of the parameters R^0 , ρ^0 , etc., with the impurity content were reasonably smooth. The calculations of ρ^0 , $\Delta\rho$ and R^0 involved the dimensions of the specimen. Since each specimen was carefully cut and lapped into parallelepiped shape, the uniformity of the thickness and width was always better than 0.5 %. However, due to the finite width of the electrical contacts to the specimen,

0.1-0.2 mm, the error involved in l was about 2 %. Hence in all cases, the errors involved in R^0 , ρ^0 and $\Delta\rho$ were approximately: $\Delta(R^0)/R^0 = 1 \%$; $\Delta(\rho^0)/(\rho^0)$, $\Delta(\Delta\rho)/(\Delta\rho) = 3 \%$, which were slightly overestimated to account for other possible source of errors.

In the two-band analysis, the ratio $\rho^0/\Delta\rho$ was used, and hence the errors in the dimensions of the specimen had no effect on the determination of slope and intercept (s and u) of the predicted linear relation of $\rho^0/\Delta\rho$ versus B^{-2} . For all specimens investigated here, this linear relation was justified and $\Delta(s)/(s)$ was always less than 2 %. However, the intercept was relatively small and a value of $\Delta(u)/(u) = 10 \%$ was also possible in the worst case. Since in the calculation of the parameters of the individual bands as given in equations (II-39) - (II-42), the quantities $\sqrt{s}$ and $\sqrt{u}$ were used, the errors introduced by s and u would then be reduced appreciably. With all these uncertainties taken into consideration, the error involved in the parameters n_0 , n_1/F_1 , μ_0 and $\mu_1 F_1$, for each specimen, were still within 7 %.

From the above considerations, the results from the analysis of the experimental data based on the two-band model were reasonably self-consistent. However, these results would be more reliable if the assumption, in the two-band model, of neglecting the contribution to magnetoresistance due to the effect of anisotropy of the $\langle 111 \rangle$ band could be justified. Such an attempt will be presented in the following section.

332. VALIDITY OF THE TWO-BAND MODEL

The materials investigated in this work are highly degenerate, and hence the effect due to variable degeneracy of the carriers in each band does not contribute to the magnetoresistance at helium temperature as mentioned earlier in Sections II-312 and II-313.

An extra contribution to magnetoresistivity due to anisotropy of the $\langle 111 \rangle$ conduction band has been completely ignored in the two-band model, and will now be considered. In analyzing the magnetoresistivity data of heavily-doped GaSb and InSb by the two-band model, Harland (65H1) and Aubin (69A1) have shown that the contribution due to anisotropy is negligible. It is expected that this would also apply to the analysis on heavily-doped InAs in the present work.

When electrons are present in both (000) and $\langle 111 \rangle$ bands, the total conductivity must be due to contributions from both types of electrons, even in the absence of the two-band effect. In this case, the total conductivity is the superposition of the conductivities from the individual bands. Since the (000) conduction band is isotropic, the magnetic field dependent part of conductivity must originate from the anisotropic $\langle 111 \rangle$ band alone. Then

$$\sigma(B) = \sigma_0 + \sigma_1(B) \quad (\text{II-85})$$

In an equivalent expression, the total resistivity $\rho(B)$ takes the form

$$\frac{1}{\rho(B)} = \frac{1}{\rho_0} + \frac{1}{\rho_1(B)}$$

$$\text{or } \rho(B) = \frac{\rho_0 \rho_1(B)}{\rho_0 + \rho_1(B)} \quad (\text{II-86})$$

By representing the magnetic field dependent resistivities $\rho(B)$ and $\rho_1(B)$ in terms of their zero-field resistivities and magnetoresistivities,

$$\begin{aligned} \rho(B) &= \rho^0 + \Delta\rho \\ \rho_1(B) &= \rho_1^0 + \Delta\rho_1 \end{aligned} \quad (\text{II-87})$$

the total magnetoresistivity $\Delta\rho$ due to anisotropy can be expressed as

$$\begin{aligned} \left(\frac{\Delta\rho}{\rho^0}\right)_{\text{anisotropy}} &= \frac{\rho(B)}{\rho_1(B)} \cdot \frac{\Delta\rho_1}{\rho_1^0} \\ &\approx \frac{\sigma_1}{\sigma_0 + \sigma_1} \cdot \frac{\Delta\rho_1}{\rho_1^0} \end{aligned} \quad (\text{II-88})$$

As given by equations (II-24) and (II-25),

$$\frac{\Delta\rho_1}{\rho_1^0} = H_1 (R_1 \sigma_1 B)^2 \quad (\text{II-89})$$

$$\text{where } H_1 = \frac{(K_1-1)^2}{3K_1(K_1+2)} [1 - (il+jm+kn)^2 + (i^2l^2+j^2m^2+k^2n^2) \cdot \frac{2(2K_1+1)}{(K_1+2)}]$$

(II-90)

Then

$$\left(\frac{\Delta\rho}{\rho}\right)_{\text{anisotropy}} = \frac{H_1}{G+1} (R_1 \sigma_1 B)^2 \quad (\text{II-91})$$

where $G = \sigma_0/\sigma_1$.

In order that the contribution to magnetoresistivity from the effects of two-band conduction and of anisotropy can be compared, the expression in $(\Delta\rho)_{\text{two-band}}$ in equation (II-34) must be conveniently rearranged to a form similar to equation (II-91). By using the ratio $L = R_0/R_1$ as well as $G = \sigma_0/\sigma_1$, equation (II-34) may be written, to first order in B^2 , as

$$\left(\frac{\Delta\rho}{\rho}\right)_{\text{two-band}} \approx \left[\frac{G (GL-1)^2}{(G+1)^2} \right] (R_1 \sigma_1 B)^2 \quad (\text{II-92})$$

Hence equations (II-91) and (II-92) only differ by the constant factors $H_1/(G+1)$ and $G(GL-1)^2/(G+1)^2$. A comparison can be made between the two contributions when the constants H_1 , G and L are known. The calculation of H_1 is based on the parameter K_1 which is still not determined for InAs. However, by analogy with the cases of germanium and GaSb which have the value of $K_1 = 8.6$ (Piller 64Pl), it is expected that the value for InAs would be in the range 4-10. The comparison of the effects of anisotropy and of two-band conduction on two typical specimens is shown in the following: (Here, the values of G and L are obtained from the two-band results given in the preceding section. The specimen current is in the x-direction and magnetic field in the z-direction.)

Specimen label	L	G	$\Delta\rho/\rho^0$ anisotropy	$\Delta\rho/\rho^0$ two-band
B3-1	0.4	5.6	$0.02-0.03(R_1\sigma_1B)^2$	$0.20(R_1\sigma_1B)^2$
B11-1	1.4	2.4	$0.04-0.06(R_1\sigma_1B)^2$	$1.40(R_1\sigma_1B)^2$

The two-band effect usually contributes over 90 % of the total magnetoresistivity, while the effect due to the anisotropy of the $\langle 111 \rangle$ band contributes about 10 % or less. If $(\Delta\rho)_{\text{anisotropy}}/(\Delta\rho)_{\text{total}} = \text{constant}$, over the whole range of magnetic field in this work, the correction for $(\Delta\rho)_{\text{two-band}}$ would lead to same percentage change in u and s . In the calculation of σ_0 , σ_1 , R_0 and R_1 from equations (II-39) - (II-42), the quantities $\sqrt{u}$ and $\sqrt{s}$ are used, and this would reduce the uncertainty in the results introduced by u and s . Even a contribution of 15 % to magnetoresistance by anisotropy would result in the errors involved in σ_0 , σ_1 , R_0 and R_1 by less than 5 %. Therefore the model for two-band conduction is reasonably valid.

333. SEPARATION OF THE (000) AND $\langle 111 \rangle$ CONDUCTION BAND MINIMA

If the shape of the conduction band were unaffected by the amount of selenium or tellurium content in the compound, both n_0 and n_1 would increase with increasing y . However the experimental results show that n_0 stops increasing as electrons start to enter the $\langle 111 \rangle$ conduction band minima. This can be explained by the high density of states of the $\langle 111 \rangle$ band. The noticeable decrease in n_0 with increasing y for $y > 0.3$ atomic % tends to indicate the effect of heavy doping on the band structure of this compound. If ΔE is the energy separation of the (000) and $\langle 111 \rangle$ minima, and E_{F0} and E_{F1} are the values of the Fermi energy measured from the bottom of the (000) and $\langle 111 \rangle$ bands respectively,

$$\Delta E = E_{F0} - E_{F1} \quad (\text{II-93})$$

The decrease in n_0 and increase in n_1 with increasing y indicates the decrease of E_{F0} and increase of E_{F1} with increasing y . This consequently leads to the conclusion that ΔE decreases with increasing impurity content.

In order to analyze such an effect, some $(E, \hbar)$ or (E, n) relations for the two bands concerned must be assumed. Here the Kane model is applied to the (000) band. As given in equation (II-4), the $(E, \hbar)$ relation takes the form

$$(E - a\hbar^2)(E + E_0 - a\hbar^2)(E + E_0 + \Delta_0 - a\hbar^2) - a\hbar^2 P^2 (E + E_0 + \frac{2}{3}\Delta_0 - a\hbar^2) = 0 \quad (\text{II-93})$$

The use of E_o^* rather than E_o in this equation as pointed out by Ehrenreich (57E1) is no problem here, since at helium temperature, the effect due to lattice vibrations is negligible, and hence $E_o = E_o^*$. With complete degeneracy and spherical constant-energy surfaces, the value of k at the Fermi energy is given by (Smith et al 59S2)

$$k_{FO}^2 = (3 \pi^2 n_o)^{2/3} \quad (II-94)$$

Upon substituting this expression into equation (II-93), an (E_{FO}, n_o) relation is obtained:

$$\begin{aligned} & (E_{FO} - b n_o^{2/3}) (E_{FO} + E_o - b n_o^{2/3}) (E_{FO} + E_o + \Delta_o - b n_o^{2/3}) - \\ & - b n_o^{2/3} p^2 (E_{FO} + E_o + \frac{2}{3} \Delta_o - b n_o^{2/3}) = 0 \end{aligned} \quad (II-95)$$

$$\text{where } b = a(3\pi^2)^{2/3} = (3\pi^2)^{2/3} \frac{\hbar^2}{2m_e} \quad (II-96)$$

As for the $\langle 111 \rangle$ band, due to the high density of states of the band, a parabolic form of the (E, k) relation can be used. At present, no detailed form of the (E, k) relation of this band is available. For a parabolic band, the Fermi energy is

$$E_{F1} = \frac{\hbar^2 k_{F1}^2}{2 m_1^*} \quad (II-97)$$

where m_1^* is the density-of-states effective mass independent of n_1 , and k_{F1} the magnitude of the wave vector at the Fermi

energy E_{F1} . An (E_{F1}, n_1) relation can be obtained by assuming

$$\kappa_{F1}^2 = \left(\frac{3 \pi^2 n_1}{M_1} \right)^{2/3} \quad (\text{II-98})$$

in analogy with the (κ_{F0}, n_0) relation. Here the multiplicity factor M_1 is introduced to account for the four equivalent conduction band minima at $\langle 111 \rangle$, i.e. $M_1 = 4$. Then

$$\begin{aligned} E_{F1} &= \left(\frac{3}{4} \pi^2 n_1 \right)^{2/3} \frac{\hbar^2}{2 m_1^*} \\ &= \left(\frac{3 \pi^2 n_1}{4 F_1} \right)^{2/3} \frac{\hbar^2}{2 (m_1^*/F_1)^{2/3}} \end{aligned} \quad (\text{II-99})$$

From the results obtained in the magnetoresistance work alone, it is very difficult to determine whether the decrease in ΔE is due to the presence of the total impurity content y or due to the total ionized impurity concentration $n_0 + n_1$. Hence both cases are considered here. By assuming a linear variation of ΔE with y or with $n_0 + n_1$,

$$\Delta E = E_{01} (1 - C z) \quad (\text{II-100})$$

where E_{01} is the energy separation of the two conduction band minima in pure InAs, C is a constant (labeled C_{Se} and C_{Te} for In_2Se_3 - and In_2Te_3 -doped systems respectively) and z represents y or $(n_0 + n_1)$. As will be seen in the following section, results of infrared absorption measurements on these materials indicate

that the latter explanation (that the decrease in ΔE is due to the ionized impurities) is more appropriate.

In order for the value of ΔE to change, the position of the (000) or $\langle 111 \rangle$ minima or both must change relative to the highest valence band. This can affect the value of E_o in equation (II-95). Two limiting cases are considered here. If the change in ΔE is solely due to movement of the $\langle 111 \rangle$ minima relative to the valence band, E_o will remain constant independent of the presence of the impurity or ionized impurity content. If, however, movement of the (000) minimum only occurs, then E_o will vary with y or $(n_o + n_1)$, and

$$E_o = E_{oo} + E_{o1} C z \quad (\text{II-101})$$

where E_{oo} is the intrinsic band gap at (000) for pure InAs.

As judged from the relative positions of selenium, tellurium, and arsenic in the periodic table, it could be predicted that the doping of In_2Se_3 had less effect on the band structure of InAs than the doping of In_2Te_3 . Furthermore, since more specimens were used in the In_2Se_3 -doped system than the In_2Te_3 -doped system at the start of the two-band conduction, the two-band results of (n_o, y) and $(n_1/F_1, y)$ relations of the In_2Se_3 -doped specimens were more useful for the calculation of the value of E_{o1} , the separation of the (000) and $\langle 111 \rangle$

minima of pure InAs. At the onset of two-band conduction, i.e. $E_{FO} = \Delta E$, $n_1 = 0$ and $E_{F1} = 0$, ΔE was obtained by solving equation (II-95) for E_{FO} with values of $n_0 = 3.4 \times 10^{25} \text{ m}^{-3}$, $E_{oo} = 0.425 \text{ eV}$, $\Delta_o = 0.43 \text{ eV}$ (Madelung 64ML) and $P^2 = 20 \text{ eV}$ (Pidgeon et al 67Pl, Summers and Smith 67S5). Since, when $n_1 = 0$, the selenium percentage was very low, the term $E_{O1}C_{Se}z$ could be expected to be very small as compared to ΔE . Here a value of

$$E_{O1} = 0.70 \pm 0.03 \text{ eV}$$

was obtained. The error in this result was introduced by the scatter of the experimental value of n_0 and by the correction term $E_{O1}C_{Se}z$ involved in the analysis.

In the calculation of the constants C_{Se} and C_{Te} in equation (II-100) by assuming linear variation of ΔE with y , the experimental values of (n_0, y) and $(n_1/F_1, y)$ for both systems were correlated with equations (II-95), (II-99) and (II-100). The calculations were carried out for two cases of E_o assumed independent of y , and E_o dependent on y as given by equation (II-101). It was found that the values of C_{Se} and C_{Te} for these two cases differed only within the limits of the experimental error and hence the question of whether the (000), $\langle 111 \rangle$ minima or both move relative to the valence band is not important in determining these constants. The values obtained for these parameters are:

$$C_{\text{Se}} = 0.18 \pm 0.03 \text{ /atomic \% selenium}$$

$$E_{\text{Ol}} C_{\text{Se}} = 0.13 \pm 0.03 \text{ eV/atomic \% selenium}$$

$$C_{\text{Te}} = 0.24 \pm 0.04 \text{ /atomic \% tellurium}$$

$$E_{\text{Ol}} C_{\text{Te}} = 0.17 \pm 0.03 \text{ eV/atomic \% tellurium}$$

The errors in the above calculations were attributed to the experimental errors as well as the uncertainty involved in the values of E_{F1} . Although E_{F1} could not be accurately determined without a given value of $m_1^*/F_1^{2/3}$, the uncertainty involved in ΔE was within 0.01 to 0.04 eV for all specimens with reasonable values of $m_1^* > 0.2m_e$ and $F_1 = 0.82$. E_{F1} was in all cases considerably smaller than E_{F0} and ΔE , and hence the data were practically not sensitive to the value of $m_1^*/F_1^{2/3}$. Thus no accurate value of this parameter could be determined here.

In the case that linear variation of ΔE with $(n_0 + n_1)$ was assumed, the experimental results in correlation with equations (II-95), (II-99) and (II-100) could also be analyzed in the same way as above. The results of the analysis of the In_2Se_3 -doped system are

$$C_{\text{Se}} = (1.6 \pm 0.4) \times 10^{-27} \text{ m}^3$$

$$E_{\text{Ol}} C_{\text{Se}} = (1.1 \pm 0.3) \times 10^{-27} \text{ eV.m}^3$$

This indicates that in an In_2Se_3 -doped specimen with ionized impurity concentration, for instance, of $6 \times 10^{25} \text{ m}^{-3}$, the decrease

in ΔE is 0.066 ± 0.020 eV. As for the In_2Te_3 -doped system, the values of $n_0 + n_1$ in all specimens of this system under investigation are in a small range of $(3.3-3.7) \times 10^{25} \text{ m}^{-3}$, and hence the analysis presented above cannot be used for calculating an accurate value of C_{Te} .

4. AUXILIARY MEASUREMENTS

The Hall effect and magnetoresistance data as based on the two-band model have indicated a decrease in the energy separation ΔE between the (000) and $\langle 111 \rangle$ conduction band minima in InAs with increasing selenium or tellurium content. However, it was still very uncertain whether the (000) band moves up or the $\langle 111 \rangle$ band drops down relative to the highest valence band. Therefore an attempt has been made here to solve this problem, and measurements capable of treating the (000) and $\langle 111 \rangle$ bands separately were of primary interest. With this aim, the electrodiflectance, infrared absorption and thermoelectric power measurements were chosen. These investigations were carried out at room temperature. Nevertheless, these would at least present a qualitative picture correlating the work at lower temperatures.

From the study of interband transitions by electrodiflectance measurements, the separation between the conduction and valence bands in the Λ direction in $\vec{k}$ -space could be determined. The variation of such a separation of the bands at some position in the Λ direction with the impurity content, if observed, would indicate whether or not the $\langle 111 \rangle$ conduction band moves due to the presence of these impurities. The original purpose of correlating the infrared absorption and thermoelectric power measurements was to deduce the value of the fundamental band gap E_0 , and from the variation of E_0 with y , to examine the movement of the (000) conduction band minimum. Unfortunately,

due to the involvement of two types of electrons, the thermoelectric power data could not be analyzed successfully with the existing theories, and hence the initial aim was not achieved. However, the information obtained from these three types of measurements, though inconclusive, was consistent with the Hall and magnetoresistance work. These investigations are now presented in the following.

41. ELECTROREFLECTANCE

The detail of this differential technique in reflectance measurements will be presented in the next chapter. This is a measure of the relative change in reflectance ($\Delta R/R$) as a result of the modulating electric field on the polished specimen surface. The peaks in the reflectance (or electroreflectance) spectra of R (or $\Delta R/R$) versus the photon energy $h\nu$ of the incident light correspond to singularities in the joint density of states of the valence and conduction bands. The necessary condition for interband transitions is (Phillips 66Pl)

$$\vec{v}_k (E_c - E_v) = 0 \quad (\text{II-102})$$

where E_c and E_v represent the energy values of the conduction and valence bands at certain wave vector $\vec{k}$.

In the electroreflectance measurements on InAs, four peaks are observed in the energy range 2-5 eV. These are labeled as E_1 , $E_1+\Delta_1$, E_0' , and E_2 . It is fairly well established that E_1 and $E_1+\Delta_1$ are due to transitions in the Λ direction in $\vec{k}$ -space, the transitions being $\Lambda_{3v}-\Lambda_{1c}$ (as shown in Figure I-4), and Δ_1 being due to the spin-orbit splitting of the Λ_{3v} valence band. E_0' corresponds to the transitions $\Delta_{5v}-\Delta_{1c}^u$ which are very close to the Γ point so that the energy value can be approximated to that for $\Gamma_{15v}-\Gamma_{15c}$. There is some uncertainty about the interpretation of the E_2 peak. It may be due to $X_{5v}-X_{1c}$ transitions but more probably to $\Sigma_{1v}\Sigma_{2v}-\Sigma_{1c}^l$ transitions

possibly close to the X point.

From reflectance measurements, Greenaway and Cardona (62G4) have shown the variations of E_1 and E_2 peaks with composition in the alloy system $\text{InAs-In}_2\text{Te}_3$. In electrodreflectance measurements made here on the In_2Te_3 -doped specimens, the variations in energy of E_1 , $E_1 + \Delta_1$, E_0' and E_2 for the composition range of interest were obtained. The results together with those in the alloy system near InAs end by Greenaway and Cardona (62G4) are shown in Figure II-11. These results indicate that the energy values of all these peaks vary very slowly with y , the atomic percentage of tellurium in InAs. The main interest in this part of the project is to measure the position of the conduction band minima relative to the highest valence band of InAs with various impurity concentrations. Therefore the variation of the E_1 peaks with y is of importance here. The reduction in energy of the E_1 peak is about 0.01 eV even at $y = 1.12$ atomic % tellurium, and is certainly much smaller than the value determined for $E_{01}\text{C}_{\text{Te}}$ from the magnetoresistance results. While the interband transitions corresponding to the E_1 peak do not occur at the $\langle 111 \rangle$ minima (L point) but at some point in the Λ direction in $\vec{k}$ -space, these electrodreflectance and reflectance results must be carefully interpreted. If the transitions occur at a value of Λ very close to the L point, then the results here would indicate a fairly constant position

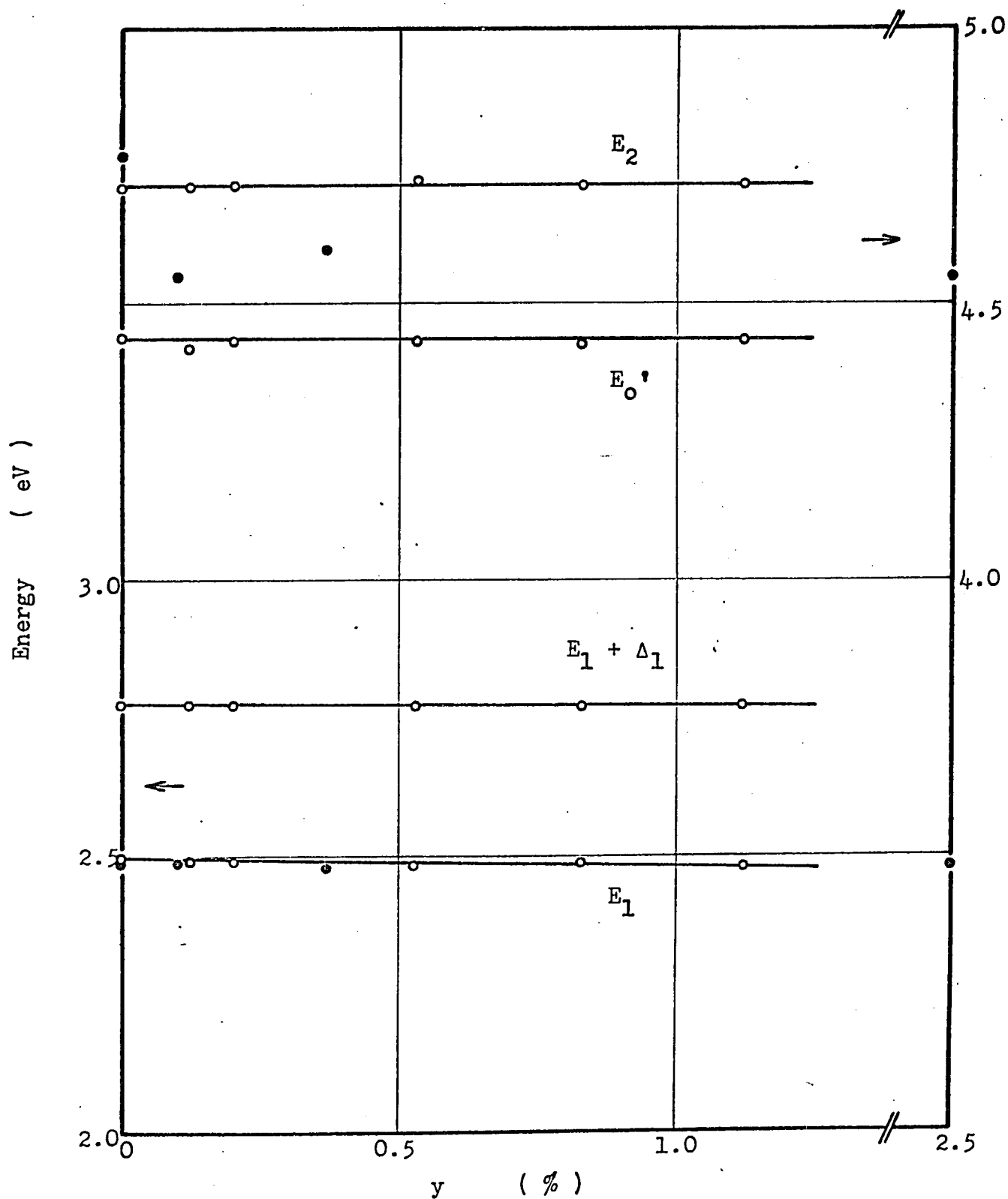


Figure II-11 Variation of E_1 , $E_1 + \Delta_1$, E_0' and E_2 interband transition energies with atomic % of tellurium y at room temperature for In_2Te_3 -doped samples: o, Electrorreflectance results (present work); •, Reflectance results (62G4).

of the $\langle 111 \rangle$ conduction band minima. However, in these heavily-doped materials, the electron concentration of the $\langle 111 \rangle$ minima was up to $2 \times 10^{25} \text{ m}^{-3}$, and hence the energy states at and near the minima would have already been occupied. The E_1 transitions must occur at a value of Λ where empty states in the conduction band are still available, and in this case probably not very close to the L point. Therefore even an appreciable lowering of the $\langle 111 \rangle$ minima would possibly show only a slight decrease of the energy values of the E_1 transitions. Here the decrease in the energy values of these E_1 peaks of $\sim 0.01 \text{ eV}$ due to the presence of tellurium, though insignificant, has definitely excluded the possibility of the rising of the $\langle 111 \rangle$.

Belle (66B5) has also made reflectance measurements on selenium- and tellurium-doped InAs samples in the energy range for E_1 transitions at 100 and 290°K . The electron concentrations of these materials were in the range $1 \times 10^{23} - 3.7 \times 10^{25} \text{ m}^{-3}$. The author observed no significant change in the E_1 transition energies with electron concentration at room temperature, but observed a decrease up to 0.025 eV in the heavily-doped samples at 100°K . It is therefore expected that the decrease in the E_1 transition energy with increasing impurity content would be more considerable at helium temperature. As based on all these electroreflectance and reflectance results, it seems reasonable that the reduction in ΔE contains some contributions from the lowering of the $\langle 111 \rangle$ band.

42. INFRARED ABSORPTION

421. GENERAL CONSIDERATIONS AND METHODS OF ANALYSIS

The absorption measurements in this work are only dealing with the direct interband transitions from the highest valence band to the lowest conduction band at and near the Γ point. When the photon energy of the radiation is slightly higher than the fundamental energy gap of a pure semiconductor, the absorption coefficient α is very high ($\sim 10^4 \text{ cm}^{-1}$). As the photon energy decreases gradually past the band gap, a marked drop in α by some orders of magnitude occurs, and this is called the absorption edge. Here, only the interpretation of absorption near the fundamental edge relevant to the experimental measurements will be presented. The development of the detailed theory has been reviewed by Johnson (67J1).

In an absorption measurement, the intensity of the incident light I_o and the intensity of the transmitted light I_t through a thin specimen of thickness d , corresponding to certain photon energy $h\nu$ of the monochromatic incident light, are measured. The transmission T is given by

$$T = \frac{I_t}{I_o} = \frac{(1-R)^2 \exp(-\alpha d)}{1 + R^2 \exp(-2\alpha d)} \quad (\text{II-103})$$

where R is the reflectivity defined by the ratio I_r/I_o , I_r being the intensity of the reflected light from the specimen

surface at normal incidence, and

$$R = \frac{I_r}{I_o} = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (\text{II-104})$$

where n is the index of refraction and κ the extinction coefficient of the material. Usually, the reflectivity varies slowly with the photon energy, and the change in transmission is basically due to the drastic variation of the absorption coefficient. Therefore, near the absorption edge, equation (II-103) can be approximated as

$$I_t/I_o = c \exp(-\alpha d) \quad (\text{II-105})$$

Here the constant c can easily be eliminated by considering the absorption at the energy gap and the background absorption (denoted by the subscripts E and B separately). Equation (II-105) then becomes

$$\log_{10}(I_o/I_t)_E - \log_{10}(I_o/I_t)_B = (\alpha_E - \alpha_B)d/2.303 \quad (\text{II-106})$$

The optical energy gap E_g is determined from the experimental relation of I_o/I_t versus $h\nu$ evaluated at $(I_o/I_t)_E$, the value of which is obtained from equation (II-106) by taking an appropriate value of $(\alpha_E - \alpha_B)$. The values of $(\alpha_E - \alpha_B)$ of pure compounds can be obtained by using the accepted value of the fundamental band gap in the absorption data. Then, for alloys

or impure materials, the values of $(\alpha_E - \alpha_B)$ can be deduced by comparing with those of pure compounds.

This approach of analyzing the absorption data has been applied on various alloy systems including InAs-In₂Se₃ (Woolley and Keating 61W3) and InAs-In₂Te₃ (Woolley et al 61W4). In the present work, the investigation is made on the InAs end of these systems in order to obtain more accurately the variation of E_g of InAs with selenium and tellurium content.

Another approach in determining E_g is by using the expression of the absorption coefficient for allowed direct interband transition:

$$\begin{aligned} \alpha &= A (h\nu - E_g)^{\frac{1}{2}} && \text{for } h\nu > E_g \\ &= 0 && \text{for } h\nu \leq E_g \end{aligned} \quad (\text{II-107})$$

where A is a constant. This expression is derived under the assumption of a filled parabolic valence band and an empty parabolic conduction band. Although equation (II-107) is not strictly valid for the interpretation of the absorption data of the highly degenerate specimens of InAs, a qualitative picture can still be obtained from this. The calculation of the energy dependence of absorption according to Kane's theory has been given in the work by Stern (60S1).

Equation (II-107) predicts a linear variation of α^2 versus $h\nu$ at photon energy above the fundamental band gap.

Since α is not obtained directly in the absorption measurements, its values at different photon energies can be calculated from

$$\alpha = \frac{2.303}{d} [\log_{10}(I_o/I_t) - \log_{10}(I_o/I_t)_B] \quad (\text{II-108})$$

by assuming equation (II-105) to be correct.

Due to the high degeneracy of the specimens, the values of E_g obtained from the absorption measurements do not necessarily correspond to the actual intrinsic band gap E_o of the material. The shift of absorption edge towards higher energy as the result of an increase of electron concentration has been explained by Burstein (54B1). Due to the low density of states of the (000) conduction band, the lower states have already been occupied by electrons in the extrinsic material. Then the direct transitions can take place slightly away from $\vec{k} = (0,0,0)$ where empty states are still available. At helium temperature, the Fermi level defines the position of the lowest available states, and therefore the photon energy corresponding to a transition near (000) in $\vec{k}$ -space is

$$E_g = E_o + E_F$$

However, at finite temperatures, the tail of the Fermi distribution function extends over an energy effectively $4kT$ below E_F (k being the Boltzmann constant). Hence, when $E_F > 4kT$, the lowest

available states lie at $E_F - 4kT$ above the conduction band minimum. If $E_F \leq 4kT$, there are still empty states at the bottom of the conduction band. Therefore E_o and E_g are related by

$$E_o = E_g - E_F + 4kT \quad \text{for } E_F > 4kT \quad (\text{II-109})$$

and $E_o = E_g \quad \text{for } E_F \leq 4kT$

Because of the Burstein effect, the band gap E_o cannot be obtained directly from the absorption measurements. Nevertheless, the variation of E_g with y , and with the electron concentration, can also give some information about the movements of the bands.

422. SPECIMEN PREPARATION, EQUIPMENT AND EXPERIMENTAL TECHNIQUE

The experimental study of optical absorption involves two separate measurements for the incident and the transmitted light intensities at various photon energies. In order to obtain high intensity and stable signals, very thin specimens, as well as a stable source of monochromatic light and a sensitive detector capable of covering the energy range of interest, are required.

Each specimen was lapped into a thin platelet with grit 1000-3200 grinding powder on a glass plate. A lapping block was used to ensure good uniformity of the thickness of the specimen. When the thickness was reduced to below 100 microns, one surface of the specimen was polished with 5 micron powder. Each crack-free specimen was then mounted on the specimen holder, which was a brass plate of about 1 mm thick with a $5-10 \text{ mm}^2$ circular or oval-shape hole at the center. The edges of the specimen were glued to the brass plate with masking tape or glyptol cement, such that the hole was completely covered by the thin specimen. After the measurement, the glue was dissolved by acetone, and then the thickness of the specimen was measured with a Moore and Wright micrometer.

A "Baird Atomic" double beam infrared spectrometer which had been modified as a single beam monochromator by Thomas of this laboratory, was used in this work. The infrared

radiation from the light source (a silicon carbide rod under the trade name "globar") was chopped at 10 cps, and a monochromatic light was obtained by using a 60° NaCl prism. The schematic diagram of the experimental setup is shown in Figure II-12. M_1 and M_3 are plane mirrors, and M_2 , M_4 and M_5 are concave mirrors with focal lengths 70.5, 20.7 and 5.8 cm, respectively. The optical path from the monochromator slit to M_2 was adjusted to be equal to the focal length of M_2 , such that a parallel beam was obtained from M_2 to M_3 and from M_3 to M_4 . Then the beam was focused to a size of approximately 10 mm x 1 mm where the thin specimen was placed. The transmitted beam was focused on a Bolometer detector. This optical setup was originally designed for both absorption and magnetoabsorption measurements by Thomas, such that the specimen could also be fitted in the pole gap of the Magnion-Harvey-Wells Model L158 15" electromagnet.

The signal from the Bolometer detector was produced by the variation of the resistance of the detector elements caused by the infrared light. The signal voltage was amplified by a PAR Model 120 lock-in amplifier, tuned to 10 cps, the frequency of the chopped light, and then measured by a Hewlett-Parkard Model 3440A digital voltmeter.

In the measurements, two different methods were used. In the first case, the intensity of the transmitted light I_t

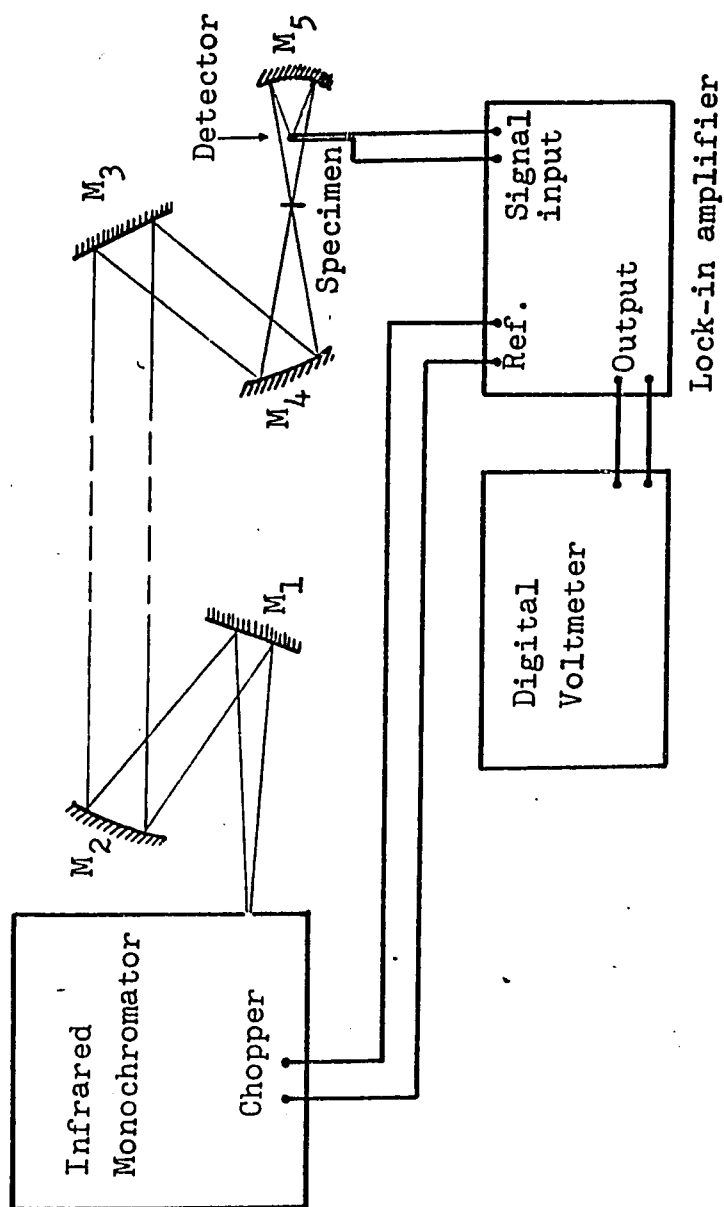


Figure II-12 Infrared absorption apparatus.

was first measured consecutively at various wavelengths in suitable steps. Then the specimen was removed from the specimen holder for measurements of the intensity of the incident light I_0 for the corresponding wavelengths. An alternative method was to take consecutive measurements of each I_t and I_0 at a given wavelength. This required two identical specimen holders, one with the mounted specimen and one without. Therefore the specimen-in and specimen-out configurations could be obtained by interchanging the two specimen holders with a simple mechanical arrangement. The advantage of the first method was that the position of the specimen subject to radiation was fixed and therefore no resetting errors were involved. The second method had the advantage of minimizing the effects due to fluctuations in the light intensities, the electronics, etc. However in practice, both methods were equally accurate for the measurements.

423. RESULTS

Room temperature optical absorption measurements were made on In_2Se_3 - and In_2Te_3 -doped InAs specimens. The experimental data were analyzed by two methods as given in Section II-421. The first approach was by using equation (II-106). The optical energy gap E_g for each specimen was determined from the experimental relation of I_o/I_t versus $h\nu$, evaluated at $(I_o/I_t)_E$ by taking appropriate values of $(\alpha_E - \alpha_B)$, e.g. 150 or 300 cm^{-1} . These values of $(\alpha_E - \alpha_B)$ have been used in various cases, e.g. InAs-GaAs (Woolley et al 68W2), InAs- In_2Se_3 (Woolley and Keating 61W3) and InAs- In_2Te_3 (Woolley et al 61W4).

Another approach was by using the linear relation of α^2 versus $h\nu$ at photon energy above the fundamental band gap as given by equations (II-107) and (II-108). The value of E_g was the intercept on the $h\nu$ -axis.

Typical results for some specimens analyzed with these two approaches are shown in Figures II-13 and II-14. In all cases, the differences in the values of E_g obtained by taking $(\alpha_E - \alpha_B)$ as 150 or 300 cm^{-1} were between 0.02 and 0.08 eV. The linear relation of α^2 versus $h\nu$ above the fundamental band gap was also satisfied in all cases. The value of E_g for each specimen, deduced from it, was between the two values determined from the first approach.

The variation of E_g with y , for the two systems of specimens, deduced from different methods are shown in Figure

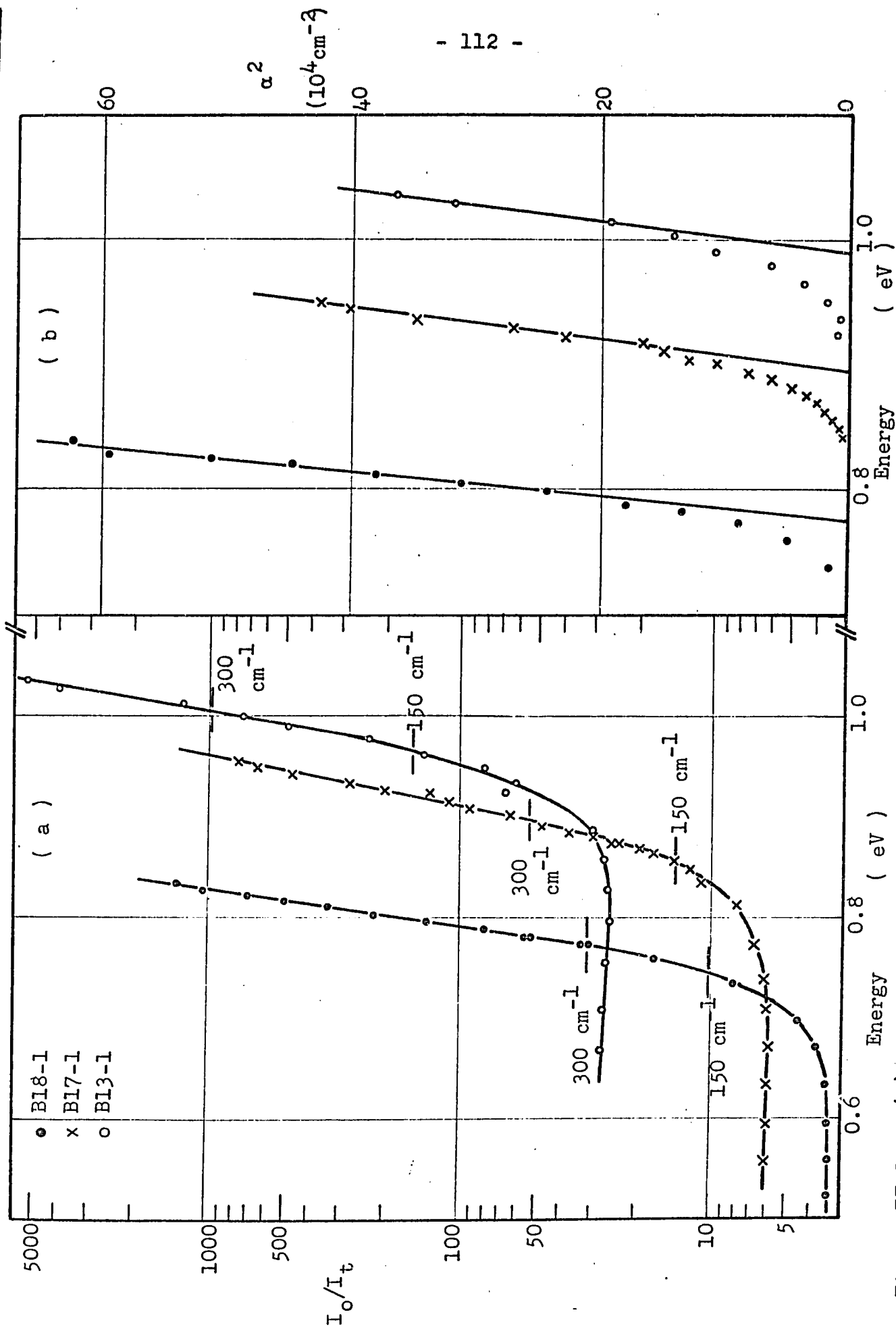


Figure II-13 (a) Variation of I_0/I_t with photon energy at room temperature for typical In_2Se_3 -doped InAs samples, and absorption edge values corresponding to absorption of 300 cm^{-1} and 150 cm^{-1} , respectively, above the background. (b) Variation of the square of the absorption coefficient α^2 with photon energy for these samples.

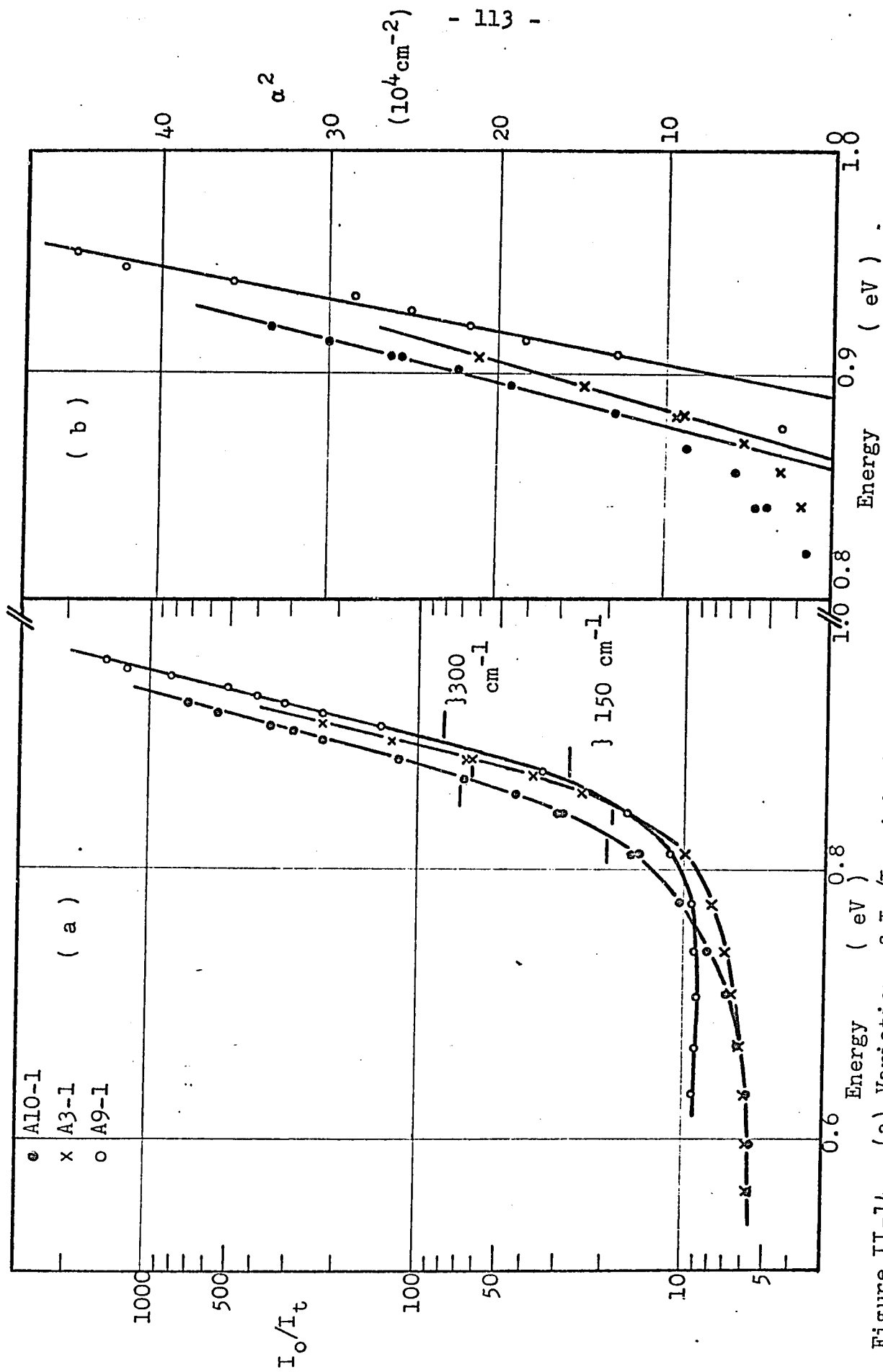


Figure II-14 (a) Variation of I_0/I_t with photon energy at room temperature for typical In_2Te_3 -doped InAs samples, and absorption edge values corresponding to absorption of 300 cm^{-1} and 150 cm^{-1} , respectively, above the background. (b) Variation of the square of the absorption coefficient α^2 with photon energy for these samples.

II-15. The curves obtained by the different methods of determining E_g are qualitatively compatible. It is seen that the value of E_g rises rapidly from 0.35 eV, the value for pure InAs, due to Burstein effect as the Fermi level enters the conduction band, but for y greater than ~ 0.3 atomic percent of selenium or tellurium, the values of E_g increase only very slowly with y . The saturated values of E_g in these two systems differ by approximately 0.1 eV. This is in reasonable agreement with the magnetoresistance results which also indicate the saturation of the total electron concentration with increasing impurity content. The saturated value of the total electron concentration in the In_2Se_3 -doped specimens was $\sim 7 \times 10^{25} \text{ m}^{-3}$, while that in the In_2Te_3 -doped specimens was only $\sim 4 \times 10^{25} \text{ m}^{-3}$. Hence the position of the Fermi level of the former must be higher than that of the latter.

Another contribution to the leveling out of the E_g versus y curve is due to the high density of states of the $\langle 111 \rangle$ conduction band. After E_F has reached the bottom of the $\langle 111 \rangle$ conduction band, the high density of states of this band prevents the rapid rise of E_F . Hence the saturated value in E_g is effectively a measure of the height of the $\langle 111 \rangle$ minima above the valence band maximum. The explanation is clarified by plotting E_g versus $(n_0 + n_1)$, as shown in Figure II-16. Here the results of E_g as determined from the three methods are

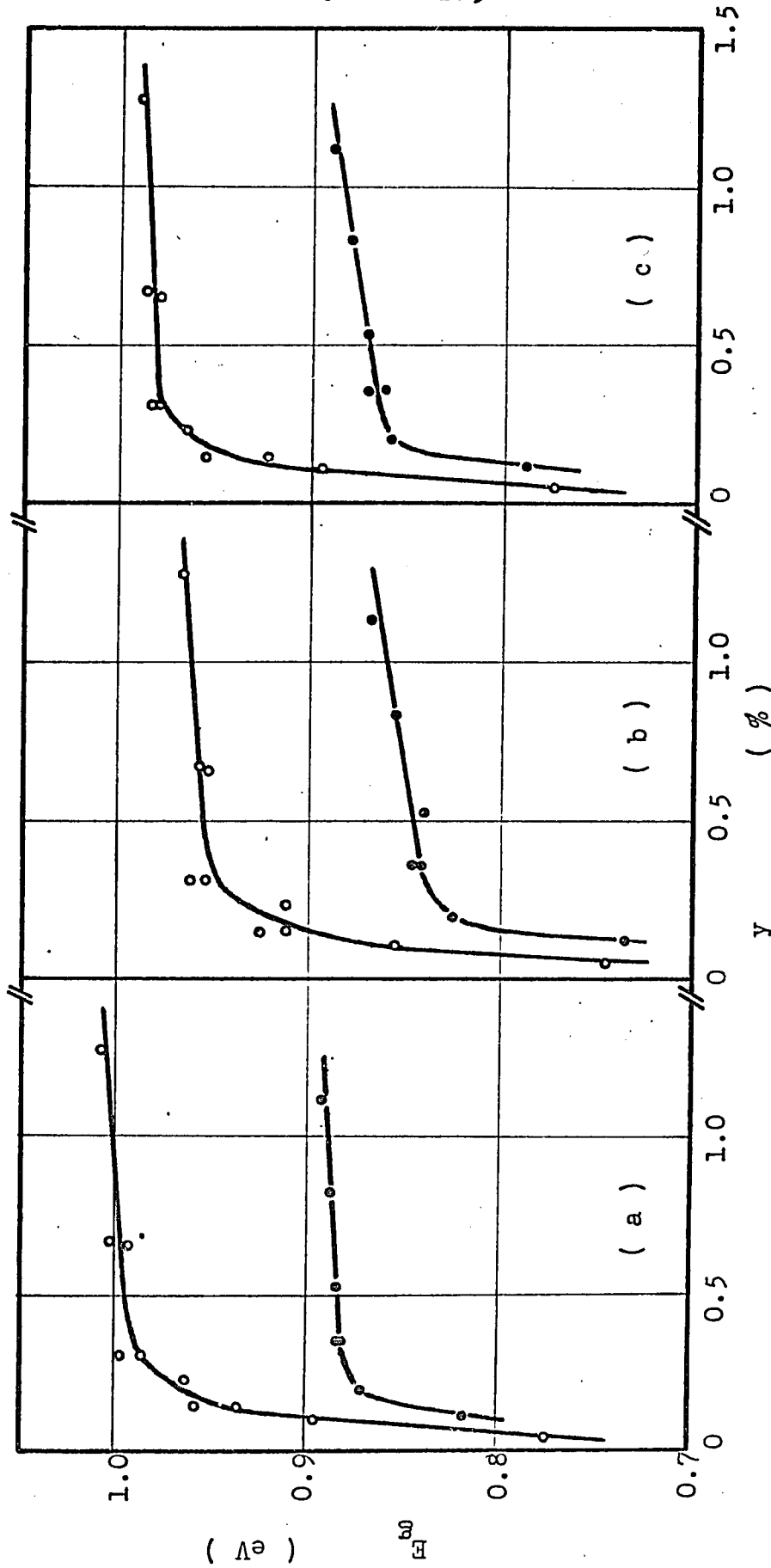


Figure II-15 Variation of room-temperature optical energy-gap E_g with atomic % of selenium or tellurium y : ○, In_2Se_3 -doped; ●, In_2Te_3 -doped samples. (a) Absorption edge values corresponding to absorption of 300 cm^{-1} above the background. (b) Absorption edge values corresponding to absorption of 150 cm^{-1} above the background. (c) Absorption edge values obtained from the linear plot of the square of the absorption coefficient α^2 with photon energy at energy above the fundamental band gap.

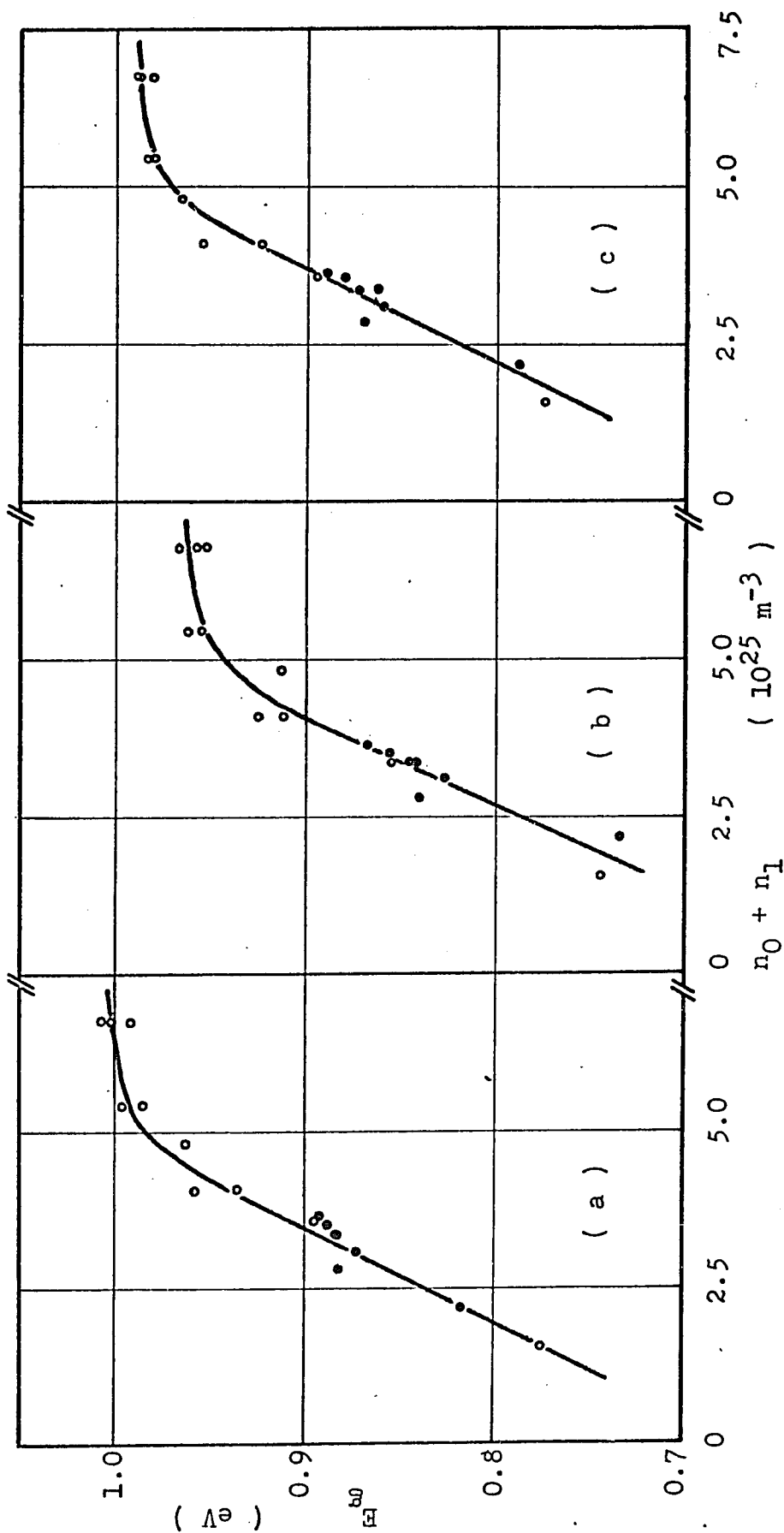


Figure II-16 Variation of room-temperature optical energy-gap E_g with total electron concentration $n_0 + n_1$ for In_2Se_3 -doped (o) and In_2Te_3 -doped (●) samples. [(a), (b) and (c): same as in Figure II-15.]

included. The values of n_0+n_1 are taken from the results of the magnetoresistance work at 4.2°K , based on the two-band model. Since these materials are highly degenerate, the carrier concentrations can be expected to be temperature independent, at least between helium and room temperatures. If the value of E_{01} , the separation between the (000) and $\langle 111 \rangle$ conduction band minima for pure InAs, is assumed to remain as 0.70 ± 0.03 eV at room temperature, the separation between the $\langle 111 \rangle$ conduction band minima and the highest valence band maximum is then 1.05 ± 0.03 eV. (Note that the fundamental band gap E_g of pure InAs at room temperature is 0.35 eV.) The decrease of ΔE due to the concentrations of ionized impurities will now be estimated, by using the saturated values of E_g :

	In ₂ Se ₃ -doped InAs	In ₂ Te ₃ -doped InAs
Value of (n_0+n_1) corresponding to saturated value of E_g	$\sim 6 \times 10^{25} \text{ m}^{-3}$	$\sim 3.5 \times 10^{25} \text{ m}^{-3}$
Saturated value of E_g	$\sim 0.98 \text{ eV}$	$\sim 0.88 \text{ eV}$
Saturated value of $E_g + 4kT$ *	$\sim 1.08 \text{ eV}$	$\sim 0.98 \text{ eV}$
Decrease in ΔE	-	$\sim 0.07 \text{ eV}$
Decrease in ΔE per ionized impurity atom in 1 m^3	-	$\sim 2 \times 10^{-27} \text{ eV.m}^3$

(* At room temperature, a term $4kT$ is added to account for the tailing of the Fermi distribution function.)

Since the "saturated value of E_g " + $4kT$ of the In_2Se_3 -doped system is within the range of the estimated value of the separation between the $\langle 111 \rangle$ conduction band minima and the highest valence band maximum (1.05 ± 0.03 eV), the decrease in ΔE due to ionized impurity content of this system cannot be determined here. As for the In_2Te_3 -doped system, an estimated value of the rate of decrease in ΔE , $\sim 2 \times 10^{-27}$ eV.m³, is obtained. Apparently, the decrease in ΔE for the In_2Se_3 -doped system can be expected to be somewhat smaller. In fact, in the magnetoresistance work at 4.2°K , the rate of decrease in ΔE has been determined as $E_{01}C_{\text{Se}} = (1.1 \pm 0.3) \times 10^{-27}$ eV.m³. From the above results, it is easily seen that tellurium has more effect than selenium on the band structure of InAs. Here, only a qualitative picture can be presented. In order to improve the accuracy of the results, it would be advisable to make further infrared absorption measurements of these materials at lower temperatures. Then the uncertainty introduced by the temperature dependence of E_{01} could be eliminated.

43. THERMOELECTRIC POWER

431. GENERAL CONSIDERATIONS

Due to the problem of Burstein shift in optical absorption results, the actual value of E_0 of a heavily-doped semiconductor is not obtainable from absorption work alone. The extra information needed for the determination of E_0 could be obtained from thermoelectric power measurements which give the value of the Fermi energy. The correlation of optical absorption and thermoelectric power measurements has been demonstrated in the study of the variation of E_0 with x in the $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloy system by Woolley et al (68W2).

Experimentally, the thermoelectric power of a semiconductor is the ratio $\Delta V/\Delta T$, where ΔV is the voltage developed between two positions on the specimen with a temperature difference ΔT . In case of a single conduction band with spherical constant-energy surfaces, the thermoelectric power θ is expressed as (Zawadzki 62Z1):

$$\theta = \frac{1}{eT} \left[\frac{\int_0^\infty E \kappa^{2s+1} (\partial f_0 / \partial E) (\partial E / \partial \kappa)^2 dE}{\int_0^\infty \kappa^{2s+1} (\partial f_0 / \partial E) (\partial E / \partial \kappa)^2 dE} - \frac{E_F}{kT} \right] \quad (\text{II-110})$$

where f_0 is the Fermi-Dirac distribution function. From this equation, it is seen that θ depends on the (E, κ) relation and the scattering mechanism involved in the electronic conduction

process as characterized by the parameter s . The expression for θ when electrons are present in two bands would be more complicated. Ehrenreich (61E2) has given, for two non-interacting bands, the relation

$$\theta = \frac{\sigma_0 \theta_0 + \sigma_1 \theta_1}{\sigma_0 + \sigma_1} \quad (\text{II-111})$$

where θ_0 and θ_1 are the thermoelectric power contributions of the (000) and $\langle 111 \rangle$ bands separately. Such involvement of two-band contributions consequently complicates the analysis of the experimental data of θ for finding the position of the Fermi energy. In this work, that the data of θ could not be analyzed successfully are attributed to two reasons:

(1) It is well established that the magnitude of the thermoelectric power decreases with increasing carrier concentration and Fermi energy. Since the Fermi energy is much closer to the $\langle 111 \rangle$ minima than the (000) minimum, θ_1 would contribute appreciably to the total thermoelectric power. The difficulties in obtaining precise information about the $\langle 111 \rangle$ band, as indicated earlier, then hinder the analysis of the experimental data of θ .

(2) Interband interaction between the (000) and $\langle 111 \rangle$ bands probably contributes to the value of θ and this could not be taken into account.

432. EQUIPMENT AND EXPERIMENTAL TECHNIQUE

The specimens used for thermoelectric power measurements were cut and lapped into a parallelepiped shape of dimensions 10x3x1 mm. The apparatus used in this work is shown in Figure II-17. The heater was a cylindrical copper rod wound by enamelled copper wire as the heating element. The heat sink was also a cylindrical copper rod. The two junctions of the ribbon type copper-constantan thermocouple were glued to the ends of the two copper rods. Good thermal contact between the specimen and the junctions of the thermocouple was maintained by pressing the copper rods against the specimen. Two small indium wires were also placed between these mechanical contacts to avoid cracking of the thermocouple junction and the specimen, as well as to serve as the electrical contacts for the measurement of the voltage produced by the temperature difference. A thin mica sheet was placed between one cold junction of the thermocouple and one indium wire to ensure electrical insulation.

A temperature difference of up to several degrees was maintained between the ends of the specimen by applying a regulated d. c. voltage to the wire heater with a Harrison Laboratories Model 6343A constant voltage supply. The voltage between the thermocouple junctions and between the indium-specimen junctions were amplified by an Astrodata Model 120 nanovolt amplifier, and then measured with a Hewlett-Parkard Model 3440A digital voltmeter.

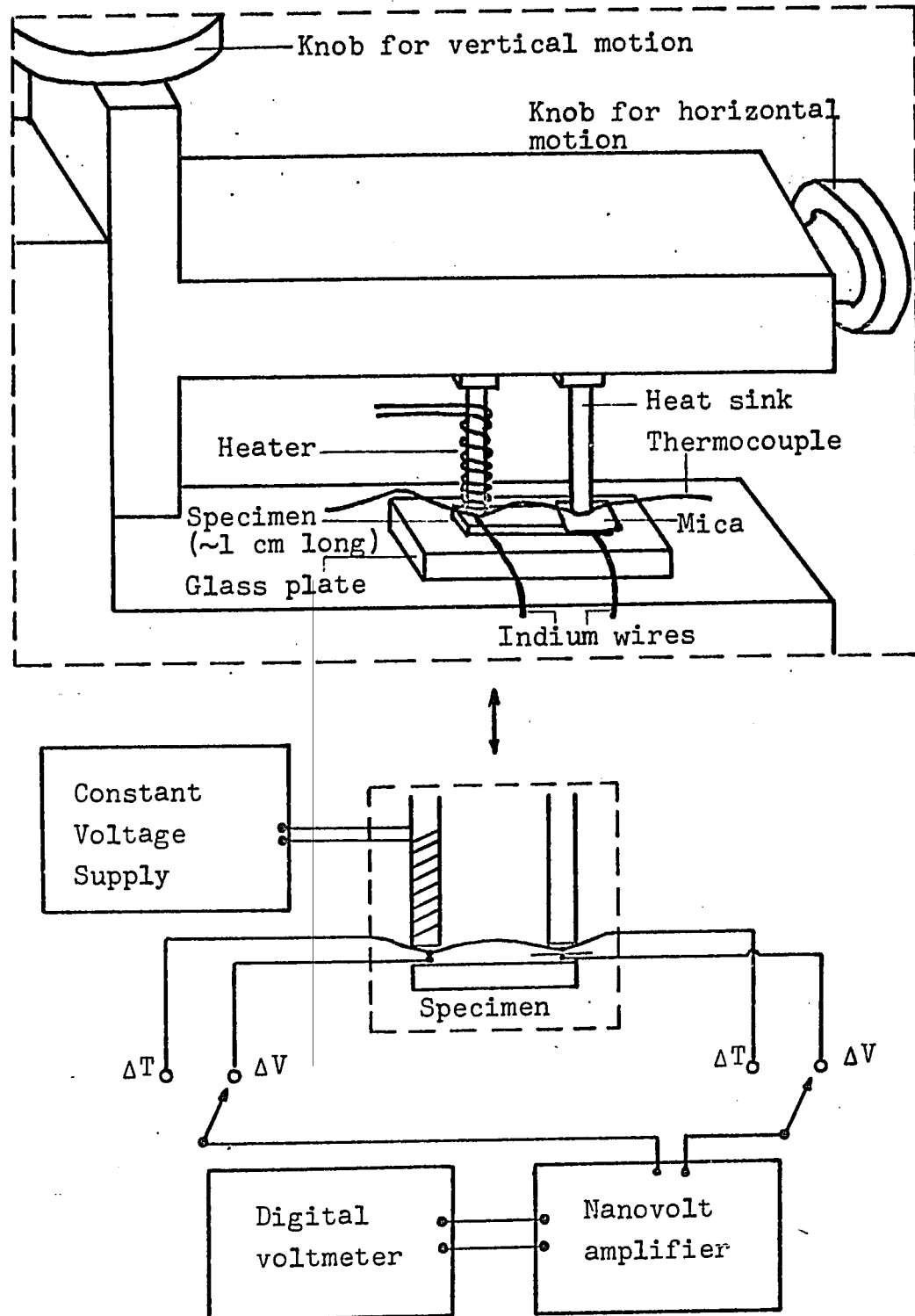


Figure II-17 Thermoelectric power apparatus.

433. RESULTS

Room temperature measurements of thermoelectric power were made on both In_2Se_3 - and In_2Te_3 -doped InAs samples. For each specimen, values of ΔV were taken for each ΔT over a range of temperature difference 0.2 to 2.5°C . It was found that in all cases, ΔV was proportional to ΔT as illustrated by some typical examples shown in Figure II-18. The thermoelectric power θ of each specimen was obtained from the slope of the ΔV versus ΔT line. The graph of the variation of $-\theta$ with y for both systems is shown in Figure II-19. The rapid decrease of the magnitude of θ with increasing y at $y < 0.3$ atomic % indicates the rise of the energy of the Fermi level. At higher values of y , the leveling of θ is seen. Since the materials with $y > 0.1$ atomic % have electrons in both (000) and $\langle 111 \rangle$ conduction band minima, equation (II-110) for a single band cannot be applied here. The difficulties encountered in the data analysis with the model given in equation (II-111) consequently prevent the calculation of the intrinsic band-gap values E_0 for the specimens under investigation.

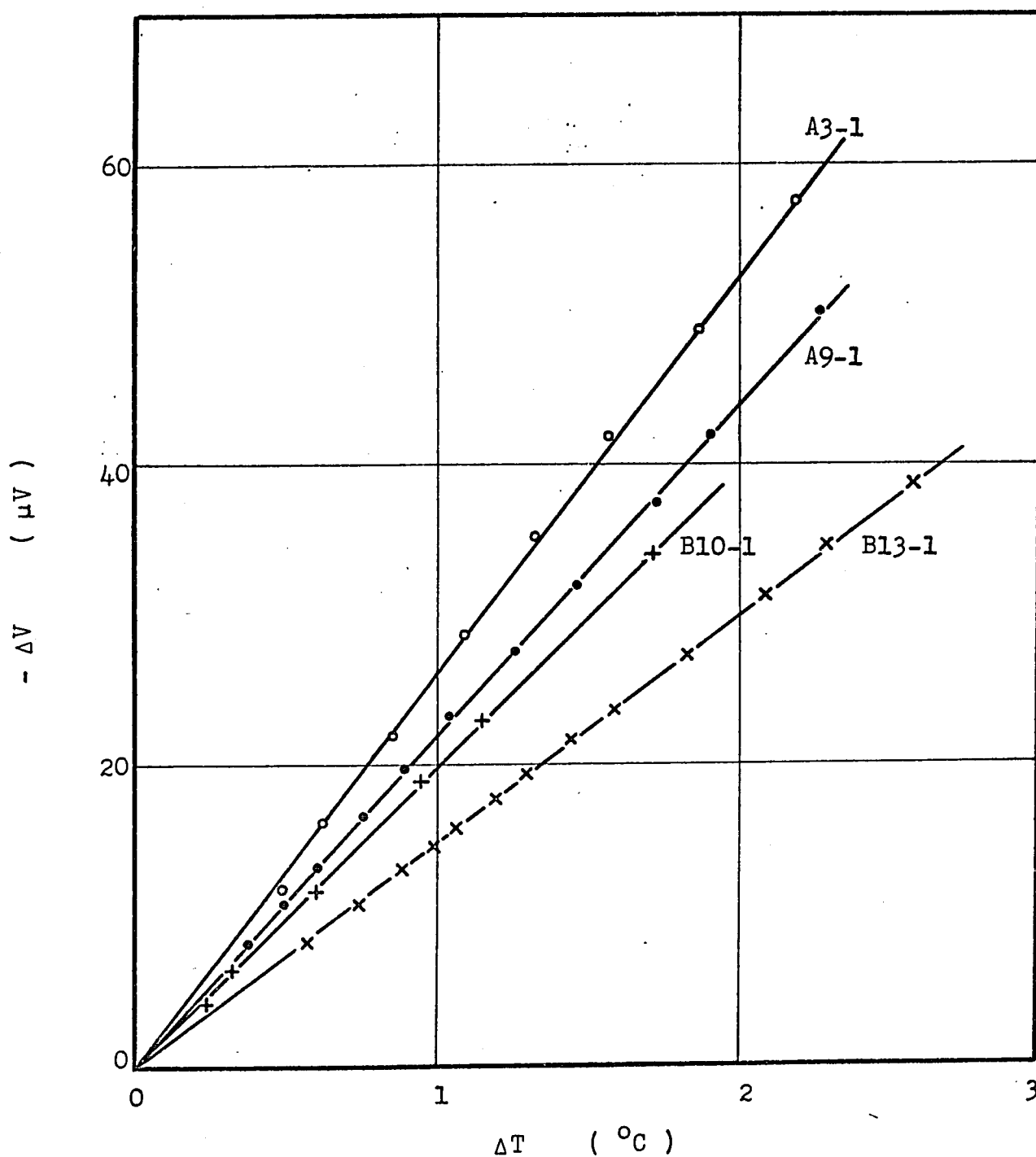


Figure II-18 Variation of voltage difference ΔV with temperature difference ΔT at room temperature for typical In_2Se_3 -doped and In_2Te_3 -doped InAs samples (in thermoelectric power measurements).

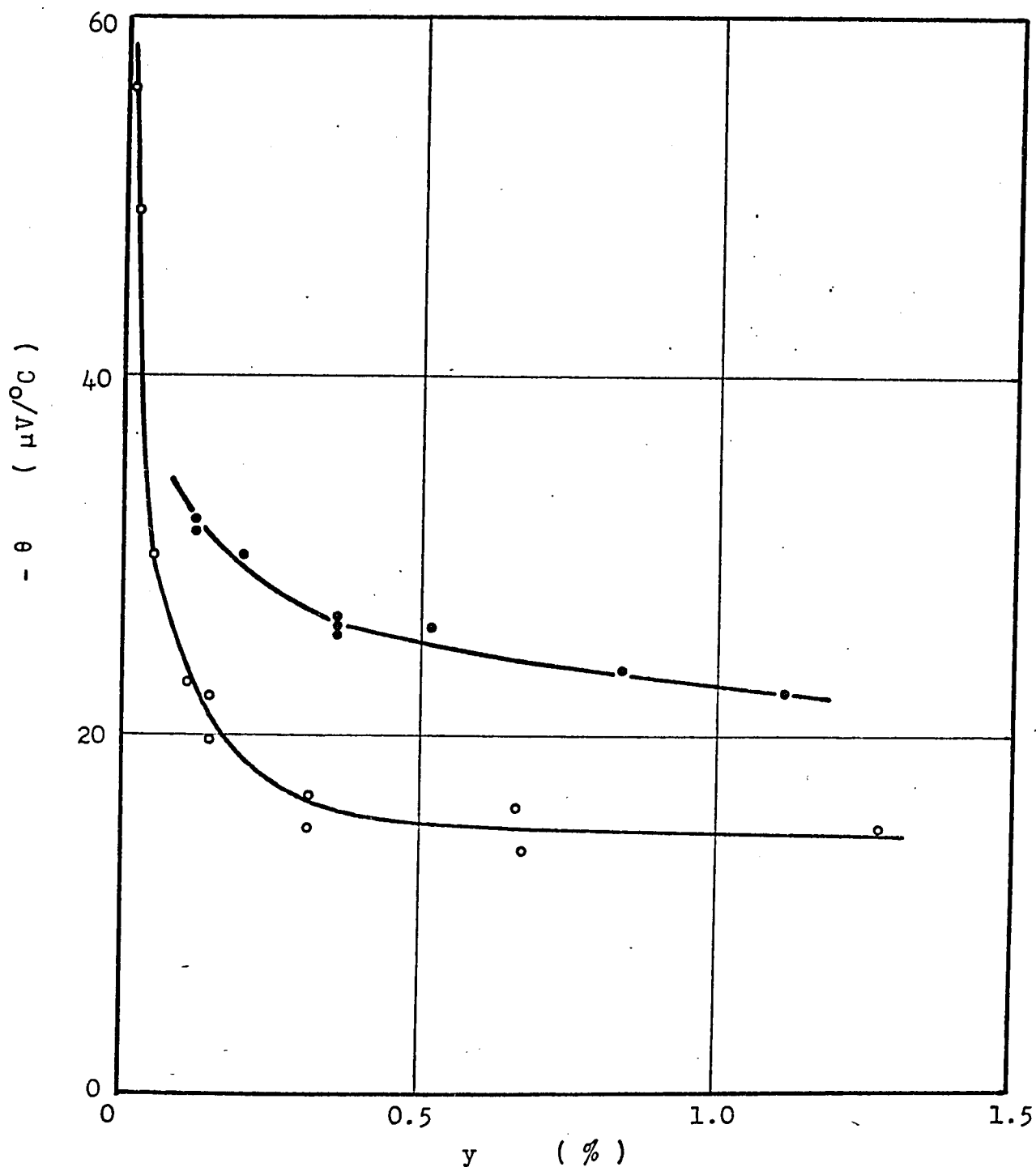


Figure II-19 Variation of room temperature thermoelectric power θ with atomic % of selenium or tellurium y : o, In_2Se_3 -doped; •, In_2Te_3 -doped samples.

5. DISCUSSION

From the Hall effect and magnetoresistance measurements on In_2Se_3 - and In_2Te_3 -doped InAs samples, the energy separation of the (000) and $\langle 111 \rangle$ conduction band minima for pure InAs was determined, and a decrease in this energy separation ΔE due to the presence of selenium or tellurium in the InAs lattice was also observed. In the analysis of the effect of doping on ΔE , calculations were made for two different cases: ΔE assumed to vary linearly with y , the atomic percentage of selenium or tellurium in the lattice, or with $n_0 + n_1$, the total ionized impurity concentration. Self-consistent results were obtained for the two cases by considering the magnetoresistance results alone. However in both cases, the contribution to the decrease in ΔE as to whether it is due to the movement of the (000), $\langle 111 \rangle$, or both could not be determined at that stage. Hence the auxiliary measurements: electroreflectance, infrared absorption and thermoelectric power, were also made at room temperature.

The electroreflectance measurements on In_2Te_3 -doped InAs samples indicated a very slight decrease of the $\Lambda_{3v} - \Lambda_{1c}$ interband transition energy with increasing tellurium content. This suggested that the decrease of ΔE in heavily-doped InAs contains the contribution of the lowering of the $\langle 111 \rangle$ band. This suggestion is supported by some evidence : One of the common features of the band structures of the compounds GaSb, InSb and InAs is that the $\langle 111 \rangle$ minima are the next lowest

conduction band minima above the (000). The investigations of the two bands in these compounds have been carried out extensively by Woolley's group. Van Tongerloo and Woolley (69V1) have reported the decrease of ΔE in GaSb due to tellurium doping from Faraday rotation measurements, correlating the magnetoresistance results by Harland and Woolley (65H1, 66H1). The authors (69V1) also concluded that such a decrease in ΔE is due to the lowering of the $\langle 111 \rangle$ minima. The magnetoresistance work on In_2Se_3 - and In_2Te_3 -doped InSb by Aubin (69A1) has also indicated the decrease of ΔE due to doping. With the additional information from reflectance results on selenium-doped InSb by Belle and Galvanov (66B6), who observed a decrease of the $\Lambda_{3v}-\Lambda_{1c}$ interband transition energy due to the presence of selenium atoms in the lattice, it can be concluded that the decrease in ΔE is contributed, at least partly, by the lowering of the $\langle 111 \rangle$ band. In the measurements of Pressure dependence of transport properties of semiconductors, Kosicki and Paul (66K2, 69P1) noted the existence of selenium donor levels in GaSb, and tellurium donor levels in InSb, associated with the $\langle 111 \rangle$ conduction band. The lowering of the $\langle 111 \rangle$ minima could be the consequence of the merging of the impurity levels with the conduction band. By comparing the above results, it would be quite acceptable that this also the case for InAs.

Both optical absorption and thermoelectric power measurements showed a rapid rising of the Fermi energy E_F with

increasing selenium and tellurium content up to $y \sim 0.3$ atomic %, and leveling out of E_F at higher values of y . The rapid rising of E_F at lower values of y can be explained by the filling up of the available states in the (000) conduction band by the extrinsic carriers, and the leveling out of E_F at higher values of y can be attributed to two factors:

(1) The additional selenium and tellurium atoms are compensated by lattice vacancies corresponding to those occurring in defect zincblende structure of In_2Te_3 , and then no further electrons are obtainable from the donor atoms.

(2) The high density of states of the $\langle 111 \rangle$ conduction band prevents the rapid rising of E_F .

Due to the difficulties encountered in analyzing the thermoelectric power data, the intrinsic band gap E_0 cannot be obtained, and consequently the effect of doping on the energy position of the (000) conduction band minimum relative to the highest valence band maximum cannot be deduced. Therefore the contribution to the decrease of ΔE by the movement of the (000) minimum is still unknown at present. From the results deduced from the correlation of the magnetoresistance and infrared absorption work, it is seen that the interpretation of the decrease in ΔE as due to the presence of ionized impurities is more appropriate than that as due to the total impurity content. This interpretation is supported by the fact that increasing number of vacancies is formed in the lattice, and such compensation to the additional selenium or

tellurium atoms would probably prevent further effect on the band structure of the material by the impurities.

Another close correlation between the magnetoresistance results on In_2Se_3 - and In_2Te_3 -doped InAs and InSb obtained in this work (68K4) and by Aubin (69A1) can be seen from the comparison of the values of C of equation (II-100). Although the interpretation of the decrease of the energy separation by a linear variation of ΔE with y is not strictly valid, this is still a good indication of the effect of the impurities on the band structure of the compounds. The values of C_{Se} and C_{Te} in these investigations are summarized in the following:

	InAs	InSb
Selenium	(a) 0.18/atom.%	(b) 0.46/atom.%
Tellurium	(c) 0.24/atom.%	(d) 0.16/atom.%

The relative values of the numbers a, b, c, d should be consistent with the relative positions of the elements involved in the periodic table:

III	IV	V	VI
		As	Se
In		Sb	Te

There are four cases:

- (1) Se should fit in InAs substitutionally more easily

than Te does, and hence it would be expected that $a < c$.

(2) Te should fit in InSb substitutionally more easily than Se does, and hence it would be expected that $d < b$.

(3) Se should fit in InAs substitutionally more easily than in InSb, and hence it would be expected that $a < b$.

(4) Te should fit in InSb substitutionally more easily than in InAs, and hence it would be expected that $d < c$.

The above experimental values show that all these four conditions are satisfied.

CHAPTER III

INTERBAND TRANSITIONS IN InAs

1. INTRODUCTION

An interband transition is the excitation of an electron from a state in the valence band to an available state in the conduction band. The experimental study of interband transitions includes transmission and reflectance measurements among others. In practice, the transmission work is useful for the study of the absorption edge, as has been presented in Section II-42. The high absorption coefficients encountered throughout the fundamental absorption region (i.e. above the absorption edge) make transmission measurements very impractical in many cases. However, the reflectance work is quite capable of covering a wide energy range from near infrared to vacuum ultraviolet.

Each reflectance spectrum, which shows the variation of the ratio of the intensities of the reflected and incident light R with photon energy $E (= h\nu)$, usually consists of a number of maxima and shoulders. The structure of the reflectance spectrum of each material is closely related to its optical properties which can be described by some optical constants, such as the complex refractive index and the complex dielectric constant. Thus the extrema in the reflectance spectrum must correspond to some kind of extrema or singularities in the optical constants. The theoretical approach in handling this

is to correlate the optical constants with electronic excitations in the solid, and then to calculate the line shapes of the energy dependence of optical constants in the neighborhood of such threshold energy in various cases. However, the correlation of experimental results with theoretical presentations can only be established qualitatively. The difficulty lies in the fact that reflectance measurements for a given material usually show poor reproducibility in the absolute values of R , mainly due to variations in the sample surface treatment. What the measurements provide in reflectance work is the overall appearance and structural features including the energy positions of the extrema, which are reproducible. The identification of the reflectance extrema, as concerning where the transitions take place in $\vec{k}$ -space, can be a formidable problem, because it involves correlating a one-dimensional set of transition energies with positions in a three-dimensional Brillouin zone. Group theory is of considerable help, since it suggests symmetry positions in the Brillouin zone where certain types of interband transitions are likely to occur. However, strong assistance for the identification of the reflectance peaks comes from existing band structure calculations, either for the material under consideration or for analogous materials, which permit a very straightforward comparison of the energy values. Such collaboration if interpreted correctly helps to improve the band structure calculations.

The recent development of differential techniques in

reflectance measurements has achieved high resolutions of some fine structures in reflectance spectra, and hence improved the accuracy of the experimental information. Each differential technique involves modulation of certain parameter, such as electric field imposed on the surface region of the specimen, temperature, or wavelength of the monochromatic radiation. Some sophisticated theoretical models have been developed to interpret various modulation effects in terms of the change of some optical constants. However, only a qualitative picture of the basic mechanisms in different cases of modulated reflectance has been obtained up to the present time. Despite the difficulties encountered in the comparison of theoretical and experimental line shapes in this type of work, these measurements are still a good source of valuable information for band structure calculations.

In the work presented here, the technique of electric field modulation, i.e. electroreflectance, was used in the study of interband transitions in InAs, the alloys $\text{In}_{1-x}\text{Ga}_x\text{As}$ and the II-IV-V₂ materials. In the study of some II-IV-V₂ materials, the conventional (static) reflectance method and the temperature modulation method, i.e. thermorefectance, were also used. In the following section, the theoretical background of these investigations will be presented.

2. BASIC THEORY

21. REFLECTANCE

The behavior of electronic excitations in a solid under electromagnetic radiation is determined by the optical constants, e.g. the complex dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$, and the complex refractive index $N = n + i\kappa$ (n and κ being the ordinary refractive index and the extinction coefficient respectively). Since $\epsilon = N^2$, the relations between ϵ_1 , ϵ_2 and n , κ are easily established. Furthermore, the real and imaginary parts of the dielectric constant at frequency ω are related through the Kramers-Kronig transformations (Stern 63S1):

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{III-1})$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} \int_0^{\infty} \frac{\epsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (\text{III-2})$$

Thus the knowledge of one of the four optical constants ϵ_1 , ϵ_2 , n and κ would be sufficient to give information about the other three.

The problem of interband transitions can be treated by using time-dependent perturbation theory in the one-electron approximation. Bassani (66B2) has calculated the transition probability per unit time and unit volume, $W_{vc}(\omega)$, for an electron from a valence band state (of energy E_v and wave vector $\vec{k}$) to a conduction band state (of energy E_c and wave vector $\vec{k}'$),

as a result of the perturbation of the system by a time-dependent vector potential of the electromagnetic wave of frequency ω and wave vector $\vec{k}_{\text{rad}}$. Since $\epsilon_2 \propto W_{\text{vc}}$ as derived from Maxwell's theory by considering the energy loss of the monochromatic wave, the expression for $\epsilon_2(\omega)$ is obtained:

$$\epsilon_2(\omega) = \frac{8\pi \hbar^2 e^2}{\epsilon_0 m_e^2 \omega^2} \int_{\text{BZ}} \frac{d\vec{k}}{4\pi^3} |M_{\text{vc}}|^2 \delta(E_c - E_v - \hbar\omega) \quad (\text{III-3})$$

where the integration is carried out over the first Brillouin zone. Here the matrix element M_{vc} is an integral over all space

$$M_{\text{vc}} = \int d\vec{r} \exp[-i(\vec{k}' - \vec{k}_{\text{rad}}) \cdot \vec{r}] u_c^*(\vec{k}', \vec{r}) \vec{e} \cdot \vec{\nabla} \exp[i(\vec{k} \cdot \vec{r})] u_v(\vec{k}, \vec{r}) \quad (\text{III-4})$$

where $\vec{e}$ is the unit vector in the direction of the vector potential, and u_c and u_v are Bloch type wave functions with the periodicity of the lattice. Equations (III-3) and (III-4) have imposed two selection rules on interband transitions:

(1) The delta function requires $E_c - E_v = \hbar\omega$, i.e. the energy difference between the states E_c and E_v must be equal to photon energy, for the transition probability to be different from zero.

(2) For non-vanishing M_{vc} , $\vec{k}' = \vec{k} + \vec{k}_{\text{rad}}$ as based on conservation of momentum. Since the wave vector of the

radiation $\vec{k}_{\text{rad}}$ is very small compared to the linear dimensions of the Brillouin zone, it can be neglected. Hence $\vec{k}' = \vec{k}$ implies allowed transitions to be vertical (or direct).

If $|M_{vc}|^2$ is assumed to be slowly varying with $\vec{k}$, the integral in equation (III-3) can be rewritten, by using property of the δ -function, as

$$\epsilon_2(\omega) = \frac{8\pi \hbar^2 e^2}{\epsilon_0 m_e^2 \omega^2} \int_S \frac{1}{4\pi^3} \frac{|M_{vc}|^2 dS}{|\vec{\nabla}_{\vec{k}}(E_c - E_v)|_{E_c - E_v = \hbar\omega}} \quad (\text{III-5})$$

where dS is a surface element of the constant-energy-difference surface $E_c - E_v = \hbar\omega$. The integral of equation (III-5) without the term $|M_{vc}|^2$:

$$J_{vc} = \int_S \frac{1}{4\pi^3} \frac{dS}{|\vec{\nabla}_{\vec{k}}(E_c - E_v)|_{E_c - E_v = \hbar\omega}} \quad (\text{III-6})$$

is defined as the joint density-of-states which has singularities (or critical points) whenever

$$\vec{\nabla}_{\vec{k}}(E_c - E_v) = 0 \quad (\text{III-7})$$

This includes two cases:

$$\vec{\nabla}_{\vec{k}} E_c(\vec{k}) = \vec{\nabla}_{\vec{k}} E_v(\vec{k}) = 0 \quad (\text{III-8})$$

$$\text{and } \vec{\nabla}_{\vec{k}} E_c(\vec{k}) = \vec{\nabla}_{\vec{k}} E_v(\vec{k}) \neq 0 \quad (\text{III-9})$$

Critical points of the first type occur only at highly symmetric points of the Brillouin zone (such as Γ , X and L in the case of zincblende), while those of the second type exist at points of lower symmetry (such as certain positions along Λ and Σ directions in the case of zincblende). The critical points can also be classified one step further. In the neighborhood of a critical point at $\vec{k}_0$ of energy difference E_g , $E_c(\vec{k}) - E_v(\vec{k})$ can be expanded in a Taylor series as

$$E_c(\vec{k}) - E_v(\vec{k}) = E_g + \sum_{l=1}^3 a_l (k_l - k_{0l})^2 \quad (\text{III-10})$$

Here the indices l indicate the three principal axes and the coefficients a_1, a_2, a_3 may take positive or negative values. Then four different types of behavior of $E_c - E_v$ about the critical points result from different number of negative a 's. The four types of critical points labeled M_0, M_1, M_2 and M_3 (where the subscript indicates the number of negative a 's), correspond to minimum, saddle point, saddle point and maximum respectively. Apparently M_0 and M_3 belong to the type described by equation (III-8), while the saddle points M_1 and M_2 belong to the type described by equation (III-9). The sketch of the joint density of states $J_{vc}(E)$ for the four different cases is shown in Figure III-1. The common feature in these four cases is that $J_{vc}(E)$ varies as the square root of the energy separation from E_g on one side of E_g on the energy scale, and is constant on the other side. In the neighborhood of E_g ,

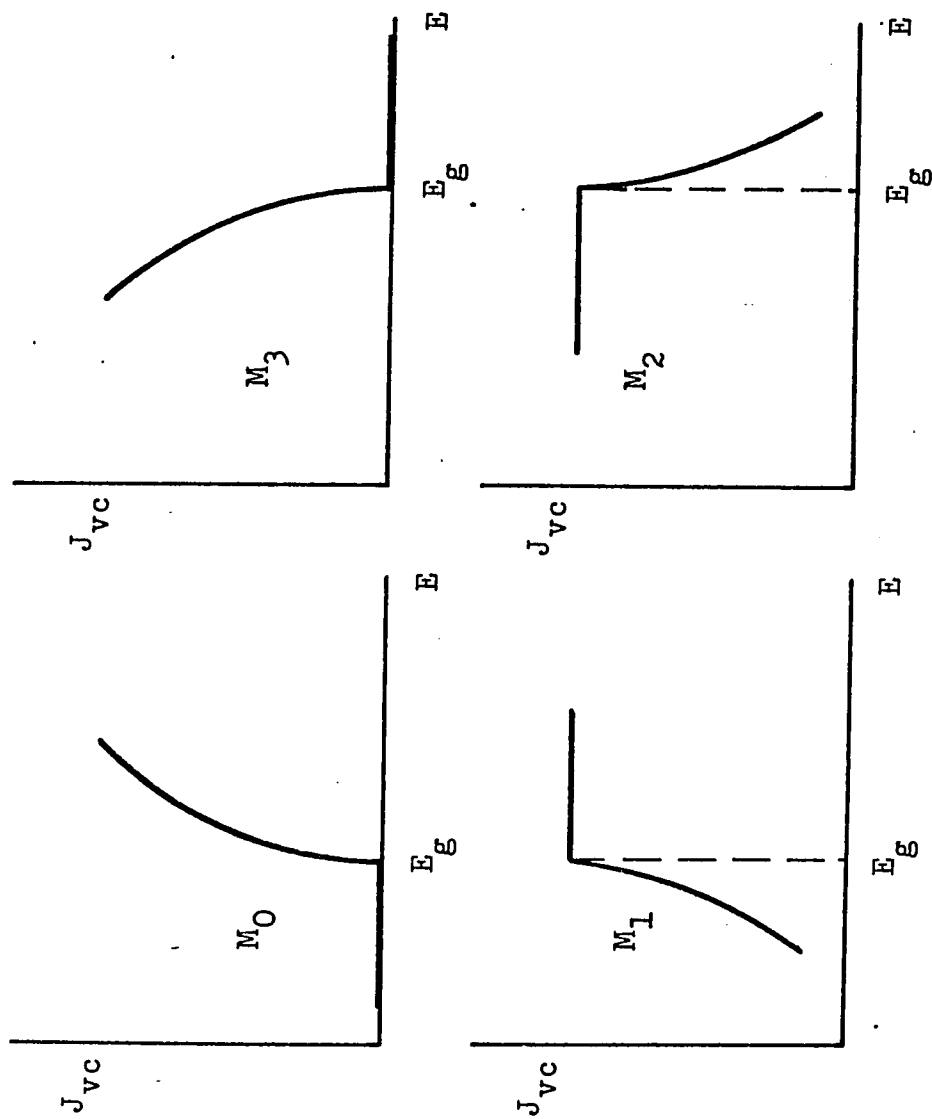


Figure III-1 Joint density-of-states function $J_{vc}(E)$ near critical points of M_0 , M_1 , M_2 , and M_3 types.

ϵ_2 also varies in the same patterns with slope discontinuity at E_g . In the analysis presented here thus far, the lifetime of the electrons in the excited states has not been considered. As a consequence of the uncertainty principle, the limited lifetime of these electrons leads to a broadening of energy of the initial and the final states, which can be described by a relaxation energy Γ (the Lorentzian broadening parameter). ϵ_2 is then described by the convolution (Seraphin and Bottka 66S2)

$$\epsilon_2(E)_{\text{lifetime broadening}} = \int_0^{\infty} \frac{\Gamma \epsilon_2(E') dE'}{(E'-E)^2 + \Gamma^2} \quad (\text{III-11})$$

However the characteristics of J_{vc} and ϵ_2 about the critical points are retained even with the inclusion of the lifetime broadening effect, and the sketch of these two quantities is quite useful for identifying the singularities for interband transitions obtained from experiments such as reflectance.

For normal incidence, the reflectance is

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (\text{III-12})$$

Since $N^2 = \epsilon$, the reflectance can also be expressed in terms of ϵ_1 and ϵ_2 :

$$R = \frac{(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} - [2\epsilon_1 + 2(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}}]^{\frac{1}{2}} + 1}{(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} + [2\epsilon_1 + 2(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}}]^{\frac{1}{2}} + 1} \quad (\text{III-13})$$

where ϵ_1 and ϵ_2 are related through the Kramers-Kronig transformations (III-1) and (III-2). It is evident that the reflectance extrema must correspond to singularities in ϵ_2 . As has been mentioned in the preceding section, the absolute reflectances of the same material are not reproducible due to variations in sample surface treatment. Consequently, only approximate values of the optical constants ϵ_1 and ϵ_2 (or n and κ) can be obtained from the Kramers-Kronig relations and reflectance data. Nevertheless, a qualitative picture, such as the types of critical points for interband transitions, can be studied through such results.

22. MODULATED REFLECTANCE

221. GENERAL CONSIDERATIONS

Since the optical properties of a material can be described in terms of the complex dielectric constant, the effect of modulation parameters on these properties must depend upon the change of the dielectric constant. The general expression for modulated reflectance for normal incidence is obtained by taking the total differential of equation (III-13) (Seraphin and Bottka 65S3):

$$\Delta R/R = \alpha(\epsilon_1, \epsilon_2) \Delta \epsilon_1 + \beta(\epsilon_1, \epsilon_2) \Delta \epsilon_2 \quad (\text{III-14})$$

Here $\alpha(\epsilon_1, \epsilon_2)$ and $\beta(\epsilon_1, \epsilon_2)$, which are also functions of photon energy through $\epsilon_1(E)$ and $\epsilon_2(E)$, describe the "macroscopic" aspects common to all different types of modulated reflectance. However, the "microscopic" contributions $\Delta \epsilon_1$ and $\Delta \epsilon_2$ are distinguished by the choice of modulating parameters. From $\epsilon_1(E)$ and $\epsilon_2(E)$ obtained experimentally, the energy dependence of α and β has been obtained for a number of semiconductors, e.g. germanium, silicon and GaAs (Philipp and Taft 60P2, Seraphin and Bennett 67S3). The forms of $\alpha(E)$ and $\beta(E)$ are very similar for these materials. The low-energy region, which contains the fundamental absorption edge, is " $\Delta \epsilon_1$ -dominated" through a value of α much larger than β (both α and β being positive). Toward higher photon energy, diminishing α and increasing β make $\Delta \epsilon_1$ and $\Delta \epsilon_2$ contribute evenly to the reflectance change.

Then a " $\Delta\epsilon_2$ -dominated" region appears as β becomes larger than α before both coefficients become negative. As can be seen in equation (III-14), the signs and relative magnitudes of the two coefficients are important factors in determining the phase and the magnitude of $\Delta R/R$.

Although $\Delta\epsilon_1(E)$ and $\Delta\epsilon_2(E)$ vary with different modulation parameters, there are still certain features in the "microscopic" parts which are common to various versions of modulated reflectance. For example: the modulation parameter affects the spectral position E_g of a critical point. This is quite valid in the modulation of lattice parameter or temperature, i.e. piezoreflectance and thermoreflectance, and is probably acceptable for the interpretation of other modulating mechanisms. It is seen from this simple picture that the modulation of the spectral position E_g of the critical point is related to ϵ_2 through the joint density-of-states function given in equations (III-5) and (III-6). $d\epsilon_2/dE_g$ is proportional to dJ_{vc}/dE_g provided $|M_{vc}|^2$ is a slowly varying term. It has been mentioned earlier that for all four types of critical points, $J_{vc}(E)$ varies as the square root of the energy separation from E_g , on one side of E_g on the energy scale, and is constant on the other side. Hence, the derivative $d\epsilon_2/dE_g$ or dJ_{vc}/dE_g has a singularity of the type $|E-E_g|^{-\frac{1}{2}}$ about the critical point. This then offers a qualitative explanation of the spectral selectivity of modulated reflectances. The response is especially sharp at the critical point but diminishes as the spectral

distance from the critical point increases. However for further understanding of modulated reflectance, the "microscopic" contributions $\Delta\epsilon_1$ and $\Delta\epsilon_2$ characterized by each type of modulation must be dealt with individually. The theoretical aspects of electreflectance and thermoreflectance, the only differential techniques used in this work, will be presented in further detail here. The theories in other types of modulated reflectance can be found in the review article by Seraphin (69S1).

222. ELECTROREFLECTANCE

The theory by Franz (58F1) and Keldysh (58K1) has predicted the effect of an electric field on the fundamental absorption edge of semiconductors and insulators. This is an effect of photon-assisted tunneling between conduction and valence bands, which gives rise to an apparent decrease of the energy gap. The Franz-Keldysh theory has been generalized and developed further for a detailed study of electric-field effect on interband transitions by Aspnes (66A2, 67A1), Aspnes et al (68A2) and Aymerich and Bassani (67A2). The theoretical aspects of electroreflectance as presented in the following are set at a conceptual level. Useful references concerning the detailed development and refinement of the theory can be found in the review article by Seraphin (69S1).

The effect of an electric field $\vec{E}$ on the electrons in the crystal can be treated by the removal of the invariance of lattice translations in the direction of $\vec{E}$. The component of the wave vector of an electron in this direction is no longer a good quantum number, and the perturbed wave functions can be formed from linear combinations of the unperturbed Bloch functions with wave vectors parallel to $\vec{E}$. With such considerations, Aspnes et al (68A2) have investigated the effect of mixing these wave functions on the dielectric function, and derived the field dependence of ϵ_2 . The expression of $\epsilon_2(\omega, \vec{E})$ is similar to the zero-field case given in equation (III-3). Here, the delta function $\delta(E_c - E_v - \hbar\omega)$ in the zero-field case is replaced

by a term, which involves an Airy function $Ai(x)$,

$$\{ |\hbar\Omega|^{-1} \cdot Ai[\frac{E_c - E_v - \hbar\omega}{\hbar \Omega(\hbar)}] \}$$

$$\text{where } \hbar \Omega(\hbar) = \left[\frac{e^2 e^2 \hbar^2}{2 \mu_{\parallel}(\hbar)} \right]^{1/3} \quad (\text{III-15})$$

$$\frac{1}{\mu_{\parallel}} = \frac{1}{\hbar^2} \frac{\partial^2}{\partial \hbar^2} (E_c - E_v) \quad (\text{III-16})$$

Here the extra variables are the electric field $\vec{E}$ and the reduced interband mass $\mu_{\parallel}$ in the direction of $\vec{E}$. The Airy function is highly unsymmetric, since it decays exponentially for positive argument but extends in damped oscillations in the region of negative argument. Aspnes (67A1) has solved the integral for $\epsilon_2(\omega, \vec{E})$ and obtained the change in ϵ_2 for four types of critical points:

$$\begin{aligned} \Delta \epsilon_2 &= \epsilon_2(\omega, \vec{E}) - \epsilon_2(\omega, 0) \\ &= \left\{ \begin{array}{l} \pm U F[\pm(E_c - E_v - \hbar\omega)/(\hbar\Omega)] \\ U G[\pm(E_c - E_v - \hbar\omega)/(\hbar\Omega)] \end{array} \right\} \quad (\text{III-17}) \end{aligned}$$

where U is a non-oscillatory term, whilst $F(x)$ and $G(x)$, defined by Aspnes (67A1) as two electro-optic functions, contain the squares of Airy functions and their derivatives of the same argument $\pm(E_c - E_v - \hbar\omega)/(\hbar\Omega)$.

The inclusion of the effect of lifetime broadening in the above treatment gives rise to a complex argument

$$[\pm(E_c - E_v - \hbar\omega) + i\Gamma] / (\hbar\Omega)$$

instead of the real argument in the Airy functions and hence in the two electro-optic functions.

$\Delta\epsilon_1$ can also be obtained through the Kramers-Kronig relation

$$\Delta\epsilon_1(\omega, \vec{E}) = \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \Delta\epsilon_2(\omega', \vec{E})}{\omega^2 - \omega'^2} d\omega' \quad (\text{III-18})$$

obtained from equation (III-1) by using $\epsilon_1 + \Delta\epsilon_1$ and $\epsilon_2 + \Delta\epsilon_2$ for ϵ_1 and ϵ_2 . The line shapes of these $\Delta\epsilon_1(\omega, \vec{E})$ and $\Delta\epsilon_2(\omega, \vec{E})$ for different types of critical points have been described in detail by Hamakawa et al (68H1). If these line shapes could ideally be recognized from electroreflectance spectra, the types of critical points involved would be identified. However in practice, due to the complexity of the field effect, limitations of the experimental techniques and variations in sample surface treatments, the correspondence between the experimental results and the ideal line shapes is very difficult to establish at present.

223. THERMOREFLECTANCE

The basic mechanisms in thermorefectance are less complicated as compared to other types of modulated reflectance, since it is a scalar effect. Hence the assumption that the temperature change shifts the spectral position of an interband edge E_g is reasonably valid. In order to include the effect of lifetime broadening, relation (III-11) is used in conjunction with the approximation

$$\epsilon_2(E, E_g) = Y J_{vc}(E, E_g) \quad (\text{III-19})$$

Y being taken as a constant. Thus the "microscopic" contribution $\Delta\epsilon_2$ due to the change in E_g is given by

$$\Delta\epsilon_2 = Y (dE_g/dT)(\Delta T) \int_0^\infty \frac{\Gamma}{(E' - E)^2 + \Gamma^2} \frac{dJ_{vc}(E', E_g)}{dE_g} dE' \quad (\text{III-20})$$

and $\Delta\epsilon_1$ can be derived from $\Delta\epsilon_2$ through the Kramers-Kronig relation. The expressions for $\Delta R/R$ can then be calculated by using equation (III-14). Batz (67B3) has obtained the results for $\Gamma \ll E_g$ for the four types of critical points M_0 , M_1 , M_2 and M_3 respectively:

$$\Delta R/R = \left\{ \begin{array}{l} -\alpha H(-x) - \beta H(x) \\ \alpha H(x) - \beta H(-x) \\ \alpha H(-x) + \beta H(x) \\ -\alpha H(x) + \beta H(-x) \end{array} \right\} \cdot Z \cdot (dE_g/dT) \cdot \Delta T \quad (\text{III-21})$$

where $H(x) = (x^2+1)^{-\frac{1}{2}}[(x^2+1)^{\frac{1}{2}}+x]^{\frac{1}{2}}$

$$x = (E - E_g)/\Gamma$$

and Z is a constant. Balzarotti and Grandolfo (68B2) and Matatagui et al (68M1) have also considered the effect of the variation of Γ on ϵ_2 for refinement of the theoretical presentation. However the existing theory of thermorefectance only gives some qualitative pictures of experimental results.

3. REVIEW OF THE LITERATURE

31. REFLECTANCE

The first reflectance measurements on semiconductors at energies above the fundamental band gap were reported on germanium and silicon (Philipp and Taft 59P1, 60P2). Since then, this type of measurements has been made on a large number of semiconductors, accompanied by a gradual development of higher degree of sophistication in the experimental techniques. The correlation of experimental results and theoretical presentations has also been established qualitatively for a number of materials.

The review presented here is mainly concerned with group IV and III-V semiconductors. The work on II-IV-V₂ compounds will be reviewed in Chapter IV. The development of reflectance work on other semiconducting materials will not be considered here, and useful references about this can be found in the review articles by Phillips (66P1) and Harbeke (68H2), and the monograph by Greenaway and Harbeke (68G3).

The first reflectance measurements on III-V compounds were reported on InSb, InAs, InP, GaSb, GaAs, GaP and AlSb by Tauc and Abraham (60T1) and Cardona (61C1, 61C2, 61C4). These measurements at photon energies lower than 5.2 eV included room temperature work on all these compounds, and lower temperature work (down to liquid nitrogen temperature) on InP and AlSb. Shortly afterwards, reflectance measurements on InSb, InAs, GaSb and GaAs were made at 80°K by Greenaway (62G3),

and in the range 130-650°K by Lukeš and Schmidt (62L2). Room temperature measurements on InSb, InAs, GaAs and GaP were made to cover the energy range 1-12 eV by Ehrenreich et al (62E1), and then extended to 25 eV by Philipp and Ehrenreich (63P1) who calculated the dielectric functions $\epsilon_1(E)$ and $\epsilon_2(E)$ of these compounds over this wide energy range. More recently, the detailed structures in reflectance spectra of seven III-V compounds in the energy range 3.5-7.5 eV were reported by Vishnubhatla and Woolley (68V1).

Since group IV elements and III-V compounds have very similar features in their band structures and reflectance spectra, a detailed study of the reflectance work on germanium and silicon would form a guide line for the interpretation of the reflectance results of the III-V materials. The correlation of experiment and theory in the reflectance work of germanium is illustrated in Figure III-2 by the comparison of $\epsilon_2(E)$ as derived from the room temperature reflectance measurements by Philipp and Taft (59P1) and Tauc and Antončík (60T2), and from pseudopotential energy-band calculations by Brust et al (62B1) and Brust (64B2). The explanation of the symbols (in Figure III-2) showing the types of interband transitions is given in Figure I-4. The interpretation of the reflectance peaks can then be made:

- (1) The reflectance measurement does not show any structure for the M_0 type critical points: $\Gamma_{25'v}-\Gamma_{2'c}$ and $L_{3'v}-L_{1c}$ transitions.

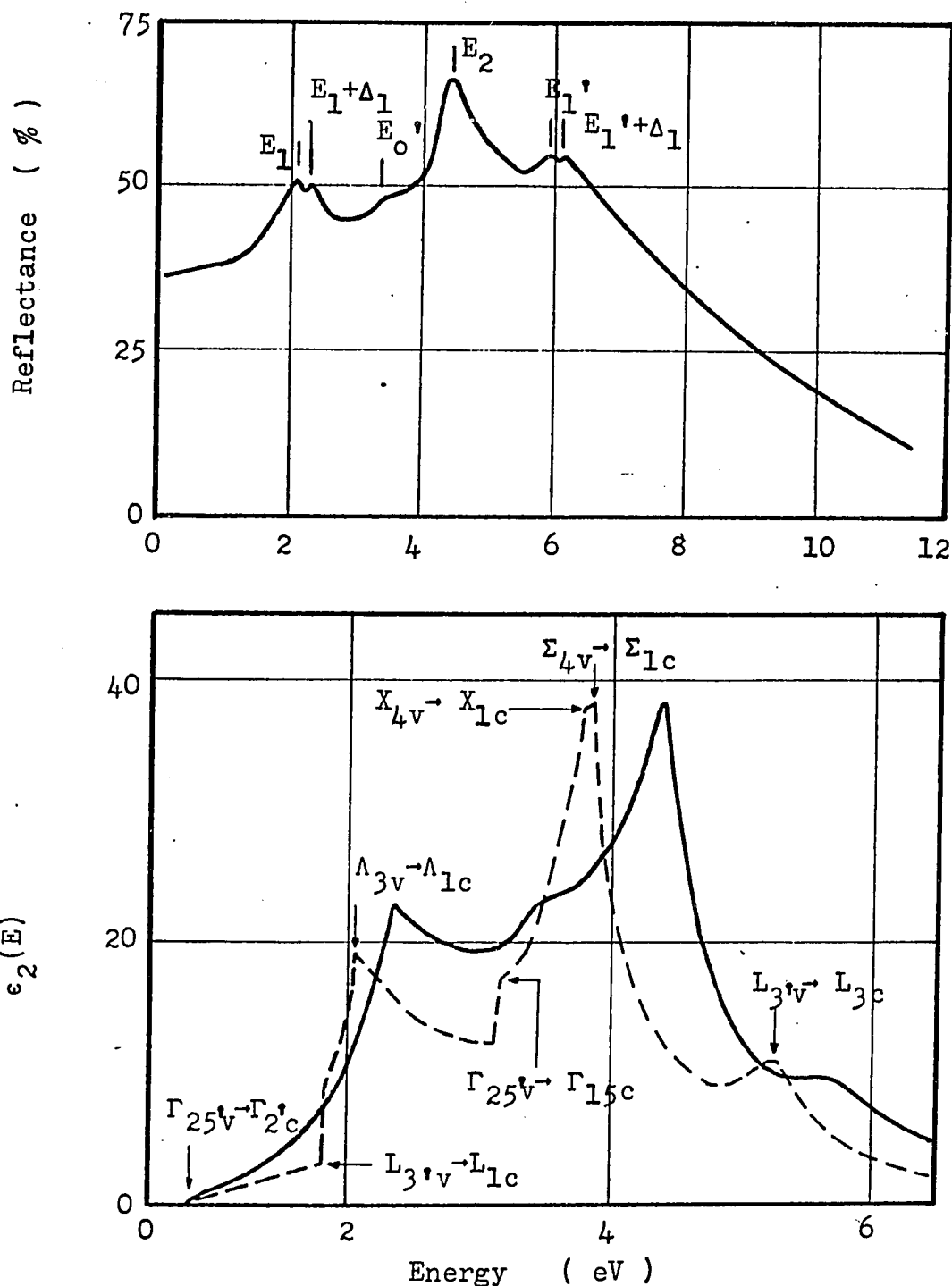


Figure III-2 (a) Room temperature reflectance spectrum of Ge (59P1, 60T2, 68G3), (b) Imaginary part of dielectric constant $\epsilon_2(E)$ for Ge, solid line: experimental; dotted line: theoretical (62B1, 64B2, 66P1).

(2) The doublet E_1 and $E_1 + \Delta_1$ corresponds to M_1 saddle point transitions $\Lambda_{3,v} - \Lambda_{1c}$. The splitting term $\Delta_1 = 0.2 \text{ eV}$ is attributed to the spin-orbit splitting of the $\Lambda_{3,v}$ band at a certain position between Γ and L points (closer to L than to Γ).

(3) The assignment of the E_0' peak as transition $\Gamma_{25,v} - \Gamma_{15c}$ must be examined. The nearly parallel nature of the Δ_{1c} and Δ_{5v} bands in the $\langle 100 \rangle$ directions indicates the possibility of having more than one critical point in the neighborhood of Γ (Brust 64B2, Cardona et al 67C1). Furthermore, the observation of the splitting of the E_0' peak from modulated reflectance measurements, such as electroreflectance (Cardona et al 67C1), suggests that this is from the splitting of the Δ_{5v} band. Since this highest valence band is degenerate at $\Gamma_{25,v}$, it would be more reasonable that the E_0' peaks correspond to the transitions $\Delta_{5v} - \Delta_{1c}$ at a position close to Γ .

(4) The strongest structure E_2 arises from the accidental degeneracy of an M_1 saddle point due to $X_{4v} - X_{1c}$ transitions and an M_2 saddle point due to $\Sigma_{4v} - \Sigma_{1c}$ transitions, i.e. in the $\langle 110 \rangle$ directions.

(5) The high energy peaks labeled E_1' and $E_1' + \Delta_1$ correspond to M_3 type critical point: $L_{3,v} - L_{3c}$ transitions. These peaks give the splitting of $L_{3,v}$, $\Delta_1 = 0.2 \text{ eV}$, since the L_{3c} spin-orbit splitting is considerably smaller than that of $L_{3,v}$ (Cardona and Pollak 66C2).

The correspondence between the reflectance peaks and interband transitions in III-V compounds can then be established

accordingly. This is illustrated by the reflectance spectrum of InAs (Ehrenreich et al 62E1) as shown in Figure III-3.. The similarity between this spectrum and that of germanium (Figure III-2) is readily seen. Since different labels are used in the band structure presentations of diamond and zincblende materials (Figure I-4), the reflectance peaks must be interpreted in terms of the appropriate ones. In the zincblende case, the correspondence is:

$$\begin{aligned} E_1 \text{ and } E_1 + \Delta_1 &: \Lambda_{3v} - \Lambda_{1c} \\ E_0' \text{ and } E_0' + \Delta_0' &: \Delta_{5v} - \Delta_{1c}^u, \text{ close to } \Gamma \text{ point} \\ E_2 &: X_{5v} - X_{1c} \text{ and/or } \Sigma_{1v} \Sigma_{2v} - \Sigma_{1c}^l \text{ close to } \\ &\quad X \text{ point} \\ E_2 + \delta &: X_{5v} - X_{3c} \text{ and/or } \Sigma_{1v} \Sigma_{2v} - \Sigma_{1c}^u \text{ close to } \\ &\quad X \text{ point} \\ E_1' \text{ and } E_1' + \Delta_1 &: L_{3v} - L_{3c} \end{aligned}$$

The interband transition energies of III-V compounds, as obtained from reflectance measurements, have been tabulated in the monograph by Greenaway and Harbeke (68G3).

Reflectance work has also been extended to mixed III-V alloys in the study of variations of various interband transition energies with composition over the whole composition range. The first report was on InSb-GaSb and InAs-GaAs systems by Woolley and Blazey (64W1). The system InAs-GaAs was studied later by Jones (66J1). Further reports of reflectance work on mixed III-V alloys included the systems: InAs-InP by Krioturu et al (66K3), and GaAs-GaP by Woolley et al (65W1) and

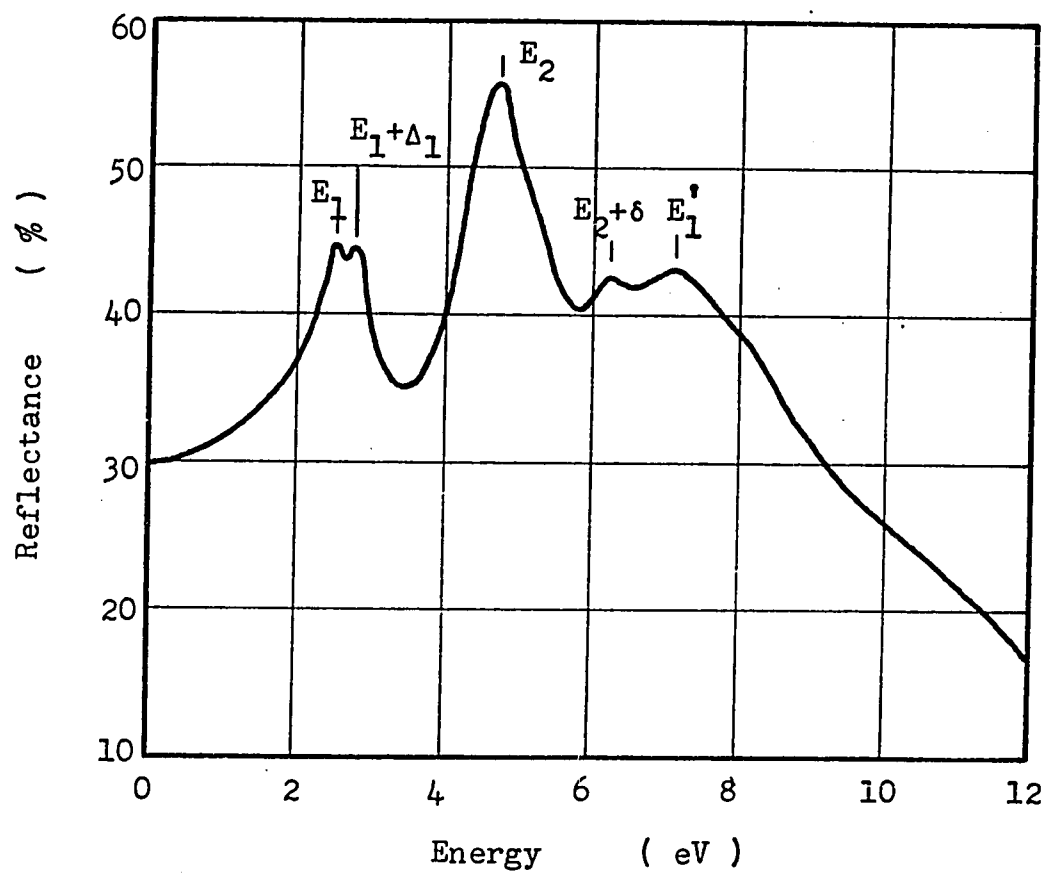


Figure III-3 Room temperature reflectance spectrum of InAs (62E1).

Thompson et al (66T2). In these investigations, the variations of some interband transition energies with composition were found to be linear within the limits of experimental error. However in the work on InAs-GaAs and GaAs-GaP systems, the authors (65W1, 66T2, 66J1) observed a non-linear composition dependence of the E_1 peaks. This situation therefore called for further investigation by using modulated reflectance methods to determine the interband transition energies more accurately.

32. MODULATED REFLECTANCE

Electroreflectance was the first modulation method used to achieve greater sensitivity and resolution in reflectance measurements. The electroreflectance method was developed by Seraphin who used a field-effect configuration (64S2). In this, the polished and etched specimen and a transparent conductor (SnO_2 deposited on fused quartz) were used as two plates of a condenser, separated by a thin dielectric film (mylar or saranwrap). Such an arrangement allows the incident monochromatic light in the range ~ 0.2 -4.5 eV to be reflected from the specimen surface. The d.c. biasing and a.c. modulating voltages of up to 600 V were applied across the plates to produce field strength and modulation of the field in the order of 10^5 V/cm on the semiconductor surface. By using the field effect configuration, Seraphin and co-workers have reported electroreflectance work on germanium (64S2, 65S4, 65S5, 65S6, 67S2), silicon (65S1, 65S4, 66S2, 67S2) and GaAs (65S2, 66S1). These investigations have also been summarized by Seraphin (67S1).

Cardona and co-workers have reported electroreflectance measurements by using an electrolyte technique. In this, the semiconductor-electrolyte interface is biased with respect to a platinum electrode to form a blocking contact in order to cause dropping of the voltage in the space-charge layer in the semiconductor surface (Williams 60W1). With this method, an electric field of the order of 10^5 V/cm can be produced with

a biasing voltage of the order of 1 V for most semiconductors (Cardona et al 67C1). The photon energy range is approximately 1-7 eV in this case. A marked advantage of this technique is that irregularly shaped surfaces can also be used without affecting the results. However this technique has a temperature limitation in operation as set by the freezing point of the electrolyte. Cardona's group has reported electroreflectance measurements on a large number of semiconductors including grey tin (66C1), germanium (65S7, 66C4, 66C6), silicon (66C4), InSb (65S7, 66C3, 66C4), InAs (66S3), InP (65S7, 66S3), GaSb (65S7, 66S3), GaAs (66C4, 66S3), GaP (66S3) and AlSb (66C5). These investigations have also been summarized by Cardona et al (67C1) who compared the experimental and calculated values of several spin-orbit splittings in these semiconductors.

Recently, more detailed electroreflectance studies on germanium were reported in several publications: Hamakawa et al (67H1, 68H1), Ghosh (68G1), Ballarò et al (68B1) and Nishino and Hamakawa (68N1).

Electroreflectance work on alloy semiconductors was first reported on Ge-Si system (Cardona et al 66C6) and GaAs-GaP system (Thompson et al 66T1). Since then electroreflectance work on mixed III-V alloys has been carried out extensively by Woolley's group. The work has covered InAs-GaAs alloys (Thompson and Woolley 67T1, Kwan et al, this thesis 68K3), InAs-InSb, InSb-GaSb and InAs-InP alloys (Vishnubhatla et al 69V3).

Thermoreflectance measurements on group IV and III-V semiconductors have been reported on germanium (Batz 66B3, 67B3), on silicon and GaAs (Berglund 66B7, Matatagui et al 68M1) and on InSb, InAs, InP, GaSb, GaP and AlSb (Matatagui et al 68M1). The interband-transition energies as obtained from these measurements were in good agreement with those from reflectance and electoreflectance work.

Other versions of modulated reflectance have also been reported in various publications, e.g.

(1) Wavelength-modulated reflectance (Balslev 66B1, Matatagui et al 68M1).

(2) Piezo-reflectance, i.e. stress modulation of reflectance (Engeler et al 65E1, Balslev 67B1, 67B2).

(3) Piezo-electoreflectance, i.e. electoreflectance with static stress (Pollak et al 66P2, Pollak and Cardona 68P1).

(4) Magneto-electoreflectance, i.e. electoreflectance in the presence of a magnetic field (Groves et al 66G1).

(5) Magneto-piezo-reflectance, i.e. piezo-reflectance in the presence of a magnetic field (Aggarwal et al 66A1).

Further detail and development of various versions of modulated reflectance can be found in the review article by Seraphin (69S1) and will not be expounded here.

4. ELECTROREFLECTANCE OF InAs

4.1. INTRODUCTION.

The electroreflectance method, which has been used to investigate singularities in the joint density-of-states for optical transitions in semiconductors, has been found to give greater resolution in energy than the conventional (static) reflectance method. In electroreflectance, the electric field imposed normal to the specimen surface consists of a d.c. bias and an a.c. modulation voltage. The resulting structure in $\Delta R/R$ as a function of photon energy $h\nu$ consisted of peaks corresponding to the interband transitions plus subsidiary oscillations which may occur before or after the peaks, depending upon the particular conditions concerned. Thus there can be uncertainty in the initial identification of the peaks corresponding to the interband transitions. Extensive studies of electroreflectance on various semiconductors have been reported by various groups (Section III-32).

It is usually found in electroreflectance measurements that for n-type material, the peak values of $\Delta R/R$ are negative, while for p-type material, $\Delta R/R$ is positive under normal conditions of d.c. biasing and a.c. modulating voltages. However, under normal conditions, the behavior of InAs is anomalous in that n-type InAs appears to give positive peaks in $\Delta R/R$ (Cardona 67C1). Such behavior will clearly depend on surface effects, which in turn will be influenced by carrier concentration, biasing voltage, etc., and hence an investigation

of the effects of both doping and biasing voltage on the electroreflectance spectra of InAs has been made here. Two further results have then been obtained. Firstly, the possible variation of the E_1 interband transition energy with doping has been checked. Cardona et al (67Cl) have used the electrolyte technique to study the variation of various electroreflectance peaks with doping in GaAs and their results tend to indicate a small increase in E_1 at high values of both n and p . Secondly, an understanding of the anomalous effects in InAs-like materials has enabled the electroreflectance data on InAs-GaAs alloys to be correctly interpreted. This will be given in detail in Section III-5.

42. MATERIALS, EQUIPMENT AND EXPERIMENTAL TECHNIQUE

421. PREPARATION OF SPECIMENS

The p-type specimens were prepared by doping InAs with zinc to give hole concentrations of up to $p = 1.6 \times 10^{25} \text{ m}^{-3}$, and the n-type specimens by doping with In_2Se_3 to give electron concentrations of up to $n = 4 \times 10^{25} \text{ m}^{-3}$. The method of preparation of these materials has been given in Section II-321. For the low doped materials, the synthesized ingots were annealed under vacuum at 800°C for 1 to 2 weeks only, and this was sufficient for good equilibrium conditions.

The specimens were cut from the annealed ingots into platelets 1-2 mm thick. In every case, a specimen was lapped on both sides and polished on one side with alumina powder down to 0.05 micron grain size on cloth covered wheels. It was then mounted on a brass rod, good electrical contact between the specimen and the rod being made with silver paint (GC no. 21-1). Both specimen and rod were painted with insulating liquid tape (GC no. 176-2) except the polished specimen surface and the upper end of the rod as shown in Figure III-4. Therefore when the mounted specimen was immersed in the electrolytic bath, only the area of $\sim 4 \times 8 \text{ mm}^2$ of the uncovered specimen surface was in electrical contact with the electrolyte. Immediately prior to the measurement, the mounted specimen was etched in Wolsky solution ($7\text{HCl} : 1\text{HNO}_3 : 8\text{CH}_3\text{COOH}$) for a few seconds to remove damaged layers on the polished surface.

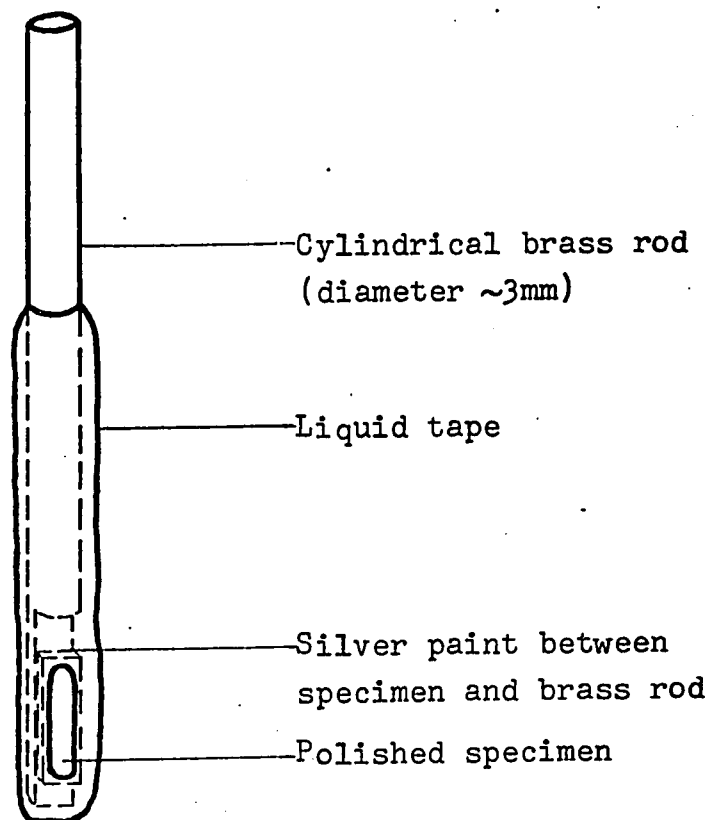


Figure III-4 Mounted specimen for electroreflectance measurement.

422. EQUIPMENT

A diagram of the experimental setup is shown in Figure III-5, and the description of this is given in the following:

4221. OPTICAL SYSTEM

The light source was a Hanovia (Model 970C-1) 600 W d.c. xenon arc lamp, installed in an Orion (Model C-60-50) lamp housing, and powered by a Hanovia (Model 27801-1) 1000 W power system. The monochromator was a grating type: Bausch and Lomb 500 mm Model 33-86-45. The wavelength control of this monochromator was motor driven. Kodak filters were used to filter out second order diffractions:

no filter	for	2000-4000 Å	(3.1-6.2 eV)
glass filter	for	3200-6200 Å	(2.0-3.9 eV)
Wratten no. 2A	for	4200-8000 Å	(1.5-3.0 eV)
Wratten no. 29	for	6100-12000 Å	(1.0-2.0 eV)

The monochromatic light was focused on the specimen surface by a quartz lens, and the reflected beam from the specimen was reflected again by an aluminum-coated mirror to a detector. The detectors used here were a Dumont 6911 photomultiplier for the 1-3 eV region, and an EMI 6255S photomultiplier for the 2-6 eV region. The optical system was arranged in a light-tight box.

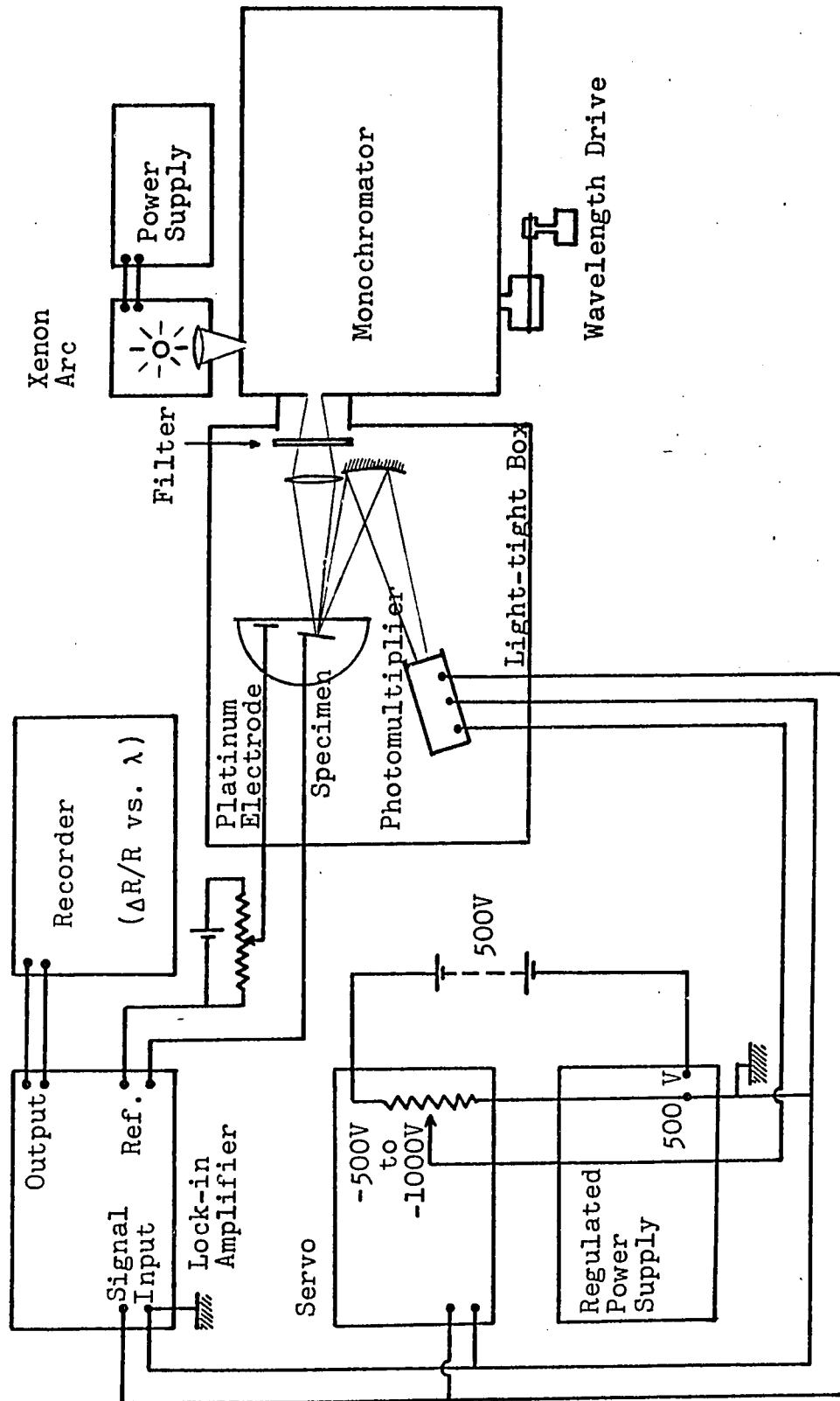


Figure III-5 Electroreflectance apparatus.

4222. ELECTROLYTIC CELL

The main parts of the electrolytic cell used in this work consisted of a thin quartz window, two electrodes, and an electrolyte. One of the electrodes was the mounted specimen, while the other was a piece of platinum foil. The electrolyte must be colorless and transparent in a wide energy range (1-6 eV), and hence KCl or glycerol aqueous solution was used.

4223. MEASURING EQUIPMENT

A biasing voltage of -3 to 3 V relative to the platinum electrode was applied to the specimen by a battery-potentiometer combination. A modulating voltage of up to 5 V peak-to-peak on the specimen was supplied by a PAR Model JB-6 lock-in amplifier. In this work, the modulation frequency was tuned at 70 or 75 cps. The high tension on the photomultiplier tube was maintained by a Keithley Model 240 and an NJE Corp. Model S-326 high voltage supplies. The output signal of the photomultiplier consisted of two parts. The part which was proportional to the reflectance R was kept constant (~ 1 V) by means of a Heathkit recorder (Model EUW-20) operating as a servo for adjusting the photomultiplier voltage in the range of -500 to -1000 V. The other part of the output signal, which was proportional to the change of reflectance ΔR due to the modulation, was amplified by the JB-6 lock-in amplifier and

then displayed on a Heathkit recorder (Model EUW-20) with chart speed 2 in/min. Since R was kept constant, the display on the chart recorder was effectively a plot of $\Delta R/R$ versus the wavelength.

423. PROCEDURE OF MEASUREMENTS

The mounted specimen was placed in the electrolytic bath and the optical system was aligned by using the green light. Then by experimentation, the gain and phase settings of the lock-in amplifier were adjusted to give the optimum signal and least noise with appropriate biasing and modulating voltages applied to the specimen. When covering different regions of the spectrum, different photomultiplier tubes and filters were used. In each case, the spectrum was scanned first with a wavelength drive speed of 40 Å/min to give approximate positions of the peaks, and then with a speed of 8 Å/min for ample resolution of the spectrum.

43. MODIFICATIONS TO THE EQUIPMENT FOR REFLECTANCE AND THERMOREFLECTANCE MEASUREMENTS, AND ASSOCIATED EXPERIMENTAL TECHNIQUE

In the study of interband transitions of II-IV-As₂ compounds, reflectance and thermoreflectance measurements were made in addition to electoreflectance. The equipment required in these three types of measurements was very similar, and after some modifications, the experimental setup for electoreflectance work was also suitable for the other two types of measurements.

431. REFLECTANCE

The reflectance of a material is usually obtained from two separate measurements: the intensities of the incident light (I_0) and reflected light (I_r). The methods for reflectance measurements are reasonably well established. There are essentially two types of procedure analogous to the two approaches in optical absorption work:

(1) The scanning technique - this involves the measurements of I_0 over an energy range and then I_r over the same range.

(2) Point-by-point procedure - this involves measurements of I_0 and I_r alternately for each wavelength.

The advantages and disadvantages of both methods are readily seen. The first method involves errors due to the

fluctuation and drifting of the light intensity and electronics, while the second method introduces resetting errors in optical alignment of specimen and detector.

To minimise the complication in the modifications of the optical system of the electreflectance setup for reflectance measurements, the scanning technique was used. The diagram of this experimental setup is shown in Figure III-6. Here the same light source, monochromator, filters, photomultipliers and regulated power supply were used. For the measurements of I_r , the monochromatic light was focused on the polished specimen, and then reflected to the photomultiplier tube. For the measurements of I_o , the specimen was removed and the photomultiplier tube was moved around to face the beam. In each case, the output from the photomultiplier tube was fed into a Keithley Model 409 picoammeter, the output of which was read on a Hewlett-Packard Model 3440A digital voltmeter. Then the reflectance of a specimen was obtained from the quotient of the voltages for I_r and I_o measurements at corresponding wavelengths.

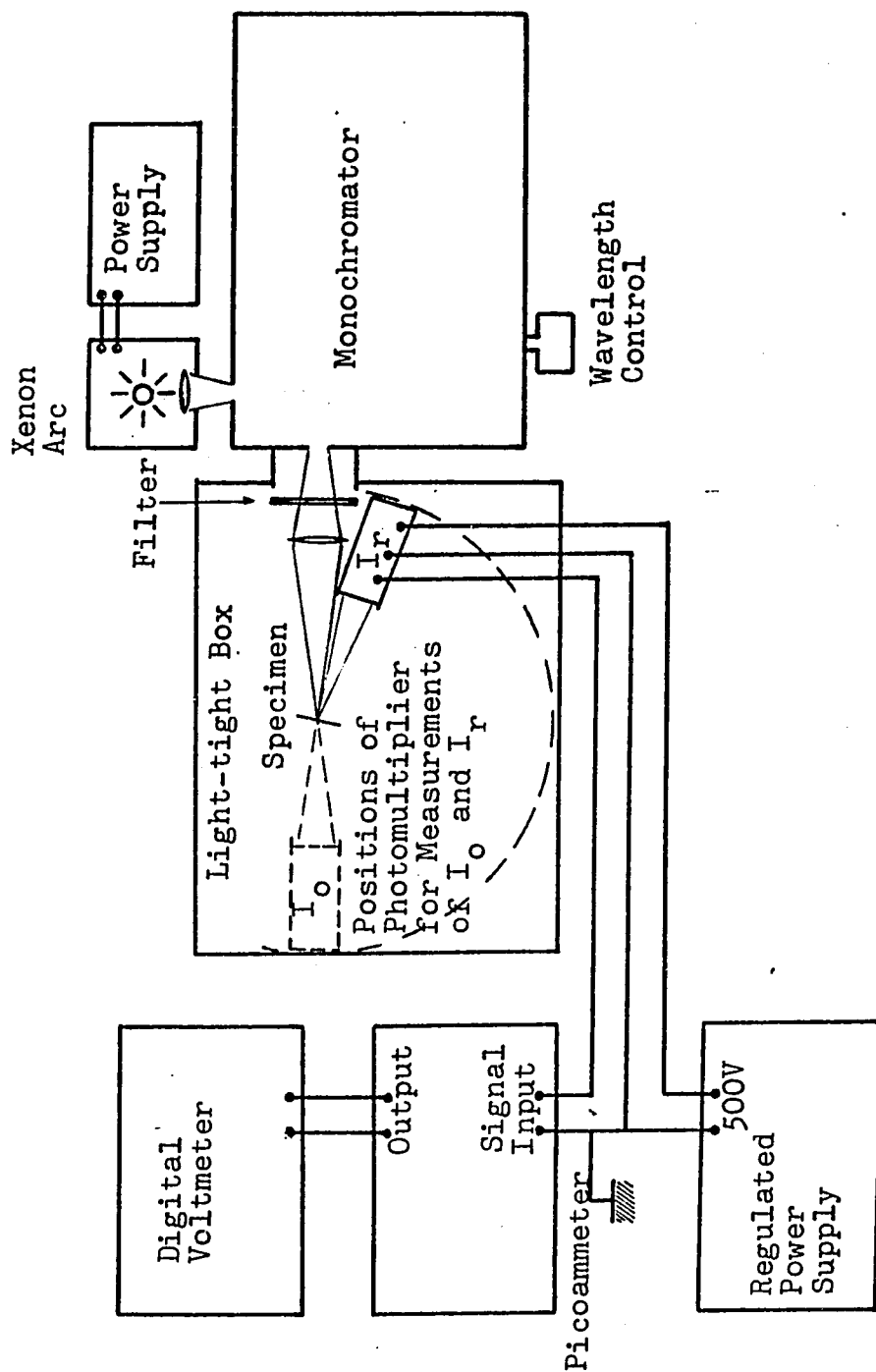


Figure III-6 Reflectance Apparatus

432. THERMOREFLECTANCE

In this work, the temperature modulation was achieved by direct heating of the specimen with square pulse of current. The mounted specimen is shown in Figure III-7. To obtain a good thermal response, the specimen was cut and lapped to the shape of a thin platelet of thickness ~ 0.3 mm. The polished specimen was mounted against a thin sapphire plate (which was glued to the copper cooling-system by silver paint) by pressure contacts with two strips of phosphor bronze at the two ends. Hence the specimen was in good thermal contact with, and in electrical insulation from, the cooling system. Some silver paint was also used to improve the electrical connections between the phosphor bronze strips and the ends of the specimen.

The apparatus used for thermorefectance measurements, as shown in Figure III-8, was very similar to that for electroreflectance. However, instead of feeding the modulation and the d.c. bias voltages to the specimen via the electrolyte in the case of electroreflectance work, the modulation voltage from the reference channel of the lock-in amplifier (PAR Model 122) was voltage and current amplified, and then square pulse of current was sent through the specimen. A modulation frequency of 19 cps was found suitable in the measurements.

After proper alignment of the optical system, the square pulse of current, which was sent through the specimen, was slowly increased until the scanning of the spectrum showed measurable peaks. For ample resolution of the spectra, a current of 0.2-1.2 amp (rms) was usually required.

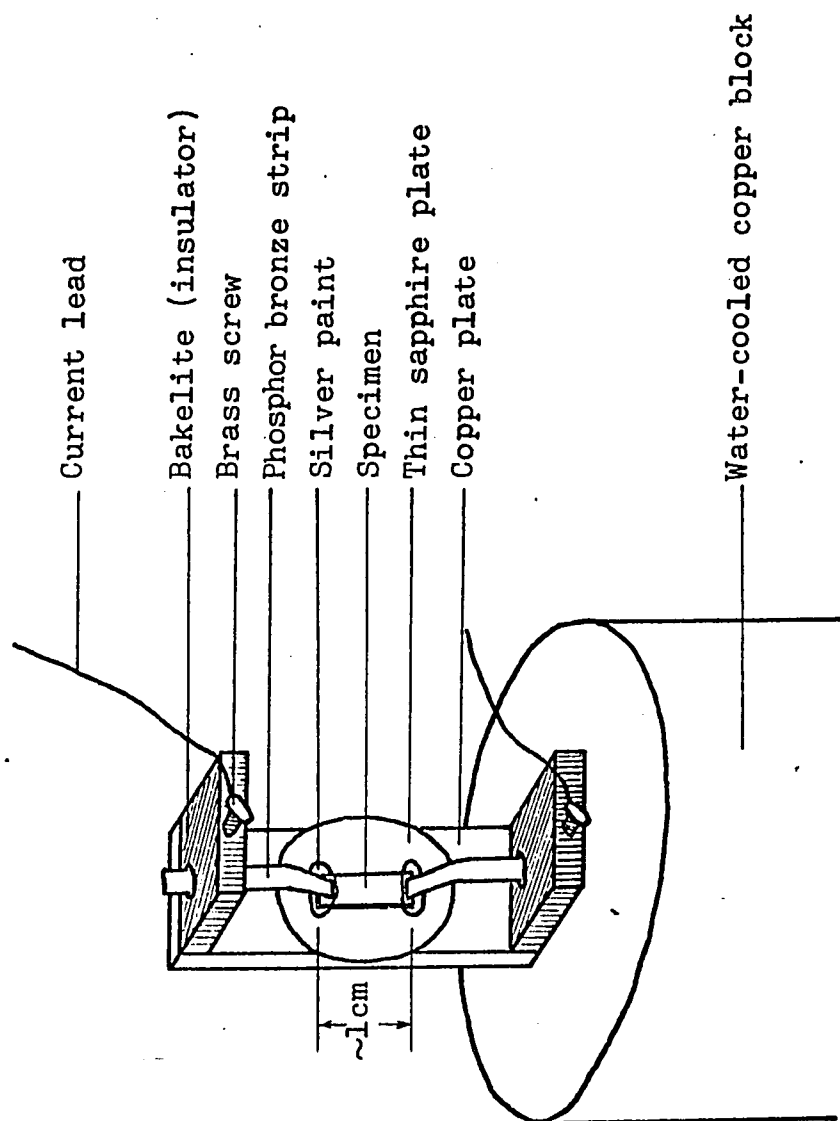


Figure III-7 Mounted specimen for thermorefectance measurement.

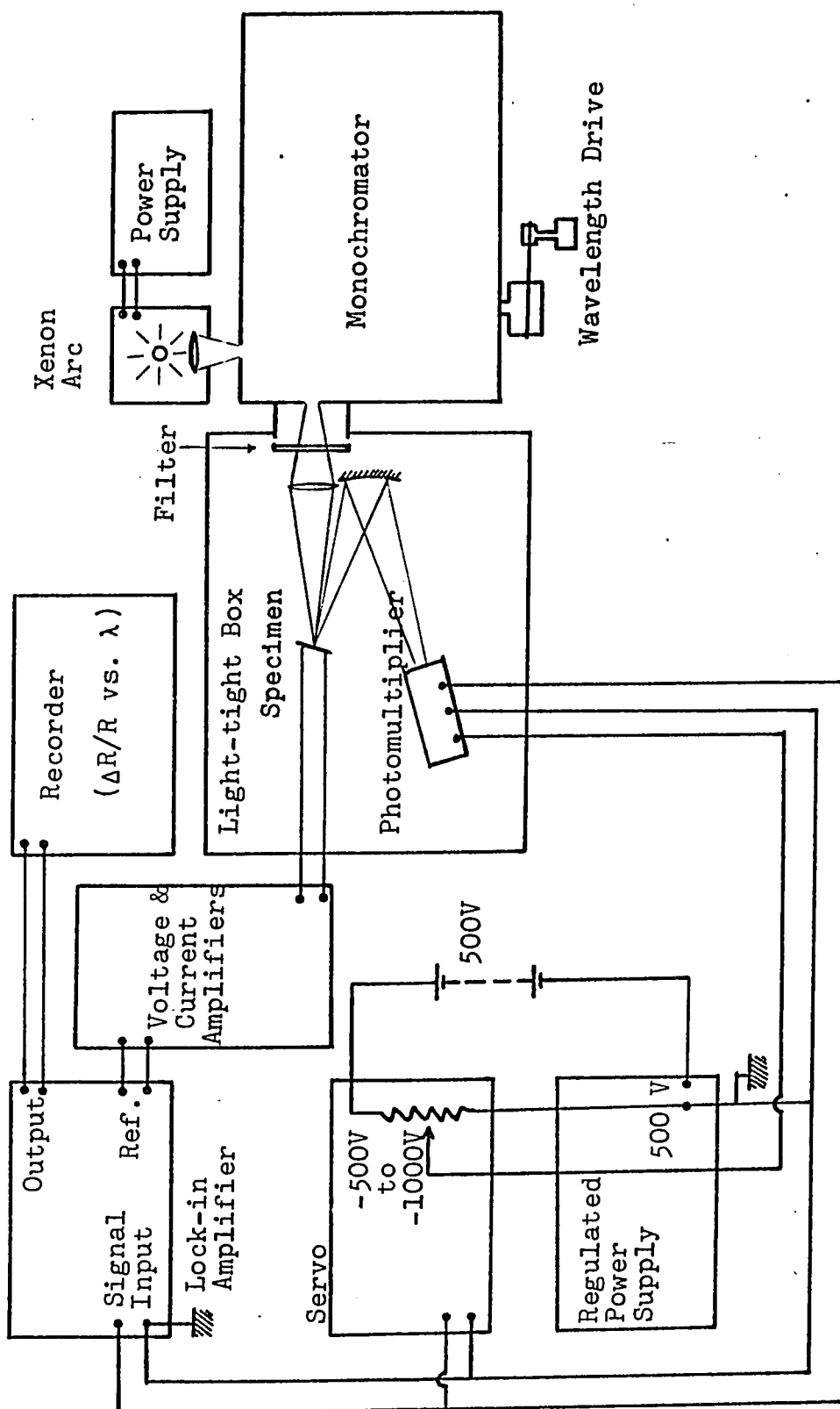


Figure III-8 Thermoreflectance apparatus.

44. RESULTS

In the initial measurements, a 0.3 N KCl solution was used as the electrolyte, a negative d.c. biasing voltage (V_{dc}) of 1.0 V was applied, and various a.c. modulation voltages (V_{ac}) of up to 3 V were used. It was found that, within the limits of experimental error, the value of the modulation voltage did not affect the characteristics of the spectra or the energy of the peaks, but strongly affected the intensity of the spectra. Hence, to investigate the effect of doping, the electroreflectance spectra in the energy range 2 to 5 eV were determined with fixed values of biasing and modulation voltage for a complete range of p- and n-type samples. In order to overcome the noise level and to avoid tarnishing of the specimen surface, a modulation of 1.5 V was found to be suitable for almost all n-type specimens and 0.6 V for all p-type specimens under investigation. The E_1 complex was investigated in detail, while for the ultraviolet (u.v.) peaks (E_o' and E_2), only the sign and energy were observed. It was found for these u.v. peaks that the energy values appeared to be independent of doping:

$$E_o' = 4.44 \pm 0.03 \text{ eV}$$

$$E_2 = 4.70 \pm 0.03 \text{ eV},$$

but the peaks could not be observed for electron concentrations close to $6 \times 10^{24} \text{ m}^{-3}$ where the change from p- to n-type behavior occurred. It was found that with this KCl electrolyte, after the detailed measurements of the E_1 region, the specimen

surface was frequently slightly tarnished.

Spectra for some typical specimens, both n-type and p-type, obtained with 0.3 N KCl electrolyte and -1.0 V d.c. bias are shown in Figure III-9. It was found that for the E_1 complex, $\Delta R/R$ was largest for p-type samples of low carrier concentration and quite small for n-type samples with carrier concentrations close to $6 \times 10^{24} \text{ m}^{-3}$, the value at which the u.v. peaks changed sign.

The energies of both positive and negative peaks in the E_1 complex were determined and are shown in Figure III-10 as a function of carrier concentration, corresponding peaks as assumed from the structure of the complex being shown by the same symbol. It is seen on this basis that for n-type material of electron concentration n greater than 10^{24} m^{-3} , the peak energies increase with n . However, if the sign of the u.v. peaks is taken into account and the E_1 and $E_1 + \Delta_1$ transitions are identified as the E_1 peaks having the same sign as these u.v. peaks, then the correlation of peaks above and below $10^{25} \text{ electrons/m}^3$ is different. The full lines in Figure III-10 indicate the peaks associated with E_1 and $E_1 + \Delta_1$ transitions and the dotted lines show the subsidiary oscillations. From these data, it appears that the energy of the E_1 and $E_1 + \Delta_1$ transitions are independent of carrier concentration within the range considered, i.e.

$$E_1 = 2.50 \text{ eV}$$

$$E_1 + \Delta_1 = 2.78 \text{ eV},$$

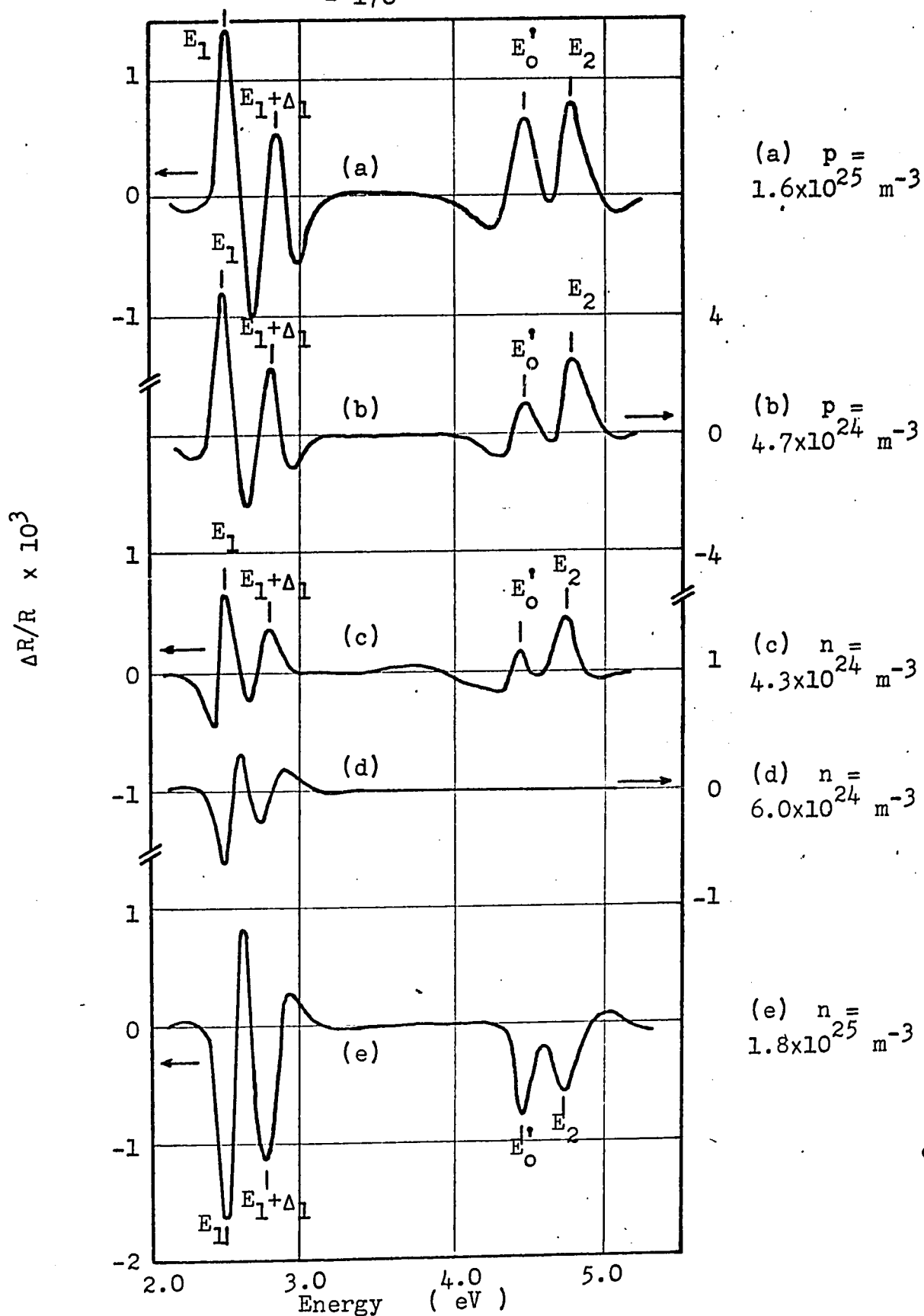


Figure III-9 Electoreflectance spectra of typical specimens of InAs, Electrolyte: 0.3N KCl; d.c. biasing voltage: 1.0 V. Note the change of scale of $\Delta R/R$ for curve (b).

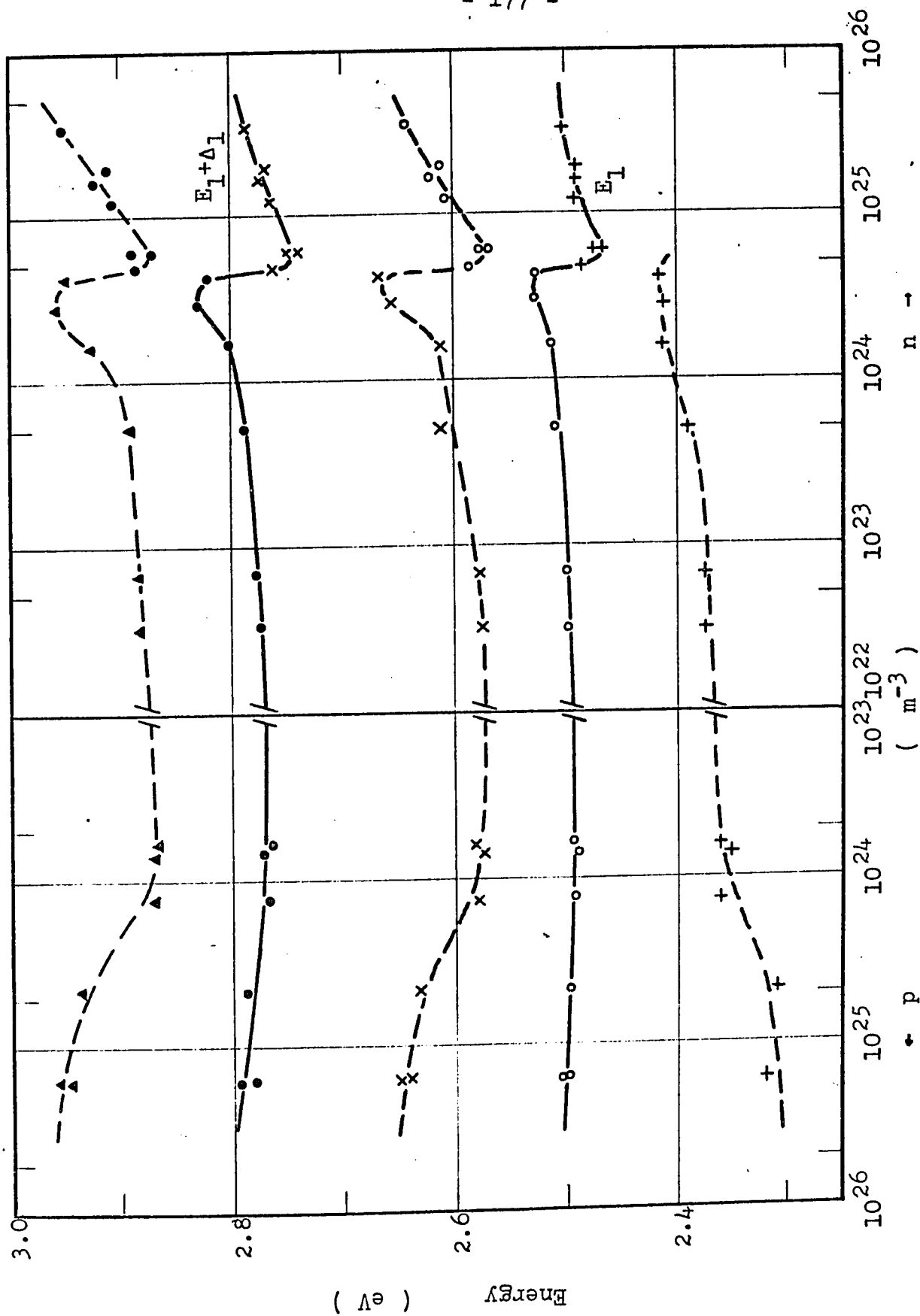


Figure III-10 Variation of energy values of peaks in the E_1 complex as a function of carrier concentration, Electrolyte: 0.3N KCl; d.c. biasing voltage: -1.0V.

while the energy values of the subsidiary oscillations do vary somewhat with carrier concentration. However, in the range of n from 10^{24} to 10^{25} m^{-3} , the energy of the E_1 and $E_1 + \Delta_1$ peaks show an oscillation, while $\Delta R/R$ is changing sign, i.e. to achieve the change of sign, the peak structure moves continuously in energy. Thus, in the range of n from 10^{24} to 10^{25} m^{-3} with this particular biasing voltage and electrolyte, no peak in the spectrum corresponds exactly with the E_1 or $E_1 + \Delta_1$ transition.

In order to investigate the effect of biasing voltage in a sample of given carrier concentration, it was desirable to eliminate the slight tarnishing which occurred during measurements in the 0.3 N KCl electrolyte. For this reason, a 25 % aqueous solution of glycerol was investigated and it was found that the surface was unaffected even by high modulation voltages. The measurements with the KCl electrolyte were repeated with the glycerol solution, using the same d.c. bias and modulation voltage. The same general behavior was observed, but because of lower ionicity of the glycerol solution, the range of the "transition region" was found to be reduced to $6 \times 10^{24} \text{ m}^{-3} < n < 1.2 \times 10^{25} \text{ m}^{-3}$. Typical spectra for n-type samples on either side of this transition region are shown in Figure III-11, and the variation of peak energies with carrier concentration given in Figure III-12. The actual form of the variation of the peak values in the transition region was not investigated in detail, but it is seen that again the values

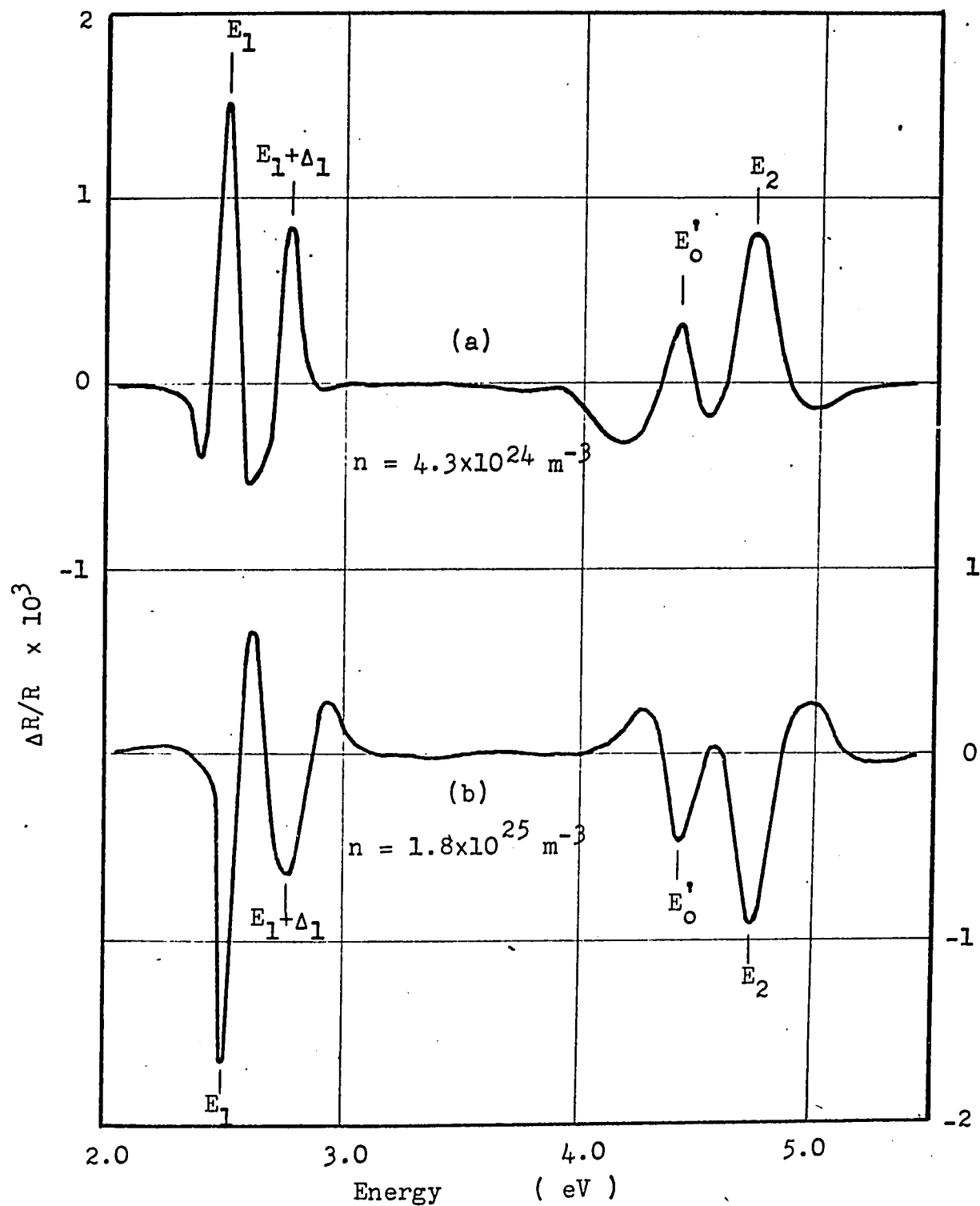


Figure III-11 Electroreflectance spectra of typical specimens of InAs, Electrolyte: 25% aqueous solution of glycerol; d.c. biasing voltage: -1.0V.

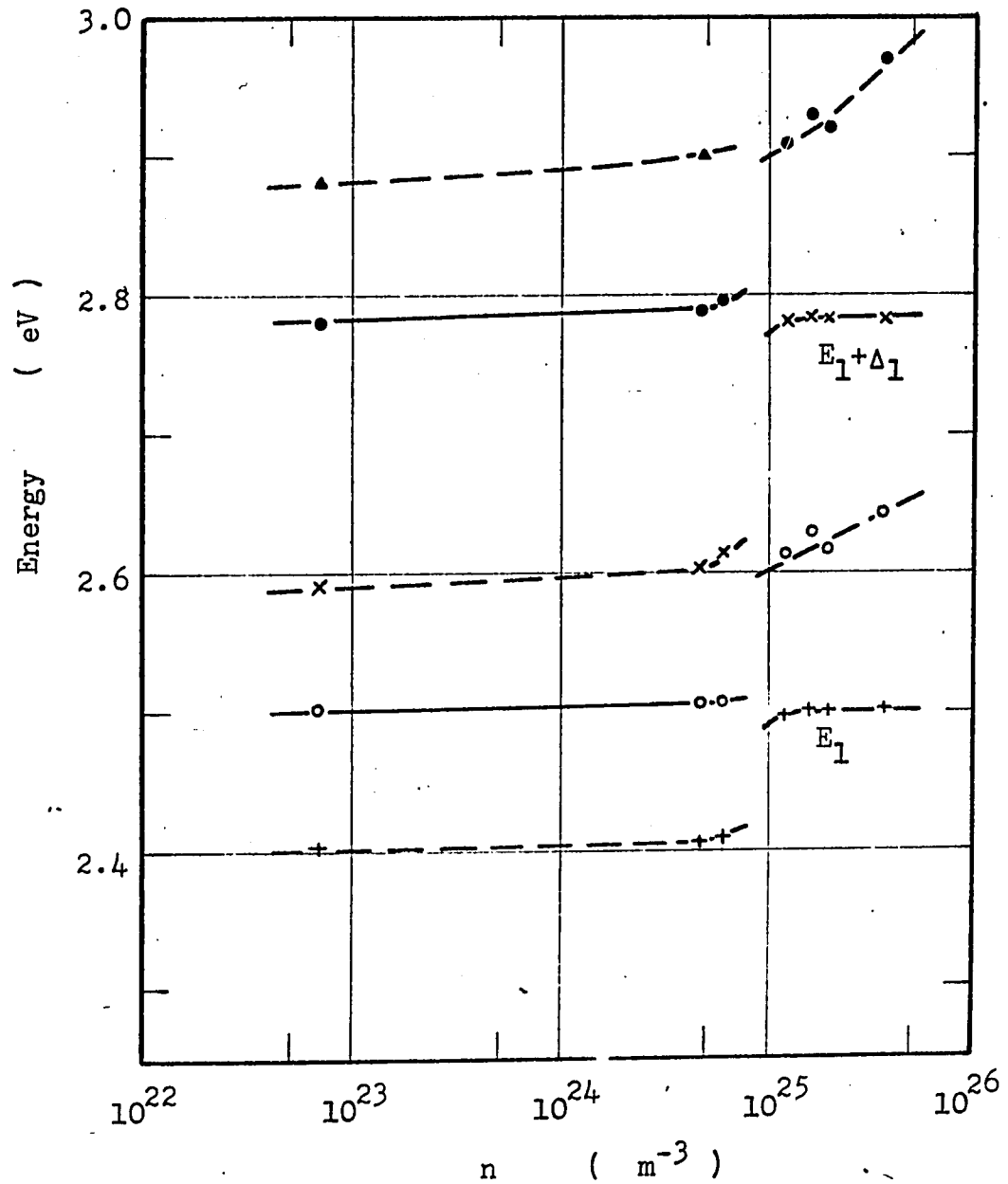


Figure III-12 Variation of energy values of peaks in the E_1 complex as a function of carrier concentration, Electrolyte: 25% aqueous solution of glycerol; d.c. biasing voltage: -1.0V.

of the E_1 and $E_1 + \Delta_1$ transition appear independent of carrier concentration.

In the present work, no attempt was made to search for an ideal biasing voltage to obtain a flat-band position which has been studied extensively on germanium by Hamakawa et al (68H1). However, various positive and negative d.c. biasing voltages were applied to a specimen of $n = 6.0 \times 10^{24} \text{ m}^{-3}$ in order to investigate the variation of the energy of transitions, the changeover of the peaks, and the shape of the spectra for the E_1 complex. The spectra and the energy values are shown in Figures III-13 and III-14. It can be seen that, with positive and low negative d.c. biasing voltages, the spectra were n-like, and with higher negative bias, the spectra were p-like. There was a narrow region in biasing voltages where the u.v. peaks were too weak to be observed and the identification of the E_1 peaks and the subsidiary oscillations was ambiguous in this transition region.

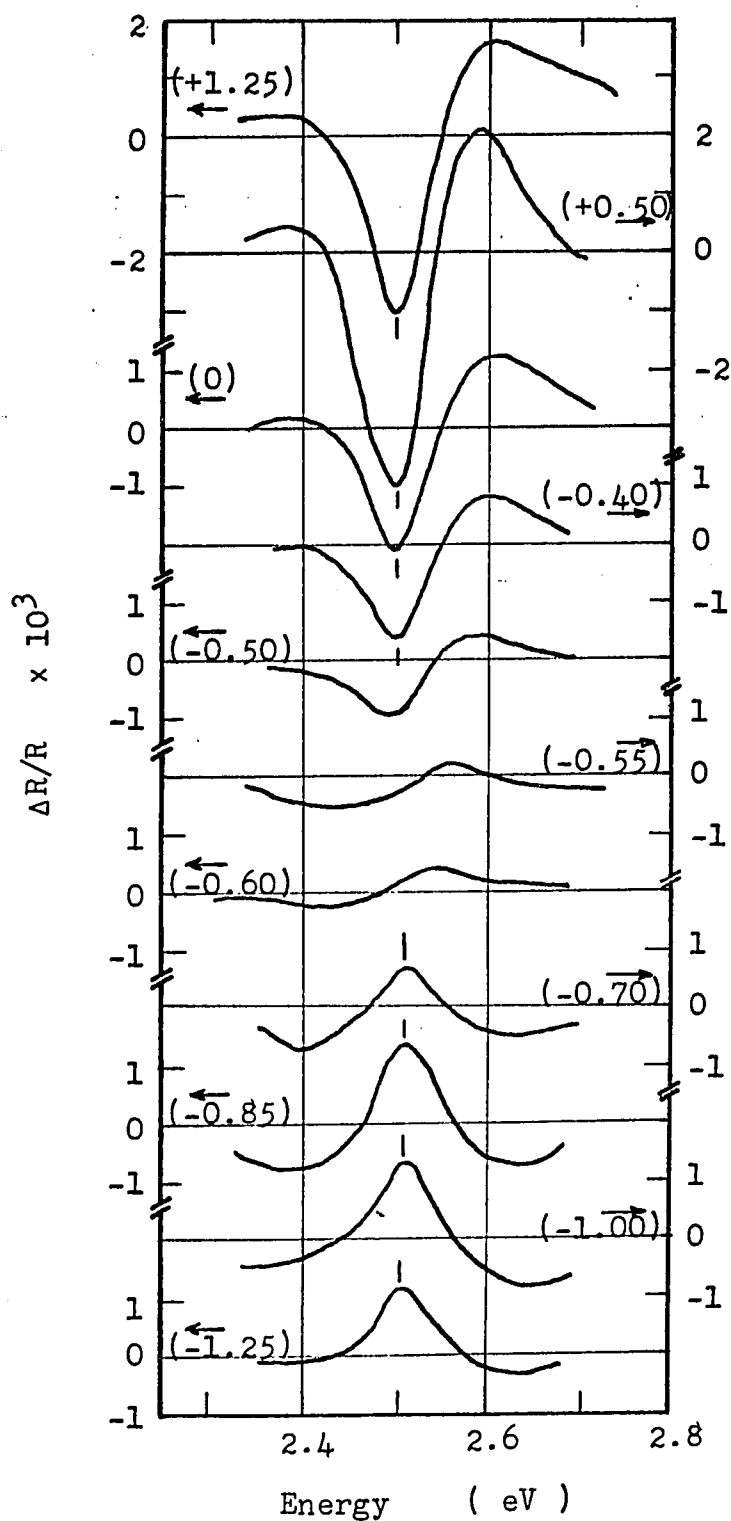


Figure III-13 Variation of the spectrum of the E_1 complex as a function of biasing voltage V_{dc} for specimen B4-2 ($n = 6.0 \times 10^{24} \text{ m}^{-3}$). Electrolyte: glycerol solution. [Value of V_{dc} shown inside brackets (in V)].

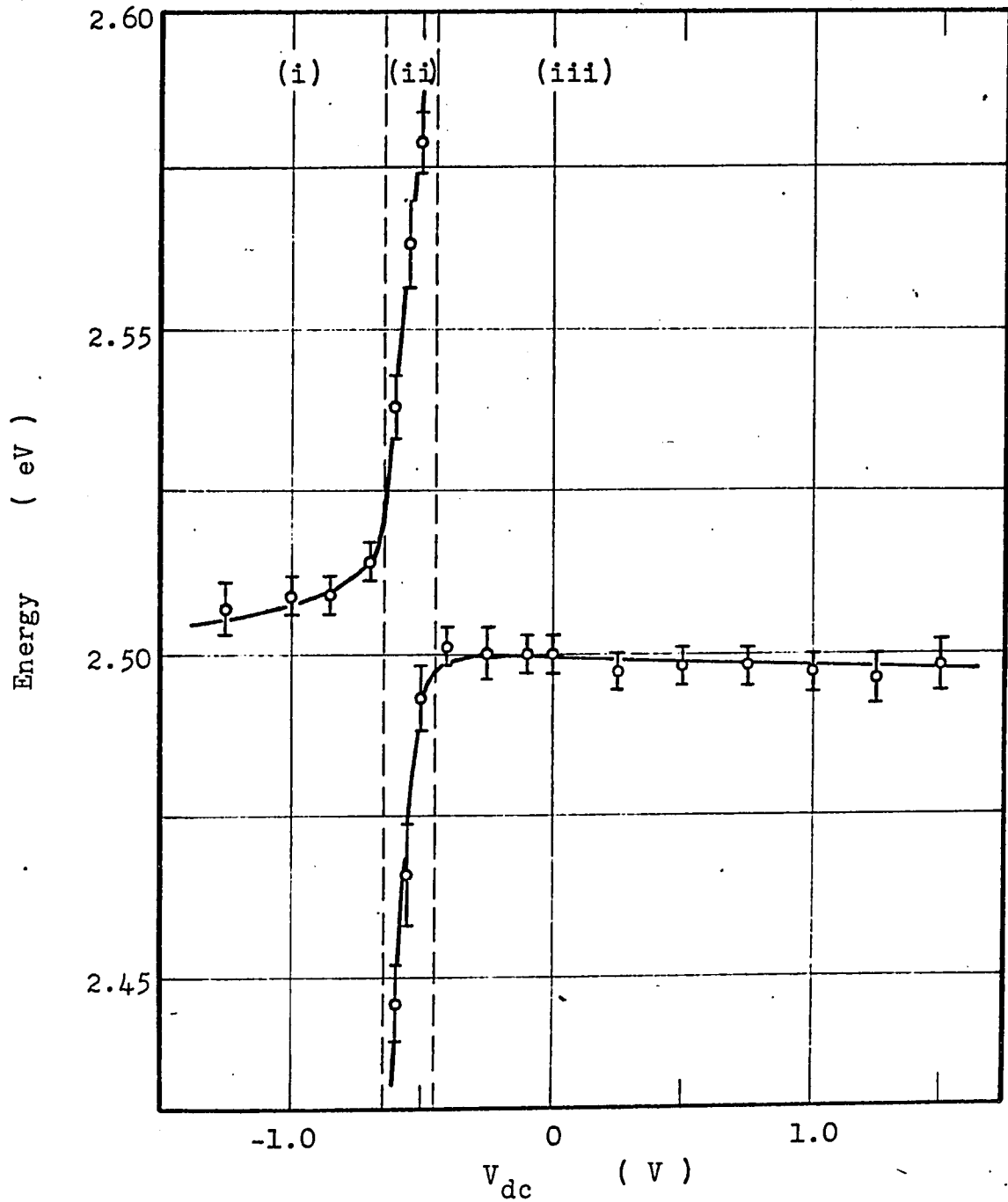


Figure III-14 Variation of energy of E_1 peak with biasing voltage V_{dc} for specimen B4-2 ($n = 6.0 \times 10^{24} \text{ m}^{-3}$). Electrolyte: glycerol solution. Region (i) p-like, (ii) u.v. peak too weak to be identified, and (iii) n-like.

45. DISCUSSION

For most III-V compounds, the transition from p-like to n-like electroreflectance spectra occurs when the sample itself is changed from p-type to n-type under normal experimental conditions. However, when InAs is investigated by the electrolyte technique, because of surface effects, band-bending, etc., p-like behavior is observed with n-type materials and the p-like to n-like transition occurs only when the electron concentration is close to 10^{25} m^{-3} . This value changed little between the two electrolytes used here, and it is probable that a similar value would be obtained for most electrolytes suitable for this technique. In this "transition region", it is found that the form of the E_1 complex of the spectrum depends critically both on the carrier concentration of the sample and on the d.c. biasing voltage applied, and that none of the peaks observed may give an accurate value for the E_1 and $E_1 + \Delta_1$ transitions. This problem is partly due to the fact that in this region, when the p- to n-like transition occurs, the associated oscillations move through the E_1 and $E_1 + \Delta_1$ peaks. In the transition region, it is seen that with the KCl electrolyte, if the value of E_1 and $E_1 + \Delta_1$ are assumed to be given by any one of the $\Delta R/R$ peaks, the resulting energy value can be different from the true band-to-band gap by as much as $\pm 0.05 \text{ eV}$. Hence, in using this technique to determine band parameters for InAs-like materials, care must be taken to make measurements well away from the

transition region. Provided that the carrier concentration of the sample satisfies this condition, it is found that the value of biasing voltage has little effect on the energy of the peaks and the resulting error in determining E_1 is certainly less than 0.01 eV.

When the values of E_1 and $E_1 + \Delta_1$ are thus correctly determined in InAs, it appears that their values are practically independent of carrier concentration from $p = 2 \times 10^{25} \text{ m}^{-3}$ to $n = 3.5 \times 10^{25} \text{ m}^{-3}$. The specimen with the highest electron concentration used here contains 0.11 atomic % of selenium (Specimen B17-1). Hence it is quite consistent with the data for the E_1 peak of InAs alloyed with In_2Te_3 (Greenaway and Cardona 62G4, this thesis: Section II-41) where it was found that the value of E_1 drops slightly only at higher impurity content.

5. ELECTROREFLECTANCE OF THE $\text{In}_{1-x}\text{Ga}_x\text{As}$ ALLOYS

5.1. PREVIOUS WORK

The first reflectance work on the InAs-GaAs system was reported by Woolley and Blazey (64W1). In this early work, it was found that the E_1 , $E_1 + \Delta_1$, E_0' and E_2 transitions all varied linearly with alloy composition within the limits of experimental error. However the reflectance work by Jones (66J1) indicated that the E_1 transition energy was non-linear with composition at the InAs end of the alloy series. Optical absorption studies of the fundamental band gap in the alloy system have been reported in a number of publications (Abrahams et al 59A1, Woolley et al 61W1, Hockings et al 66H2, and Woolley et al 68W2), and the variation of E_0 with composition was found to be non-linear in all cases. This situation has then motivated further studies of interband transitions in this alloy system by modulated reflectance method.

The first electroreflectance work on this system was reported by Thompson and Woolley (67T1) who used the electrolyte technique and obtained the variations of E_1 complex, E_0' , $E_0' + \Delta_0'$, E_2 and $E_2 + \delta$ transition energies with composition. In the above work, $\text{In}_{1-x}\text{Ga}_x\text{As}$ samples of electron concentration on the order of 10^{24} - 10^{25} m^{-3} were used, and it was found that the E_2 peaks gave p-type behavior for alloys close to the InAs end, were weak or unobservable in the range $0.15 < x < 0.35$, and gave n-type behavior when $0.35 < x < 1.0$. For the E_1

complex, a group of five alternately positive and negative peaks were observed for all values of x (0 to 1), and the energy of each peak varied smoothly with x . It was thus more difficult to determine where the transition from p- to n-type behavior occurred and hence to determine the form of the variation of the E_1 interband transition with x . Two alternative interpretations of the data were presented by the authors (67T1):

- (1) The p- to n-type transition occurs at $x \sim 0.9$, and hence the experimental results give a linear variation of E_1 and $E_1 + \Delta_1$ with x .
- (2) The p- to n-type transition occurs at $x \sim 0.1$, and hence the experimental results indicate parabolic variation of E_1 and $E_1 + \Delta_1$ with x .

By comparing this with the reflectance and electro-reflectance work on other mixed III-V alloys, such as GaAs-GaP (Woolley et al 65W1, Thompson et al 66T1, Thompson et al 66T2), the second interpretation of parabolic variation seems more appropriate. With such interpretation, none of the peaks in $\Delta R/R$ for $x < 0.2$ in the system $\text{In}_{1-x}\text{Ga}_x\text{As}$ would correspond to the exact value of E_1 and $E_1 + \Delta_1$, since the measurements on these materials with such electron concentrations were probably made in the "transition region" as described in Section III-44. Therefore the E_1 and $E_1 + \Delta_1$ transitions of this system in the InAs-rich section were remeasured in the present

investigation by using materials with lower electron concentrations to avoid the "transition region" that would complicate the data interpretations.

52. SOURCE OF MATERIALS

Samples of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys were prepared by Coderre (69Cl) with the horizontal Bridgman method. In this method, an evacuated quartz capsule of diameter $\frac{1}{2}$ " and length 5"-6", containing approximately 50 gm of the constituent compounds InAs and GaAs with mean composition $x = 0.3$ to 0.7 , was motor-driven slowly through a horizontal furnace consisting of two independent zones. The two zones were set at 1200°C and 600°C respectively. The temperature of the "cool" zone was low enough to allow the ingot to solidify at all compositions, but high enough to prevent condensation of arsenic and to maintain arsenic vapor pressure over the ingot. With a travelling rate of 1 cm/day through the furnace, each ingot was n-type with extrinsic carrier concentrations $\leq 10^{23} \text{ m}^{-3}$, and showed gradual variation of composition across the length, as seen from powder x-ray photographs which showed sharp resolution. The spread in a 1 mm thick cross-sectional slice was 1 mol. percent or even less. The accurate composition of each slice was determined from the value of its lattice parameter as deduced from the x-ray photographs. The lattice parameters of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys have been determined previously (Woolley and Smith 58W1).

In the present work, electoreflectance measurements were made on six specimens of the alloys with $x < 0.5$, by using a glycerol electrolyte (25 % aqueous solution). Each

specimen was prepared by the method described in Section III-421, and the mounted specimen was etched in Wolsky solution ($7\text{HCl} : 1\text{HNO}_3 : 8\text{CH}_3\text{COOH}$) for a few seconds prior to measurement.

53. RESULTS

In electroreflectance measurements of these alloys, various d.c. biasing voltages were applied. Since the electron concentrations of these samples were reasonably low ($n \leq 10^{23} \text{ m}^{-3}$), the "transition region" was not involved, and hence the E_1 and $E_1 + \Delta_1$ interband transition energies for each alloy was unaffected by these biasing voltages within a reasonable range of -1 to 1 V. An a.c. modulating voltage of 1.5 V was found suitable for all these specimens for ample signals and low noise in the measurements. The electroreflectance spectra of these alloys were all p-like, typical ones being shown in Figure III-15. Here $\Delta R/R$ is shown on an arbitrary scale, since this is sufficient to indicate interband transition energies. The variation of the energy values of E_1 and $E_1 + \Delta_1$ transitions with x is shown in Figure III-16, together with the previous data for alloys with $x > 0.2$. It is seen that a smooth variation of both E_1 and $E_1 + \Delta_1$ with x is now obtained. Curve fitting shows that both curves can be fitted reasonably well to a parabolic equation of the form

$$E = \alpha + \beta x + \gamma x^2 \quad (\text{III-22})$$

where $\alpha = 2.51$, $\beta = -0.16$, $\gamma = 0.52$ for E_1 ;

and $\alpha = 2.78$, $\beta = -0.14$, $\gamma = 0.49$ for $E_1 + \Delta_1$.

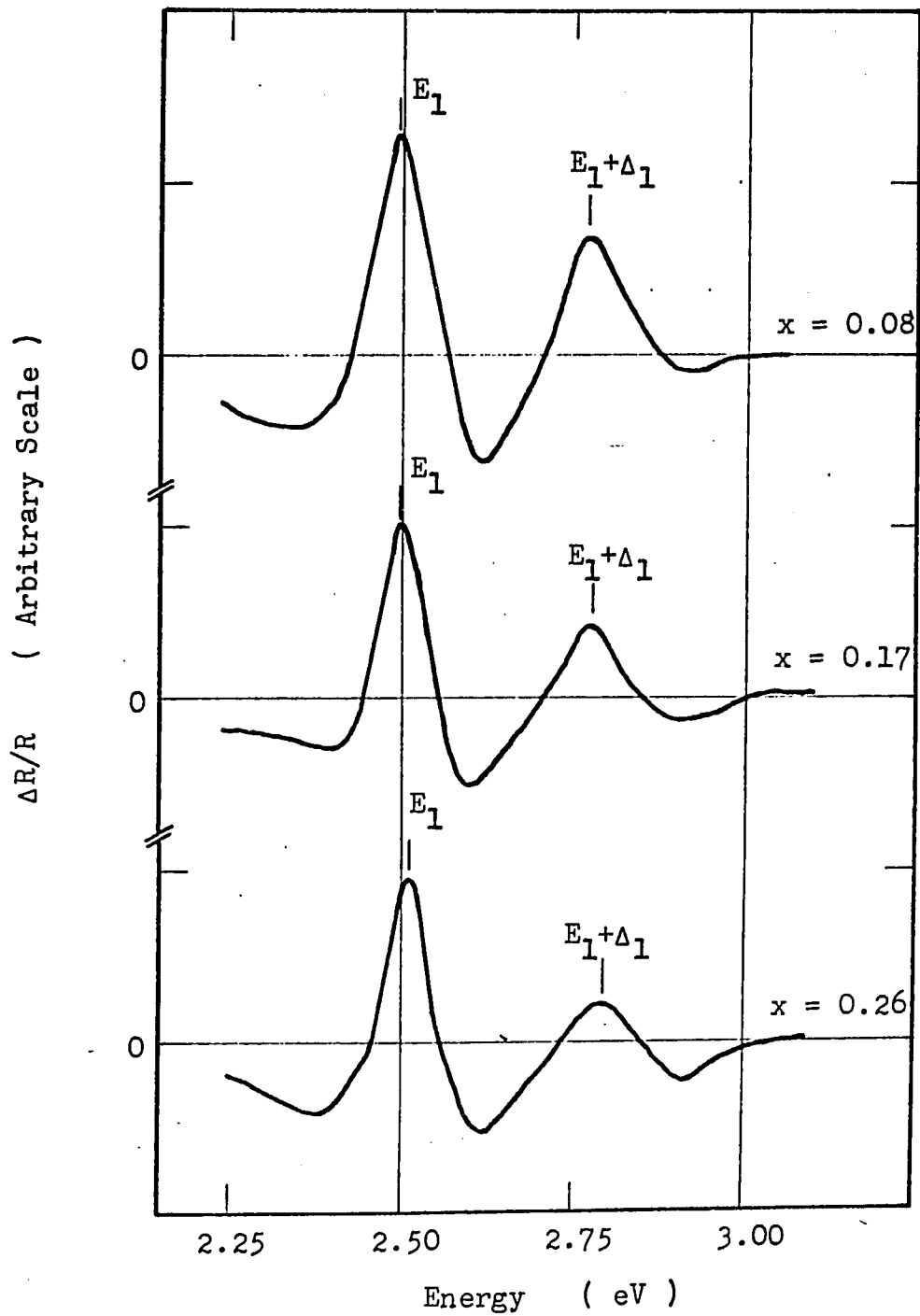


Figure III-15 Electroreflectance spectra of typical specimens of the alloy system $\text{In}_{1-x}\text{Ga}_x\text{As}$ (in the InAs-rich section). Electrolyte: glycerol solution.

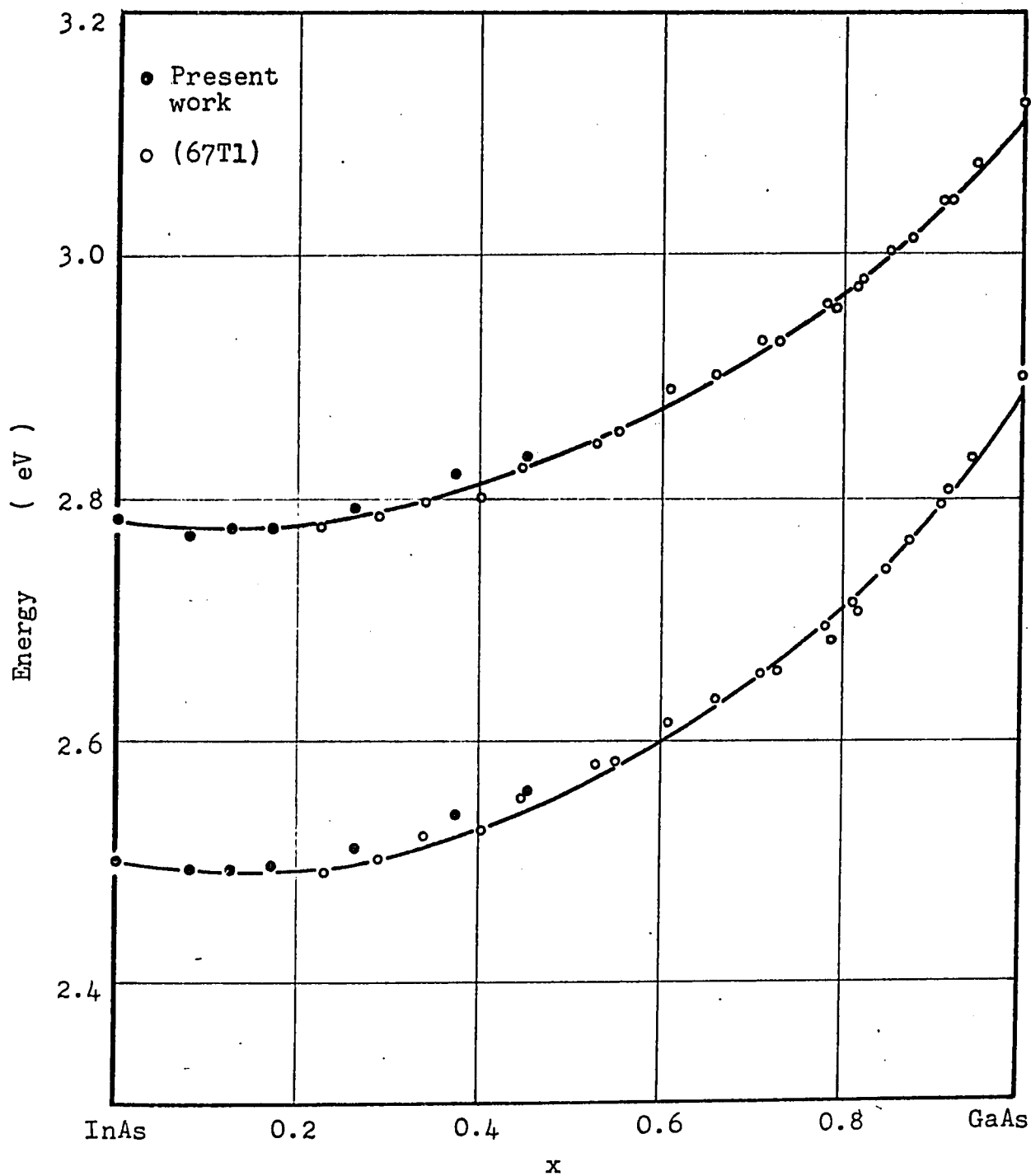


Figure III-16 Variation of the energy of E_1 and $E_1 + \Delta_1$ interband transitions with composition for $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys.

54. DISCUSSION AND CURRENT INTERESTS

In an alloy system, the energy separation E between bands at a given position in $\vec{k}$ -space is expected to vary with alloy composition in a parabolic form (equation I-13, Section I-5):

$$\begin{aligned} E &= (\alpha + \beta x) + \gamma x(1-x) \\ &= \alpha + \beta'x + \gamma'x^2 \end{aligned} \quad \text{(III-23)}$$

α , β , γ , β' and γ' being constants. Here the constant γ (or γ') indicates the magnitude of deviation from linearity ($E = \alpha + \beta x$) due to the contribution from the alloying effect, i.e. from the virtual crystal and the disordered alloy lattice.

The problem in analyzing the E_1 and $E_1 + \Delta_1$ data is that the non-linearity in the E_1 and $E_1 + \Delta_1$ energy values versus x graph can also be attributed partly to the movement of the transitions in $\vec{k}$ -space along the Λ direction. Since the expected deviation as contributed by the alloying effect is symmetric in x about the position $x = 0.5$, the difference δ between the experimental value for E_1 (or $E_1 + \Delta_1$) and the value obtained by linear interpolation between the two compounds is a good indicator for examining this effect. The curves of δ versus x for E_1 and $E_1 + \Delta_1$ interband transition energies, as shown in Figure III-17, are practically symmetric about the position $x = 0.5$. This indicates that such a deviation from

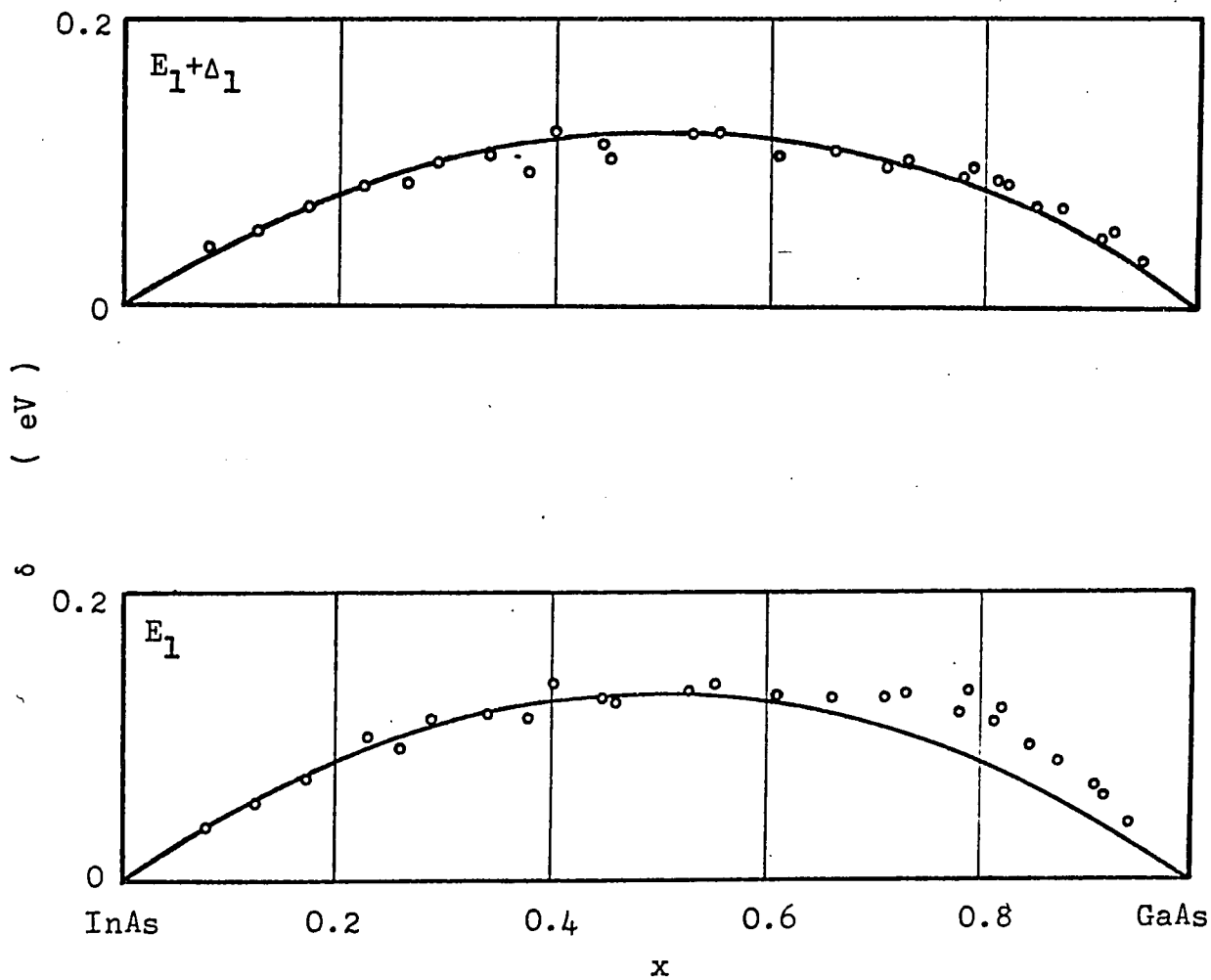


Figure III-17 Variation of δ with composition for $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys. (See text).

linearity is practically due to the alloying effect.

Recently the results of this work (68K3) have been used by Vishnubhatla et al (69V3) in a systematic study of the disorder effects in the alloy lattice by analyzing the parabolic variation of the E_0 , E_1 , $E_1+\Delta_1$, E_0' and E_2 interband transition energies in five mixed III-V alloy systems.

Electroreflectance studies on the $\text{In}_{1-x}\text{Ga}_x\text{As}$ alloys have also been made concurrently and independently by Williams and Rehn (68W1, 69W1) who also obtained the parabolic variation of the E_1 and $E_1+\Delta_1$ transition energies with x . Although the value of $\gamma = 0.6$ as obtained by these authors in the parabolic fit is slightly higher than the value obtained here, an overall agreement between both results is readily seen.

CHAPTER IV
INTERBAND TRANSITIONS IN II-IV-As₂

1. INTRODUCTION

Due to close similarities in crystal structures and various physical properties between the III-V and II-IV-V₂ compounds, band structure investigations on these ternary compounds can usually be made by taking the III-V compounds as the guideline. There are three types of methods for such an approach:

(1) The use of the closest binary analogs of the II-IV-V₂ compounds - This method can be illustrated by the band structure calculation of ZnGeAs₂ by Poplavnoi and Karavaev (68P3). The authors placed the energy spectrum (the E, $\hbar$ relation) of GaAs, the closest binary analog of ZnGeAs₂, in the Brillouin zone of the chalcopyrite, and treated the replacement of 2Ga by ZnGe with a perturbation potential. The pseudopotential method has given some indication about the values of the fundamental band gap and the valence band splitting due to the crystal field, and an approximate shape of the conduction band along the (001) direction, i.e. between Γ and T. (The notations of the symmetry points have been given in Section I-4.)

(2) The comparison of band structure parameters of both modifications of a II-IV-V₂ compound - This method can be illustrated by the band structure investigations of ZnSnP₂

by Goryunova et al (68G2). The authors have observed very similar reflectance spectra of the chalcopyrite and zincblende modifications of this compound except for a slight shift in energy of the peaks. The band structure of the zincblende modification of this compound was calculated based on the reflectance results with techniques similar to those applicable to the III-V compounds. Then the change from zincblende to chalcopyrite lattice is taken care of by a perturbation potential similar to the treatment in case (1).

(3) The alloying of the ternary compounds with some III-V compounds - This method is applicable whenever complete solid solutions between the two constituent compounds can be obtained. One advantage of this method is that a gradual and systematic change of physical properties and band structure characteristics can be observed along the composition range.

In the present investigations on the ternary arsenides, the second and the third methods have been applied in parallel in room temperature electroreflectance work, supported by reflectance and thermorefectance measurements. The materials included five compounds: CdSnAs_2 , CdGeAs_2 , ZnSnAs_2 , ZnGeAs_2 and ZnSiAs_2 , and two alloy systems $2\text{InAs}-\text{CdSnAs}_2$ and $2\text{InAs}-\text{ZnSnAs}_2$. No attempt has been made here to carry out the band structure calculations. The purpose of this work is to provide as much as possible the experimental evidence concerning the band structures of the chalcopyrite lattices, in order that the number of adjustable parameters in the theoretical band calculations can be reduced.

2. REVIEW OF THE LITERATURE

21. THE COMPOUNDS

The existence of the II-IV-V₂ compounds was first reported by Goodman (57G1). Accompanying the improving techniques of producing good quality crystals, the growing importance of these materials was gradually recognized. The bibliography by Ray (67R1) and the review article by Borshchevskii et al (67B4) have summarized the available information concerning these compounds with references up to 1966-7. Up to the present time, only six II-IV-As₂ compounds have been produced, as derived from the combinations of II: Cd, Zn, and IV: Sn, Ge, Si, with As. These ternary arsenides have two modifications: chalcopyrite and zincblende (plus the amorphous state in the case of CdGeAs₂) as has been mentioned in Section I-3. However, most of the investigations on these compounds thus far has been of their basic structure, the chalcopyrite form. The band structure parameters at (000) of the direct band-gap II-IV-As₂ compounds are summarized in Table IV-1. The compound CdSiAs₂ is not included in the table, since the only available band structure information about this compound is $E_0 = 1.62$ eV (at 80°K) from radiative recombination measurements by Borshchevskii et al (68B4). Further band structure information about the ternary arsenides will be reviewed individually in the following.

Table IV-1 Summary of band structure parameters of the (000) bands of the ternary compounds: CdSnAs₂, CdGeAs₂, ZnSnAs₂ and ZnGeAs₂.

Energy parameter, effective mass #	Temperature (°K)	CdSnAs ₂	CdGeAs ₂	ZnSnAs ₂	ZnGeAs ₂
E _o	295-300	0.25-0.275eV, OA(61SL, 66EL, 66S4)##	0.41-0.53eV, OA(63LL, 63G2, 65G2) 0.50eV, PC(65K3)	0.65-0.66eV, OA(64KL, 66ML)	0.85eV, OA(65G3)
	80-88		0.54eV, PC(65K3) 0.607eV, RR(68B4)	0.72eV, OA(66ML)	
	0	0.254-0.26eV, HR(62G2, 65G1)	0.73eV, HR(65G2)	0.59-0.89eV, HR(66ML, 67VL)	1.3eV, TC(68P3)
dE _o /dT (Temperature coefficient)	80-300	-2.0 to -2.5 x10 ⁻⁴ eV/°K, OA(66S4, 67KL)	-1.9x10 ⁻⁴ eV/°K, PC(65K3)	-2.8x10 ⁻⁴ eV/°K, OA(66ML)	
ΔE _k	300	0.01-0.03eV, OA(66LL, 67KL)	0.01eV, TC(65G2)	0.03eV, EV(67VL)	0.04eV, TC(68P3)
Δ _o	300	0.45eV, EV(63G1)	0.33eV, TC(65G2)		
m _n [*] /m _e	300	0.019, MT(67K2) 0.02, MS(62M2) 0.034, TC(66LL)	<0.027, MT(63G2, 65G2) 0.20, HR(63L4) TC(65G2)	0.029, TC(67V2)	0.038, TC(67V2)
	0	0.014, TC(63G1)			

Table IV-1 Continued.

Energy parameter, effective mass	Temperature (°K)	CdSnAs ₂	CdGeAs ₂	ZnSnAs ₂	ZnGeAs ₂
$d(m_n^*/m_e)/dT$ (Temperature coefficient)	130-295	$2.4 \times 10^{-5}/^\circ K$, FR(66S4) $1.8 \times 10^{-5}/^\circ K$, IR(66S4) O,MR(66S4)			
m_p^*/m_e (Average of heavy and light holes)	100-557	0.11,FR(67K1) 0.1, HR(66P4)		0.43-0.59, TP(66M1) 0.6,MT(64K1,65K2) 0.30,HR(63L1)	0.17-0.74, TP(63L1,66C9,67B4)
m_{p2}^*/m_e	300		0.035,TC(65G2)		0.04, EV(67V1)
m_{p3}^*/m_e	300		0.12, TC(65G2)		

Meaning of symbols given in Figure I-5, Section I-4.

Meaning of the abbreviations:

- | | |
|-----------------------------------|------------------------------------|
| EV - Estimated value, | MT - Magneto-thermoelectric power, |
| FR - Faraday rotation, | OA - Optical absorption, |
| HR - Hall effect and resistivity, | PC - Photoconductivity, |
| IR - Infrared reflectance, | RR - Radiative recombination, |
| MR - Magneto-reflectance, | TC - Theoretical calculation, |
| MS - Magnetic susceptibility, | TP - Thermoelectric power. |

(1) CdSnAs_2

Chalcopyrite structure - The investigations of magnetoresistance measurements by Polyanskaya et al (66P4), Leroux Hugon (66L1) and Matyáš et al (67M2) have verified the theoretical presentation of a spherical constant-energy surfaces of the (000) conduction band for this compound. However in recent magnetoresistance work, Polyanskaya et al (68P2) have observed some anisotropic effect of the conduction band.

Some authors have studied the variation of the electron effective mass at the Fermi level with electron concentration. These investigations are summarized in Figure IV-1. It is seen that there is some discrepancy in the results obtained by Leroux Hugon (66L1) and other authors, in particular Kesamanly and Korshak (67K2). Since the $\vec{k} \cdot \vec{p}$ approach for the band calculation of this compound is only at a very preliminary stage, it will still be some time before a more reliable semi-empirical presentation of its band structure can be obtained.

Some investigations on the higher bands have also been reported. Mal'tsev et al (67M1) have observed the interband transitions at 0.28 and 0.41 eV from room temperature optical absorption measurement. This gives a value of the fundamental band gap of 0.28 eV and a separation of 0.13 eV between the lowest conduction band minimum at (000) and a higher conduction band minimum. However, further information about such a postulated sub-band is still not available. Chang and Chang (66C7) and Sikharulidze et al (67S4) have investigated interband

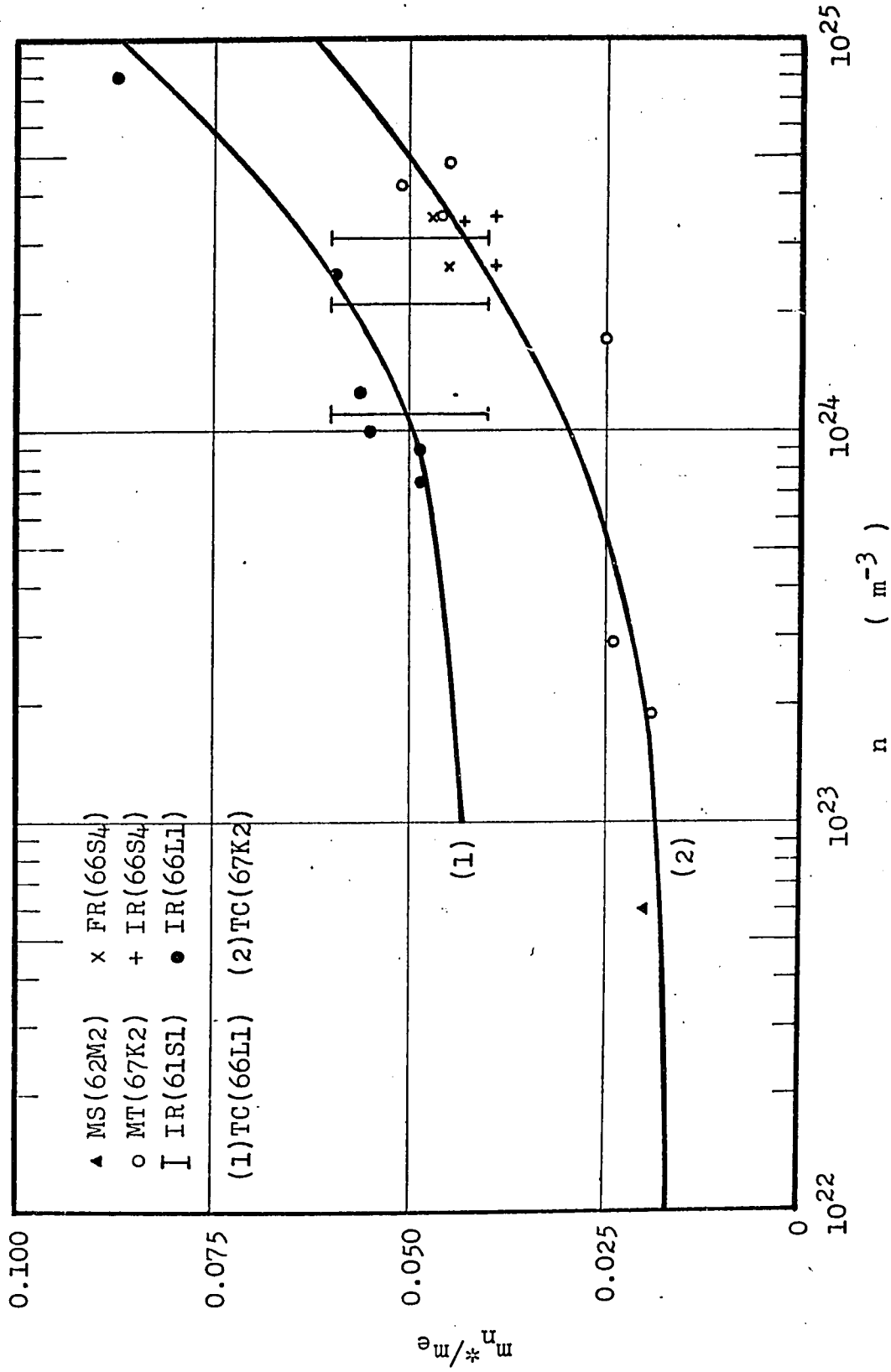


Figure IV-1 Variation of electron effective mass (at the Fermi level) with electron concentration for CdSnAs₂ (chalcopyrite structure). (61S1, 62M2, 66L1, 66S4, 67K2).

transitions in this compound by room temperature reflectance measurements. Chang and Chang observed reflectance peaks at 2.10, 2.39, 2.98 and 4.46 eV, while Sikharulidze et al reported values of 1.88, 2.44, 2.88, 3.82 and 5.75 eV. (See Figure IV-4.) The disagreement between these two results may be attributed to the fact that in the former case polycrystalline material was used, while in the latter case the sample was a single crystal. Due to low symmetry and tetragonal compression of the crystal lattice, the single crystal could be optically anisotropic. However the crystal orientation and the field direction of the polarized light were not specified in the above work of Sikharulidze et al. Chang and Chang have interpreted the four peaks in their measurement as E_1 , $E_1 + \Delta_1$, E_0' and E_2 transitions by using the Brillouin zone of the III-V compounds.

Zincblende structure - Osmanov et al (6801) have observed temperature independence of Hall coefficient and conductivity of CdSnAs_2 crystals of both structures in the range of impurity conduction. From the similar transport properties, the authors indicated that the conduction band structures [the (000) band] for both CdSnAs_2 modifications are similar.

(2) CdGeAs_2

Chalcopyrite structure - The band structure information of this compound is still very preliminary at this stage. Even the fundamental band gap is not accurately determined as can be seen

from the wide range of values of 0.4-0.7 eV reported from various measurements.

Abrahám et al (68A1) have reported the reflectance of this compound at room temperature in the energy range 0.6-5.5 eV. Two intense maxima at 2.15 and 3.9 eV together with some less intense ones at ~0.8, 1.6, 2.1, 2.25, ~2.6, ~3.2, 3.85 and ~4.7 eV were observed. (See Figure IV-5.) No interpretation of these peaks was given by the authors (68A1).

Amorphous state - This material shows n-type conduction with a resistivity of $\sim 10^4$ ohm.m. Vaipolin et al (65V1) have obtained an approximate value of the fundamental band gap of 0.6 eV from room temperature optical absorption and photoconductivity measurements. More recent results from optical absorption measurements give $E_0 = 0.73$ eV (at 300°K) and $dE_0/dT = -(5 \pm 1) \times 10^{-4}$ eV/°K (Borisova et al 68B3). The room temperature reflectance spectrum of this material shows no noticeable peaks in the energy range 0.6-5.5 eV (Abrahám et al 68A1).

(3) ZnSnAs_2

Chalcopyrite structure - At present, ZnSnAs_2 (as well as ZnGeAs_2 and ZnSiAs_2) crystals can only be grown as p-type samples. As for the band structure investigations of ZnSnAs_2 , Rud' et al (68R1) have reported a detailed study of the room-temperature absorption spectrum in the range 0.45-0.75 eV, and Kesamanly et al (65K1) have reported the room-temperature

reflectance spectrum in the range 1-6 eV. The three peaks observed in the reflectance work, 1.91, 2.25 and 4.7 eV (as shown in Figure IV-8), were interpreted by the authors (65K1) as interband transitions near L and at X by using the Brillouin zone of the III-V compounds.

(4) ZnGeAs_2

Chalcopyrite structure - The disagreement among the reported values of m_p^*/m_e (Table IV-1) of this compound can be attributed to the uncertainty in the scattering mechanism of the holes.

The band calculation of this compound by Poplavnoi et al (68P3) has given, besides E_0 and ΔE_k , an approximate value of the separation 0.3 eV of the lowest conduction bands at Γ and T.

(5) ZnSiAs_2

Chalcopyrite structure - The ZnSiAs_2 crystals are usually p-type with relatively low hole concentrations (10^{20} - 10^{21} m^{-3}) and high resistivity ($\sim 10 \text{ ohm}\cdot\text{m}$). This compound is an indirect band-gap material with its lowest conduction band minima located along the $\langle 100 \rangle$ directions (Karavaev et al 68K1). This indirect band-gap has been determined to be 1.64 eV at room temperature and a temperature coefficient of $-4.5 \times 10^{-4} \text{ eV}/^\circ\text{K}$ from optical absorption measurements (Vaipolin et al 64V2). However, a different value of the band-gap has also been obtained from photoconductivity measurements, the room temperature value

and temperature coefficient being 2.10 eV and -4.2×10^{-4} eV/ $^{\circ}$ K respectively (Kesamanly et al 65K3). These photoconductivity results could possibly indicate the separation between the highest valence band and a conduction band at (000) rather than the indirect band-gap.

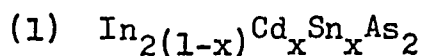
Vaipolin et al (67V2) have indicated a theoretical value of $0.071m_0$ of the electron effective mass without explanation. The reflectance of the compound in the range 3-6 eV at room temperature has been investigated by Kesamanly et al (65K1). The reflectance spectrum (as shown in Figure IV-10) consists of two peaks 3.35 and 4.2-4.5 eV which were assigned by the authors (65K1) as interband transitions near L and at X in terms of the nomenclature of the symmetry points of the III-V compounds.

22. THE ALLOY SYSTEMS OF TERNARY ARSENIDES WITH III-V COMPOUNDS

Since the group IV elements, the III-V and II-IV-V₂ compounds are isoelectronic analogs, the study of the cross alloy systems based on these materials would lead to further correlations of their physical properties and band structure characteristics. In the study of the (II-IV-V₂)-(IV) systems so far, the group IV element is usually a component of the ternary compound, since this circumstance may favor, to a certain extent, the formation of solid solutions between IV and II-IV-V₂. Goryunova et al (63G3) have investigated the system ZnGeAs₂-4Ge and observed high solubility of up to 25 mol. % of (4Ge) in ZnGeAs₂. Borshchevskii et al (67B4) have also indicated that the solubility of Ge in ZnGeP₂ and that of Si in ZnSiP₂ are also very high. These observations are in contrast with the low solubilities of the group IV elements in the III-V compounds partly due to the absence of any common component involved.

The study on the alloy systems (II-IV-V₂)-(III-V) are still at a preliminary stage. The systems investigated so far are those with common group IV elements, such as CdSnSb₂-2InSb (Khalilov and Aliev 68K2), CdSnAs₂-2InAs (Goryunova and Prochukhan 60G1), ZnSnAs₂-2InAs, ZnGeAs₂-2InAs, CdGeAs₂-2InAs (Borchers and Maier 63B1), ZnGeAs₂-2GaAs and ZnSiAs₂-2GaAs (Nazarov et al 67N1). For the purpose of correlating the band structures of the II-IV-V₂ and the III-V compounds by studying the gradual

change in various physical properties along the composition range, complete solid solutions between these compounds are required. Among these systems, this has been achieved in CdSnAs_2 -2InAs and ZnSnAs_2 -2InAs only. The equilibrium diagrams of these two systems (Borshchevskii et al 67B4, Borchers and Maier 63B1) are reproduced in Figure IV-2. Further information about these systems are reviewed in the following.



Since InAs is the closest binary analog of CdSnAs_2 , the system CdSnAs_2 -2InAs was one of the first (II-IV-V₂)-(III-V) sections investigated (Goryunova and Prochukhan 60G1). The authors have obtained a continuous sequence of solid solutions over the whole composition range ($x = 0$ to 1). The alloys were of zincblende structure in the InAs-rich section, and of chalcopyrite structure in the CdSnAs_2 -rich section. Mamaev et al (61M1) have obtained the variation of the fundamental band gap E_0 with composition of this system by transport measurements. A non-linear variation with a minimum of 0.2 eV at $x = 0.6$ was observed. (Note that $E_0 = 0.254$ eV for CdSnAs_2 and 0.425 eV for InAs at 0°K, Galvanov et al 65G1, Dixon and Ellis 61D3.) Leroux Hugon (62L1) has attempted to measure the effective mass of the (000) electrons by thermoelectric power and Hall effect measurements, values in the range 0.01-0.04 m_e being obtained for specimens over the whole composition range. From similar measurements, Nasledov et al (63N1) have obtained an approximate

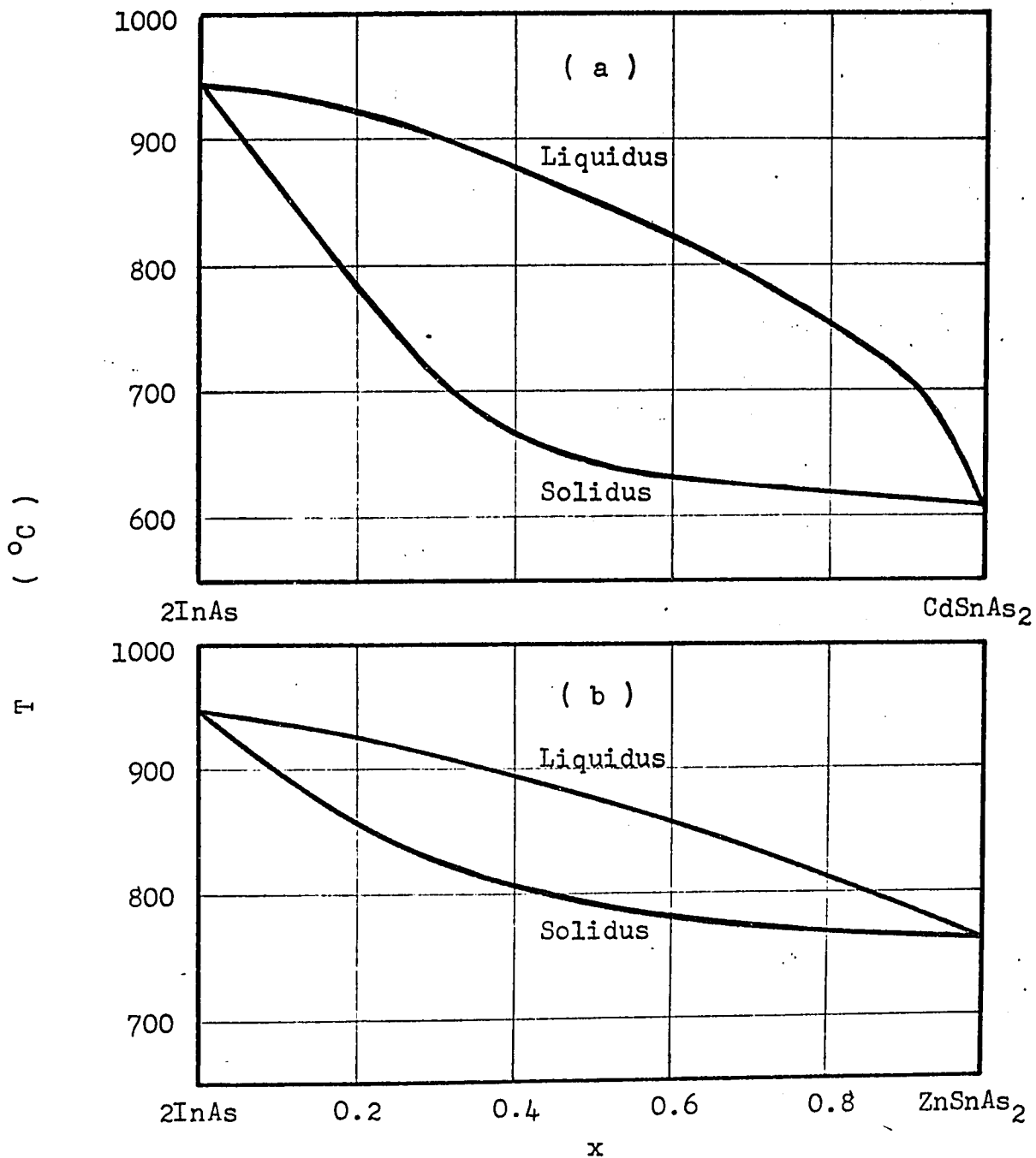
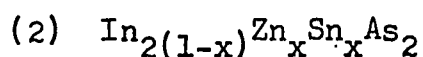


Figure IV-2 Equilibrium diagrams of (a) $\text{In}_2(1-x)\text{Cd}_x\text{Sn}_x\text{As}_2$ system (67B4), and (b) $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$ system (63B1).

value of the electron effective mass of $\sim 0.045m_0$ for all specimens over the whole composition range of this system.



The compound ZnSnAs_2 does not show any tetragonal contraction in the lattice, and hence the band structure characteristics of its chalcopyrite and zincblende modifications are expected to be more similar than other ternary arsenides. Borchers and Maier (63B1) have obtained complete solid solutions of the system ZnSnAs_2 - 2InAs in zincblende structure. Since this ternary compound transforms into chalcopyrite from zincblende when the temperature is lowered to $632\text{--}635^\circ\text{C}$ from its melting point 778°C (Masumoto and Isomura 66M1, Vaipolin et al 67V1), alloys of the chalcopyrite structure are expected to be obtainable near the ZnSnAs_2 end of the alloy system with suitable methods of preparation. Voitsekhovskiy et al (63V1) have reported some transport measurements of this alloy system over a temperature range $80\text{--}300^\circ\text{K}$.

3. MATERIAL PREPARATION

31. THE COMPOUNDS

As has been mentioned in the preceding section and in Section I-3, these ternary compounds transform from zincblende to chalcopyrite structure at temperatures somewhat below their melting point. Accompanying the change in crystal structure, a tetragonal contraction occurs in the lattice in most ternary arsenides with the exception of ZnSnAs_2 . Therefore cracks could be formed during the zincblende-chalcopyrite transition while the compounds are cooled from their molten state. These ternary arsenides are usually prepared by direct synthesis of stoichiometric amounts of the elements concerned. Various methods for obtaining good quality and preferably crack-free materials have been reported. These include:

- (1) Slow cooling of the furnace -
 CdSnAs_2 , Spitzer et al (61S1)
 ZnGeAs_2 , Constantinescu et al (66C9)
 ZnSiAs_2 , Masumoto et al (66M2)
- (2) Vertical Bridgman method -
 ZnSnAs_2 , Masumoto and Isomura (66M1)
 ZnSiAs_2 , Masumoto et al (66M2)
- (3) Zone refining method -
 CdSnAs_2 , Leroux Hugon (66L1), Goryunova et al (67G1),
Kesamanly and Korshak (67K2)
- (4) Directional cooling of the melt -
 CdGeAs_2 , ZnSnAs_2 , ZnSiAs_2 , Borshchevskii et al (67B4)

The fast cooling of the molten compounds leads to crystallization in the zincblende modification (CdSnAs_2 , Strauss and Rosenberg 61S2; ZnSnAs_2 , Gasson et al 62G1; ZnGeAs_2 , Vaipolin et al 67V2) and in the amorphous state (CdGeAs_2 , Vaipolin et al 65V1).

In the present investigations, the method of "slow cooling of the furnace" has been used to prepare the chalcopyrite modifications of the compounds CdSnAs_2 , CdGeAs_2 , ZnSnAs_2 and ZnGeAs_2 . The elements used for the synthesis of the compounds were of at least 99.999 % purity. For the preparation of each compound, the stoichiometric amounts of the elements concerned, a total of about 12 gm, were placed in an argon-filled quartz ampoule of inner diameter $\frac{1}{2}$ ". In the case of the Zn compounds, the constituent elements were placed in a cylindrical-shaped graphite crucible fitted nicely inside the quartz tube. Each graphite crucible had been cleaned by hot nitric and hydrochloric acids, rinsed thoroughly by boiling water and baked in a furnace of temperatures $\sim 500^\circ\text{C}$ for a few hours, prior to use. The graphite crucible served the purpose of avoiding the reaction of Zn with quartz at high temperatures. The ampoule was suspended inside a vertical furnace at its hottest zone. The power consumption of the furnace was varied slowly by changing the output voltage, from the powerstat to the heating element of the furnace, with a low speed motor. The furnace temperature was increased at the rate of 20°C/hr from $\sim 100^\circ\text{C}$ to somewhat above the highest melting point of the constituent

elements and the melting point of the compound. Such a precaution was taken to reduce the chance of cracking the quartz ampoule by the arsenic vapor. The argon gas, which was at a pressure of 0.5-1 atm at room temperature, was used as a counter-pressure of the arsenic vapor for the same purpose. The furnace temperature was kept constant for about 1 day. After a period of mixing with the aid of a mechanical vibrator to remove blow holes and voids, the furnace temperature was lowered uniformly to room temperature at a rate of about 10°C/hr .

The four compounds synthesized by this method were polycrystalline with very coarse grain size. The ingots of CdGeAs_2 , thus obtained, contained a network of fine cracks as a result of appreciable tetragonal compression in the lattice ($c/a = 1.888$). The mechanical conditions of CdSnAs_2 ingots were much better since $c/a = 1.957$, and crack-free crystals of a few mm in size were usually obtained. The ingots of the two Zn compounds were completely crack-free, since $c/a = 1.966$ and 2.000 for ZnGeAs_2 and ZnSnAs_2 respectively. [These c/a values were given in the review article by Borshchevskii et al (67B4).]

The zincblende modifications of CdSnAs_2 and ZnSnAs_2 were prepared by quenching in water the synthesized compounds from the melt. The ingots obtained were crack-free, and polycrystalline with fine grains (~ 1 mm).

Some ZnSnAs_2 and ZnSiAs_2 crystals of chalcopyrite structure were supplied by Isomura of the National Research Institute for Metals, Japan. These materials were prepared by

the vertical Bridgman method (Masumoto and Isomura 66M1, 66M2). The difference between this method and the "slow-cooling" method used in this work is that the ampoule containing the melt is lowered out of the vertical furnace very slowly, instead of reducing the furnace temperature. In this case, the lowering rate was 0.05 mm/min. The ZnSnAs_2 specimens were single crystals while the ZnSiAs_2 specimens were polycrystalline with fine cracks.

32. THE ALLOY SYSTEMS $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$ AND $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$

Each alloy, corresponding to a value of x between 0 and 1, in the systems $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$ and $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ was prepared by mixing appropriate amounts of compounds concerned (InAs , and CdSnAs_2 or ZnSnAs_2), of total weight 4-5 gm, in an argon-filled quartz ampoule of inner diameter $\frac{5}{16}$ ". The furnace temperature was gradually increased to 1000°C , exceeding the melting point of InAs . After extensive mixing by mechanical vibrations, the ampoule was quenched in water. Then long annealing of the ingots at temperatures somewhat below the solidus curve of the phase diagram (Figure IV-2) was required to ensure good equilibrium conditions. The materials prepared in this way were polycrystalline with grain size ~ 1 mm. Since these alloy systems were formed from compounds with different crystal structures, the alloys in the InAs -rich section were expected to be of zincblende structure, and those near the ternary arsenide end could assume zincblende or chalcopyrite structure under different conditions.

The temperature for the structural transformation of CdSnAs_2 is within 40°C below its melting point 595°C (Leroux Hugon 63L1, Borshchevskii et al 66B8), and hence this phase-change temperature of each alloy near the CdSnAs_2 end in $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$ is probably close to the solidus curve of the equilibrium diagram. For alloys near the InAs end, the annealing at temperature 100 - 200°C below the solidus curve for about 2 months was quite sufficient to ensure good equilibrium

conditions. However for alloys with $x > 0.4$, the annealing temperature was initially set at 570°C , gradually reduced to about 450°C in 6 weeks, and maintained at this temperature for 6 weeks or more. With such treatments, the alloys with x up to 0.7 retained zincblende structure, and those with $x > 0.7$ tended to assume chalcopyrite structure, as observed from the x-ray diffractions on powdered specimens.

The alloys of the system $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ were annealed at $700\text{--}750^{\circ}\text{C}$ for 2-3 months. Since in ZnSnAs_2 , the temperature of structural transformation 632°C was well below its melting point 778°C (Masumoto and Isomura 66M1), only the zincblende modification of the alloys in this $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ system was obtained by this treatment. The chalcopyrite form of the alloys near the ZnSnAs_2 end could also be obtained at lower annealing temperatures. Here an alloy of $x = 0.95$ was prepared by slow-cooling of the melt from 1000°C to 400°C at the rate of about 5°C/hr . Then the ampoule was kept at that temperature for 1 week. This alloy then showed chalcopyrite structure.

33. SPECIMEN-SURFACE TREATMENTS

The methods of cutting, lapping, polishing and mounting of specimens for reflectance, electoreflectance and thermo-reflectance measurements have been described in Sections II-321, III-421 and III-43. Since these ternary arsenides, especially CdGeAs_2 and ZnSiAs_2 , were very brittle, the samples had to be cut into thicker slices and reduced in thickness very slowly by lapping with grit 3200 grinding powder on a glass plate.

In order to remove the damaged layers on the specimen surfaces caused by cutting, lapping and polishing of the specimens, different combinations of hydrochloric, nitric and glacial acetic acids, glycerol and other chemicals with various proportions had been attempted. After a period of testing, three etching solutions were found to be suitable for the materials investigated in this work:

(1) Wolsky solution ($7\text{HCl} : 1\text{HNO}_3 : 8\text{CH}_3\text{COOH}$) was suitable for the alloy systems $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$ and $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ in the InAs-rich section.

(2) ($1\text{HCl} : 1\text{CH}_3\text{COOH} : \text{a trace of HNO}_3$) was suitable for the compounds CdGeAs_2 , ZnSnAs_2 , ZnGeAs_2 and ZnSiAs_2 , the system $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ over the whole composition range, and the alloys with $x < 0.5$ in the system $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$.

(3) ($1\text{HNO}_3 : 1\text{CH}_3\text{COOH} : 1 \text{ Glycerol}$) was suitable for the compounds CdSnAs_2 , ZnSnAs_2 and ZnGeAs_2 , and the alloys with $x > 0.4$ in both systems.

4. RESULTS AND DISCUSSION

The experimental methods for the three types of reflectance measurements have been presented in Sections III-42 and III-43. In the electroreflectance measurements, the glycerol electrolyte was used for all specimens.

4.1. THE COMPOUNDS

4.1.1. CdSnAs_2

The two polycrystalline specimens of zincblende and chalcopyrite modifications of this compound (labeled G5-1 and G4-1 respectively) used here, were n-type and of the same electron concentration $1.8 \times 10^{24} \text{ m}^{-3}$. Such a coincidence in electron concentrations would strengthen the correlation of the results on these two modifications. The reflectance and electroreflectance spectra of specimen G5-1 are shown in Figure IV-3. This specimen showed a p-like electroreflectance spectrum with two broad peaks at 2.15 ± 0.05 and 2.46 ± 0.05 eV. Since in the electroreflectance spectrum, interband transitions in the ultraviolet (u.v.) region were not observable, the measurements were supplemented by the conventional reflectance method and a peak at 4.35 ± 0.10 eV was observed. At this stage, these three peaks of this zincblende modification can only be assumed to correspond to E_1 , $E_1 + \Delta_1$ and E_2 transitions, i.e. interband transitions $\Lambda_{3v} - \Lambda_{1c}$, and $X_{5v} - X_{1c}$ (or $\Sigma_{1v} \Sigma_{2v} - \Sigma_{1c}^t$) respectively as explained in Section III-2. The justification

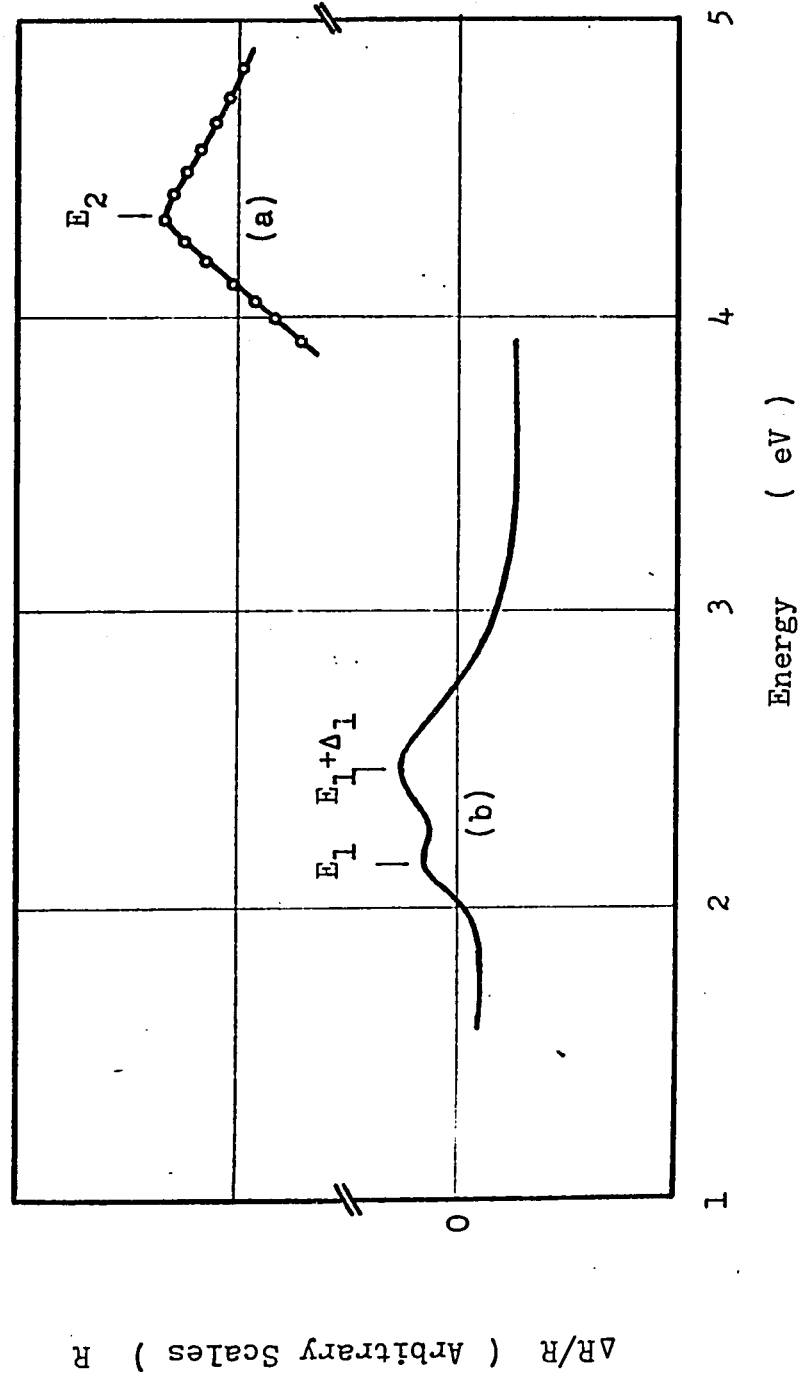


Figure IV-3 Reflectance and electroreflectance spectra of CdSnAs₂ with zincblende structure (Specimen G5-1). (a) Reflectance, (b) Electroreflectance: $V_{dc} = -1.0$ V, $V_{ac} = 1.5$ V.

for this will be seen later by following through the reflectance and electroreflectance peaks of the alloy system $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$.

The reflectance and electroreflectance spectra of G4-1, the specimen of chalcopyrite structure, are shown in Figure IV-4. Here the reflectance spectra as reported by Chang and Chang (66C7) and Sikharulidze et al (67S4) are also included. The reason for the appreciable difference in shape as well as positions of the maxima in the spectra, as reported by these authors, has been given in Section IV-21. In the present work, since same experimental conditions were imposed on both specimens G5-1 and G4-1 in electroreflectance measurements (e.g. the same electron concentration, bias and modulating voltage), the spectrum of specimen G4-1 was also expected to be p-like. In fact, the energy values of the two main peaks in $+\Delta R/R$ of this specimen: 2.125 ± 0.005 and 2.425 ± 0.005 eV, were very similar to those of the E_1 and $E_1 + \Delta_1$ peaks of specimen G5-1, the zincblende modification of this compound. Furthermore, these energy values were in good agreement with the results by Chang and Chang: 2.10 and 2.39 eV. Beside the two main peaks in the electroreflectance spectrum of specimen G4-1, there were two less intense peaks at 2.23 ± 0.03 and 2.62 ± 0.03 eV in the form of shoulders. The electroreflectance spectrum of this specimen did not show any structure in the u.v. region, and hence the measurements were again supplemented by the conventional reflectance method. A fairly broad maximum at 4.40 ± 0.10 eV,

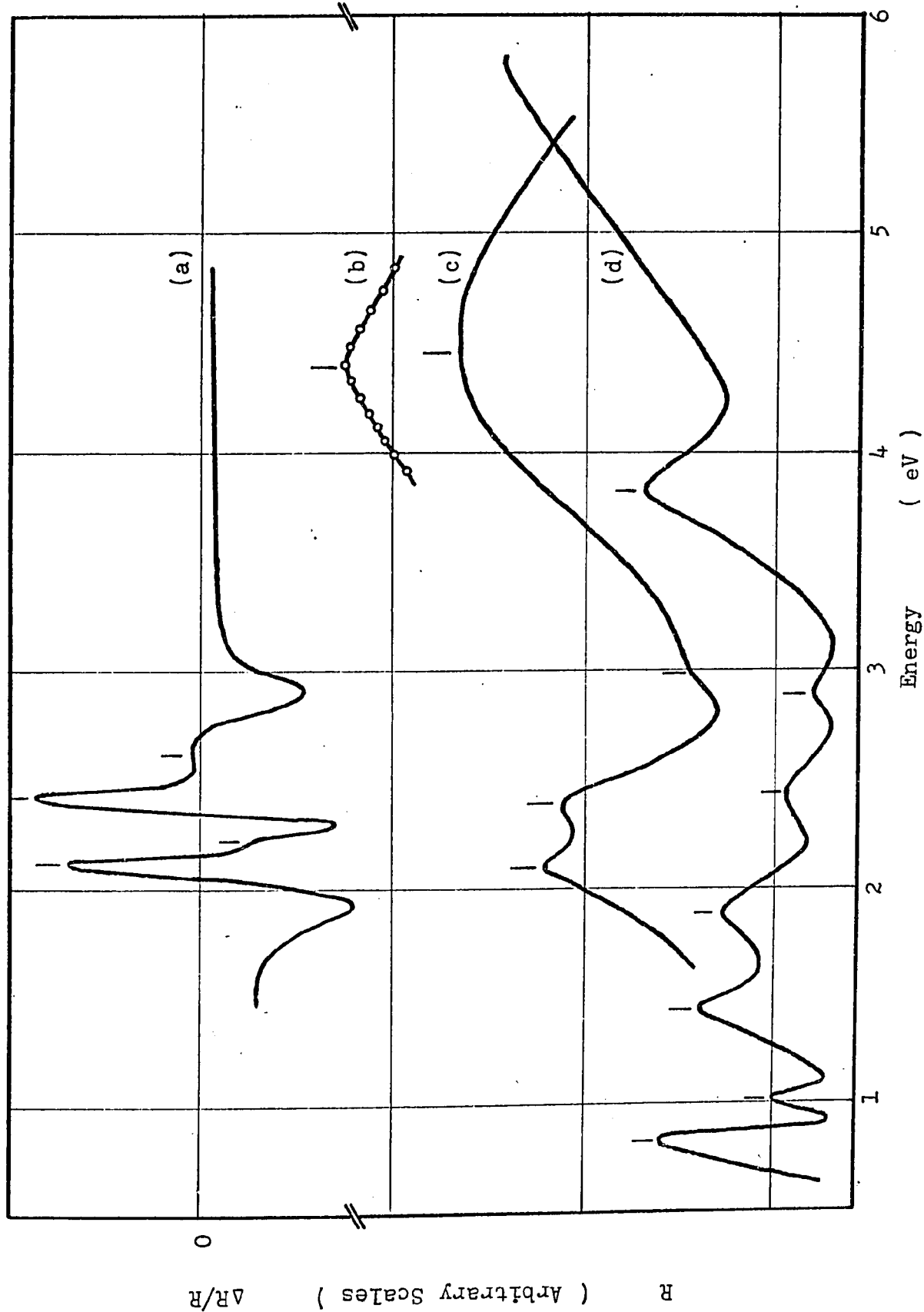


Figure IV-4 Reflectance and electroreflectance spectra of CdSnAs_2 with chalcopyrite structure.
 (a) Electroreflectance: Specimen G4-1, $V_{dc} = -1.0\text{V}$, $V_{ac} = 1.5\text{V}$; (b) Reflectance: Specimen G4-1; (c) Reflectance: (66C7); (d) Reflectance: (67S4).

similar to the value obtained for specimen G5-1, was observed. This value was again in good agreement with the result of 4.46 eV reported by Chang and Chang (66C7).

412. CdGeAs_2

As a result of the appreciable tetragonal compression in the crystal lattice, the band structure and the nature of the critical points for interband transitions in this compound were expected to be very complicated. The electroreflectance spectrum from the present work and the reflectance spectrum as reported by Abraham et al (68A1) on polycrystalline specimens of the chalcopyrite modification of this compound are shown in Figure IV-5. The specimen used in this work (labeled I2-1) was n-type with electron concentration $\lesssim 10^{24} \text{ m}^{-3}$. Since this material had a network of cracks, its carrier concentration could not be accurately determined. Both spectra exhibited a number of peaks and most of the electroreflectance peaks in $+\Delta R/R$ were compatible with those of the reflectance spectrum, e.g. the peaks at 2.175 ± 0.005 , 2.32 ± 0.05 , 2.490 ± 0.008 , 2.65 ± 0.01 and $3.16 \pm 0.01 \text{ eV}$ of the electroreflectance spectrum, and those at 2.1, 2.25, ~ 2.6 and $\sim 3.2 \text{ eV}$ of the reflectance spectrum. In both cases, the most intense peak appeared at approximately the same energy (2.175 and 2.1 eV), and this should correspond to same type of interband transitions as the one at 2.125 eV of CdSnAs_2 .

The remaining peaks: 1.84, 2.87 and 3.50 eV, in the electroreflectance spectrum of specimen I2-1 were not observed in the reflectance work by Abraham et al. From repeated electroreflectance measurements on this compound, it was found that with various biasing and modulating voltages the energy

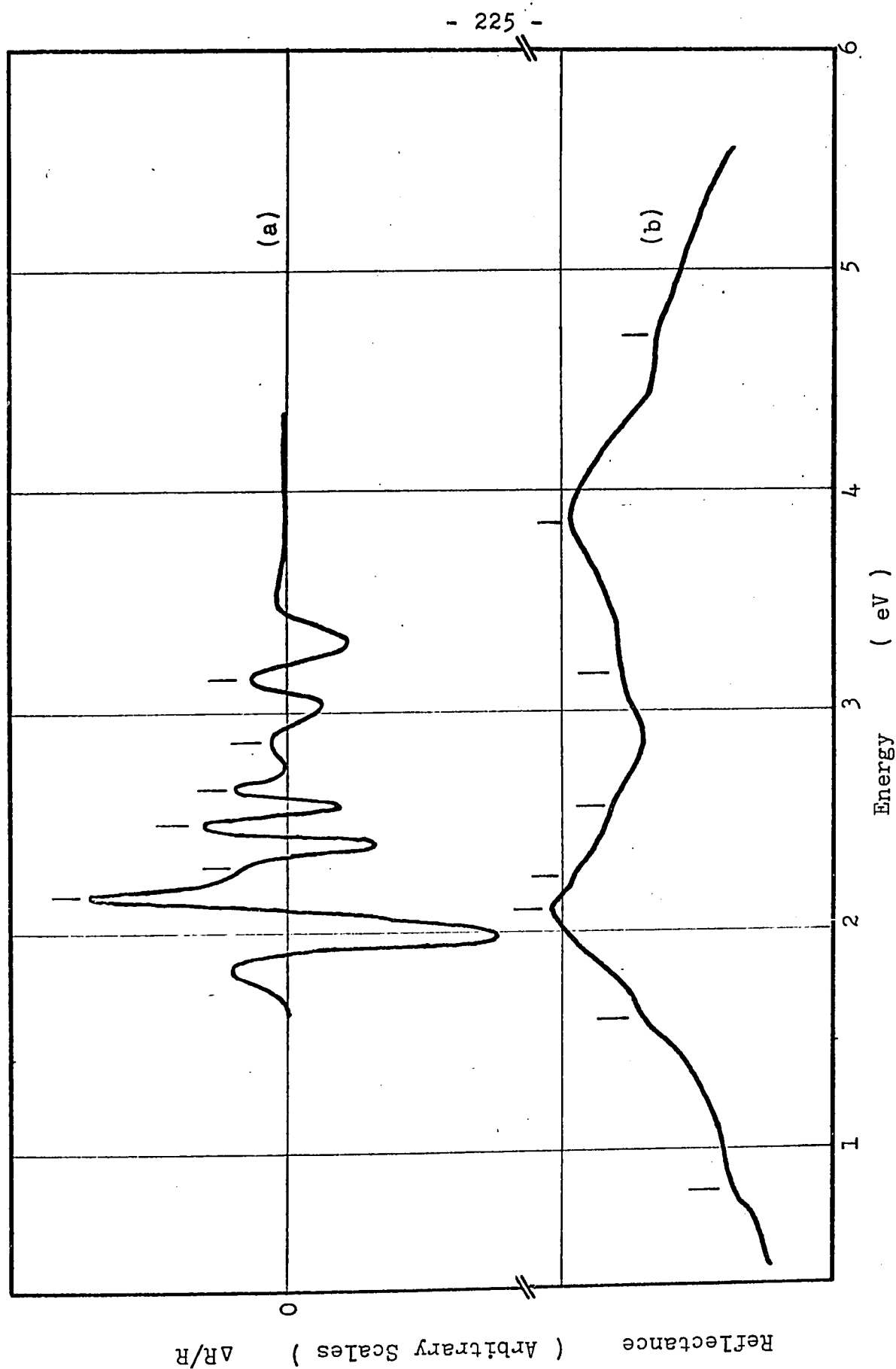


Figure IV-5 Reflectance and electroreflectance spectra of CdGeAs_2 with chalcopyrite structure.
 (a) Electroreflectance: Specimen I2-1, $V_{dc} = -0.5\text{V}$, $V_{ac} = 1.5\text{V}$; (b) Reflectance: (68Al).

positions of most peaks, except those at 1.84 and 3.50 eV, were reproducible. Hence these two maxima could be attributed to subsidiary oscillations.

This electroreflectance spectrum did not show any structure at energies higher than 3.5 eV, and unfortunately no accurate reflectance and thermorefectance measurements could be made on the available samples of this compound because of the presence of fine cracks. Nevertheless, the energy values of fine structures of interband transitions in the range 2.0-3.5 eV have been accurately measured in the present work.

413. ZnSnAs_2

Specimen J2-1, the zincblende modification of this compound, was p-type with high carrier concentration of $1 \times 10^{26} \text{ m}^{-3}$. The reflectance, electroreflectance and thermorefectance spectra of this polycrystalline specimen are shown in Figure IV-6. Here only one p-like peak at $2.14 \pm 0.03 \text{ eV}$ was observed in the electroreflectance measurements. Hence, the measurements in the u.v. region were supplemented by the conventional reflectance method, and a maximum at $4.70 \pm 0.08 \text{ eV}$ was obtained. The thermorefectance spectrum of this specimen contained two broad peaks, and the intensity of the spectrum was still very low even with a high specimen current of 1.1 amp. However, the energy positions of these two peaks could be measured with reasonable accuracy: 2.23 ± 0.05 and $4.70 \pm 0.08 \text{ eV}$. These two peaks observed in the three types of measurements were practically self-consistent, and at this stage, they could only be assumed to correspond to the E_1 and E_2 transitions (defined earlier). This will be justified later by following through the reflectance and electroreflectance peaks in the alloy system $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$.

The specimens of the chalcopyrite structure of this compound used in this work were also p-type but with much lower hole concentrations. The hole concentration of the polycrystalline specimen J1-1, prepared by the "slow-cooling" method, was $1.6 \times 10^{24} \text{ m}^{-3}$, while that of the single crystal (specimen J5-1), grown by the vertical Bridgman method by Masumoto and Isomura, was $1.1 \times 10^{24} \text{ m}^{-3}$.

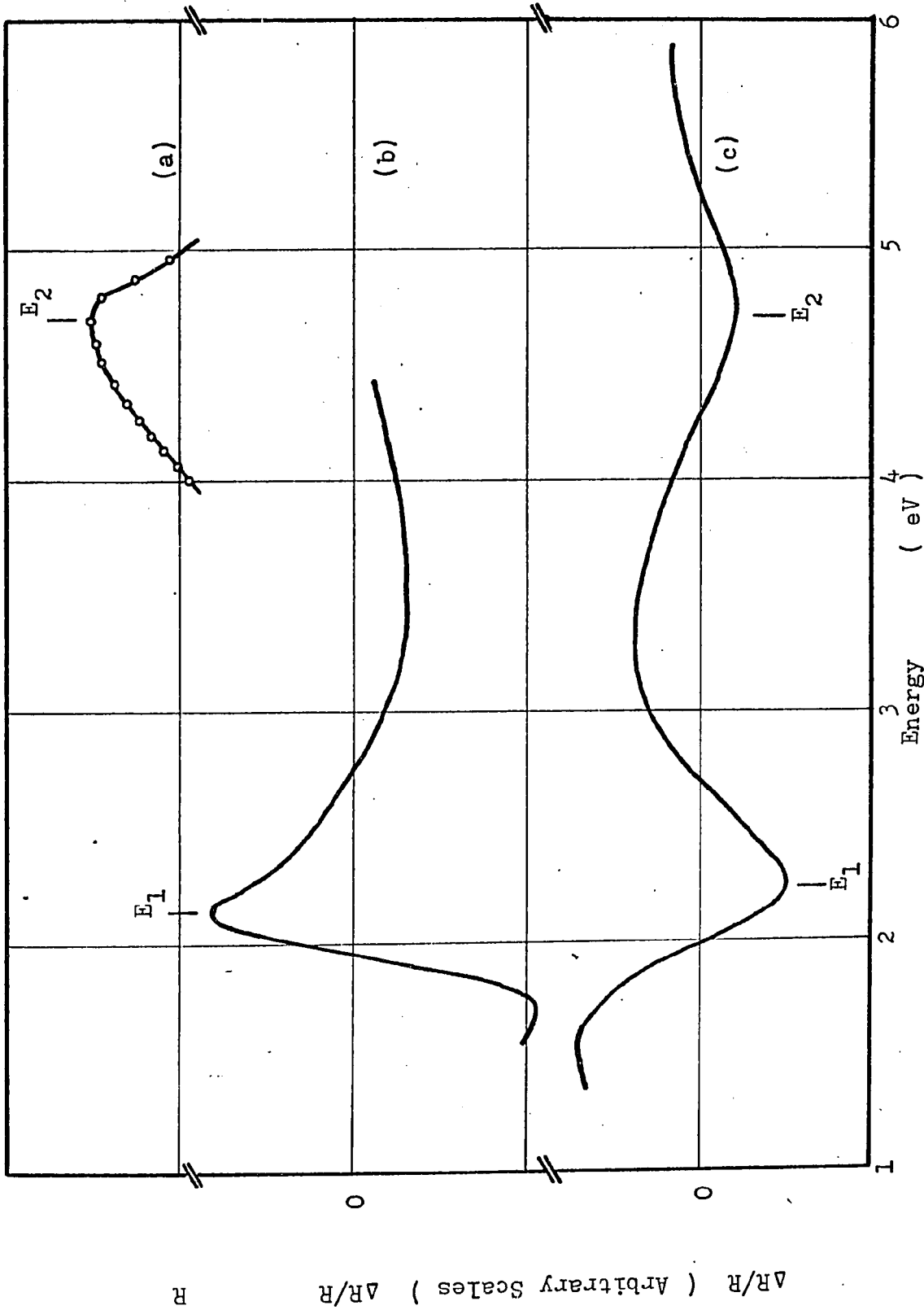


Figure IV-6 Reflectance, electroreflectance and thermoreflectance spectra of ZnSnAs_2 with zincblende structure (Specimen J2-1). (a) Reflectance; (b) Electroreflectance; (c) Thermoreflectance: specimen current 1.1 amp. $V_{dc} = -1.0V$, $V_{ac} = 1.5V$;

The electroreflectance spectra of these two specimens are shown in Figure IV-7. These two spectra were practically identical. Since there was no tetragonal compression in the crystal lattice, the anisotropy in optical properties of this compound would be less significant than in other II-IV-V₂ compounds. The electroreflectance spectra of these specimens contained a large number of peaks with energy values at:

(J1-1)	(J5-1)	
2.230±0.006,	2.260±0.006,	
2.310±0.005,	2.335±0.005,	
2.545±0.005,	2.550±0.008,	
2.75,*	2.78,*	
3.050±0.006,	3.075±0.008,	
4.34±0.04,	4.40±0.05,	
4.72±0.03,	4.77±0.04,	
5.05,*	5.17,*	(in eV).

The maxima marked by a * sign could be interpreted as subsidiary oscillations, since the energy positions of these two maxima shifted slightly with various biasing and modulating voltages while those of other peaks remained unchanged.

In order to confirm the observations in the electroreflectance work, thermorefectance measurements were also made on specimen J5-1. The spectrum is shown in Figure IV-8. Here the reflectance spectrum as reported by Kesamanly et al (65K1) is also included. The intensity of the thermorefectance spectrum was reasonably high even with specimen current ~0.3 amp.

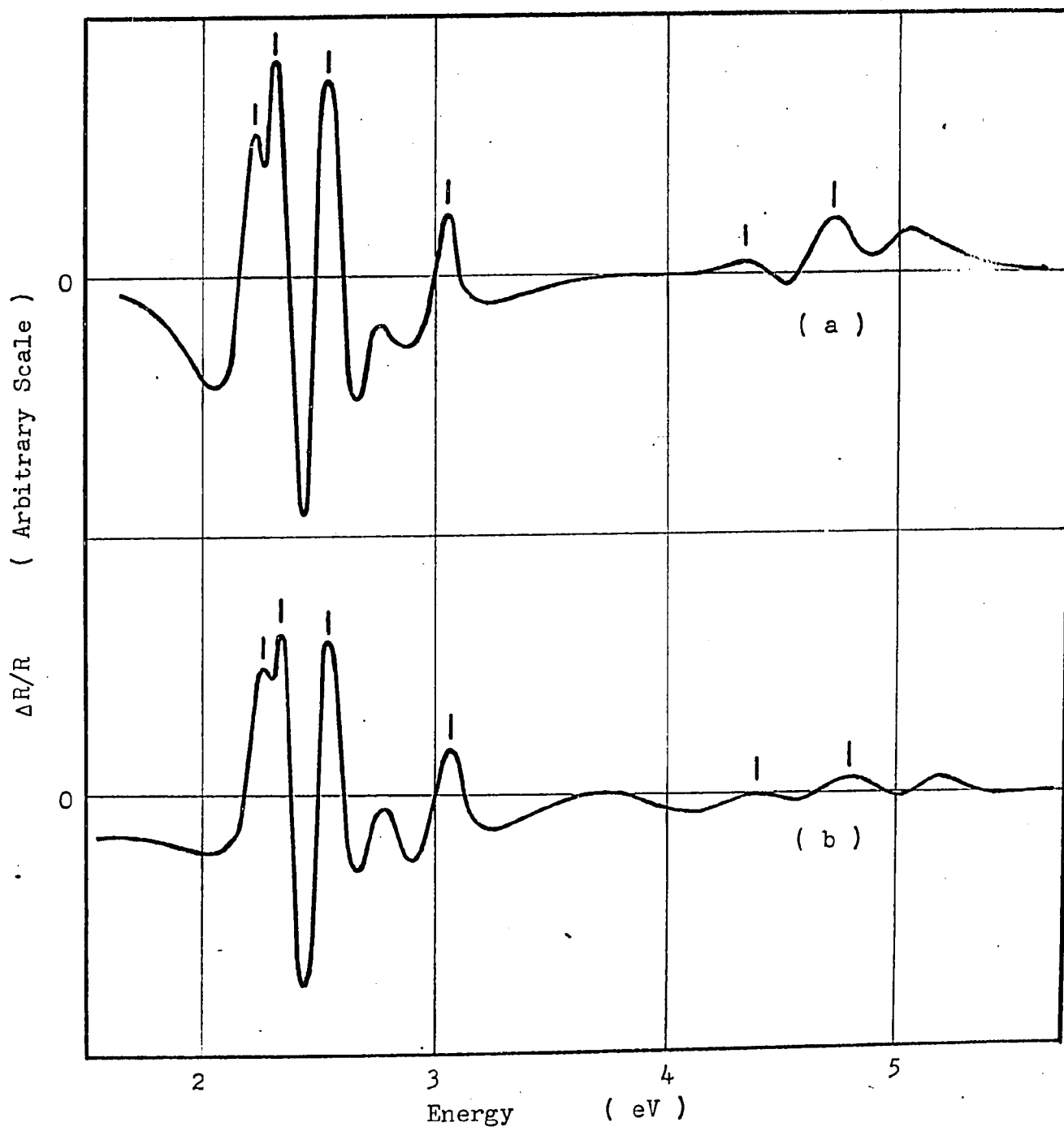


Figure IV-7 Electroreflectance spectra of ZnSnAs_2 with chalcopyrite structure. (a) Specimen J1-1 (prepared by "slow-cooling" method), $V_{dc} = -0.5\text{V}$, $V_{ac} = 1.5\text{V}$; (b) Specimen J5-1 (prepared by "vertical Bridgman" method), $V_{dc} = -0.25\text{V}$, $V_{ac} = 1.5\text{V}$.

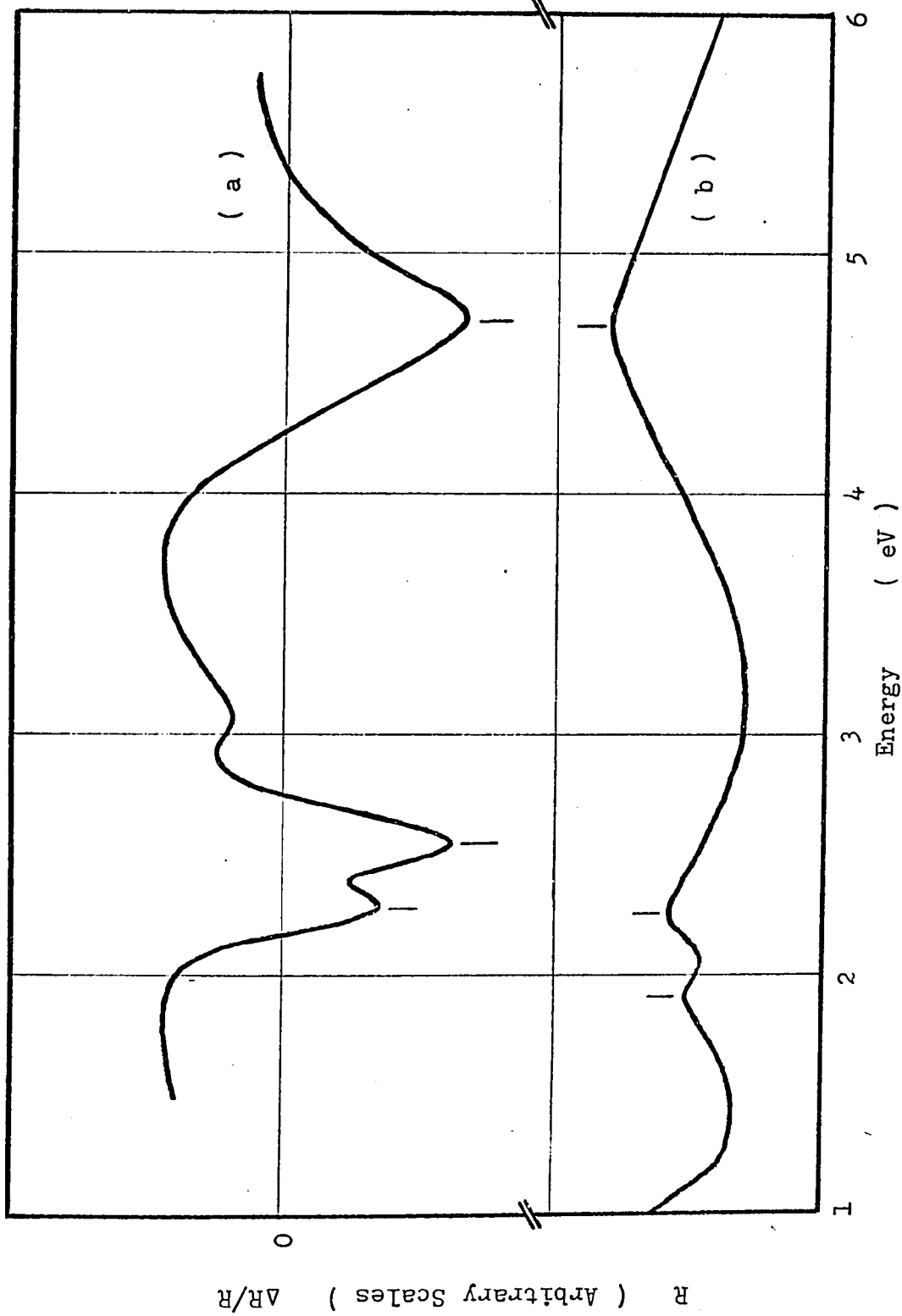


Figure IV-8 Reflectance and thermoreflectance spectra of ZnSnAs_2 with chalcopyrite structure. (a) Thermoreflectance: Specimen J5-1, specimen current 0.5 amp; (b) Reflectance: (65K1).

For better resolution of the spectrum, a slightly higher specimen current of 0.5 amp was used. This spectrum contained four peaks at 2.28 ± 0.01 , 2.55 ± 0.01 , 3.07 ± 0.03 , and 4.72 ± 0.02 eV which were in excellent agreement with the electroreflectance results. However, the doublet in the region 2.2-2.4 eV was not resolved here. The reflectance spectrum by Kesamanly et al contained three intense maxima, two of which (2.25 and 4.7 eV) were in good agreement with the present investigations. A peak at 1.91 eV reported by these authors, however, was not observed in this work.

By comparing the reflectance and modulated reflectance spectra of the two modifications of this compound, it was found that the energy values of the two peaks at 2.2-2.4 eV and 4.7 eV of the chalcopyrite modification were almost the same as the peaks E_1 and E_2 of the zincblende modification, although the hole concentrations of these specimens differed by almost two orders of magnitude. This obviously indicates that the presence of high-concentration extrinsic holes has little effect on the band structure of this material.

414. ZnGeAs_2

The polycrystalline specimen L1-1 of the chalcopyrite modification of this compound was p-type with hole concentration $8.2 \times 10^{24} \text{ m}^{-3}$. The reflectance, electroreflectance and thermorefectance spectra of this specimen are shown in Figure IV-9. The compatibility of these results could easily be seen by comparing the energy positions of the peaks of the spectra:

Reflectance	Electroreflectance	Thermorefectance
2.30±0.06	2.260±0.008	2.28±0.03
	2.410±0.008	
2.70±0.04	2.740±0.008	2.57±0.04
3.2±0.2	3.23±0.01	3.21±0.04
4.4±0.1	4.37±0.03	4.37±0.05
	4.92±0.03	4.94±0.05 (in eV)

These spectra were also very similar to those of ZnSnAs_2 of the same crystal structure. It was apparent that the peaks at 3.2 and 4.4 eV of this compound corresponded to same types of interband transitions as the peaks at 3.07 and 4.7 eV of ZnSnAs_2 . The correspondence between the peaks in the region 2-3 eV of these two compounds was more difficult to establish. However, as judged from the intensity of the reflectance peaks, it was very probable that the peak at 2.7 eV of ZnGeAs_2 would correspond to the one at 2.2-2.4 eV of ZnSnAs_2 .

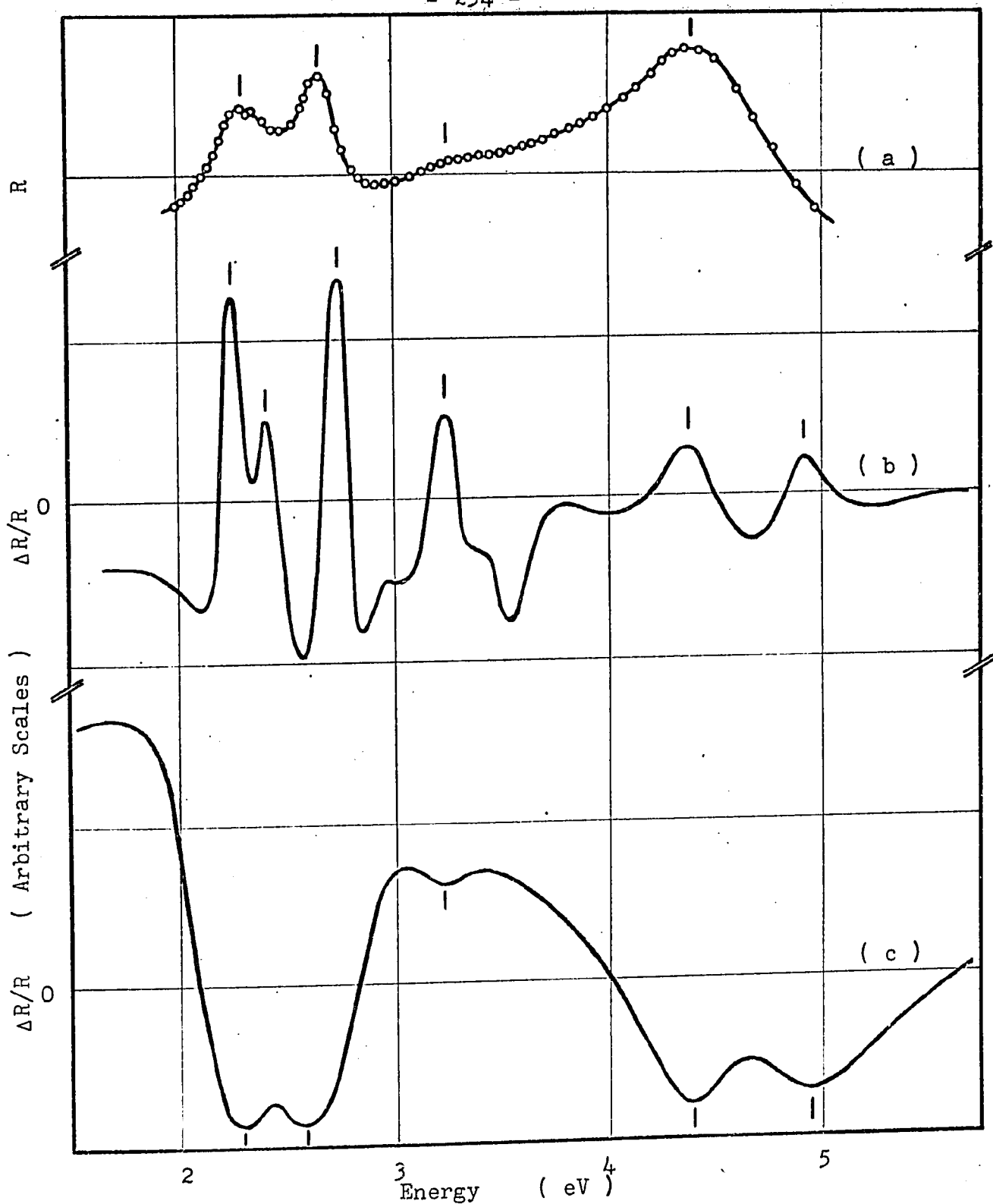


Figure IV-9 Reflectance, electroreflectance and thermorefectance spectra of ZnGeAs_2 with chalcopyrite structure (Specimen L1-1). (a) Reflectance; (b) Electroreflectance: $V_{dc} = -0.25\text{V}$, $V_{ac} = 1.5\text{V}$; (c) Thermorefectance: Specimen current 0.6 amp.

415. ZnSiAs_2

The polycrystalline specimen M1-1 of the chalcopyrite modification of this compound was p-type with very low carrier concentration ($\sim 10^{20}$ - 10^{21} m^{-3}). The electroreflectance spectrum of this specimen and the reflectance spectrum reported by Kesamanly et al (65K1) are shown in Figure IV-10. The electroreflectance spectrum consisted of a large number of peaks: 2.130 ± 0.005 , 2.228 ± 0.008 , 2.477 ± 0.006 , 2.76 ± 0.01 , 2.900 ± 0.006 , 3.26 ± 0.01 , 4.32 ± 0.02 and 4.73 ± 0.03 eV. The most intense peak 2.130 ± 0.005 eV was in very good agreement with the photoconductivity result of 2.10 eV by Kesamanly et al (65K3). This value indicated the separation between the highest valence band and the lowest conduction band at Γ : E_0 . The small peak adjacent to this intense maximum 2.228 ± 0.008 eV could be attributed to the transitions $E_0 + \Delta_0$. Hence the spin-orbit splitting of the valence band at Γ was deduced: $\Delta_0 = 0.10 \pm 0.01$ eV. The splitting due to the crystal field, ΔE_k , was too small to be measurable in this work.

The only two peaks observed in the reflectance measurements (Kesamanly et al 65K1), 3.35 and 4.2-4.5 eV, were compatible with the peaks 3.26 and 4.32 eV in the electroreflectance spectrum obtained here. By comparing the spectra of this compound with those of other II-IV- As_2 compounds, it was seen that these two peaks corresponded to same types of interband transitions as the peaks at 2.2-2.4 and 4.7 eV of ZnSnAs_2 , and that the peak at 4.73 eV (of ZnSiAs_2) corresponded to that of the 4.9 eV peak of ZnGeAs_2 .

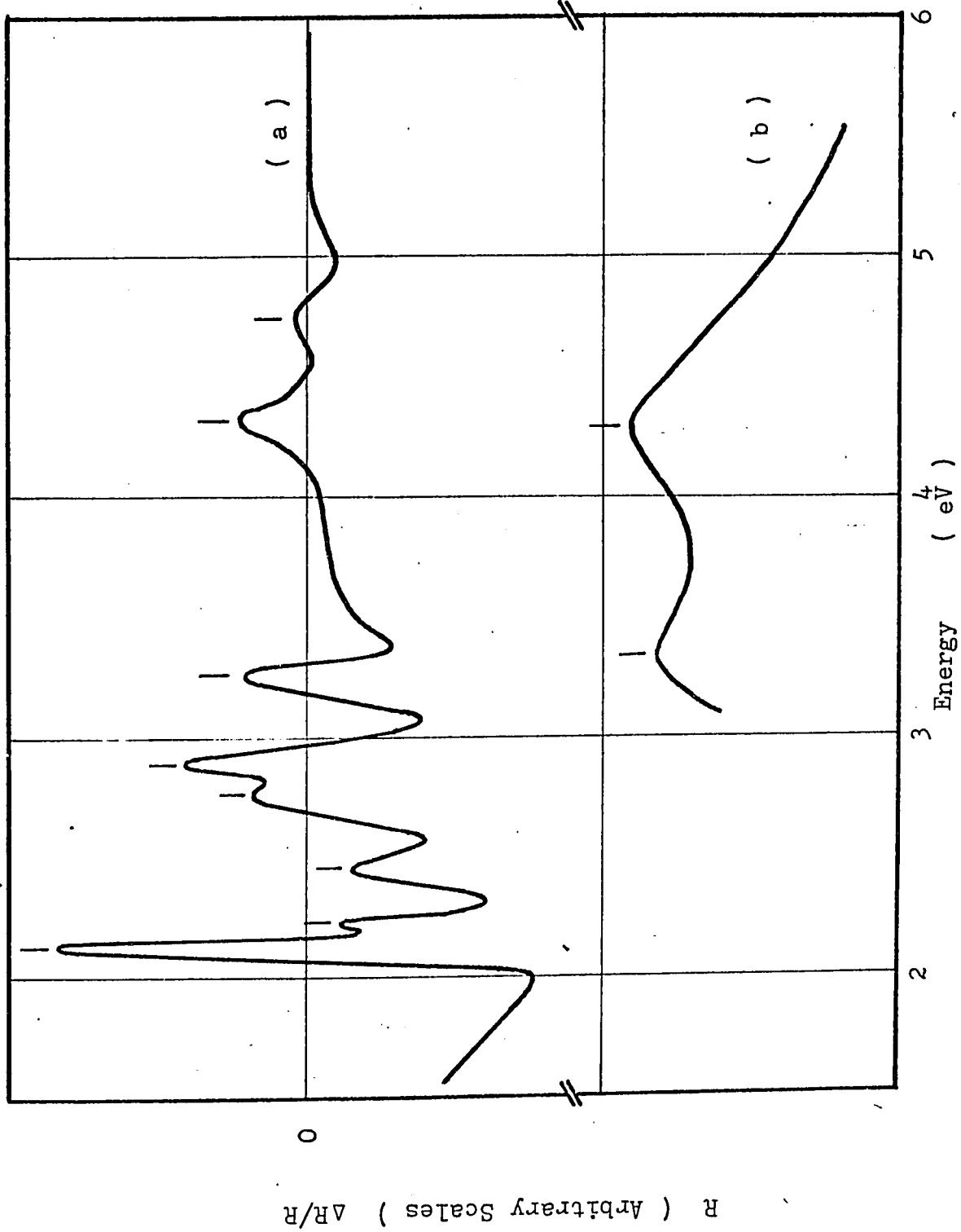


Figure IV-10 Reflectance and electroreflectance spectra of ZnSiAs_2 with chalcopyrite structure. (a) Electroreflectance: Specimen M1-1, $V_{dc} = -0.25\text{V}$, $V_{ac} = 1.5\text{V}$; (b) Reflectance: (65K1).

42. THE ALLOYS

421. $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$

All specimens of this alloy system investigated here were n-type with electron concentrations in the range of $1-4 \times 10^{24} \text{ m}^{-3}$. The electroreflectance spectra of the alloys over the whole composition range, including the zincblende modification of CdSnAs_2 , in the energy range of 1.5-4.0 eV are shown in Figure IV-11. The two p-like peaks, 2.500 and 2.778 eV in the spectrum of InAs have been identified as corresponding to E_1 and $E_1 + \Delta_1$ transitions. It is seen that as x increases, the energy positions of the E_1 and $E_1 + \Delta_1$ peaks decrease gradually to the values of 2.125 and 2.425 eV at the CdSnAs_2 end, and as the structure gradually changes from zincblende to chalcopyrite at $x = 0.7-0.8$, some less intense peaks appear in the form of shoulders on the main peaks. These shoulders do not seem to be split-off peaks from the main peaks, and their origin is still unknown at this stage. The variation of the energy values of all these peaks over the whole composition range is shown in Figure IV-12. A question is raised at this point: The experimental results have indicated smooth variations of these two main peaks with composition of the alloys, regardless of the structural change of the alloys from zincblende to chalcopyrite. In the zincblende lattice, the E_1 and $E_1 + \Delta_1$ peaks correspond to interband transitions $\Lambda_{3v} - \Lambda_{1c}$. Then in the chalcopyrite lattice, what interband transitions do these two peaks represent?

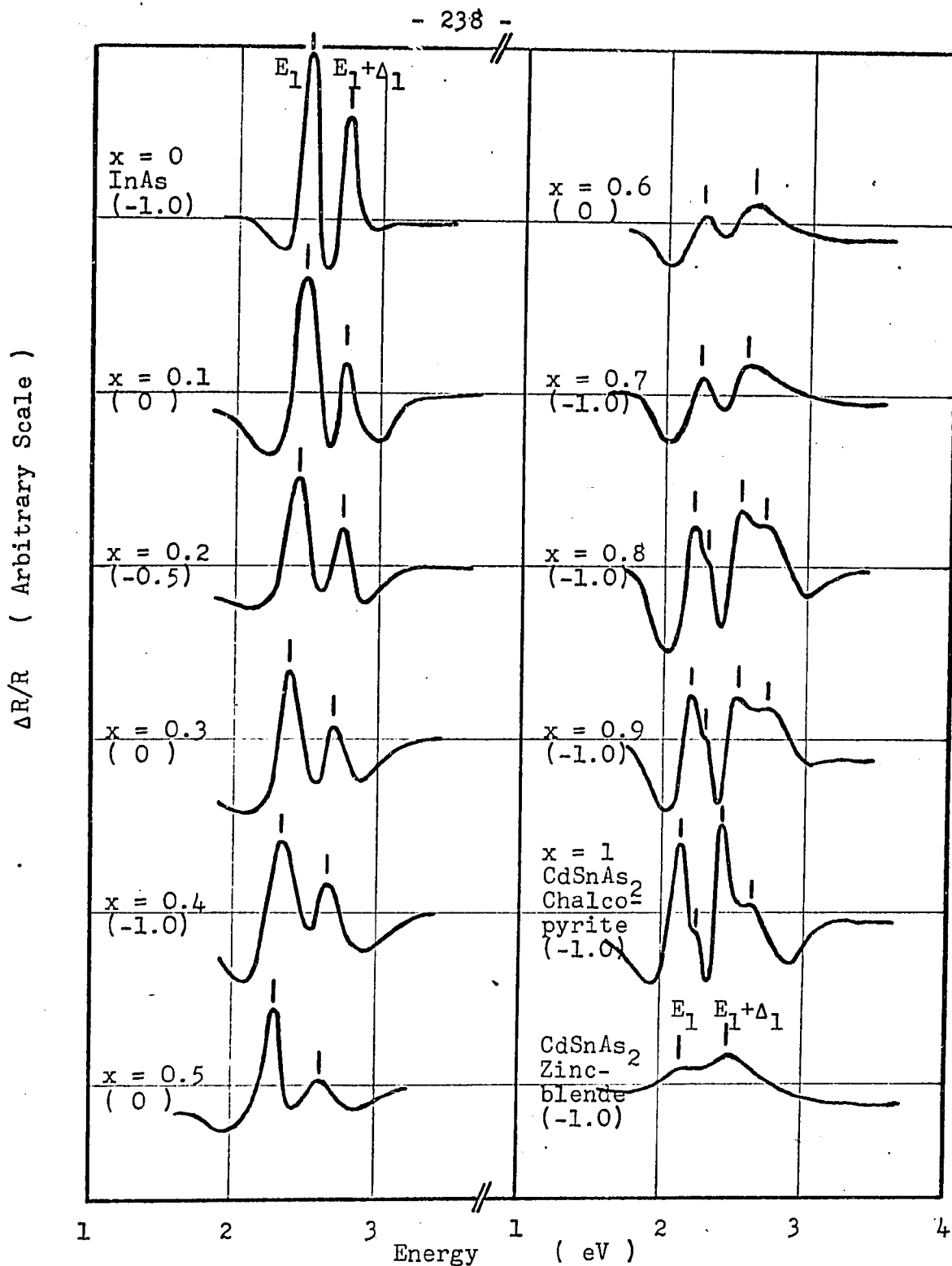


Figure IV-11 Electroreflectance spectra of the E_1 complex of the system $\text{In}_2(1-x)\text{Cd}_x\text{Sn}_x\text{As}_2$. [$V_{ac} = 1.5\text{V}$, Values in brackets are biasing voltages (V_{dc}).]

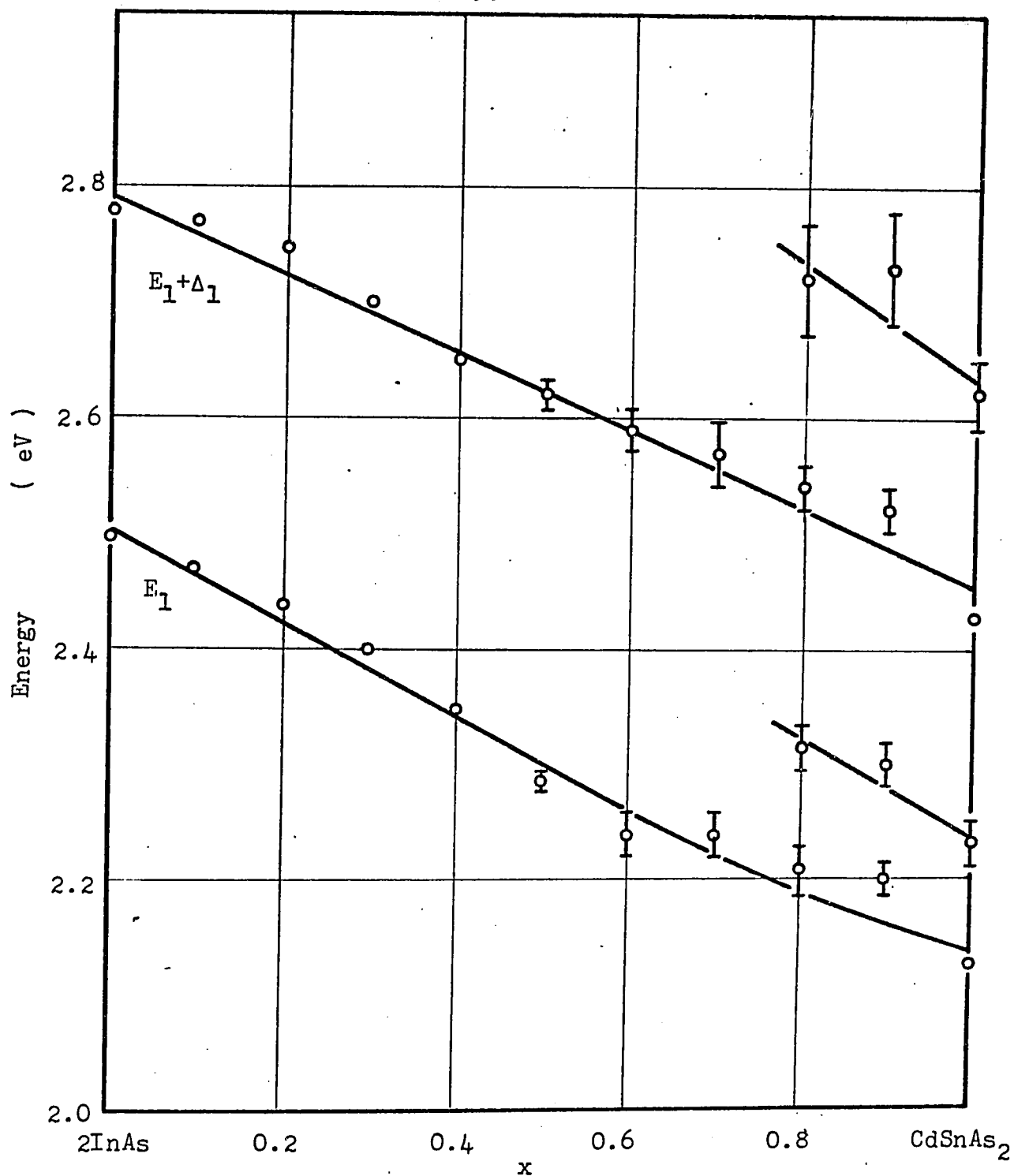


Figure IV-12 Variation of the energy of E_1 and $E_1 + \Delta_1$ interband transitions with composition of the system $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$.

By comparing the Brillouin zones of these two structures, correspondence has been established between some symmetry points in them, such as

$$\Gamma \text{ (zincblende)} \longleftrightarrow \Gamma \text{ (chalcopyrite)}$$

$$L \text{ (zincblende)} \longleftrightarrow N \text{ (chalcopyrite)}$$

Since the E_1 and $E_1 + \Delta_1$ transitions in the zincblende case take place at a position along the Λ direction, which is much closer to L than to Γ , it is seen that in the chalcopyrite case these E_1 and $E_1 + \Delta_1$ peaks correspond to transitions in the neighborhood of the N point. Here the same labels (E_1 , $E_1 + \Delta_1$, etc.) are used to indicate the close correlations of these peaks in the two modifications of this compound.

The structures of the electroreflectance spectra of this alloy system in the u.v. region were only observed for specimens with $x \leq 0.5$. These spectra are shown in Figure IV-13. The two p-like peaks: 4.44 and 4.70 eV of InAs, have been identified as corresponding to E_0' and E_2 transitions, i.e. $\Delta_{5v} - \Delta_{1c}^u$ near Γ , and $X_{5v} - X_{1c}$ (or $\Sigma_{1v} \Sigma_{2v} - \Sigma_{1c}^l$). As x increases, the peaks became weaker and finally disappeared. This was therefore supplemented by the conventional reflectance measurements. As shown in Figure IV-14, the reflectance spectra of the alloys with $x = 0.5-1.0$ are relatively broad and less accurate, and the E_0' peaks are completely unobservable. However, a decrease in energy of the E_2 peaks is easily seen. The variation of these ultraviolet peaks with x is shown in Figure IV-15. Here the same label E_2 is still used for these

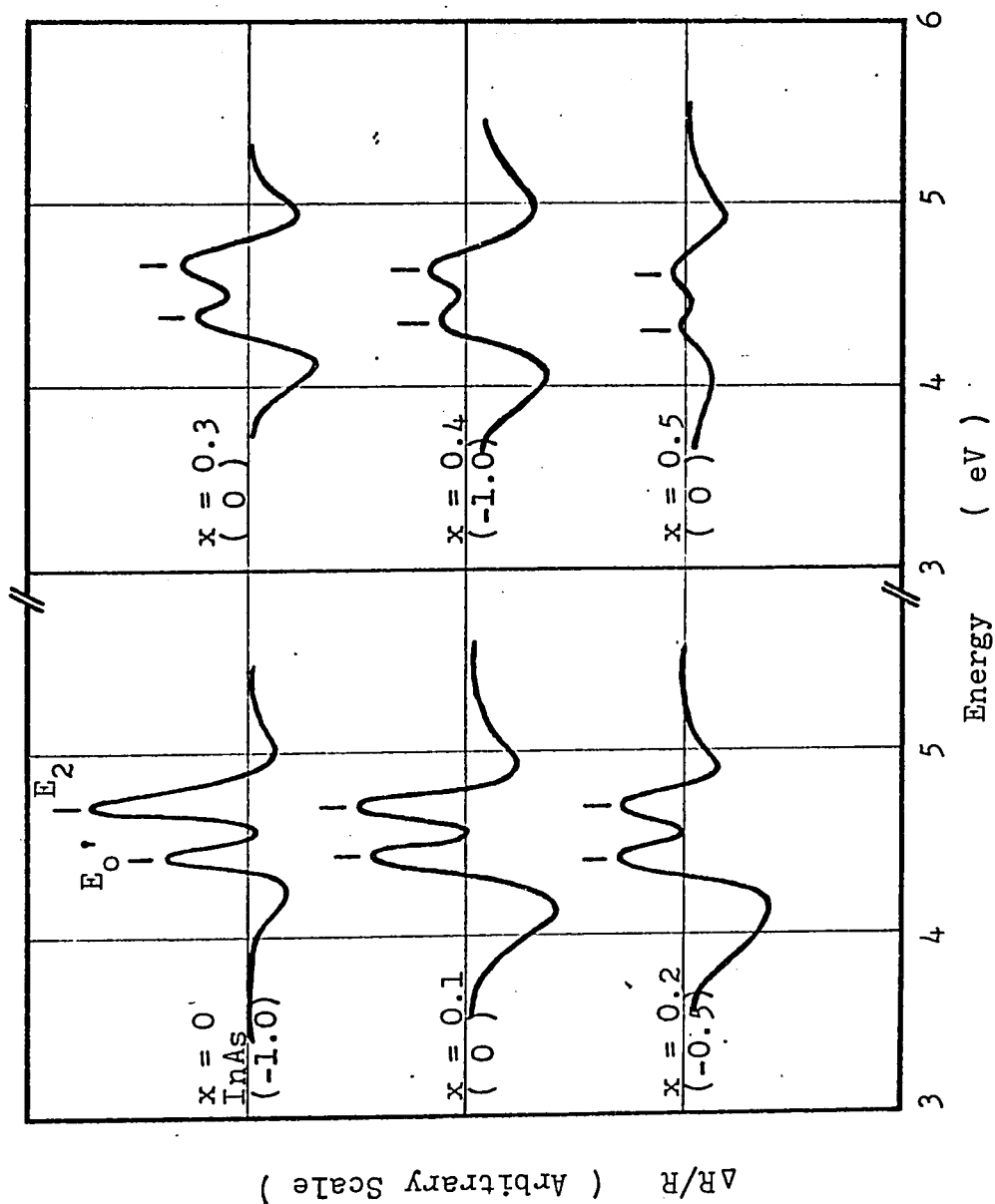


Figure IV-13 Electrorreflectance spectra in the u.v. region of the system $\text{In}_2(1-x)\text{CdSnAs}_2$ up to $x = 0.5$. [$V_{ac} = 1.5V$, Values in brackets are biasing voltages (V_{dc}).]

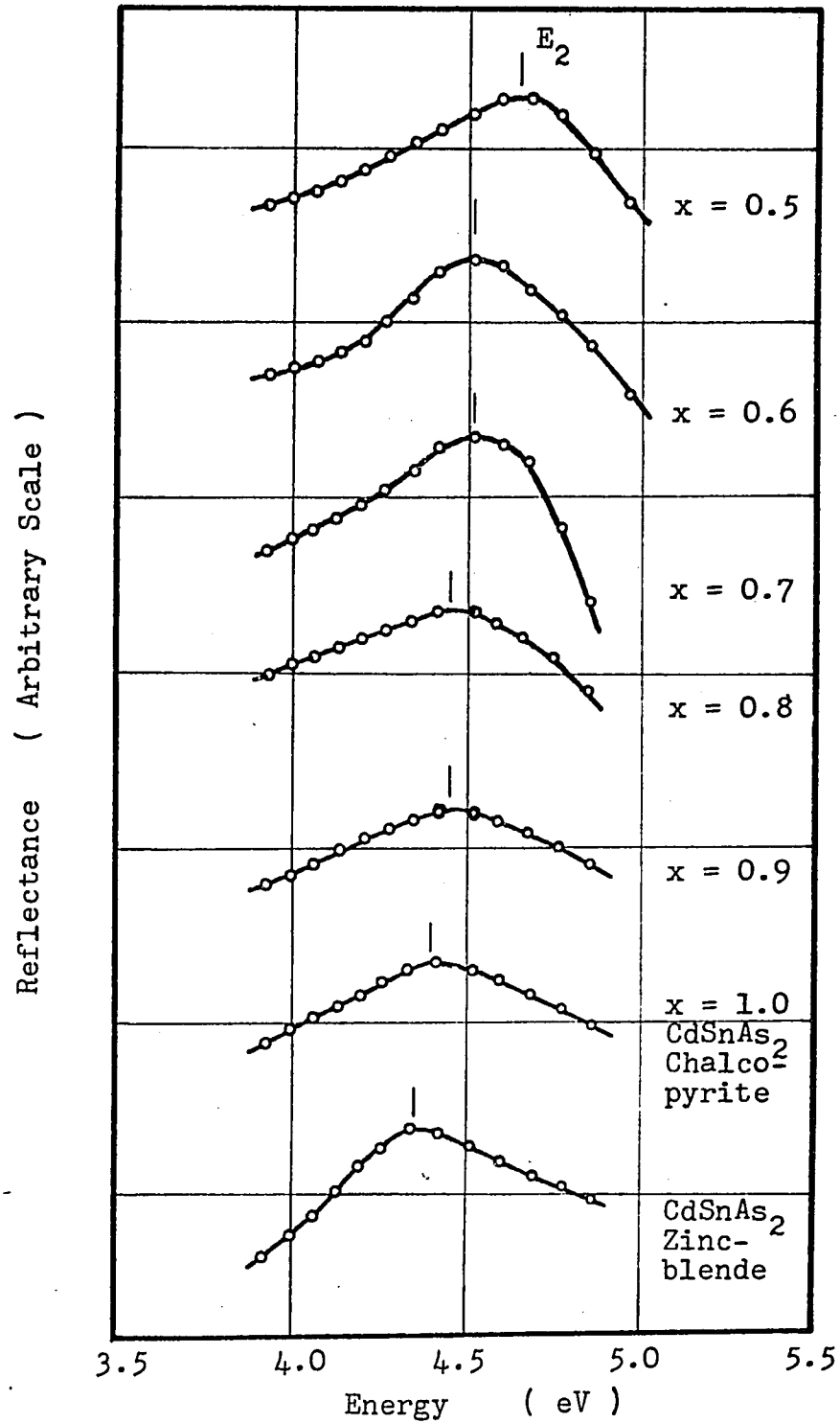


Figure IV-14 Reflectance spectra of the system $\text{In}_2(1-x)\text{Cd}_x\text{Sn}_x\text{As}_2$ in the u.v. region.

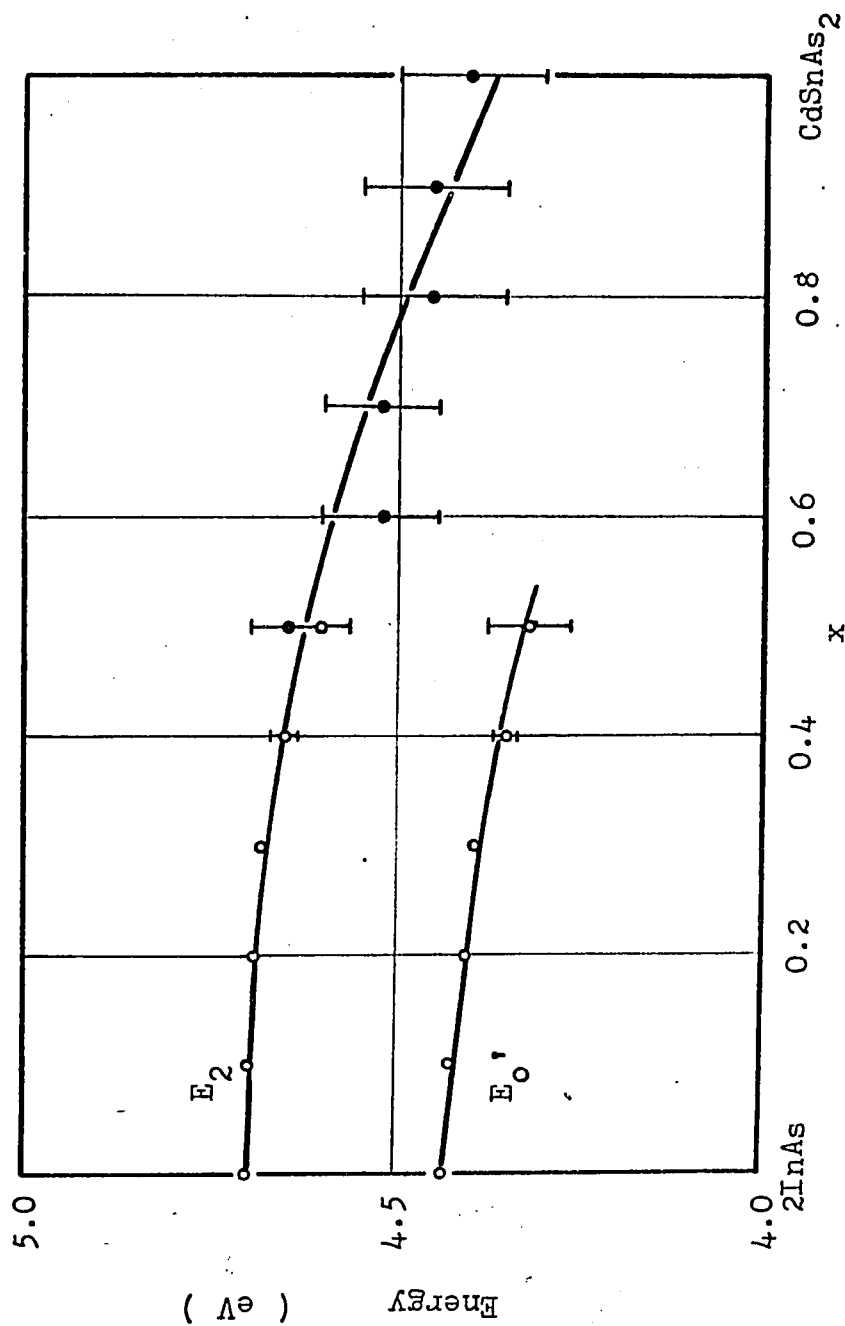


Figure IV-15 Variation of the energy of E_0' and E_2 interband transitions with composition of the system $\text{In}_2(1-x)\text{CdSn}_x\text{As}_2$. (o, electroreflectance results; ●, reflectance results.)

peaks of the chalcopyrite lattice to correlate the peaks of both modifications. The correspondence can be established if the E_2 peaks represent the transitions at the X point of the Brillouin zone of the zincblende lattice, because the X point here corresponds to both Γ and T of chalcopyrite.

However, the correspondence of the Σ direction in the Brillouin zone of zincblende with the symmetry directions in that of chalcopyrite is still uncertain at this stage.

422. $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$

The specimens of the zincblende modification of the alloys of this system were p-type with hole concentrations in the range of $0.9\text{--}2.4 \times 10^{25} \text{ m}^{-3}$. For these materials, there will be no ambiguity in the interpretation of the electroreflectance or reflectance peaks, since no structural change is involved. The electroreflectance spectra of the E_1 and $E_1 + \Delta_1$ peaks for this system over the whole composition range are shown in Figure IV-16. The spectra are all p-like. As x increases, the $E_1 + \Delta_1$ peaks become less prominent and gradually become shoulders on the main E_1 peaks. The E_1 peaks also become broader as x increases. The variation of the energy values of E_1 and $E_1 + \Delta_1$ with alloy composition is shown in Figure IV-17. The non-linear variation of E_1 with x can be fitted to a parabola. The broadening of the E_1 peaks and the disappearance of the $E_1 + \Delta_1$ peaks near the ZnSnAs_2 end can intuitively be interpreted as due to the smallness of the splitting Δ_1 which is beyond the resolution of the spectra. Such variations of the energy values of these E_1 and $E_1 + \Delta_1$ peaks will be discussed later.

The electroreflectance peaks in the u.v. region (E_0' and E_2 transitions) were observed only in the alloys near the InAs end. As shown in Figure IV-18, these ultraviolet peaks become weaker as x increases. The measurements of the energy values of the ultraviolet peaks of the rest of this alloy

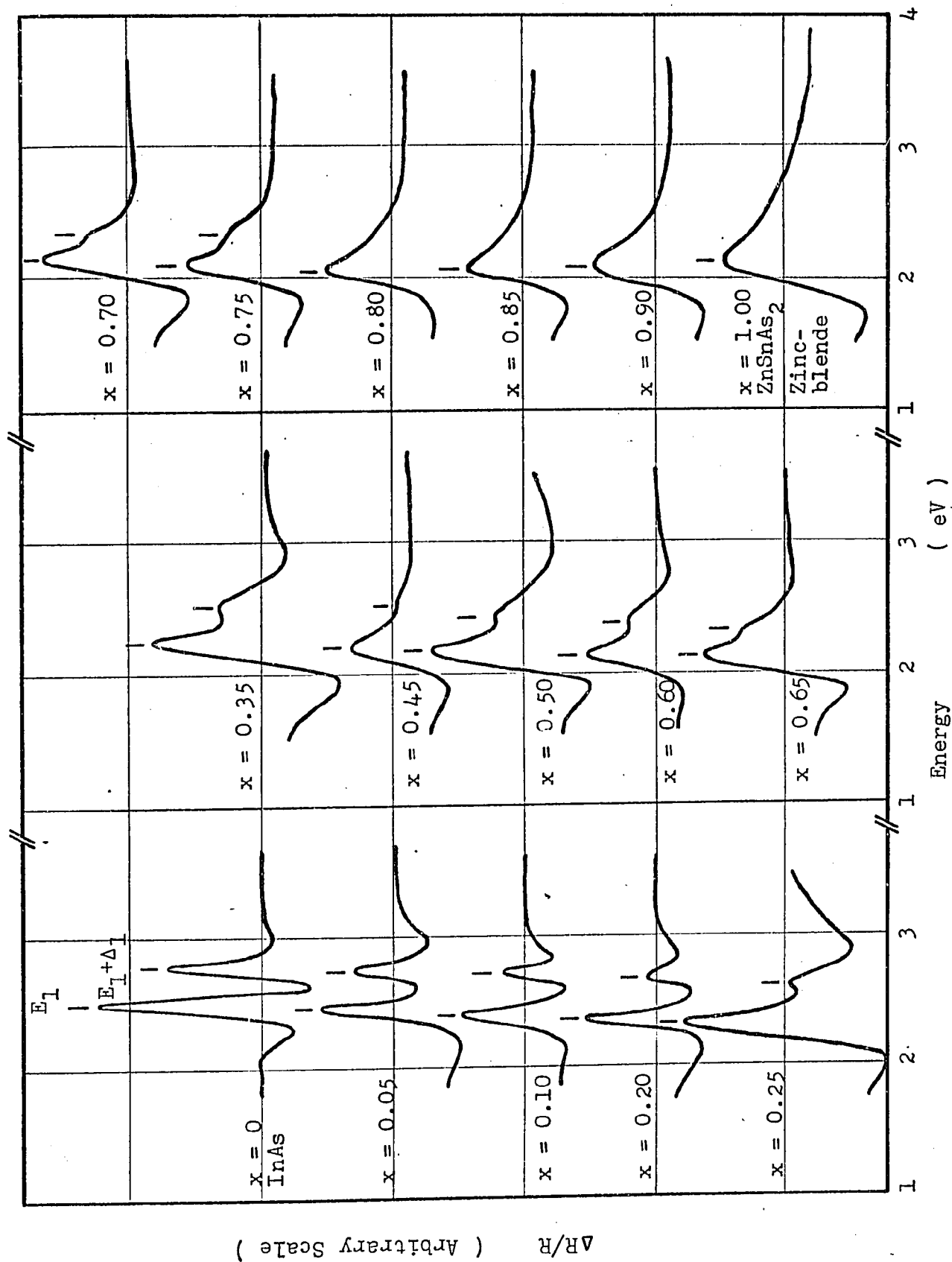


Figure IV-16 Electrorreflectance spectra of the E_1 complex of the system $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$.
($V_{dc} = -1.0V$, $V_{ac} = 1.5V$.)

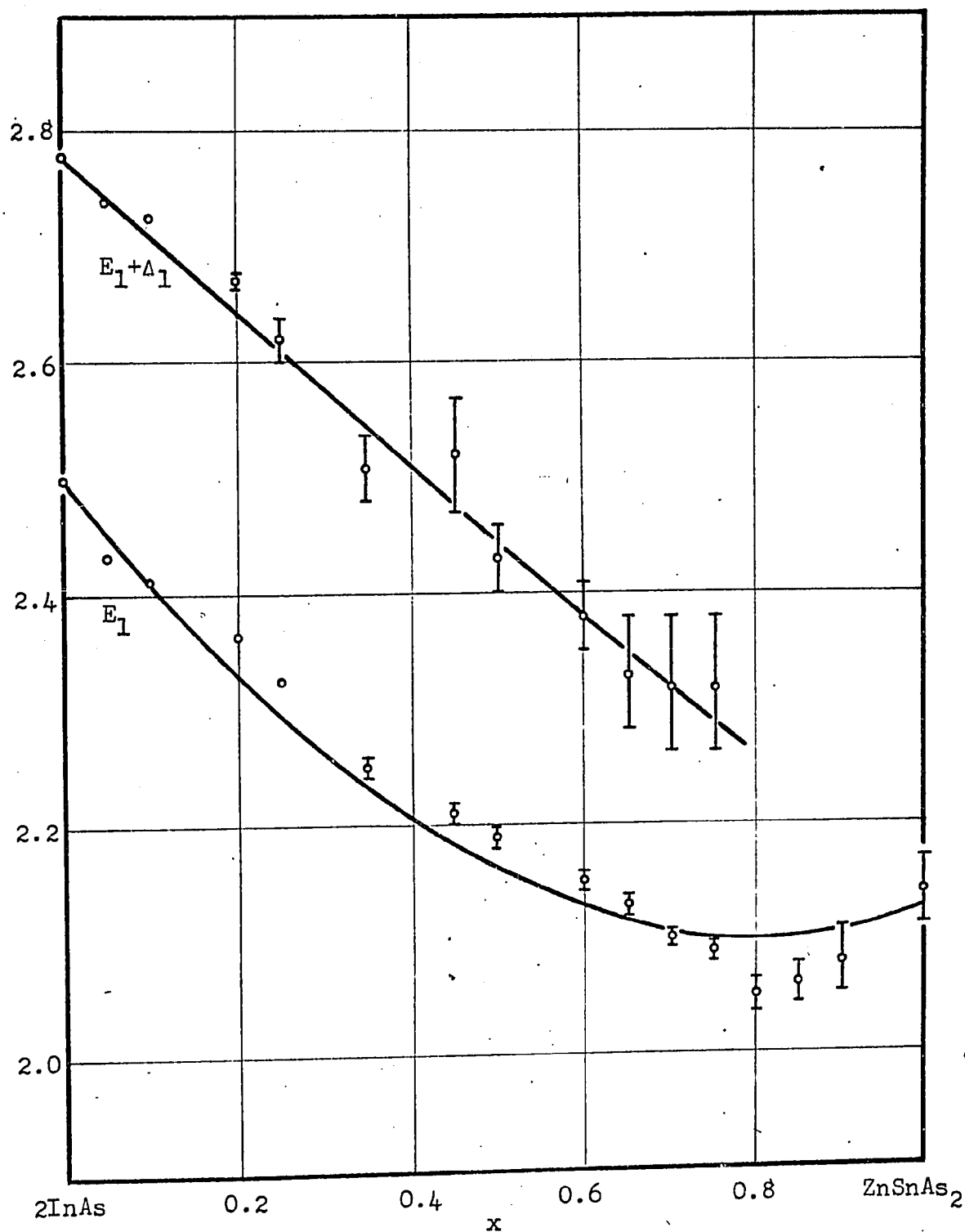


Figure IV-17 Variation of the energy of E_1 and $E_1 + \Delta_1$ interband transitions with composition of the system $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$.

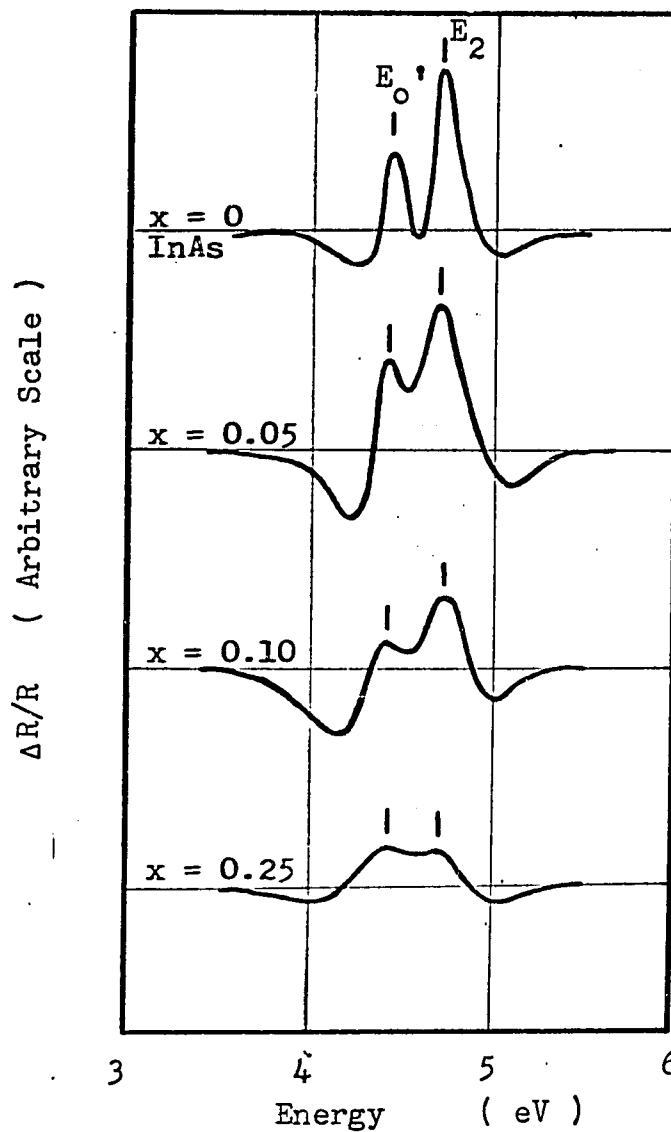


Figure IV-18 Electroreflectance spectra in the u.v. region of the system $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ up to $x = 0.25$. ($V_{dc} = -1.0\text{V}$, $V_{ac} = 1.5\text{V}$.)

system was then supplemented by reflectance work. The reflectance spectra and the variation of the energy values of the E_0' and E_2 transitions with x obtained from these two types of measurements are shown in Figures IV-19 and IV-20. The reflectance peaks were very broad and less accurate, and the E_0' transitions were only observed near the InAs end. The energy values of the E_2 peaks showed a shallow minimum. However, due to the large errors involved in the experimental results in the energy positions of these E_2 peaks from reflectance measurements, the variation of these peaks with alloy composition could not be accurately determined.

By following through the reflectance and electroreflectance peaks of this alloy system in the energy range of 1.5-5.5 eV, the two peaks at 2.2 and 4.7 eV of the zincblende modification of ZnSnAs_2 are definitely identified as the E_1 and E_2 transitions. Hence the assumptions made in Section IV-413, concerning the reflectance, electroreflectance and thermorefectance peaks of ZnSnAs_2 , are now shown to be justified.

Electroreflectance measurements were also made on the alloy $\text{In}_{0.10}\text{Zn}_{0.95}\text{Sn}_{0.95}\text{As}_2$ of chalcopyrite structure. This specimen was p-type with hole concentration $2.7 \times 10^{25} \text{ m}^{-3}$, and since it consisted of 95 mol. % of ZnSnAs_2 , its band structure was expected to be close to that of this ternary arsenide. The electroreflectance spectrum of this specimen, as shown in Figure IV-21, exhibits three peaks: 2.26 ± 0.01 , 2.53 ± 0.01 and

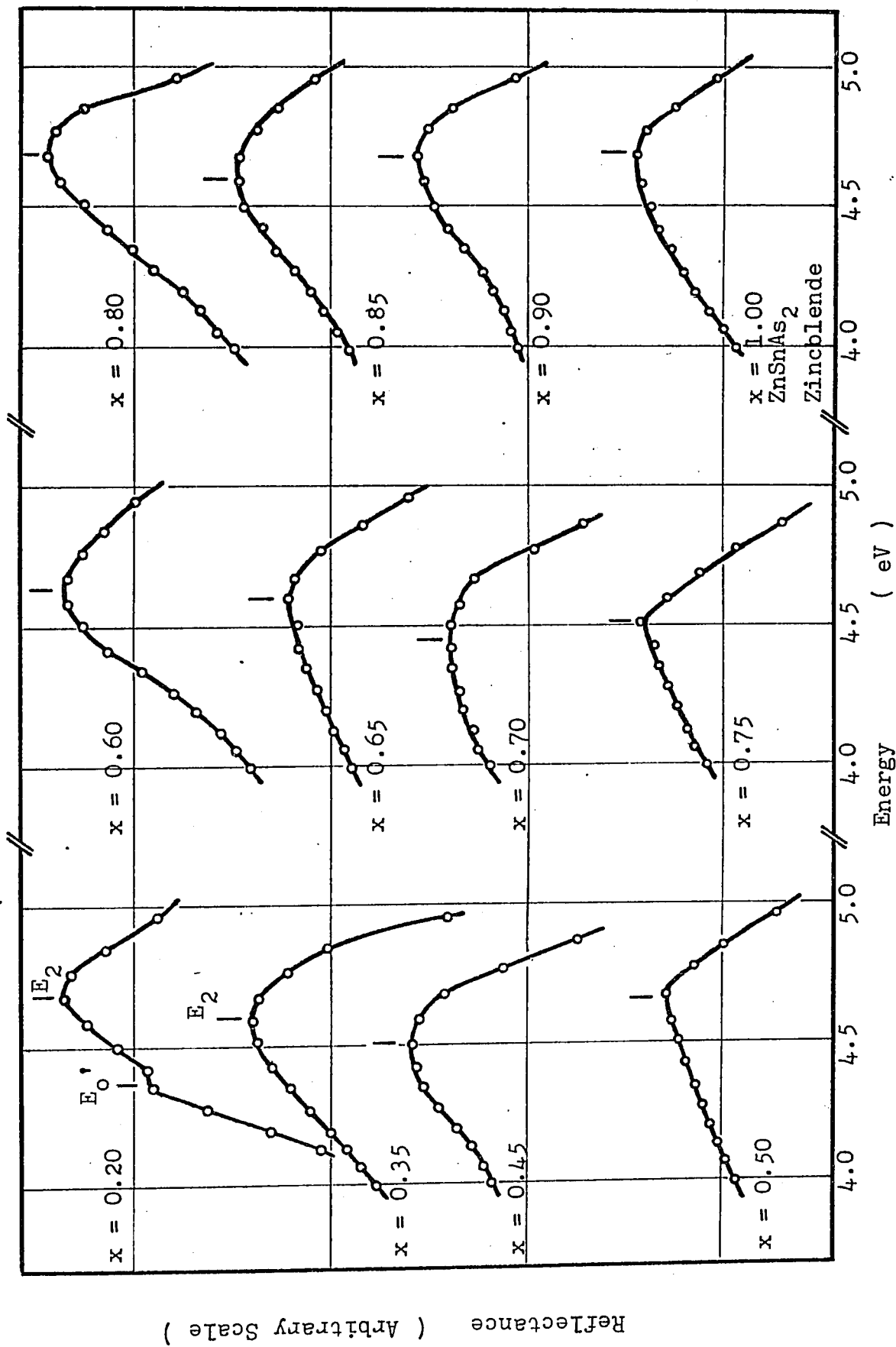


Figure IV-19 Reflectance spectra of the system $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$ in the u.v. region.

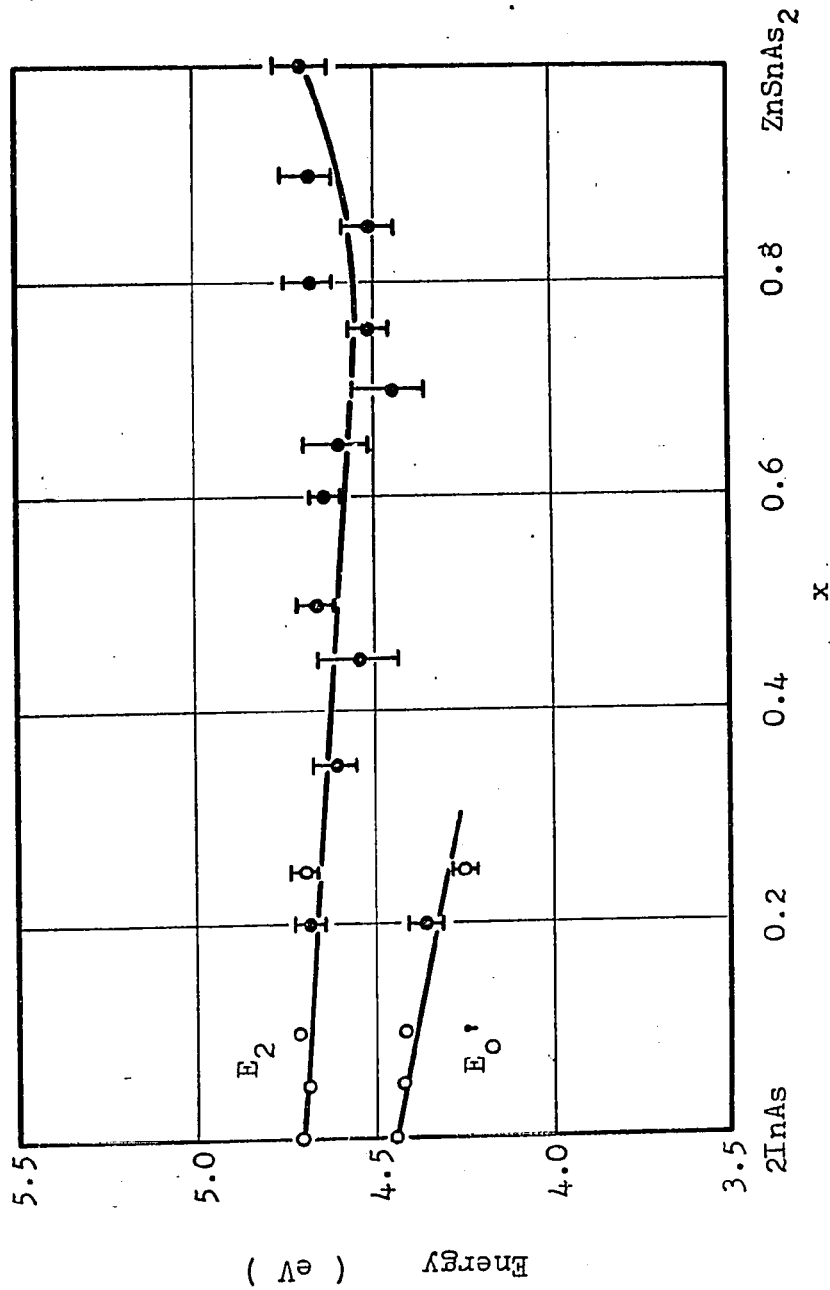


Figure IV-20 Variation of the energy of E_0' and E_2 interband transitions with composition of the system $\text{In}_2(1-x)\text{ZnSn}_x\text{As}_2$. (o, electroreflectance results; •, reflectance results.)

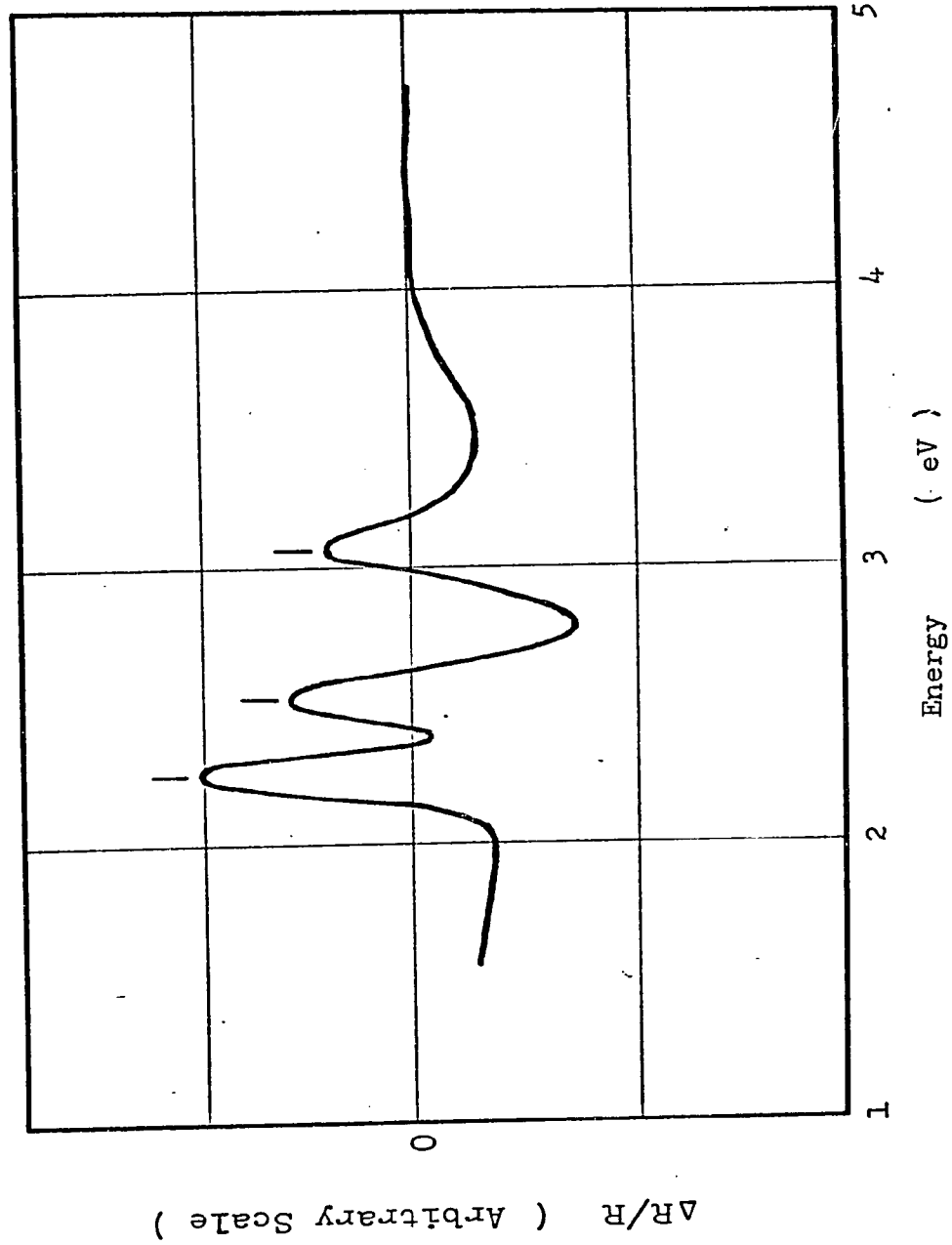


Figure IV-21 Electroreflectance spectrum of the alloy $\text{In}_{0.10}\text{Zn}_{0.95}\text{Sn}_{0.95}\text{As}_2$.
 ($V_{\text{dc}} = -0.4\text{V}$, $V_{\text{ac}} = 1.5\text{V}$.)

3.07 ± 0.01 eV, which are very close to the energy positions of the peaks in ZnSnAs_2 of chalcopyrite structure. However, no splitting of the 2.26 eV peak was observed. This can be attributed to the incomplete ordering of the atoms of Zn and Sn with the presence of In. The higher energy structure of this alloy was not observed in the measurements.

43. SUMMARY AND DISCUSSION OF THE RESULTS

In the present work, reflectance and modulated reflectance measurements have been made on five ternary arsenides and two alloy systems. By following through the peaks in R and $\Delta R/R$ of the alloy systems, the main peaks in the spectra of CdSnAs_2 and ZnSnAs_2 have been found to be closely related to certain interband transitions in InAs . Such correspondence therefore gives further support to the interpretation of the spectra of the five ternary arsenides. The results of the above work on these compounds are summarized in Table IV-2. Here the values of the peaks corresponding to the same type of interband transitions are tabulated in the same row.

In the study of the variation of band structure with composition in the alloys, a simple parabolic form has been suggested (Section I-5) for alloys with the constituent compounds of the same crystal structure. This has been verified for various mixed III-V alloys (Section III-54). In the $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$ system of zincblende structure investigated in this work, a non-linear variation of E_1 versus x has been observed (Figure IV-17). The experimental results can be fitted to a parabola

$$E = \alpha + \beta x + \gamma x^2$$

with $\alpha = 2.50 \pm 0.01$, $\beta = -0.98 \pm 0.02$ and $\gamma = 0.62 \pm 0.04$.

As has been discussed in Section III-54, the problem in analyzing

Table IV-2 Room temperature reflectance (R), electroreflectance (ER) and thermorelectance (TR) results on 5 II-IV-As₂ compounds.

	CdSnAs ₂ Chalco- pyrite (G4-1)	Zinc- blende (G5-1)	CdGeAs ₂ Chalco- pyrite (I2-1)	ZnSnAs ₂ Chalco- pyrite (J1-1)	Chalco- pyrite (J5-1)	Zinc- blende (J2-1)	ZnGeAs ₂ Chalco- pyrite (L1-1)	ZnSiAs ₂ Chalco- pyrite (M1-1)
E ₀								2.130 ₅ ER
E ₀ +Δ ₀								2.228 ₈ ER
								2.477 ₆ ER
							2.260 ₈ 2.410 ₈ ER 2.28 ₃ TR 2.30 ₆ R	
E ₁	2.125 ₅ ER	2.15 ₅ ER	2.175 ₅ ER	2.230 ₆ 2.310 ₅ ER	2.260 ₆ 2.335 ₅ ER 2.28 ₁ TR	2.14 ₃ ER 2.23 ₅ TR	2.740 ₈ ER 2.57 ₄ TR 2.70 ₄ R	2.76 ₁ [?] ER 2.900 ₆ [?] ER 3.26 ₁ ER
E ₁ +Δ ₁	2.425 ₅ ER	2.46 ₅ ER	2.490 ₈ ER					
	2.62 ₃ ER		2.65 ₁ ER					
			2.87 ₃ ER					
			3.16 ₁ ER					
				2.545 ₅ ER	2.550 ₅ ER 2.55 ₁ TR			
				3.050 ₆ ER	3.075 ₈ ER 3.07 ₃ TR		3.23 ₁ ER 3.21 ₄ TR 3.22 ₂ R	
				4.34 ₄ ER	4.40 ₅ ER			
E ₂	4.40 ₁₀ R	4.35 ₁₀ R		4.72 ₃ ER	4.77 ₄ ER 4.72 ₂ TR	4.70 ₈ TR 4.70 ₈ R	4.37 ₃ ER 4.37 ₅ TR 4.41 ₁ R	4.32 ₂ ER
							4.92 ₃ ER 4.94 ₅ TR	4.73 ₃ ER

The above values are in eV.

2.130₅ means 2.130±0.005, 4.40₁₀ means 4.40±0.10, etc.

the E_1 transition energies is the effect of possible movement in the $\vec{k}$ -space in the Λ direction besides the alloying effect, i.e., contributions from the virtual crystal and the disorder of the alloy lattice. This can be checked by plotting δ versus x (δ being the difference between the experimental value for E_1 and the value obtained by linear interpolation between the two compounds), and it is expected that this graph would be symmetric about the position $x = 0.5$ should the alloying effect dominate. However the graph of δ versus x for the E_1 transitions of this alloy system as shown in Figure IV-22 shows slight asymmetry. The variation of the $E_1 + \Delta_1$ and E_2 transitions of this system cannot be analyzed because of the scatter of the experimental data. As for the $\text{In}_2(1-x)\text{Cd}_x\text{Sn}_x\text{As}_2$ system, the effect of the structural transformation makes the simple model of alloying effect inapplicable for the analysis of the variation of various interband transition energies with alloy composition.

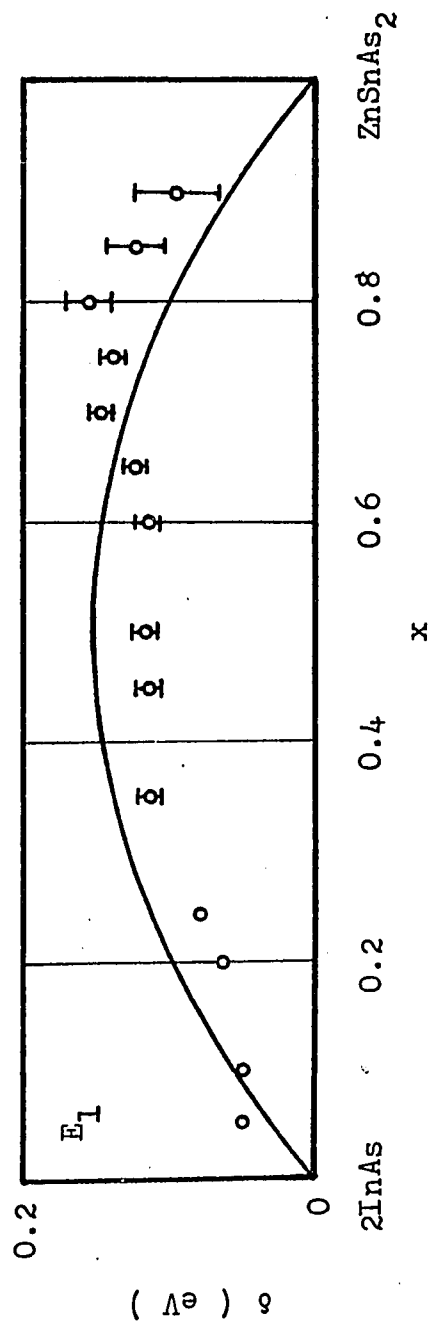


Figure IV-22 Variation of δ with composition of the $\text{In}_2(1-x)\text{Zn}_x\text{Sn}_x\text{As}_2$ system.
(See text.)

CHAPTER V

CONCLUSIONS

1. SUMMARY OF THE WORK

The work as presented in this thesis has covered a wide range of physical measurements for investigating the band structures of some semiconducting arsenides. Hall effect and magnetoresistance measurements were made on In_2Se_3 - and In_2Te_3 -doped InAs samples at 4.2°K to investigate the conduction band above the fundamental (000) minimum. The experimental data were analyzed by a two-conduction-band model [of the (000) and $\langle 111 \rangle$ bands] with a new approach developed in this work. From the analysis, the separation of these two conduction band minima for pure InAs was determined as 0.70 ± 0.03 eV, and this separation was found to decrease with increasing selenium or tellurium content. Room temperature electroreflectance, infrared absorption and thermoelectric power measurements were also made on these samples to examine the effect of heavy doping.

A thorough study of electroreflectance measurements on InAs was carried out to obtain detailed information about the structure of electroreflectance spectra of this compound under various experimental conditions, such as different carrier concentrations, electrolytes, and biasing and modulating voltages. The results of this work were applied

to the alloy system $\text{In}_{1-x}\text{Ga}_x\text{As}$ to confirm the parabolic variation of the $\Lambda_{3v}-\Lambda_{1c}$ transitions with x .

The knowledge of the band structure and interband transitions of InAs was then used to correlate that of the II-IV- As_2 compounds, through the alloy systems $\text{In}_{2(1-x)}\text{Cd}_x\text{Sn}_x\text{As}_2$ and $\text{In}_{2(1-x)}\text{Zn}_x\text{Sn}_x\text{As}_2$. Room temperature reflectance and modulated reflectance measurements were made on five ternary arsenides and these two alloy systems. The reflectance and modulated reflectance peaks were interpreted through comparative studies.

[Presented in the Appendix is an analysis of Harland's oscillatory magnetoresistance data on n-type GaSb samples (65H1).]

2. FUTURE WORK AND SUGGESTIONS

Some suggestions concerning further investigations of the work presented in this thesis can be made here:

(1) The two-band magnetoresistance results can be used in conjunction with Faraday rotation work to give further information about the (000) and $\langle 111 \rangle$ bands, as has been illustrated by Van Tongerloo and Woolley (69V1) in the work on tellurium-doped GaSb samples. Such an approach is expected to be applicable for the study of heavily-doped InAs materials.

(2) For closer correlation with the results from low-temperature magnetoresistance work on heavily-doped InAs samples, it would be more appropriate to carry out the infrared absorption and the electroreflectance measurements at lower temperatures. Because of the limitation set by the freezing points of the electrolytes, the electroreflectance work with electrolyte technique is not very suitable for this purpose. Hence it is advisable to carry out other versions of modulated reflectance, such as thermorefectance, on these materials at lower temperatures.

(3) The band structure investigations on the II-IV-V₂ materials are still at a preliminary stage at present. The reflectance and modulated reflectance work can be extended to the studies on II-IV-P₂ compounds and mixed II-IV-V₂ alloys with an approach similar to the work presented in this thesis.

APPENDIX

ANALYSIS OF HARLAND'S DATA OF SHUBNIKOV-DE HAAS EFFECT IN GaSb

1. INTRODUCTION

Shubnikov-de Haas effect has been observed in various III-V semiconductors, e.g. n-type InAs (Frederikse and Hosler 58F2, Sladek 58S1, Shalyt and Efros 62S1, Amirkhanov et al 63A1, Hyman and Siklossy 65H2, Bresler et al 66B9), n-type InSb (Frederikse and Hosler 57F1, Broom 58B1, Shalyt and Efros 62S1) and n-type GaSb (Becker and Fan 64B1, Yep and Becker 66Y1). In all of these investigations, the basic conditions

$$\mu B \gg 1$$

$$E_F > \hbar \omega > k T$$

as mentioned in Section II-3152 were satisfied. In all these compounds, the conduction band minima immediately above the main (000) minimum are in the $\langle 111 \rangle$ direction in $\vec{k}$ -space. The separations of the (000) and $\langle 111 \rangle$ minima of these compounds at 4.2°K have been obtained by magnetoresistance and Faraday rotation measurements by Woolley's group (InAs: 0.70 eV, this thesis; InSb: 0.43 eV, Aubin 69A1; GaSb: 0.078 eV, Harland and Woolley 66H1, Van Tongerlo and Woolley 69V1). The subsidiary $\langle 111 \rangle$ minima are so close to the (000) minimum in GaSb that in specimens with electron concentrations above 10^{24} m^{-3} , electrons will be present in both minima even at helium temperatures.

Harland (65H1) has observed magnetoresistance oscillations at 2-4.2°K in three highly degenerate GaSb samples. From the period of oscillations, the author (65H1) has determined the electron concentrations of the samples, which were compatible with his Hall effect and magnetoresistance results. However with the methods of data analysis of the amplitude of oscillations as presented in his work, no conclusive results regarding the cyclotron effective mass m_c^* of electrons and the Dingle temperature T' were obtained. In the present work, the two methods described in Section II-3154 were used to analyze Harland's data.

2. AMPLITUDE OF OSCILLATIONS

Harland's data of the amplitude of oscillations $\Delta\rho_A(T,B)$ on three specimens (labeled #8A, #6A and #7A) are shown in Figures A-1, A-2 and A-3. It is noted that the results on the lower concentration specimen (#8A) are less accurate than the others, because of the much smaller amplitude of oscillations in this case. (The fitted curves to the experimental data will be considered later.)

As has been presented in Section II-3154, the ratio of the oscillation amplitudes $\Delta\rho_A(T_1)/\Delta\rho_A(T_2)$, at two temperatures T_1 and T_2 and at a constant magnetic field B , was given by (equation II-65)

$$\frac{\Delta\rho_A(T_1)}{\Delta\rho_A(T_2)} = \frac{T_1 \sinh\left(\frac{2\pi^2 k m_c^* T_2}{e \hbar B}\right)}{T_2 \sinh\left(\frac{2\pi^2 k m_c^* T_1}{e \hbar B}\right)} \quad (A-1)$$

The experimental data of $\Delta\rho_A(T,B)$ of each specimen at two different temperatures were then used to calculate the value of m_c^* . In this analysis (referred to as method I), the interpolated values of $\Delta\rho_A(T_1,B)$ and $\Delta\rho_A(T_2,B)$ at different fixed field intensities in the range 1.4-2.3 W/m² were used. For each specimen, consistent values of m_c^* were obtained for various fixed field intensities in this range. The results for these three specimens are shown in Table A-1.

The Dingle temperature T' was then determined from the plot of

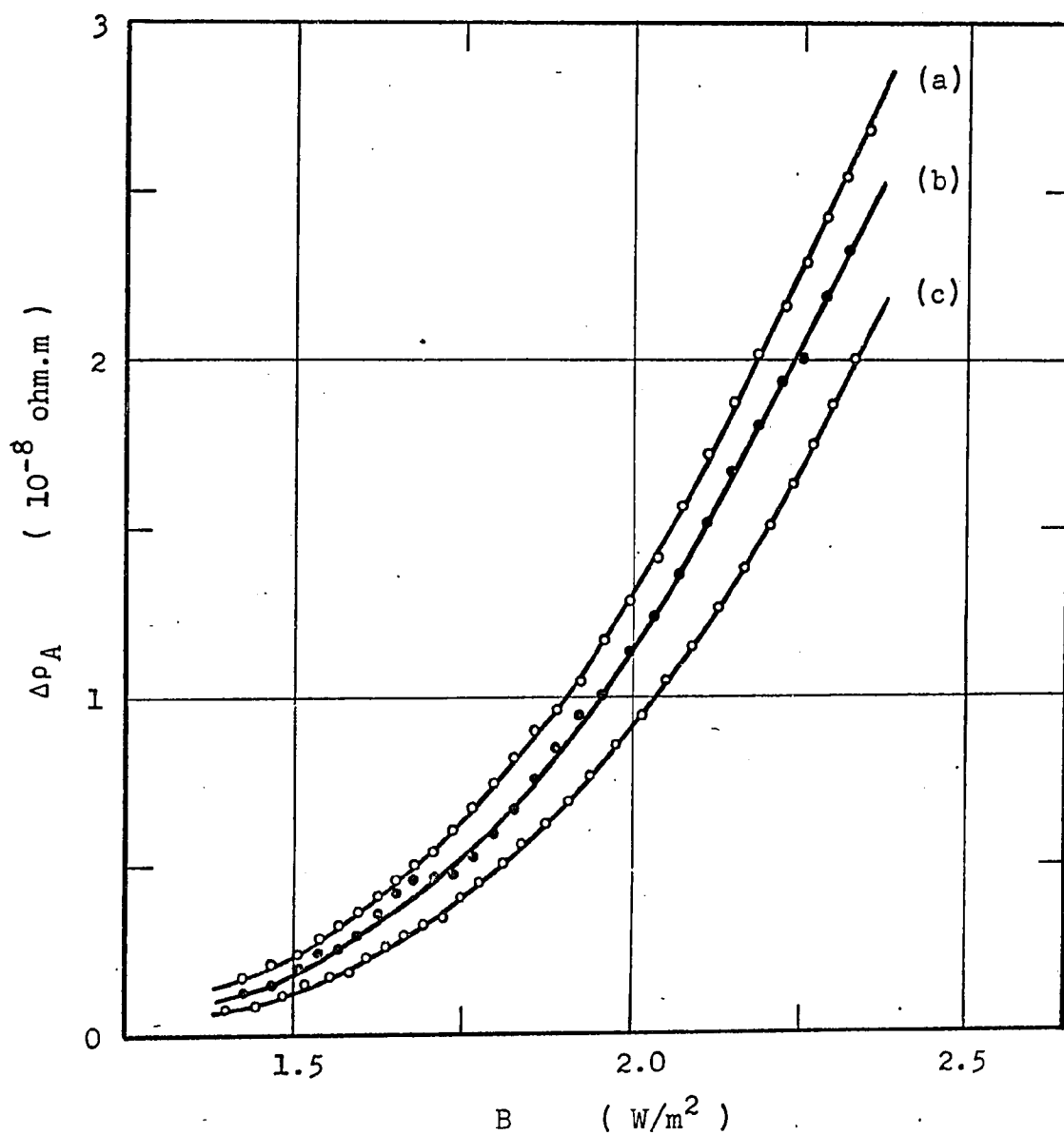


Figure A-1 Variation of magnetoresistance oscillation amplitude $\Delta\rho_A$ with magnetic field B at three temperatures for Specimen #8A. (a) $T = 2.077 \pm 0.003^\circ K$, (b) $T = 3.040 \pm 0.002^\circ K$, (c) $T = 4.203 \pm 0.001^\circ K$. [Points: Harland's data; lines: curve fitting to equation (A-3).]

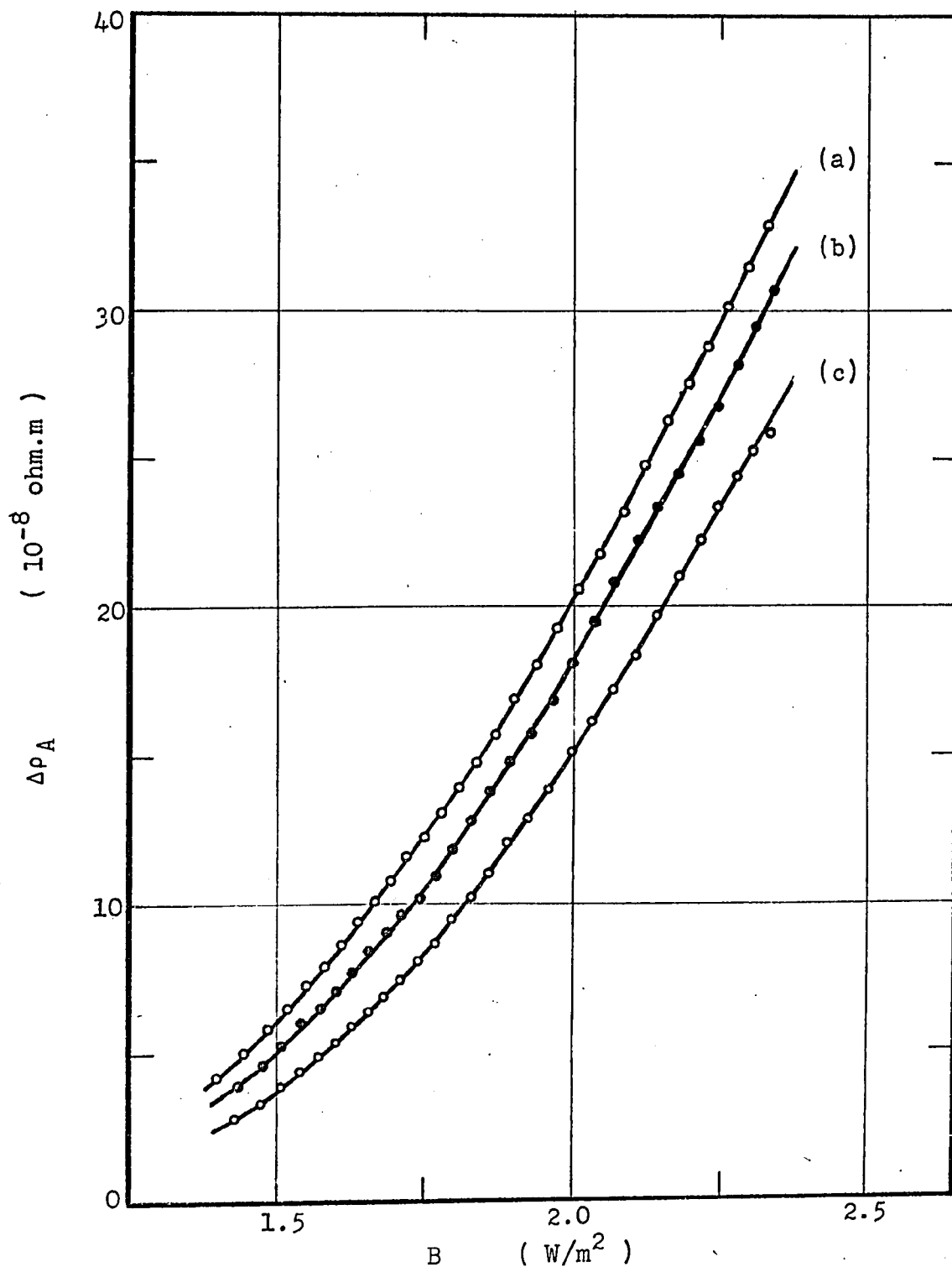


Figure A-2 Variation of magnetoresistance oscillation amplitude $\Delta\rho_A$ with magnetic field B at three temperatures for Specimen #6A. (a) $T = 2.130 \pm 0.003^\circ K$, (b) $T = 3.060 \pm 0.001^\circ K$, (c) $T = 4.201 \pm 0.001^\circ K$. [Points: Harland's data; lines: curve fitting to equation (A-3).]

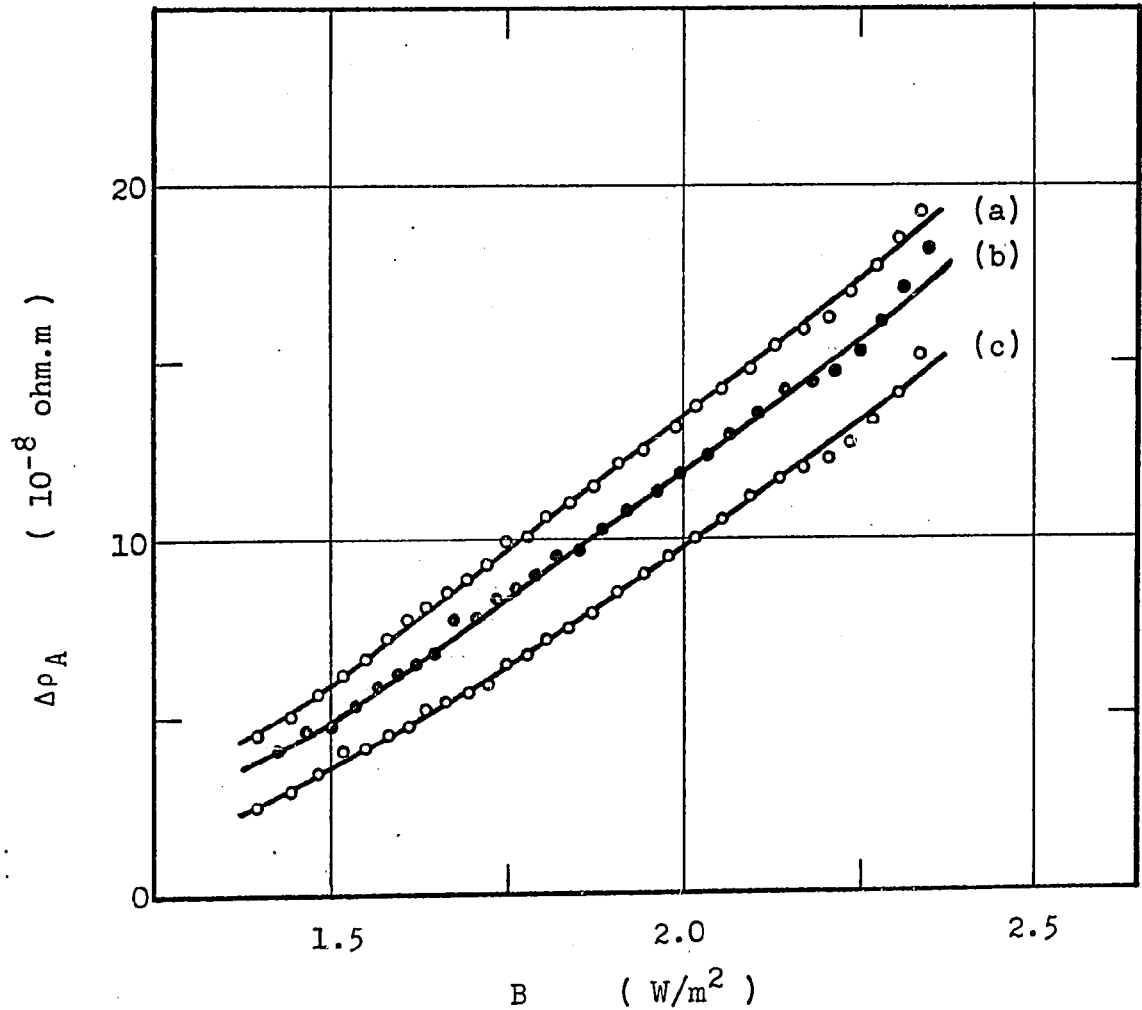


Figure A-3 Variation of magnetoresistance oscillation amplitude $\Delta\rho_A$ with magnetic field B at three temperatures for Specimen #7A. (a) $T = 2.077 \pm 0.005^\circ K$, (b) $T = 2.972 \pm 0.004^\circ K$, (c) $T = 4.204 \pm 0.001^\circ K$. [Points: Harland's data; lines: curve fitting to equation (A-3).]

Table A-1 Results of m_c^*/m_e calculated from $\Delta\rho_A(T_1, B)$ and $\Delta\rho_A(T_2, B)$ at fixed values of B , in the range 1.4-2.3 W/m², by using equation (A-1).

Specimen label	Electron concentration † n_0 (m ⁻³)	T_1 (°K)	T_2 (°K)	m_c^*/m_e	m_c^*/m_e (average)
#8A	1.21×10^{24}	3.040	4.203	0.055 ± 0.002	0.057 ± 0.003
		2.077	4.203	0.057 ± 0.001	
		2.077	3.040	0.059 ± 0.002	
#6A	1.33×10^{24}	3.060	4.201	0.0528 ± 0.0008	0.0525 ± 0.0010
		2.130	4.201	0.0526 ± 0.0004	
		2.130	3.060	0.0520 ± 0.0010	
#7A	1.54×10^{24}	2.972	4.204	0.0535 ± 0.0010	0.0535 ± 0.0015
		2.077	4.204	0.0542 ± 0.0008	
		2.077	2.972	0.0530 ± 0.0015	

† Values obtained from the period of oscillations (65H1)

$$\ln\{[\Delta\rho_A(B)] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 k m_c^* T}{e \hbar B}\right)\} \text{ versus } B^{-1}$$

at constant temperature. As shown in Figures A-4, A-5 and A-6, the relation of the plot was linear for the three specimens each at three different temperatures. Therefore relation (II-66),

$$[\Delta\rho_A(B)] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 k m_c^* T}{e \hbar B}\right) \propto \exp\left(-\frac{2\pi^2 k m_c^* T'}{e \hbar B}\right) \quad (\text{A-2})$$

was reasonably satisfied. In the calculation of T' for each specimen, the errors in the determination of m_c^*/m_e were also considered. The results are given in Table A-2. It is seen that the Dingle temperature T' for each specimen is constant over the temperature range of investigation, 2-4.2°K, as assumed in the theory. It is noted also that T' decreases with increasing electron concentration.

An alternate approach of analyzing the $\Delta\rho_A(T, B)$ data (referred to as method II) was by the method of curve fitting to equation (II-72)

$$\Delta\rho_A(B) = \frac{a}{B^b \sinh\left(\frac{c}{B}\right)} \quad (\text{A-3})$$

at fixed temperatures. The values of a , b and c for the three specimens each at three different temperatures were determined (Table A-3). A very good fit to the experimental data with these parameters (a , b , c) was obtained, as shown in Figures

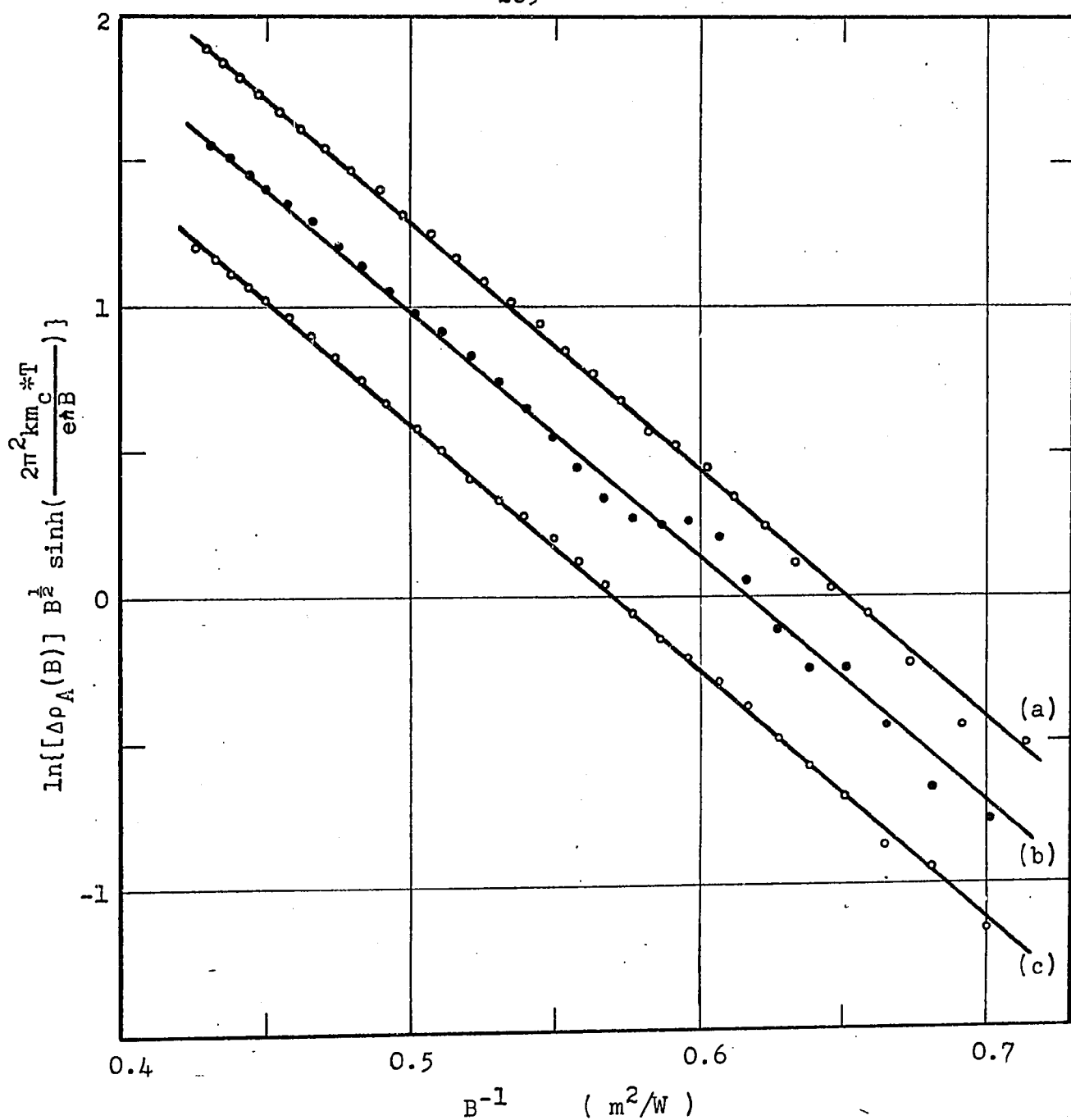


Figure A-4 Variation of $\ln\left\{\left[\Delta\rho_A(B)\right] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 k_B T}{e\hbar B}\right)\right\}$ with inverse magnetic field B^{-1} at three temperatures for Specimen #8A. (a) $T = 4.203^\circ\text{K}$, (b) $T = 3.040^\circ\text{K}$, (c) $T = 2.077^\circ\text{K}$.

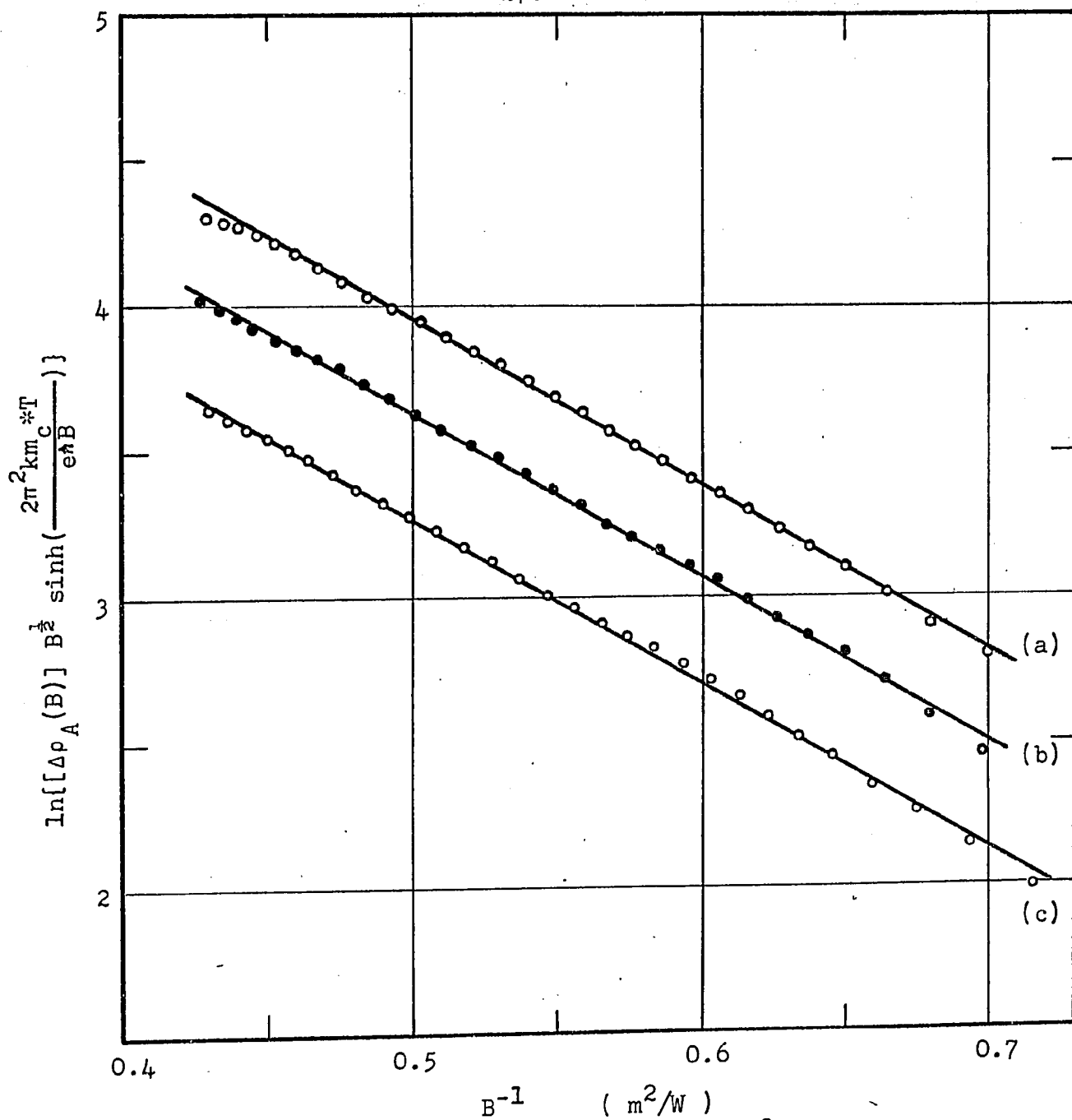


Figure A-5 Variation of $\ln[\Delta\rho_A(B)] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 k_B T}{e\hbar B}\right)$ with inverse magnetic field B^{-1} at three temperatures for Specimen #6A. (a) $T = 4.201^\circ\text{K}$, (b) $T = 3.060^\circ\text{K}$, (c) $T = 2.130^\circ\text{K}$.

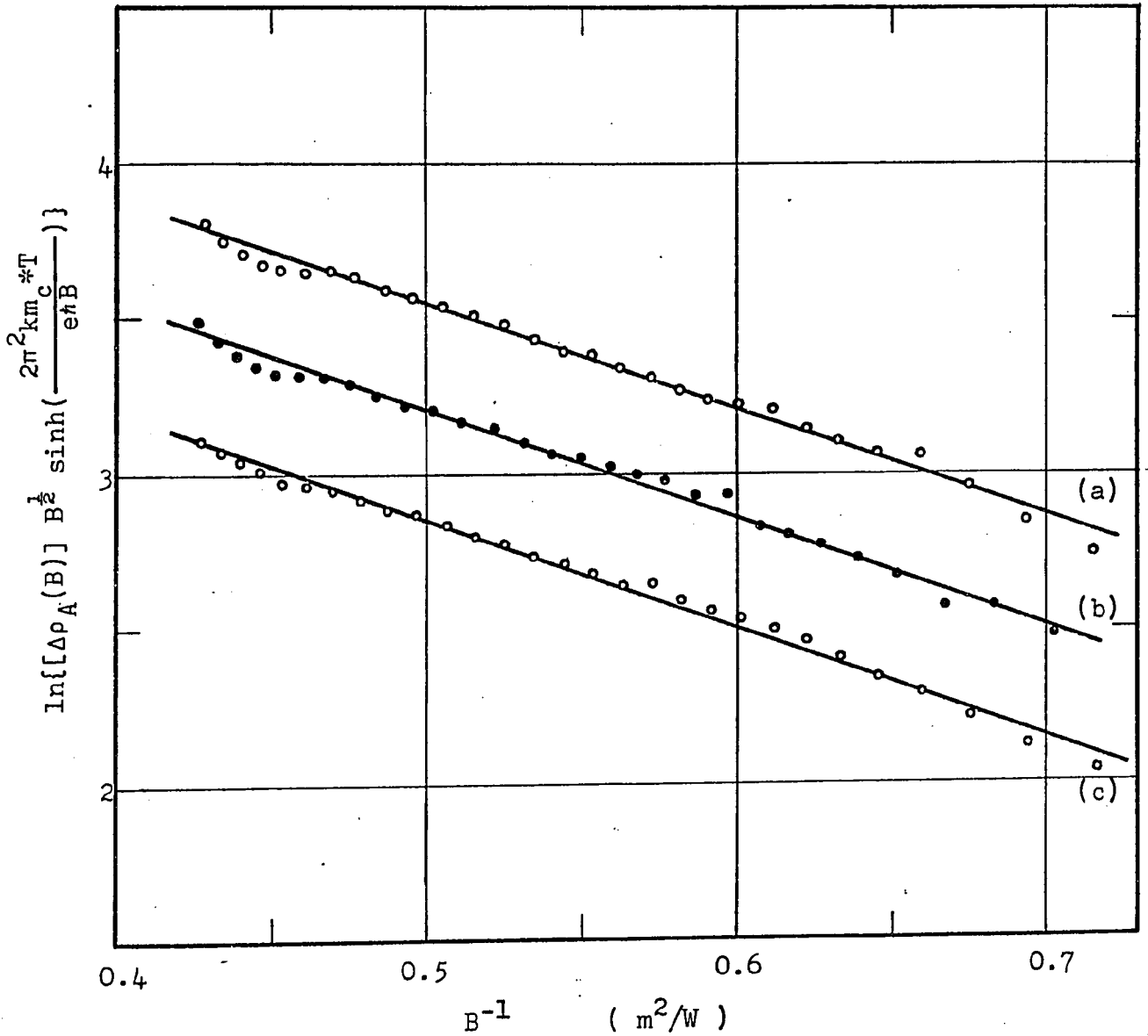


Figure A-6 Variation of $\ln[\Delta\rho_A(B)] B^{\frac{1}{2}} \sinh\left(\frac{2\pi^2 km_c * T}{e\hbar B}\right)$ with inverse magnetic field B^{-1} at three temperatures for Specimen #7A.
(a) $T = 4.204^\circ\text{K}$, (b) $T = 2.972^\circ\text{K}$, (c) $T = 2.077^\circ\text{K}$.

Table A-2 Results of the Dingle temperature T^* calculated from the linear plot of equation (A-2).

Specimen label	$m_c^*/m_e^\dagger$	T ($^\circ\text{K}$)	T^* ($^\circ\text{K}$)	T^* ($^\circ\text{K}$) (average)
#8A	0.057 ± 0.003	4.203	10.2 ± 0.6	10.2 ± 0.8
		3.040	10.2 ± 1.0	
		2.077	10.1 ± 0.6	
#6A	0.0525 ± 0.0010	4.201	7.4 ± 0.3	7.4 ± 0.3
		3.060	7.5 ± 0.3	
		2.130	7.3 ± 0.5	
#7A	0.0535 ± 0.0015	4.204	4.4 ± 0.4	4.5 ± 0.4
		2.972	4.5 ± 0.4	
		2.077	4.5 ± 0.4	

$\dagger$ from Table A-1

Table A-3 Results of curve fitting of equation (A-3).

Specimen label	T (°K)	a $\times 10^5$	b	c (W/m ²)	T' (°K)
#8A	4.203	0.91	1.2	13.52	13±2
	3.040	0.70	1.2	12.62	
	2.077	0.35	0.8	11.45	
#6A	4.201	5.58	1.5	11.02	10±2
	3.060	2.75	1.2	9.72	
	2.130	2.83	1.3	9.43	
#7A	4.204	1.65	1.8	9.16	7.0±1.5
	2.972	0.63	1.3	7.51	
	2.077	0.63	1.4	7.20	

A-1, A-2 and A-3. The values of ϵ was then plotted against T for each of the three specimens (Figure A-7). According to equation (II-70), a linear relation of

$$\epsilon = \left(\frac{2\pi^2 k m_c^*}{e\hbar} \right) T + \left(\frac{2\pi^2 k m_c^* T'}{e\hbar} \right) \quad (A-4)$$

was expected. However for each specimen, the experimental error in the three points leaves some uncertainty as to the exact value of the slope and consequently of the effective mass m_c^* . Since the electron concentrations of these three specimens are so close ($1.21-1.54 \times 10^{24} \text{ m}^{-3}$), the effective mass m_c^* could reasonably be expected to be similar such that the deviations from each other were within approximately 10 %. Therefore some consistent sets of parallel lines could be drawn through the points in the ϵ versus T graph. This gave a value of

$$m_c^*/m_e = 0.053 \pm 0.006$$

and the Dingle temperature T' for each specimen. The results of T' are shown in Table A-3. It is noted that the T' values deduced here also decrease with increasing electron concentration. The dependence of the parameter a on temperature is not clear from these results. The value of the parameter b , which appears to vary with electron concentration and temperature, lies in the range 0.8-1.8. However, these two parameters do not affect the calculation of m_c^* and T' and therefore will not be investigated further here.

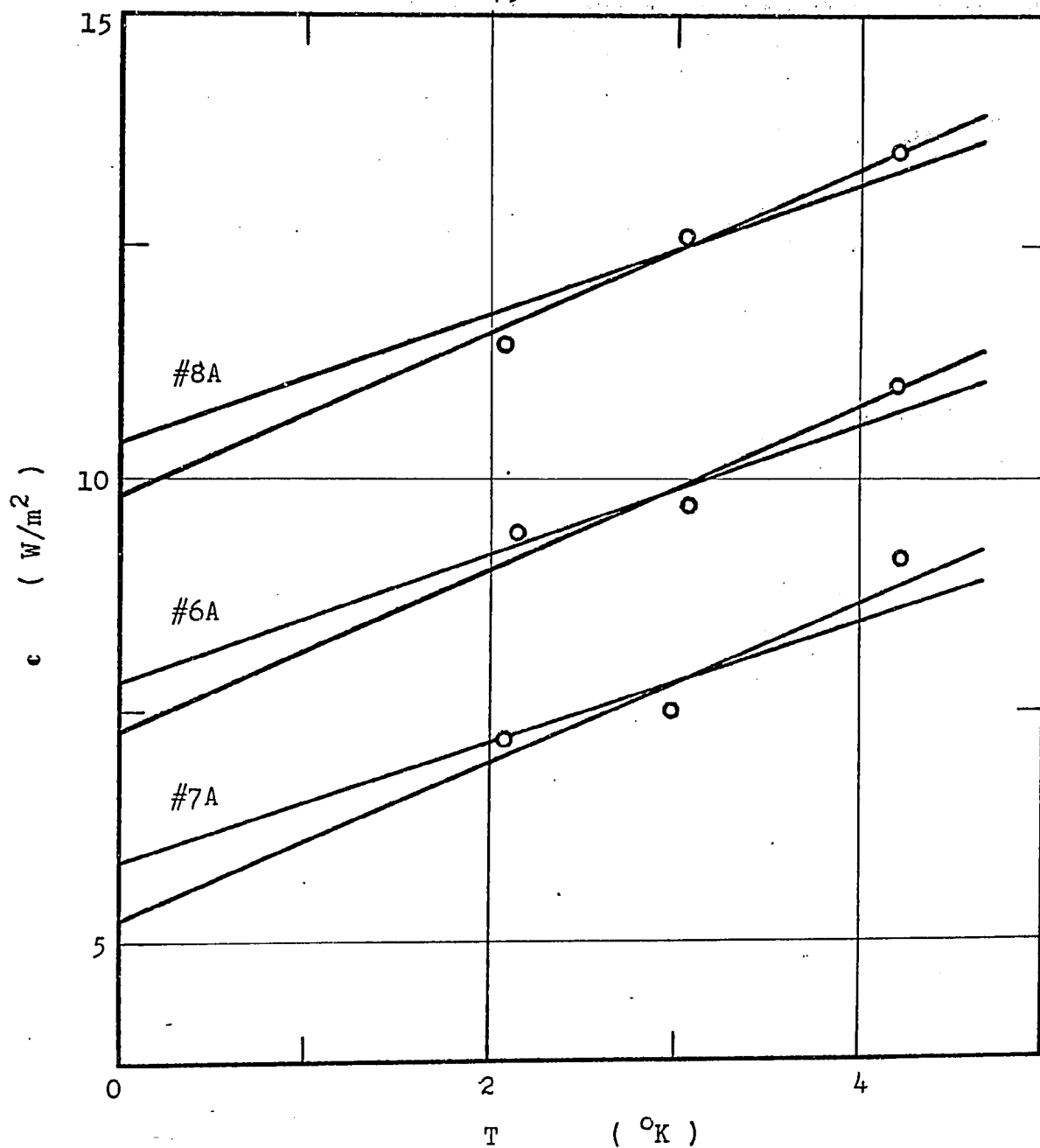


Figure A-7 Variation of ϵ with temperature T for specimens #8A, #6A and #7A. (See text.)

3. COMPARISON OF THE RESULTS, AND DISCUSSION

31. THE EFFECTIVE MASS m_c^*

Both methods (I and II) give consistent values of m_c^*/m_e in the range of 0.05-0.06 for these specimens with electron concentrations $1.21-1.54 \times 10^{24} \text{ m}^{-3}$. A calculation of the m_c^*/m_e values can also be made by applying the four-band Kane model (Section II-3155). In the calculation, a knowledge of the values of E_o , Δ_o and P^2 is required. The magnetoabsorption data (Zwerdling et al 59Z1) of relatively pure GaSb ($n \sim 10^{22}-10^{23} \text{ m}^{-3}$) gives an effective mass of $0.047 \pm 0.003 m_e$ and $E_o = 0.813 \text{ eV}$ at helium temperature. The spin-orbit splitting Δ_o has been obtained from room temperature electoreflectance measurements (Cardona et al 67C1) to be 0.80 eV. The value of P^2 has been estimated to be 20 eV (Aubin et al 69A2). These values of E_o , Δ_o and P^2 give an effective mass 0.0465m of the electrons at the bottom of the (000) conduction band in good agreement with the magnetoabsorption result of $0.047 \pm 0.003 m_e$. It was found from the calculation that m_c^*/m_e varies from 0.054 to 0.055 for electron concentrations of $1.2-1.5 \times 10^{24} \text{ m}^{-3}$. However, the difficulty in the interpretation of the term P^2 and the uncertainty of Δ_o at helium temperatures leave some doubt about the accuracy of the calculation based on this model. Nevertheless, this result is quite compatible with the deduced values of m_c^*/m_e from the measurements.

In the work of Yep and Becker (66Y1), the effective mass at the bottom of the (000) conduction band was found to be $0.040 m_e$

by applying the Kane model with the parameters $\Delta_0 = 0.86$ eV and $P^2 = 23.6$ eV. (Here this P^2 value has been converted to the unit of eV from Yep and Becker's value.) Their calculated values of m_c^*/m_e at different $\hbar_F$ (or electron concentrations n_0) are consequently lower than the results obtained here. However, the experimental value of $m_c^*/m_e = 0.052 \pm 0.002$ for GaSb specimens with $n_0 \sim 10^{24} \text{ m}^{-3}$ as reported by Becker and Fan (64B1) is quite compatible with the present results.

32. THE DINGLE TEMPERATURE T'

According to both methods (I and II), the Dingle temperature T' decreases with increasing carrier concentrations of the (000) conduction band. This can be explained by the increase in screening of the ionized impurities by the $\langle 111 \rangle$ electrons due to the filling of the $\langle 111 \rangle$ band and as a result, the scattering of the (000) electrons is reduced (Robinson and Rodriguez 64R1, 65R1).

From the definition of T' as shown in equation (II-62)

$$T' = \frac{\hbar}{\pi k \tau} \quad (\text{A-5})$$

a comparison of this Dingle temperature T' with a calculated value T_{μ}' can be made. Here, T_{μ}' is defined as the T' value given in equation (A-5) with the substitution of the collision broadening time τ by the relaxation time which relates the mobility μ_0 and an effective mass m^* of the (000) electrons. Now,

$$T_{\mu}' = \left(\frac{\hbar}{\pi k} \right) \left(\frac{e}{m^* \mu_0} \right) \quad (\text{A-6})$$

As a very crude approximation, m^* may be regarded to be similar to the cyclotron effective mass in values. The values of μ_0 were determined as 0.55, 0.97 and 0.78 $\text{m}^2/\text{V}\cdot\text{sec}$ for specimens #8, #6 and #7A respectively from two-band magnetoresistance measurements (Harland 65H1). (Note that specimens #8 and #6 were cut from the same ingots as specimens #8A and #6A respectively.)

The values of T_{μ}' of the three specimens were then obtained:

#8A - 14.7°K

#6A - 8.3°K

#7A - 10.3°K

The intervalley scattering of the (000) and $\langle 111 \rangle$ electrons also contributes to reduce the mobility of the (000) electrons slightly, and from these μ_0 values a non-monotonic variation of T_{μ}' with increasing carrier concentration is obtained as shown above. However, the effect of collision broadening is greatly affected by the screening of the ionized impurities by the less mobile $\langle 111 \rangle$ electrons, and this gives rise to a more rapid decrease of T' with the filling of the $\langle 111 \rangle$ band. Therefore a greater decrease in T' than in T_{μ}' with increasing electron concentration can be expected.

33. CONTRIBUTION OF THE $\langle 111 \rangle$ ELECTRONS

It has been found (Van Tongerloo and Woolley 69V1) that the longitudinal and transverse effective masses of the $\langle 111 \rangle$ electrons are $m_{L1}^* = 0.946m_e$ and $m_{T1}^* = 0.110m_e$. The density-of-states effective mass of the $\langle 111 \rangle$ electrons, defined as $m_1^* = (m_{L1}^* m_{T1}^{*2})^{1/3}$, is $0.226m_e$. The spacing of Landau levels in the Shubnikov-de Haas effect is inversely proportional to the effective mass of the carriers. Here the effective mass of the $\langle 111 \rangle$ electrons is approximately 4 times that of the (000) electrons. Moreover, the mobility of the $\langle 111 \rangle$ electrons is so low (e.g. Specimen #6: $0.088 \text{ m}^2/\text{V}\cdot\text{sec}$; #7A: $0.025 \text{ m}^2/\text{V}\cdot\text{sec}$, Harland 65H1) that the condition of $\mu B \gg 1$ is not satisfied. The effect of the alternating transfer of carriers between the two bands with the variation of the magnetic field has been discussed by Becker and Fan (64B1). The contribution of such an effect to the oscillatory phenomenon is only of secondary importance. Principally, the carriers in the (000) band play the important role in the Shubnikov-de Haas effect.

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