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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS REÇUE
THE PHOTOVOLTAIC EFFECT AND INTERBAND

MAGNETO-OPTICAL TRANSITIONS IN

Ge, InP, InSb, AND GaAs

by

Paul L. Rochon

Submitted to the School of Graduate Studies of the University of Ottawa in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

Department of Physics
Faculty of Science and Engineering
University of Ottawa
Ottawa, Canada

1976
to my parents....
ABSTRACT

The magneto-absorption spectra of Ge, InP, InSb and GaAs at 6K were investigated for photon energies corresponding to direct inter-band optical transitions. Magnetic fields up to 7 Tesla could be used and high sensitivity was achieved by using the photovoltaic effect as a new method for observing small variations in the absorption coefficient. The data associated with transitions between Landau levels in the valence and conduction bands were analyzed in terms of the coupled band theory of Pidgeon and Brown (66?1). Exciton participation in the spectra is also observed and discussed.

Ge was used as a test specimen to establish the method. The correspondence between the theoretical and the observed line shapes of structures is considered, the conclusion being that the Landau level positions correspond closely with the maxima of the derivative of the photoresponse.

In order to confirm the above conclusion the wavelength modulated spectra of the photovoltage, $\Delta V_{\text{PV}}$, and the wavelength modulated reflectivity spectra $\Delta R/R$ are compared in InP. The experimental positions corresponding to Landau levels are analyzed in terms of the Pidgeon and Brown theory. The best fit between theory and experiment provided the following parameter values: the conduction band effective mass $m_c/m_0 = 0.079 \pm 0.001$ and the Luttinger parameters $\gamma_1^L = 5.15 \pm 0.05$, $\gamma_2^L = 0.94 \pm 0.03$, and $\gamma_3^L = 1.62 \pm 0.03$. The direct observation of the
split-off valence band to conduction band transition gives \( \Delta_0 = 0.108 \pm 0.003 \text{ eV} \) and an approximate effective mass of \( m_{so}/m_0 = 0.21 \pm 0.02 \). The effects of exciton participation are discussed in terms of the arguments presented by Vrehen (66V1).

In InSb, Landau levels and exciton states are separately identified. The behaviour of the exciton states is analyzed in terms of the theory by Alterelli and Lipari (74Al). The data corresponding to the Landau levels are again analyzed in terms of the Pidgeon and Brown theory. In both cases the best fit to the data is obtained by using the Pidgeon and Brown (66P1) band parameters for InSb.

Impurity absorption is also observed and its behaviour in a magnetic field is considered.

The preliminary results obtained for the magneto-optical structures in GaAs are seen to be comparable to that of Vrehen (66V1). From an analysis of the data the band parameters are estimated to be:

\[
\frac{m_e}{m_0} = 0.067 \pm 0.002, \quad \gamma_1^L = 7.14 \pm 0.1, \quad \gamma_2^L = 1.6 \pm 0.1 \quad \text{and} \quad \gamma_3^L = 2.7 \pm 0.1.
\]

Impurity absorption is observed at room temperature at an energy of 50 meV below the gap. The participation of L.O. phonons of energy 35.6 meV is also detected.

Throughout this work the photovoltaic effect and its wavelength modulated derivative proved to be advantageous methods for observing magneto-optical structures. The observation of weak structures, such as those due to impurity absorption, further demonstrated the sensitivity of this method.
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INTRODUCTION

In the past two decades a considerable amount of experimental and theoretical effort has been devoted to the investigation of the electronic states of solids in the presence of an external magnetic field. In particular, since the observation of magneto-optical interband transitions in 1959 (5931, 5921), the magneto-optical properties of semiconductors have been under a great deal of investigation because they can provide very important information about the electronic band structure of these materials.

Semiconductors such as germanium and some III-V compounds, are characterized by strong direct interband transitions. In a magnetic field the valence band and the conduction band split up into a series of magnetic sub-bands called Landau levels. The energy separation between these levels and the photon energy required for interband transitions increase with increasing magnetic field strength. In addition to undergoing a band-to-band transitions the photo-excited electron in the conduction band may be bound to the hole in the valence band via Coulomb interaction. Such a hydrogenic complex, called an exciton, would in a low magnetic field display a Zeeman effect and, to second order, a diamagnetic shift. Therefore, the photon energy required to create the exciton is expected to vary as a function of magnetic field. In a high magnetic field, when the Landau levels are separated from each other by an energy greater than the exciton
binding energy, exciton states can be associated to each Landau level. The interpretation of results associated with Landau levels and exciton states with the aid of theories expressed in terms of the fundamental band parameters of the semiconductor should result in an accurate determination of these parameters.

Magneto-optical effects were first studied by optical transmission, however the rapid increase in the absorption coefficient for photon energies greater than the fundamental gap required the use of very thin samples and restricted the spectral region that could be studied. The observation of magneto-optical structures in the reflectivity spectra could remove the above restrictions, but the structures were found to be so weak that magneto-reflectivity experiments proved quite difficult to perform.

In the early 1960's differential techniques were developed to enhance the sensitivity of the absorption and reflectivity methods. An externally applied periodic perturbation, such as an electric field, a stress, or a temperature variation modulates the absorption or reflection spectrum of the material. However these modulation techniques, which directly affect the semiconductor, will often greatly perturb the parameters themselves, therefore proper and often difficult corrections must be included in the analysis of the results. An interesting alternative to the experimental complexity of the modulation techniques is to study the spectral distribution of the photo-effects of a semiconductor in a magnetic field. Pilon (73FL) has studied the photoconductivity spectra of GaSb in intense magnetic
fields and their results were comparable if not better than those
published by Reine et al. (72R2) who used a stress modulation technique.
More recently, Barbarie (74Bl) investigated the photo-electromagnetic
effect of some semiconductors and showed that this photo-effect could
also be used to observe magneto-optical structures. One purpose of
the present research was to develop and make use of yet another photo-
effect technique, specifically the photovoltaic effect produced at a
metal-semiconductor contact, for research in magneto-optics.

The photovoltaic effect at a metal-semiconductor contact has
some practical applications in the areas of detectors. The most
notable advantages of this effect over photoconductivity and the photo-
electromagnetic effect include high signal to noise ratios and fast
response time. In addition the photocell can be made to reflect small
variations in the absorption coefficient of the semiconductor with a
high degree of sensitivity.

When a Schottky barrier is made, a space charge is built up
at and near the metal-semiconductor interface. Near the semiconductor
surface the ionized donors, which form the space charge, produce a local
electric field inside the semiconductor to a depth \( W \), called the barrier
depletion width. This depletion width is in part determined by the
donor impurity concentration of the semiconductor and is therefore a
controllable parameter. If a photon of energy greater than the fun-
damental gap enters the depletion region it may be absorbed to create an
electron hole pair which, because of the electric field, will immediately
be separated and as a result produce a photocurrent.
The photocurrent produced is directly related to the generation rate of electron hole pairs within the depletion layer and is therefore directly related to the absorption coefficient, $\alpha$, of the semiconductor. The photoresponse of the cell will, in fact, best reflect small variations in the absorption coefficient when $\alpha W \approx 1$. In addition an even greater visibility of the structures in $\alpha$ can be achieved by using a modulation technique, for example wavelength modulation, to obtain the differential spectrum of the photovoltage. The advantages of the wavelength modulated photovoltaic effect has recently been used elsewhere (76NL) in order to observe small changes in the absorption coefficient of semiconductors.

In the following study the experimental results obtained on Ge, InP, InSb and GaAs are discussed. Germanium, being one of the best known semiconductors, was used as a test material to determine the feasibility of using the photovoltaic effect in magneto-optics. The results were analyzed in terms of the coupled band theory of Pidgeon and Brown, the best non-excitonic theory available. The band parameters obtained from the fit were compared to those of Aggarwal (70A1). Because of the success of the method in Ge, the photovoltaic effect and its wavelength derivative were used to observe the magneto-optical structures in a less known semiconductor, InP. New band parameters were determined by the analysis of the Landau levels. Excitonic participation was observed and is discussed. Both the exciton states and Landau levels in InSb could be observed. The analysis of these phenomena led to the conclusion that the Pidgeon and Brown (66P1)
parameters best describe the bands in InSb. Finally the band parameters of GaAs were estimated from preliminary results.

The following is separated into three main chapters:

1- In chapter I the theoretical background is recalled and those aspects used in our analysis are stressed.

2- Chapter II deals with the apparatus and experimental procedure.

3- Chapter III presents the results and analysis for the semiconductors we have studied.
CHAPTER I  THEORETICAL BACKGROUND

This chapter, separated into two sections, is a resume of the theories which were considered for the present work. In the magneto-optics section the behaviour of Landau levels and of exciton states as a function of magnetic field are reviewed. The photovoltaic effect was used to observe magneto-optical structures and the relevant properties of this photo-effect are summarized in the second section.

A. MAGNETO-OPTICS

In 1897 Zeeman (9721) made the first successful observation of the influence of a magnetic field on the properties of light emitted or absorbed by a substance. Subsequent studies and analysis of the spectra of atoms in magnetic fields helped greatly to elucidate the electron structure of the atom. In solid state physics the advent of high purity crystals combined with the availability of low temperatures and high magnetic fields later permitted the observation of magneto-optical phenomena in semiconductors. The oscillations observed in the magneto-absorption spectra of InSb (5781) and of germanium (5721) at energies just above the energy gap were immediately interpreted in terms of transitions between the quantized magnetic levels in the valence and
conduction bands. Research has been done on many magneto-optical phenomena, for example: cyclotron resonance, magneto-plasma reflection, and Faraday rotation; the present work will however be concerned with interband magneto-optical transitions.

A great deal of theoretical and experimental effort has been expended in order to understand the electronic states which give rise to the structures observed in magneto-optics and, as a result, a wealth of information related to these interband transitions and to the band parameters of the crystal can be obtained from the analysis of experimental results. Moreover, the observation of the behaviour of bound electron-hole pairs, known as excitons, in a magnetic field will result in additional information about the properties of the semiconductor.

This section is a summary of the existing theories which were used in the interpretation of our experimental results. Excellent reviews of magneto-optical phenomena can be found in the literature; for example Johnson (67W1), Lax and Mevroides (67W1), and Aggarwal (72W1) consider the behaviour of Landau levels, and Dimmock (67W1) and Knox (63K1) summarize the properties of exciton states. The optical transitions in solids have also been recently reviewed by Bassani and Pastori Parravicini (75B1).

1. Landau levels

The study of magneto-optical phenomena begins with the investigation of the effects of a magnetic field on the band structure
of a semiconductor. Consider a simple band structure consisting of two bands for which the energy-momentum relation near \( \mathbf{k} = 0 \) are given by

\[
E_c = \frac{\hbar^2 k^2}{2m_c}
\]

and

\[
E_v = \frac{\hbar^2 k^2}{2m_v} - E_g
\]

where the indices \( c \) and \( v \) denote the conduction and valence bands respectively, \( m_c \) and \( m_v \) are the electron and hole effective masses, and \( E_g \) is the energy gap between the conduction and valence bands. In the effective mass approximation, Schrödinger's equation, including a term for the presence of a magnetic field \( \mathbf{B} \), is written as

\[
\frac{1}{2m^*} \left( \mathbf{p} + \frac{e}{c} \mathbf{A} \right)^2 \psi = E\psi
\]

where \( \mathbf{p} \) is the momentum operator and \( \mathbf{A} = \frac{1}{2} (\mathbf{B} \times \mathbf{r}) \) is the vector potential of the field. The eigenvalues of equation m2 in the case where \( \mathbf{A} \) is in the \( z \)-direction and spin is neglected are given by

\[
\varepsilon_n = (n + \frac{1}{2}) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m_c}
\]

for the electron in the conduction band, where \( n \geq 0 \) is the magnetic quantum number and \( \omega_c = \frac{eB}{m_c} \) is the cyclotron frequency. Similarly the eigenvalues of equation m2 for the holes in the valence band are
given by
\[
E_m = -(m + \frac{1}{2})\hbar \omega_v - \frac{\hbar^2 k_x^2}{2m_v}
\]

The solution of equation M2 was first obtained by Landau (30LL) for the case of free electrons. The simple case considered here demonstrates that the solution can be represented as a series of harmonic oscillator-like levels, known as Landau levels, with the spacing between the levels equal to the cyclotron energy \( \hbar \omega_v \). Figure MF1 illustrates the energy levels for this case. In considering this simple model we are led to expect that the absorption coefficient as a function of energy will exhibit structures related to transitions between magnetic sublevels. Figure MF2 illustrates this phenomena for direct transitions. From the observation of such structures and the ensuing analysis the band parameters of the solid near \( \mathbf{k} = 0 \) can be determined. However, the data that is obtained for most semiconductors cannot be fully analysed in the light of the simple model presented above.

The existence and degeneracy of the light hole and heavy hole valence bands at \( \mathbf{k} = 0 \) in many semiconductors considerably complicate the study of the effects of a magnetic field. Luttinger and Kohn (56LL) investigated this problem in the framework of the effective mass approximation assuming the bands to be parabolic. Their theory also includes the effects of spin orbit coupling. Roth et al. (59K) and Burstein et al. (59B1) applied Luttinger and Kohn's theory to the case of the interband magneto-optics.
Figure MF1  Landau levels for simple bands

$E_g$ is the zero field band gap, $\hbar w_c$ and $\hbar w_v$ are the cyclotron energies of the conduction and valence bands respectively.
Figure M F 2 Magneto-optical structures in the absorption coefficient.

- - - B=0, ___ B≠0, Broadening is included such that ℏw x γ=5.
The theory in magneto-optics was further developed by Pidgeon and Brown (66P1) in order to take into account the effects of the non-parabolicity of the bands due to k·p interactions (Kane 56KL). This was done by treating the two conduction bands (spin degenerate) and the six valence bands (heavy hole, light hole, split-off spin degenerate) simultaneously. The theory also includes the interactions of the conduction band with higher bands as well as the effects of the anisotropy of the bands.

In the Pidgeon and Brown theory, the energy positions of the Landau levels are found to be the eigenvalues of an 8 x 8 matrix representation of the hamiltonian. If the magnetic field is in the (110) plane, the hamiltonian can be written as

\[ D = D_0 + D_1 \]

where part of the valence band anisotropy is included in \( D_0 \). \( D_1 \) is a small perturbation also due to the anisotropy and Pidgeon and Brown show that \( D_1 \) can be neglected. At \( k_z = 0 \), \( D_0 \) is represented by two 4 x 4 matrices, table M11, whose eigenvalues are the energies of the Landau levels at a given magnetic field. A schematic representation of the Landau levels is shown in figure MP3.

The conduction band in the presence of a magnetic field splits up into two series of levels: the \( a^c \) series with spin \( m_s = \frac{1}{2} \), and the \( b^c \) series with spin \( m_s = -\frac{1}{2} \). The valence bands become four series of levels: \( a^+ \) is the light hole band with spin \( m_j = \frac{1}{2} \) or \( \frac{3}{2} \), \( b^- \) is the
heavy hole band with spin $m_j = \frac{1}{2}$ or $\frac{3}{2}$, $b^+$ is the light hole band with spin $m_j = \frac{1}{2}$ or $-\frac{3}{2}$, and $b^*$ is the heavy hole band with spin $m_j = \frac{1}{2}$ or $-\frac{3}{2}$.

In figure MF3 the allowed direct interband transitions have been indicated for both the right circular (R.C.P.) and left circular (L.C.P.) polarizations of incident light whose wavevector is parallel to the magnetic field direction. The quantum numbers of the levels are labelled as in the Pidgeon and Brown scheme and the selection rules for the interband transitions are as given by Fillion (73FL) and Reine (70RL)

$$n = (n - n') = +1 \quad \text{L.C.P.}$$

$$= -1 \quad \text{R.C.P.}$$

where $n$ is the conduction band magnetic quantum number and $n'$ is the valence band magnetic quantum number.

The matrix elements of the Hamiltonian are expressed in terms of the following parameters:

- $E_g$: the zero magnetic field band gap

- $\Delta_0$: the split-off band energy

- $\gamma_1$, $\gamma_2$, $\gamma_3$, $k$: the Luttinger (56L1) parameters which describe the valence bands

- $E_p$: the interaction energy between the conduction band and the valence bands as defined by Kane (56K1)

- $f$: a parameter describing the interaction between the conduction band and higher bands
\[ -f(\Theta) = \frac{1}{4} \left( 3 \cos^2 \Theta - 1 \right)^2 \] is a function to take into account the angle between the magnetic field and the (001) direction of the crystal (figure MF4).

These parameters which can be obtained by fitting experimental data are related to others found in the literature, for example the conduction band effective mass \( m_c \) is written as

\[
\frac{m}{m_c} = 1 + \frac{E_D}{3} \left[ \frac{2}{E_g} + \frac{1}{E_g + \Delta} \right] + 2f
\]

Aggarwal (72W1)

and the conduction band electron spin g factor is

\[
g_c = 2 \left[ 1 - \frac{E_D}{3} \left( \frac{1}{E_g} - \frac{1}{E_g + \Delta} \right) \right]
\]

Roth et al. (59R1)

Lawaetz (71L1) writes the light hole effective mass, \( m_{lh} \), and the heavy hole effective mass \( m_{hh} \), in terms of Luttinger's parameters, i.e.

\[
\frac{m}{m_{lh}} = (\gamma_1^L + \gamma_1)
\]

\[
\frac{m}{m_{hh}} = (\gamma_1^L - \gamma_1) \left( 1 + 0.05 \gamma_h + 0.0164 \gamma_h^2 \right)^{3/2}
\]

where \( \gamma_1 \) and \( \gamma_h \) are defined to be

\[
\gamma_1 = (2 \gamma_2^L + 2 \gamma_3^L)^{1/2}
\]
TABLE MT1 The Pidgeon and Brown matrix

\[
\begin{bmatrix}
s_{M_1} & s_{M_2}^{1/2} & s_{M_4}^{1/2} & s_{M_7}^{1/2} \\
- & s_{M_2}^{1/2} & s_{M_4} & s_{M_8} \\
- & s_{M_3} & s_{M_5} & s_{M_9} \\
- & s_{M_6} & s_{M_7} & s_{M_9} \\
- & s_{M_8} & s_{M_9} & s_{M_{10}} - \Delta \\
\end{bmatrix}
\]

<table>
<thead>
<tr>
<th>matrix a</th>
<th>matrix b</th>
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<tbody>
<tr>
<td>(M_1)</td>
<td>(n+2f(n+1/2))</td>
</tr>
<tr>
<td>(M_2)</td>
<td>((1/2 \ n \ E_p)^{1/2})</td>
</tr>
<tr>
<td>(M_3)</td>
<td>(- (\gamma_1 + \gamma') (n-1/2) - 3/4 K)</td>
</tr>
<tr>
<td>(M_4)</td>
<td>((1/6 (n+1) E_p)^{1/2})</td>
</tr>
<tr>
<td>(M_5)</td>
<td>(- (3n(n+1))^{1/2} \gamma'')</td>
</tr>
<tr>
<td>(M_6)</td>
<td>(- (\gamma_1 - \gamma') (n+3/2) + 1/2 K)</td>
</tr>
<tr>
<td>(M_7)</td>
<td>((1/3 (n+1) E_p)^{1/2})</td>
</tr>
<tr>
<td>(M_8)</td>
<td>((6(n+1)n)^{1/2} \gamma'')</td>
</tr>
<tr>
<td>(M_9)</td>
<td>(- 2(\gamma' (n-3/2) + (K+1)/2))</td>
</tr>
<tr>
<td>(M_{10})</td>
<td>(- \gamma_1 (n-1/2) - K - 1/2)</td>
</tr>
</tbody>
</table>

\[s = \frac{e \hbar B}{m_o} \]
\[\gamma' = \gamma_3^{L} - (\gamma_2^{L} - \gamma_2^{L'}) f(\Theta) - E_p/6E_g\]
\[\gamma'' = \gamma_3^{L} - 1/3 (\gamma_3^{L} - \gamma_2^{L}) (1-f(\Theta)) - E_p/6E_g\]
\[\gamma_1 = \gamma_1^{L} - E_p/3E_g\]
\[K = K^{L} - E_p/6E_g\]
Figure MF3

Landau levels as seen in the Pidgeon and Brown theory. (70RL)

$a^c$ and $b^c$ are the conduction bands, $a$ and $b$ are the light
hole valence bands, $a^-$ and $b^-$ are the heavy hole valence bands.

The transitions for both L.C.P. and R.C.P. are indicated for
a sample which is placed in the Faraday configuration. The
transitions originating from the split-off band have been
omitted.
Figure MF4

The angle between the magnetic field and the crystal direction [001]

The magnetic field is in the (110) plane and the angle $\Theta$ is that which is included in the function $f(\Theta)$ in the Pidgeon and Brown formalism.
\[ \gamma_h = 6 \left( \frac{\gamma_2^2}{3} \gamma_2^2 \right) / \gamma (\gamma_1 - \gamma) \]

The split-off band effective mass, \( m_{so} \), the electron spin g-factor are also given by Aggarwal (72K1) as

\[ \frac{m}{m_{so}} = \gamma_1^L + \frac{E_p}{3E_g} \left( \frac{\Delta}{E_g + \Delta} \right) \]

and

\[ g_{so} = -2 \left[ 2k^L + 1 \right] - \frac{E_p}{3E_g} \left( \frac{\Delta}{E_g + \Delta} \right) \]

The theory should now permit the determination of the band parameters from the analysis of Landau levels observed experimentally in real crystals. The above theory, however, has so far neglected the Coulomb-interaction between the electron and the hole. Excitonic participation in the spectra can be very important and, as a consequence, the origins of the oscillations observed can be ambiguous. Elliott and Loudon (60E1) demonstrated that in the presence of high magnetic fields 'exciton states can be associated with each Landau magnetic sub-level and that these states can be expected, in some cases, to be the dominating features in the absorption spectrum. Therefore in order to fully interpret the observed spectra and obtain the band parameters of a semiconductor the theory for the behaviour of exciton states in a magnetic field is a necessity.
2. Excitons in a magnetic field

Theories have been developed for the behaviour of exciton states in low and high magnetic fields. These two regions of magnetic field strength are defined by the parameter $\Theta_e$ introduced by Yafet et al (56Y1) and Elliott and Loudon (60E1). The parameter $\Theta_e$ is given as

$$\Theta_e = \frac{\hbar \omega_c^e}{2 \varepsilon_x(o)}$$

where $\omega_c^e$ is the reduced cyclotron frequency of the electron hole pair

$$\omega_c^e = \frac{eB}{m_c} \left( \frac{1}{m_c} + \frac{1}{m_0} \right)$$

and $\varepsilon_x(o)$ is the exciton binding energy in the absence of a magnetic field. The exciton binding energies and the magnetic field values for $\Theta_e = 1$ for some semiconductors are presented in table MT2. The effect of a low magnetic field, $\Theta_e \ll 1$, can be considered as a small perturbation and can be handled by using standard perturbation theory. This is the case, for example, for the Zeeman effect in atomic spectroscopy. The influence of a low magnetic field on the direct exciton states has been investigated by Altarelli and Lipari (73AL) and more recently by Cho et al (75CL1). In these papers the behaviour of the ground state of the exciton is mainly considered and the calculations are done to second order perturbation. In the present research, however, the high and intermediate magnetic field regions are investigated.
TABLE MT2
Energy gaps ($E_g$), Binding energy of exciton ($E_{ex}$), and the value of magnetic field ($B$) at which the effective field $E_{g}^{-1}$ for some semiconductors.

<table>
<thead>
<tr>
<th>material</th>
<th>$E_g$ (eV)</th>
<th>$E_{ex}$ (eV)</th>
<th>$B$ (Tesla)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.689</td>
<td>0.0019</td>
<td>1.18</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.520</td>
<td>0.0053</td>
<td>6.12</td>
</tr>
<tr>
<td>GaSb</td>
<td>0.811</td>
<td>0.0021</td>
<td>1.41</td>
</tr>
<tr>
<td>InP</td>
<td>1.424</td>
<td>0.0052</td>
<td>5.05</td>
</tr>
<tr>
<td>InAs</td>
<td>0.410</td>
<td>0.0015</td>
<td>0.60</td>
</tr>
<tr>
<td>InSb</td>
<td>0.2357</td>
<td>0.0005</td>
<td>0.11</td>
</tr>
</tbody>
</table>
The adiabatic method introduced by Elliott and Loudon (60El) was considered an excellent approach to the theoretical problem of exciton states in a high magnetic field, $\Theta > 1$. The extension of Elliott and Loudon’s work to the realistic case of semiconductors, where valence band degeneracy and anisotropy as well as band to band interactions are taken into account was investigated by Rees (72Rl) and Altarelli and Lipari (74Al). These authors express the results in terms of the zero magnetic field band parameters of the semiconductor. In order to analyze the exciton structures in our spectra of InSb, the theory for the case $\vec{B} // [111]$ had to be developed in the light of Altarelli and Lipari’s results and is presented in Appendix A. An analysis of both the exciton behaviour and the Landau level distribution should, in principle, result in an accurate determination of the band parameters. However, the experimental results obtained for many semiconductors are neither in the low or high magnetic field limits. The analysis of the results obtained at intermediate field, $\Theta \sim 1$, can become very complicated since the identification of the structures is uncertain. An estimate of the band parameters of the semiconductor can nevertheless be obtained if the experimental results are empirically corrected for exciton effects and are then analyzed using the Pidgeon and Brown theory for interband magneto-optics. (Vreken 68V1).

The binding energy of exciton states associated with Landau levels of quantum numbers $n_x > 0$ can be estimated following a qualitative argument given by Elliott and Loudon. The binding energy of an exciton
in a magnetic field depends mainly on the average radius of the state \( n_L \) with which it is associated so that its energy can be related to the binding energy of the exciton associated with the lowest level, \( n_L = 0 \), as given by:

\[
\epsilon_{\text{ex}}(n_L', \Theta_e) \sim \epsilon_{\text{ex}}(0_L, \Theta_e')
\]

where

\[
\frac{\Theta_e'}{\Theta_e} = \frac{1}{2n_L + 1} = \frac{1/2 \hbar \omega_e}{(n_L + 1/2) \hbar \omega_e}
\]

If the binding energy of the exciton associated with the lowest level is determined as a function of field, the binding energy of the excitons associated to the higher Landau levels can thus be estimated and appropriate corrections to the data can be made. It should be noted that since the binding energies decrease with \( n \), the parameters of the semiconductor can be determined by considering high levels as Landau levels only and analyzing them as such.

In our case, the Pidgeon and Brown theory for Landau levels was used to analyze the results in Ge, InP, InSb and GaAs. The exciton states were corrected for in InP and GaAs using the above arguments. An analysis of the data using Altarelli and
and Lipari's theory for the behaviour of exciton states in high magnetic fields also resulted in the determination of the band parameters of InSb.

Many experimental methods have been developed in order to obtain data to be analyzed in the light of the above theoretical considerations. The study of the spectral distribution of photo-effects such as photoconductivity (73FL) and the photoelectromagnetic effect (74Bl) has proven effective in overcoming some of the drawbacks of the absorption and reflection techniques. The advantages of the photovoltaic effect such as high signal to noise ratio and fast response time have provided an impetus to the present research.
B. THE METAL SEMICONDUCTOR CONTACT AND THE PHOTOVOLTAIC EFFECT

The barrier height of a metal-semiconductor contact is, in general, determined by both the metal's work function and by the density of surface states on the semiconductor. A detailed energy band diagram of a metal to n-type semiconductor contact is shown in figure P1 as presented by Cowley and Sze (65C1).

Before the metal is brought into close contact with the semiconductor a barrier already exists at the surface of the semiconductor due to the presence of surface states. The Fermi level at the surface is at an energy of $\phi_0$ above the valence band. When the metal of work function $\phi_m$ is made to come into contact with the semiconductor the barrier is built up even more. Electrons originating from the donor levels near the surface of the semiconductor flow into the metal and the surface states until thermal equilibrium is achieved. The barrier height $\phi_{Bn}$ resulting from this space charge distribution can be approximately written as (69S1)

$$\phi_{Bn} = C_2 (\phi_m - \chi) + (1 - C_2) \left( \frac{E_i}{q} - \phi_0 \right)$$

$$C_2 = \frac{E_i}{(E_i + q^2 \delta p_s)}$$
\( \phi_m \) work function of the metal
\( \phi_{\text{Bn}} \) barrier height of the metal-semiconductor barrier
\( \phi_{\text{Bo}} \) asymptotic value of \( \phi_{\text{Bn}} \) at zero electric field
\( \phi_o \) energy level at surface
\( \Delta \phi \) image force barrier lowering
\( \Delta \) potential across interfacial layer
\( \chi \) electron affinity of the semiconductor
\( V_{\text{bi}} \) built-in potential
\( \varepsilon_s \) permittivity of the semiconductor
\( \varepsilon_i \) permittivity of the interfacial layer
\( \delta \) thickness of the interfacial layer
\( Q_{\text{SC}} \) space-charge density in the semiconductor
\( Q_{\text{SS}} \) surface-state density on the semiconductor
\( Q_m \) surface-charge density on the metal

Figure P11 Detailed energy band diagram of a metal n-type semiconductor contact with an interfacial layer of the order of atomic distance. After Cowley and Sze (65CL).
In this expression the parameters are those shown and defined in figure P1. From equation P1 we can consider, for example, two limiting cases:

a) When the density of surface states is very large, $D_s \to \infty$, the barrier height is given by

$$q \phi_{Bn} = (E_g - q \phi_o)$$  \hspace{1cm} \text{(P3)}

In this case the Fermi level at the interface is pinned by the surface states at the value of $q \phi_o$ above the valence band and the barrier is entirely determined by the doping and surface properties of the semiconductor.

b) When the density of surface states is low, $D_s \to 0$, the barrier height is given by

$$q \phi_{Bn} = q(\rho_m - \chi)$$  \hspace{1cm} \text{(P4)}

which is the expression for an ideal Schottky barrier when surface states are neglected.

The experimental results of Mead and Spitzer (66M1) indicate that for various gold-semiconductor contacts the energy of $q \phi_o$ can be found using the relation

$$E_c - q \phi_o = \frac{2}{3} E_g$$  \hspace{1cm} \text{(P5)}

These results indicate that for most semiconductors the density of surface states is peaked at an energy of one third of the gap value above the valence band edge. It should be noted that there is of yet no generally accepted model for the formation of a Schottky barrier and intensive investigations of the problem are still underway, using tools such as external photoemission for instance (Gregory and Spicer 75G1). Mead and Spitzer (66M1) favour the idea that the Fermi level is pinned at the surface by the intrinsic semiconductor surface states. Others (74P1) suggest that the Fermi level pinning is due to various interactions between the metal and semiconductor. Our present concern is however only that a barrier exits.
The presence of a barrier at the surface of the semiconductor provides a localized electric field region in which free electrons or holes can be accelerated to give a resulting current. If the metal contact on the front surface is semitransparent, electrons and holes can be injected into this interface region by photo-excitation. (A metal-semiconductor contact is schematically represented in figure PP2 where the electric field region and the methods of electron injection by photo-excitation are indicated). Two types of photosignals are possible. In one case electrons can be excited from the metal, over the barrier, and into the electric field region, known as the depletion region. This would occur for light whose energy exceeds the barrier height, $h\nu > q\Phi_B$. On the other hand, the light which arrives into the depletion region can, if $h\nu > E_g$, create an electron-hole pair which will be immediately separated and produce a photo-current. Both of these mechanisms would normally give rise to a photosignal, however our main interest lies in the second type of transition since this photo-signal will be directly a function of the intrinsic optical properties of the semiconductor.

The expression for the photosignal of a contact barrier has been developed by Gartner (54Gl). The total short circuit current density through the depletion layer is given as

$$J_{TOT} = J_{DL} + J_{DIFF}$$

where $J_{DL}$ is the drift current density due to the carriers generated inside the depletion layer and $J_{DIFF}$ is the diffusion current density of
Figure PF2  

A—representation of a sample  
B—two types of optical transitions  
C—the electric field region
minority carriers generated outside the depletion region in the bulk of the semiconductor. The thermal generation of carriers within the junction will be neglected here. Under monochromatic radiation, the electron-hole pair generation rate at a distance $x$ from the surface of the semiconductor is given by

$$g(x) = \phi \propto \exp(-\alpha x)$$

where $\phi$ is the incident photon flux times the quantum efficiency and $\alpha$ is the absorption coefficient. If recombination is neglected for carriers created within the barrier depletion width $W$, the drift current density will then be given by

$$J_{DL} = q \int_{0}^{W} g(x) dx$$

$$= q \phi \left( \exp(-\alpha W) - 1 \right)$$

In an n-type semiconductor for $x \gg W$ the diffusion current is given by (5481)

$$J_{DIFF} = -\frac{q \phi L_p}{1 + \alpha L_p} \exp(-\alpha W) - q P_o \frac{D_p}{L_p}$$

where $L_p = (D_p \tau)^{1/2}$, $D_p$ is the diffusion coefficient for the holes, $\tau$ is the minority carrier lifetime, and $P_o$ is the equilibrium hole density. Under normal conditions the equilibrium hole density $P_o$ will be small so that the second term of equation P9 can be neglected. The
current density produced by the light is thus written as

\[ J_L = -q \frac{\phi}{\alpha} \left(1 - \frac{\exp(-\alpha W)}{1 + \alpha L_p}\right) \]

The photovoltage produced by the light can be calculated using the current-voltage characteristic equation for a diode:

\[ J = J_s \left(\exp\left(\frac{qV}{kT}\right) - 1\right) \]  

where \( J_s \) is the reverse bias saturation current density and \( V \) is the voltage needed across the junction to produce the current density \( J \).

The total current density \( J \) in the presence of light and an applied voltage is

\[ J = J_L + J_s \left(\exp\left(\frac{qV}{kT}\right) - 1\right) \]

and setting \( J = 0 \), the open circuit photovoltage is

\[ V_{PV} = \frac{kT}{q} \ln \left(1 - \frac{J_L}{J_s}\right) \]

\[ = \frac{kT}{q} \ln \left| \frac{\frac{\phi}{\alpha}}{J_s} \left(1 - \frac{\exp(-\alpha W)}{1 + \alpha L_p}\right) + 1 \right| \]

The functional dependence of the photovoltage on the absorption coefficient \( \alpha \) is mainly characterized by the value of the depletion width \( W \) as seen in figure PF3. The photovoltage becomes insensitive to small changes in \( \alpha \) for values \( \alpha W < 10^{-2} \) and \( \alpha W > 10^2 \). Small
Figure PF3  The photovoltage as a function of $\alpha W$.

For a fixed depletion width, $W$, the photovoltage is insensitive to changes in the absorption coefficient, $\alpha$, for $\alpha W < 10^{-1}$ and $\alpha W > 10^1$. The highest sensitivity to small changes in $\alpha$ occurs at $\alpha W = 1$. 
changes in the absorption coefficient can most easily be detected in samples with $\alpha W > 10^{-1}$ and $\alpha W < 10$. Assuming that the depletion width, $W$, is given as in the abrupt junction approximation (69S1),

$$W = \left| \frac{2\varepsilon_s}{qN_d} (V_{bi} - \frac{KT}{q}) \right|^{1/2}$$

and since the barrier height $V_{bi}$ is fixed for a particular metal-semiconductor contact, the proper donor concentration, $N_d$, must be selected in order to obtain a sample which will produce a measurable photovoltage as well as reflect small variation in the absorption coefficient.

The correspondence between structures in the absorption coefficient and structures in the photovoltage is easily established. For example it can be shown (Appendix B) that the maxima (minima, inflection points) in $\alpha$ correspond to maxima (minima, inflection points) in the photovoltage $V_{PV}$. One can therefore use the photovoltaic response to study the effects of an external magnetic field on the absorption coefficient of a semiconductor.

The main objective of the present work was to observe and analyze magneto-optical structures of Ge, InP, InSb, and GaAs at low temperatures using the photovoltaic effect and its derivative. In addition to the effects of a magnetic field on the samples, various temperature dependent phenomena could also be investigated. In particular an important variation in the magnitude of the photovoltage in InSb as a function of temperature was observed and an interpretation
of this phenomenon was developed (see Appendix C) following the above theoretical considerations.
CHAPTER II

EXPERIMENTAL METHOD AND APPARATUS

The apparatus used in the present magneto-optical studies has been described in some detail by Fillion, A. (73Fl), Barbarie, A. (74Bl) and Davoine, J.M.V. (75D1) and since this work necessitated very little change in the basic set-up, the design and methods of fabrication of the various components will not be stressed here. The following is a straightforward description of the equipment and how it was used. The sample preparation technique that will be presented will hold for all our samples and any specific details pertaining to individual specimens will be included in the next chapter when the results are presented.

This chapter is divided into four sections; the first section presents the method of selecting the optical radiation; section two describes the cryostats and their use; in section three the sample preparation is summarized; and in section four a brief account of the signal detection system is given.

A. THE SELECTION OF OPTICAL RADIATION

The apparatus for the selection of the required optical radiation is presented in figure AFl where the different elements of the system have been noted. Beginning at the light source, the components
are described following the light path. Two light sources were used: a quartz iodine tungsten filament lamp for the wavelength region of 600 nmeters to 2,000 nmeters and a Nepritz filament for the wavelength region 1,500 nmeters to 6,000 nmeters. The white light emitted from the source was focused onto the entrance slit of the spectrometer. Just before entering the spectrometer the light could be chopped in a square wave pattern at a frequency of 85 Hz. The Czerny-Turner, Spex model 1700, 3/4-meter spectrometer was equipped with variable entrance and exit slits allowing the selection of the spectral resolution required in a particular experiment. Wavelength modulation could be done by using the vibrating plate mechanism which had been installed by Filion (73P1) inside the spectrometer near the entrance slit. The original glass plate could easily be replaced by quartz and calcium fluoride plates of various thicknesses to select the amplitude of the modulation required in specific spectral regions. Monochromatic radiation was obtained by using the 10 x 10 cm reflection gratings: a 600 grooves/mm grating blazed at 750 nmeters, a 600 grooves/mm grating blazed at 1,600 nmeters, and a 150 grooves/mm grating blazed at 4,000 nmeters. Most of the second and higher order radiation was cut off by low pass filters (600 nmeters, 1,040 nmeters, 3,000 nmeters) placed at the exit slit. The monochromatic radiation could be circularly polarized with the help of either an H.R. polarizer and a Fresnel rhomb made of high index of refraction glass (for the visible and near infrared) of a nickel filament polarizer and a sodium chloride Fresnel rhomb
(for the medium infrared). The advantage of the rhomb over the 1/4 wave plate is that the light can be circularly polarized over an extended wavelength region. The rhombs were built by the author following the criteria given by J. M. Bennet (7081). The outgoing radiation could be separated into two beams allowing the simultaneous detection of both the intensity variation in the incident beam and the sample response variation as a function of wavelength.

The wavelength calibration and the optical resolution were checked before and after each experiment with a helium-neon laser and a mercury arc lamp. The direction of polarization of the beam incident on to the sample could be determined by using a quarter wave plate and the percentage of polarization could be estimated by measuring the ellipticity of the radiation. It should be noted that the radiation coming from the spectrometer is partially linearly polarized and that the spectral distribution of the intensity will therefore depend on the direction of the circular polarization. Cardona (69C1) pointed out that when wavelength modulation is being done the modulation amplitude to be used should be approximately equal to the spectral resolution. An experimental study of wavelength modulation and resolution was done for our apparatus by Davoine (75D1) and his results should be considered when an experiment is planned.
THE CRYOSTATS

Three types of cryostats were used throughout the experimentation period of this work. All samples underwent preliminary tests in portable liquid nitrogen cryostats which were built here in the department following the plans by Fortin (70FL). In these cryostats the samples were attached to a copper cold finger where, upon filling the cryostat with liquid nitrogen temperatures of the order of 100K could be attained.

To perform experiments at lower temperatures and in the presence of a magnetic field two cryostats equipped with superconducting solenoids were available. Although the two cryostats were basically of the same design, they differed in their maximum magnetic field available as well as differing greatly in their use and portability. Figure AF2 is a schematic representation of a cross section of both cryostats. Each cryostat shall now be described in more detail including some of their advantages and disadvantages.

The "larger" cryostat was built by Sulfrion Cryogenics Inc. A niobium titanium superconducting solenoid from Ferranti-Packard was mounted horizontally in the cryostat. The experimental chamber had an inner diameter of 3.5 cm allowing an effective f number of 4.8. The chamber was sealed in front by a removable quartz or sapphire window assembly which could withstand the thermal shock upon being quickly cooled to 4.2K. The front optical windows, CaF$_2$, were attached to stainless
Figure AF2 A cross section of the cryostats.

1 - Helium recovery and current lead
2 - Liquid nitrogen
3 - Liquid helium guide
4 - Carbon resistor as level indicators
5 - Liquid helium
6 - Magnet
7 - Leads from sample
8 - Feedthrough
9 - Sample holder
10 - Experimental chamber
11 - Indium O-ring
12 - Vacuum
13 - Copper radiation shield
14 - Rubber O-ring
15 - Capillary to exp. chamber
16 - Optical windows
steel rings with Shell Epon 628 epoxy and Shell D hardening agent as suggested by Mollenaer et al. (63M1) (Note: the epoxy may crack with thermal recycling and therefore could be a source of leakage at low temperatures). The back seal of the chamber, also capable of withstanding thermal shock, consisted of a stainless steel plate in which an eight wire ceramic electrical feedthrough was installed. (The feedthroughs may crack at low temperatures; it was found that this would occur when the ceramic had been overheated while making electrical connections). The front ring and the back plate were bolted to the chamber while an indium 'O' ring was used to assure a vacuum tight seal even at low temperatures. (The indium 'O' rings should be changed every time the seals are broken).

The experimental chamber and the liquid helium container were surrounded by a liquid nitrogen cooled copper shield. The whole apparatus was finally enclosed in a vacuum-tight stainless steel casing. The outer casing was equipped with removable front and back plates which were bolted on to the chamber while a rubber 'O' ring ensured a good seal. The space between the outer casing and the inner chamber was evacuated by an oil diffusion pump in series with a mechanicial pump. Because of the large volume and the many seals involved with this cryostat, pumping of this space would take a minimum of two days before a vacuum of the order of $10^{-3}$ pascals could be achieved.

The cryostat being pumped, the inner chamber was also evacuated through a small capillary. The liquid nitrogen reservoir for the
copper radiation shield was then filled. Liquid helium was introduced into the inner reservoir via a guide pipe which allowed the cold helium gas to cool the system from the bottom up. Primary cooling could also be done by introducing liquid nitrogen into the inner container and letting it evaporate. However, great care had to be taken that no nitrogen remained in the chamber when the liquid helium was introduced since the nitrogen would quickly solidify and, therefore, block the access of the helium to the lower part of the cryostat.

During the cooling process it was noticed that the outer chamber would sometimes cool and fog. This was not necessarily an indication of an air leak but was often the result of a poor vacuum in the chamber. Further cooling of the inner chamber often provided enough cryo-pumping to eliminate this problem. If complete freeze-out of the stray gases in the chamber did not occur, the experiment had to be stopped and once the system had returned to room temperature all seals had to be checked.

The helium level in the inner reservoir was monitored by firstly recording the resistance of the superconducting magnet; its resistance varied from 650 ohms at room temperature, to 90 ohms at liquid nitrogen temperature, and finally to zero at approximately 10K. Once the magnet was superconducting the liquid helium level was monitored by recording the values of various carbon resistors placed at regular depth intervals inside the reservoir. Under normal operating conditions 15 to 20 litres of liquid helium were required to cool the system down and an additional 3 litres per hour were required to compensate for
losses. A helium exchange gas at a pressure of 10 to 100 pascals was introduced via the capillary into the experimental chamber where temperatures of the order of 6K were attained.

Because of the time and expense involved in the preparation and use of the cryostat a minimum of four and up to eight pretested samples would be fixed onto the sample holder in order to avoid cancelling a run due to sample or contact breakage during cooling. The samples were mounted on an ebonite cylinder with silicone DC-29 grease, a compound which remains soft at low temperatures and assures that minimum stress is made on the sample while cooling. The samples were placed in the center of the experimental chamber where the magnetic field would be parallel to their surface direction. In this region the magnetic field factor of 0.1448 Tesla/Amp was found to be correct to within 0.5% by Fillion (73F1) and the radial field homogeneity over the diameter of the experimental chamber was found to be superior to 99.5%. The liquid helium temperature critical field of the magnet was estimated to be 7.37 tesla with an average rate of field increment of 0.2 Tesla/min.

The electric circuit for the magnet is presented in figure AP3. Starting at the magnet, the system was equipped with a persistent switch which could provide a field stability of one part in $10^3$ over $10^3$ seconds. We have however not used this mode of the system since we were interested in stopping at many magnetic field values for a relatively short time. The magnetic field at the sample was estimated by monitoring the current fed into the magnet through a standard resistor of $5.00 \pm 0.02 \times 10^{-4}$ ohms.
Figure AF3 - The electrical circuit for the magnet.
Figure AF4 - Current output vs time characteristic of the control circuit.

At any specific current value, the output is adjusted such that the magnetic field can be increased in a minimum time.
Should the magnet become normal during operation at high magnetic fields a high back e.m.f. would be induced into the circuit, (the magnet has a self inductance of 20 henry) and could seriously damage the power supply. To prevent damage of this type a network of protection diodes type 70H10A made by International Rectifier was installed in parallel with the power supply output. It was possible to program the Hewlett Packard model 6260A direct current power supply by varying a resistance which was monitored by the power supply. In order to obtain any specific magnetic field value in a minimum time, a non-linear current control was made. The control resistance consisted of three resistors, figure AF3, $R_1$ was motor driven to vary linearly from 0 to 500 ohms, $R_2$ could be manually set from 0 to 100 ohm and permitted the selection of the maximum allowable current, and $R_3$ 30 ohms, was added to permit a maximum field of 7.2 tesla when $R_2$ was at 100 ohms. Figure AF4 shows the current output as a function of time for this control system. It takes approximately 38 minutes to go from 0 to 7.2 tesla and, considering the rate at which helium is lost, this long rise time can be a great inconvenience if many runs are planned. In fact in order to obtain the spectra for one sample at every 0.5 tesla for both circular polarizations a minimum of 10 hours had to be reserved once the system was cooled down and ready for operation. As previously noted, four samples were normally installed in the cryostat and if scans of all the reasonable samples were to be made a minimum of 75 litres of liquid helium would be required.
Figure AFS - Sample holder with thermometers.

A - Top view
B - Side view

1 - Sample
2 - Silicone grease
3 - Feedthrough pin
4 - Ebonite cylinder
5 - Gas circulation holes
6 - Copper resistor
7 - Germanium resistor
8 - Ceramic plate
9 - Screw
10 - Feedthrough

D - Diameter
In order to circumvent some of the disadvantages of the "larger" cryostat we have built a small portable model. In this cryostat a superconducting solenoid from Supraconducteur et Cryogenie du Canada Limitée permitted fields of at least 3 tesla. The magnetic field factor was \( \sqrt{0.0693 \text{ tesla/Amp}} \) and the current could be quickly increased manually. The low temperature front window was made of sapphire obtained from Adolf Meller Co. N.Y. This window in combination with the room temperature exterior window of CaF\(_2\) allowed work to be done in the infrared up to 7,000 nmeters. Only one day of pumping was required to achieve a vacuum necessary for the experiment to proceed.

The cooling down of the system required from 3 to 5 litres of liquid helium and with a current of 40 amps flowing through the magnet and copper leads the rate of helium loss was of the order of 1.5 litres per hour. Although four samples could be placed onto ordinary sample holders, a special holder (figure AF5) with both a germanium resistance thermometer and a copper resistance thermometer was installed allowing us to put one sample with electrical leads and two or three samples on which reflectivity experiments could be done. Since the cryostat under normal operating conditions would warm up very slowly, experiments to follow the temperature variation of several phenomena in the absence of magnetic field could easily be performed. The cryostat was made to be portable so that its total liquid helium capacity was small (\( \sim 2 \) litres) and therefore many helium transfers could be required during one single run. It was found well-advised to reduce the magnetic field to zero each time a transfer was done since the initial hot helium gas could make
the magnet normal. But these are small inconveniences when we consider the total turn around time (approx. 2 days) for one run with the small cryostat in comparison to the turn around time (approx. 2 weeks) for a similar run with the larger cryostat. Moreover all samples were tested for magneto-optical structures in the small cryostat before considering putting them into the larger system. In the case of small band gap materials such as InSb the complete study can be done in the smaller cryostat.

C SAMPLE PREPARATION

Throughout this work a large number of samples were made and tested. However only a small percentage of the samples actually survived all the preliminary tests in a way as to be considered acceptable. The samples, in general, were cut from large monocrystal; the actual specimen would be a parallelipiped of approximately 4 x 6 x 1 mm. Both the front and back surfaces were lapped using 5 micron Al₂O₃ powder. The samples were then etched with appropriate etchants as suggested by Milnes (72M1) and as given in table M1. The highly polished samples were mounted on glass slides and indium was evaporated over most of the back surface. The indium was then diffused by heating the sample in a nitrogen atmosphere furnace to temperatures of up to 400°C. The front surface was re-etched and a thin gold film (30 to 800 nmeters thick) was evaporated onto this surface. The transmission spectrum of the
TABLE A11

Etch for various semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>HCl</th>
<th>H₂SO₄</th>
<th>HNO₃</th>
<th>B'</th>
<th>C'</th>
<th>D'</th>
<th>E'</th>
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<td>S</td>
<td>S,N</td>
<td>V</td>
<td>S,M</td>
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<td>M</td>
<td>M</td>
<td>M</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
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<td>M</td>
<td>M</td>
<td>N</td>
<td>N</td>
<td>M</td>
<td>N</td>
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<td>V</td>
<td>S</td>
<td>S</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

A-All solutions are at room temperature and concentrated unless otherwise noted.

V-etches material vigorously
M-etches material moderately
S-etches material slightly
N-does not perceptibly etch material

B-1 HF:4 HNO₃
C-Approximately 5% Bromine in Methanol
D-30% NaOCl
E-Approximately 20% NaOH and warm 40-50°C unless noted otherwise
f-50% NaOH and hot 90-100°C
g-Hot 90-100°C
i-20 to 100°C
Figure AF6 - Transmission spectrum of a gold film, \( t \approx 0.07 \mu m \). No sharp structures are observed.
gold films, figure AF6, was checked for sharp structures which could hinder the data interpretation. No evident structures were found in the spectral region of interest. Gold or platinum wires were attached to both front and back metal contacts with indalloy or silver paint. Finally the samples could be mounted into the various cryostats to be tested for their photovoltaic response.

The Synchronous Detection System

A schematic representation of the detection system used in most of the present experiments is included in figure AF1. Systems such as this are in general use today and we feel that a lengthy description of the components is not necessary.

As previously mentioned the monochromatic radiation coming from the spectrometer has been chopped at a frequency of 85 Hz. Once the light has gone through the optical system it is split into two beams, one of which goes to the sample and the other goes to a detector suitable for the wavelength region to be studied.

The photosignal coming from the sample was fed into a PAR 213 preamplifier whose variable input impedance permitted the matching of the different sample impedances encountered in this work. The output of the preamplifier went to a PAR 210 selective amplifier and finally the signal was fed into a PAR 220 Lock-In amplifier. The signal from the detector was similarly processed through separate preamplifier, selective
amplifier, and Lock-In amplifier. The signal to noise ratio could be maximized by matching the electronic time constant to the spectral scanning rate and the required resolution. The resultant D.C. signals from the Lock-In amplifiers were processed by a PAR 230 multiplier unit where the sample's photosignal was divided by the detector's photosignal in order to eliminate from the sample's signal any structures which might arise from variations in the input light intensity.
CHAPTER III EXPERIMENTAL RESULTS AND ANALYSIS

The spectral response of the photovoltaic effect in the presence of quantizing magnetic fields were obtained for germanium, indium phosphide, indium antimonide and gallium arsenide. The results and analysis of the experiments will be presented in chronological order. Germanium was the first semiconductor to be studied. Its primary role as test sample was to confirm that magnetic field dependent structures could be observed in the photoresponse and that such structures could be analyzed in the light of the latest magneto-optical theories. Magneto-optical structures were readily observed and from the analysis it was concluded that the energy positions of the maximum slope of these structures corresponded to Landau level energies. Indium phosphide was then studied in order that the conclusion reached in the study of germanium be verified and, more importantly, in order that its band parameters be precisely determined. Exciton participation was evident in the spectra of InP and empirical corrections of the data had to be done following the method suggested by Vreven (68V1). In InSb, both the exciton and Landau level transitions could be separately seen and as a consequence the band parameters could be made to fit both the exciton and Pidgeon and Brown theoretical developments simultaneously. Finally, the preliminary results obtained from the photovoltaic effect on gallium arsenide are analyzed.
GERMANIUM

Germanium was one of the first semiconductors to be studied in magneto-optics (57Z1) and since then it has been investigated by many authors and by the various magneto-optical techniques available. Because of this extensive research the band parameters of Ge are considered well known and from our point of view Ge could serve as an excellent test sample for our studies using the photovoltaic effect for the observation of magneto-optical structures.

The results were obtained on samples cut from a monocrystalline block of n-type Ge with a carrier concentration of $3 \times 10^{15} \text{cm}^{-3}$. A rapid estimate gives a depletion layer width of $W = 5 \times 10^{-4} \text{cm}$ and a maximum electric field of $2 \times 10^3 \text{V/cm}$ at the barrier. For this sample no Franz-Keldish* effect could be detected. The samples were polished with $\text{Al}_2\text{O}_3$ powder and etched in a solution of $15\text{HF}:25\text{HNO}_3:15\text{CH}_3\text{COOH}$. The back surface ohmic contact was made by evaporating indium onto the face and alloying in a nitrogen atmosphere furnace at 300°C. The front

* The Franz-Keldish effect (58F1). An external electric field modifies the optical properties of semiconductors because it produces a change in the electronic levels and the transition probabilities. Near critical points in the absorption coefficient this effect would give rise to a tail and oscillations in the spectral distribution. Neither of these two phenomena were observed in our samples including Ge, InP, InSb and GaAs. Therefore we believe that the electric field at the metal semiconductor contact was not high enough to affect the results in magneto-optics.
surface contact consisted of an evaporated semi-transparent gold film. The specimen was then mounted in the Faraday configuration with \( \vec{B} \parallel [110] \) within the experimental chamber of the superconducting magnet. The quartz iodine tungsten filament lamp served as light source and the 1,600 nmeter blaze grating provided the light dispersion. The monochromator was set at a one-nanometer (1 meV) resolution.

Ge-A Preliminary data and fit

Typical spectra of the photovoltage in the presence of a magnetic field are shown in figure GeF1. One such spectrum for each of L.C.P. and R.C.P. was obtained at every 0.5 tesla in the range zero to seven tesla. The signal to noise ratio was estimated to be better than 1000:1, however the actual portion of the required signal was obtained by working with a zero d.c. off-set and multiplying the basic signal by a factor of 10. Therefore the oscillations as seen in figure GeF1 represent, in amplitude, approximately \( 1 \text{/100} \) of the total signal.

Initially the energy values of the maxima of the structures were thought to correspond to the positions of Landau levels and were taken as the significant data and labelled (Table GeT1) as in the Pidgeon and Brown scheme. The energies of the maxima for L.C.P. and R.C.P. light are plotted as functions of the magnetic field in figures GeF2 and GeF3 respectively where again the labelling is in accordance with Table GeT1. A linear fit of low field, low quantum
Figure GeF1 - Spectral distribution of the photovoltaic effect at a Au-Ge barrier for both circular polarizations.
TABLE GeT1
Identification of transitions in Ge.

\[ HH(i,j) = \frac{a^c(i) a^c(j) b^c(i) b^c(j)}{2} \]

<table>
<thead>
<tr>
<th>R.C.P.</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>a^-(1) a^c(0)</td>
<td>a^-(-1) b^c(0)</td>
</tr>
<tr>
<td>B</td>
<td>a^+(1) a^c(0)</td>
<td>HH(0,1)</td>
</tr>
<tr>
<td>C</td>
<td>HH(2,1)</td>
<td>HH(1,2)</td>
</tr>
<tr>
<td>1</td>
<td>b^+(1) b^c(0)</td>
<td>b^+(0) b^c(1)</td>
</tr>
<tr>
<td>2</td>
<td>HH(3,2)</td>
<td>HH(2,3)</td>
</tr>
<tr>
<td>3</td>
<td>a^+(2) a^c(1)</td>
<td>b^+(1) b^c(2)</td>
</tr>
<tr>
<td>4</td>
<td>HH(4,3)</td>
<td>HH(3,4)</td>
</tr>
<tr>
<td>5</td>
<td>a^-(2) a^c(1)</td>
<td>(4,5)</td>
</tr>
<tr>
<td>6</td>
<td>HH(5,4)</td>
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</tr>
<tr>
<td>7</td>
<td>HH(6,5)</td>
<td>HH(6,7)</td>
</tr>
<tr>
<td>8</td>
<td>HH(7,6)</td>
<td>HH(7,8)</td>
</tr>
<tr>
<td>9</td>
<td>HH(8,7)</td>
<td>HH(8,9)</td>
</tr>
</tbody>
</table>
Figure GeP2 - Energy of maxima of the photovoltage as a function of magnetic field for left circularly polarized light.
number lines gives an extrapolated band gap of 0.8892 ± 0.0005 eV, 
a value close to 0.888 ± 0.001 eV obtained by Aggarwal (70A1) at 30 K.

The full lines on the fan diagrams (figures GeF2 and GeF3) 
represent computer fits of the experimental data to the Pidgeon and 
Brown theory. For these fits, the bandgap $E_g$ was taken from above as 
0.8892 eV; the split-off energy $\Delta = 0.296$ eV, the upper band inter-
action parameter $f = 0$, and the anisotropy factor $\gamma_3^L - \gamma_2^L = 1.38$
were taken from Aggarwal (70A1). The data were fitted with respect to 
the three most important parameters in the theory: $\gamma_1^L$, $\gamma_2^L$, and $m^*_C$
In an attempt to avoid excitonic effects (Edwards and Lazazzera (60E2)) 
the fits were made only for the field values of 3 to 7 tesla and 
quantum numbers of 2 to 7 for the heavy hole transitions. The values 
obtained for different parameters are shown in table GeT2 along with 
the values quoted from Aggarwal (70A1).

Ge-B  Excitonic participation

The effects of excitonic contributions to the spectra are easily 
seen in the data. A consistent offset of the experimental points from 
the theoretical lines at low quantum numbers (eg: lines A and B, figures 
GeF2 and GeF3) is a preliminary indication that these points are of 
excitonic origin. Moreover a precise plot (figure GeF4) of the 
average energy of the lowest light hole transition labelled "A" shows
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present work</th>
<th>Aggarwal(70Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e/m_o$</td>
<td>0.0360 ± 0.0003</td>
<td>0.0380</td>
</tr>
<tr>
<td>$\gamma_1^L$</td>
<td>12.6 ± 3</td>
<td>13.38</td>
</tr>
<tr>
<td>$\gamma_3^L$</td>
<td>5.66 ± 0.04</td>
<td>5.68</td>
</tr>
<tr>
<td>$E_p$</td>
<td>28.1 ± 2 eV</td>
<td>26.8 eV</td>
</tr>
<tr>
<td>$\gamma_2^L$</td>
<td>4.3 ± 0.5</td>
<td>4.3</td>
</tr>
<tr>
<td>$q_c$</td>
<td>-3.2 ± 0.3</td>
<td>-3.0</td>
</tr>
<tr>
<td>$L_x$</td>
<td>3.7 ± 0.6</td>
<td>3.4</td>
</tr>
<tr>
<td>Drms</td>
<td>0.8 meV</td>
<td></td>
</tr>
</tbody>
</table>
Figure GeF4 - Energy of the 'A' transition of figure GeF1 as a function of magnetic field. The error bars are the standard deviation from the mean.
a non-linear variation with magnetic field. This behaviour is exciton like (60EL) as opposed to the linear fit expected in the Pidgeon and Brown formalism for Landau levels in that magnetic field and energy range.

Ge-C Discussion

The values of the band parameters giving the best fit to the maxima of the structures observed in the spectra differ significantly from the accepted values. For example, the value of 0.036 m obtained here for the conduction band effective mass is lower than the rather well known value of 0.038 m obtained by Dresselhaus and Dresselhaus (67D1). Figure GeF5 is a reproduction of the spectrum of figure Gef1 but with the labelled transitions being those obtained from the Pidgeon and Brown theory using the parameters proposed by Aggarwal (70Al). The theoretical points lie on the low energy side of the maxima but are yet consistent in their positions on the structures. As was pointed out by Roth et al. (59R1) and Barbarie (74B1) the theoretical transition energies between Landau levels correspond to the energy positions of maxima in the absorption spectrum only when broadening of the levels can be neglected. When a finite relaxation time γ is included, the absorption coefficient is written as (67W1)

\[ \alpha = \frac{\hbar \omega}{C} \sqrt{\gamma} \sum \left[ \frac{\left( x_n^2 + 1 \right)^{\frac{1}{2}} + x_n}{2\left( x_n^2 + 1 \right)^{\frac{1}{2}}} \right]^{\frac{1}{2}} \]
Figure GeF5 - Spectral distribution of the photovoltage at a magnetic field of 3 Tesla. The positions indicated are those predicted from the Pidgeon and Brown theory using the parameters suggested by Aggarwal (70A1).
where \( X_n = (N - W_n)^T \), \( W \) is the incident photon frequency,

\[
\omega_n = \omega_c + (n + \frac{1}{2}) \omega_c^*, \quad \text{and} \quad \omega_c^* \text{ is the effective cyclotron frequency},
\]

\[
\omega_c^* = \frac{eB}{\mu}. \quad \text{The absorption coefficient and its derivative are}
\]

plotted as a function of frequency in figure GeF6 for \( \omega_c^* = 5 \).

The energy positions of the maxima do not correspond to the Landau level energies and a line shape analysis of the structures observed in the spectra would be required if high precision is needed on the positions of the Landau level transition energies. On the other hand a good estimate of the required energies can be made by taking the positions of the maximum slope and the error introduced by taking these points is usually less than the experimental error itself. This conclusion seems to be confirmed for the results on Ge (figure GeF5) as well as the results on InP.

2. INDIUM PHOSPHIDE (75P1)

Indium phosphide is a III-V compound which has not been the subject of many interband magneto-optical investigations, one reason being that this material is difficult to obtain in pure form. To our best knowledge only a partial study done by Barbaric (72B1) has been reported up to now.

The determination of the band parameters through magneto-optics presents both experimental and theoretical difficulties. Due to the
relatively high effective masses involved, high magnetic fields are required to produce observable energy quantization, and even at 7 tesla only the transitions from the light-hole valence band will produce any observable effects, these effects being small in comparison to the background. The exciton contributions to the spectrum are large because of the exciton's large binding energy; therefore the observed quantum oscillations must be corrected for these effects. The correction in the case of InP is difficult to perform explicitly since the field involved is in the intermediate region, $\Theta_e \approx 1$, where no theory has yet been developed.

Our samples were obtained from a monocrystalline block of n-type InP with a room temperature carrier concentration of $2 \times 10^{15}$ cm$^{-3}$. As in germanium the depletion layer width is estimated at $W = 5 \times 10^{-4}$ cm with a maximum electric field of $E = 2 \times 10^3$ V/cm at the barrier. The samples were polished with Al$_2$O$_3$ powder and etched in a 10%/vol Br-methanol solution. Again the contacts were placed in a "sandwich" configuration, the back ohmic contact being made of diffused indium and the front rectifying contact consisting of a semitransparent gold film. The samples were placed in the Faraday configuration with $\vec{B} \parallel [111]$. In order to obtain the wavelength modulated reflectivity spectra, a similar sample of InP was made without contacts and a low noise silicon photodiode (EG and G-type HAD-1000) was used as the detector.
InP-A Comparison of wavelength-modulated photovoltaic effect and wavelength modulated reflectivity.

In the discussion of the results on Ge, we had suggested that the energy positions for Landau levels should closely correspond to the maximum slopes of the structures observed in the direct photovoltaic spectra. The signal from InP samples was found to be noise free to the extent that wavelength modulation could easily be used to obtain the derivative of the photoresponse.

Thus in order to establish experimentally the correspondence between the structures seen in the photovoltaic spectra and the pertinent transition energies, a comparison was made between the wavelength modulated photovoltaic $\Delta V_{pv}$ spectrum and the wavelength modulated reflectivity $\Delta R/R$ spectrum. On figure InP1 the $\Delta R/R$ spectrum near the 1s exciton line at 1.4183 eV is presented together with the $\Delta V_{pv}$ spectrum. The reflectivity curve was fitted to the form (69C1)

$$\frac{\Delta R}{R} \propto C - Re \left( \frac{\alpha}{\varepsilon} \right) + 2A \ Im \left( \frac{\alpha}{\varepsilon} \right)$$

where $\alpha$ is an exciton-asymmetry broadening parameter and $\varepsilon$ is the complex dielectric constant, which includes excitonic participation, as given by Bhandari and Woolley (W151). The parameter $A$ was found to be $A = 0.6$ and the Lorentzian broadening parameter, $\Gamma$, which is included in the dielectric constant, was found to be $\Gamma = 1$ meV.
Figure PPL1. - Wavelength modulated reflectivity ($\Delta R/R$) and wavelength modulated photovoltaic ($\Delta V_{pv}$) effect near the $E_x$ exciton line.
It is noted that the exciton energy, which corresponds with the minimum in the $\Delta R/R$ curve, is associated to the zero-cross over of the $\Delta V_{pv}$ curve. As a consequence the pertinent energies to be related to excitonic behaviour will be the maximum of these structures observed in the direct photovoltaic spectra or will be the zero cross-over of the structures observed in the $\Delta V_{pv}$ spectra.

The more complete spectra of $\Delta R/R$ and $\Delta V_{pv}$ at 7 tesla are presented for comparison in figure InPF2. The pertinent transition energies (as labelled in table InPT1) which were taken as data are indicated on the figure. In the case of the Landau like oscillations having a large broadening parameter, the maxima of the $\Delta V_{pv}$ curves correspond to the minima of the $\Delta R/R$ curves to within 0.5 meV, which is as good as the resolution of the apparatus. A major difficulty in using only the $\Delta R/R$ data was that the reflectivity signal was very weak and noisy, in contrast to the photovoltage. This is clearly demonstrated in figure InPF2 by the high visibility of the split-off band to conduction band (S.O.) transitions and higher quantum number Landau level transitions in the $\Delta V_{pv}$ spectrum in comparison with that of the $\Delta R/R$ spectrum.

Figure InPF3 presents a comparison of the direct photovoltaic spectrum and its associated wavelength modulated spectrum at 5.5 tesla for L.C.P. light. The transitions which can be seen in the direct spectrum appear as very small oscillations even when the signal is amplified and offset. These oscillations, however, are quite evident
Figure InPF2 - Spectral distribution of the wavelength modulated photovoltaic ($\Delta V_{pv}$) signal and its corresponding reflectivity ($\Delta R/R$) signal at a magnetic field of 7 Tesla.
Figure InP3 - Spectral distribution of the direct photovoltage (solid line) and its associated wavelength modulated derivative (dashed line) at 5.5 Tesla.
in the modulated spectrum and the high signal to noise ratio would permit even greater amplification if it were required.

InP-B  Landau level analysis

For each magnetic field value and each polarization of incident light, the data were accumulated from the $\Delta R/R$ spectra, the $\Delta V_{pv}$ spectra, as well as from the direct $V_{pv}$ spectra. The energies of the pertinent points are plotted as functions of the magnetic field in figures InPF4 and InPF5 for right- and left- circularly polarized light respectively. Following Vreken (6SV1), it was assumed that the binding energy of excitons associated with Landau levels of higher quantum numbers (eg. $n = 4, 5, 6$) is negligible when compared to the experimental resolution. Therefore these three levels for both polarizations were simultaneously fitted to the Pidgeon and Brown theory for Landau level transitions. For the fit the band gap value of $E_g = 1.423$ eV was obtained from the zero-field convergence point of the three upper curves of both polarizations. The S.O. energy of $\Delta = 0.108$ eV was obtained directly from the spectra at $B = 0$. The higher-band interaction parameter $f = 0.0$ was estimated by minimizing the r.m.s. error of the fit with respect to this parameter. The anisotropy factor $\left(V_3^L - V_2^L\right) = 0.68$ was taken from Lawaetz (7LL1).

The fit produced the band parameters presented in table InPT2,
where the parameters such as $q_c$, $q_{so}$, $m_{so}$ and $F_p$ are calculated using the approximate equations of Aggarwal (72W1). The parameters obtained differ somewhat from the theoretical values but are however in good agreement with the latest experimental values obtained by cyclotron resonance; for example, $m_{lh}/m_0 = 0.12$ of Leotin et al. (74L1) and $m_c/m_0 = 0.0803$ of Chamberlain et al. (72Cl).

The theoretical lines produced in figures InPF4 and InPF5 are derived from the parameters obtained in the fit and are identified in table InPT1. The lines are labelled according to the Pidgeon and Brown notation in the case of Landau levels; in the case of exciton levels, the lines are labelled as the corresponding Landau level (which is $R(H)/(2n + 1)$ above the exciton level). For example, in the R.C.P. data both the Landau transition $a^+ (1) \rightarrow (0)$, line 3, and its associated exciton level, line 1, are seen. The higher quantum number lines, $n = 4, 5, 6$, stem from an unresolved mixture of Landau and associated exciton levels. Due to the admixture of a number of possible Landau and associated exciton levels, the exact identity of the data at low energy was difficult to establish. Thus, among the possible overlapping theoretical lines, the line which best described the data was chosen as label.
Figure InP4 - Energy positions of the spectral oscillations as a function of magnetic field for R.C.P. light. The lines represent the theoretical transitions labeled in table InPTL.
Figure InP5 - Energy positions of the spectral oscillations as a function of magnetic field for L.C.P. light. The lines represent the theoretical transitions labeled in table InPT1.
TABLE INPT1 IDENTIFICATION OF TRANSITIONS IN INP.

The notation used is as in the Pidgeon and Brown scheme. In the table the transitions are identified as Landau levels (L) or as the exciton states associated with the pertinent Landau level. For n>4 the experimental resolution does not allow the differentiation between a Landau level and its associated exciton.

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<thead>
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<th>L.C.P.</th>
</tr>
</thead>
<tbody>
<tr>
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<td>notation</td>
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<td>(a^+ (1)) (a^- (0))</td>
</tr>
<tr>
<td>2</td>
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<td>3</td>
<td>(a^+ (1)) (a^- (0))</td>
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<tr>
<td>4</td>
<td>(a^- (2)) (a^- (1))</td>
</tr>
<tr>
<td>5</td>
<td>(b^- (2)) (b^- (1))</td>
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<td>(a^+ (3)) (a^- (2))</td>
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<tr>
<td>9</td>
<td>(a^+ (6)) (a^- (5))</td>
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<tr>
<td>10</td>
<td>(a^+ (7)) (a^- (6))</td>
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### TABLE IMPT2
BAND PARAMETERS OF INDIUM PHOSPHIDE

<table>
<thead>
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<th>parameter</th>
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<th>theory</th>
<th>others (exp.)</th>
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</thead>
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<tr>
<td>(E_g)</td>
<td>1.423±.0005 ev</td>
<td>1.42*</td>
<td>1.424(^d)</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>0.108±.002 ev</td>
<td>.13*</td>
<td>0.11(^d)</td>
</tr>
<tr>
<td>(E_P)</td>
<td>17±1 ev</td>
<td>20.4*</td>
<td>16(^b)</td>
</tr>
<tr>
<td>(f)</td>
<td>0.0</td>
<td>-2.0*</td>
<td></td>
</tr>
<tr>
<td>(m_c/m_0)</td>
<td>.079±.001</td>
<td>.080*,.072(^a)</td>
<td>.0803(^c)</td>
</tr>
<tr>
<td>(\gamma_1^L)</td>
<td>5.15±.05</td>
<td>6.28*</td>
<td></td>
</tr>
<tr>
<td>(\gamma_2^L)</td>
<td>.94±.03</td>
<td>2.08*</td>
<td></td>
</tr>
<tr>
<td>(\gamma_3^L)</td>
<td>1.62±.03</td>
<td>2.76*</td>
<td></td>
</tr>
<tr>
<td>(m_{hh}/m_0)</td>
<td>.12±.01</td>
<td>.089*,.086(^a)</td>
<td>.12(^b)</td>
</tr>
<tr>
<td>(m_{lh}/m_0)</td>
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<td>.85*,.50(^a)</td>
<td>.60(^b)</td>
</tr>
<tr>
<td>(m_{so}/m_0)</td>
<td>.21±.01</td>
<td>.17*,.16(^a)</td>
<td></td>
</tr>
<tr>
<td>(\kappa^L)</td>
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<tr>
<td>(g_{so})</td>
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<td></td>
</tr>
<tr>
<td>Drms</td>
<td>.5 meV</td>
<td></td>
<td></td>
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</tbody>
</table>

\(^a\) - Cardopa (65C2)
\(^b\) - Lecott et al. (74LL)
\(^c\) - Chamberlain et al. (72CL)
\(^d\) - Fishback et al. (72F1)
InP-C S.O. transition energy shift

The high visibility of the S.O. transition in the $\Delta V_{pv}$ and $V_{pv}$ spectra permitted the observation of the energy shift of the S.O. structure as a function of magnetic field. A comparison of this shift to that predicted by the theory verified the band parameters obtained above.

Because of the observed spectral width of the S.O. transition the exact energy positions of these transitions were limited to a resolution of approximately 1 meV. It was therefore difficult to observe differences between the L.C.P. and R.C.P. spectral positions at a given magnetic field. A general shift as a function of magnetic field was, however, observed and is presented in figure InPF6. In the figure the points represent the average shift in energy $\Delta E_{so}$ of both polarizations. The theoretical line shown is given by (72W1).

$$
E_{so} = \frac{1}{2} \left( \frac{m}{m_c} - \frac{m}{m_{so}} \right) \frac{e\hbar B}{m_o}
$$

which is a first order approximation for the energy shift of the S.O. transition. In this equation, the values of $m_c = 0.079 m_o$ and $m_{so} = 0.21 m_o$ from table InPT2 were used. The agreement of the data with the fit again increases our confidence in the parameters derived from the Landau-level analysis, specifically the values of $m_c$, $\Gamma_L^1$ and $m_{so}$. 
Figure InP6 - Energy shift of the split-off to conduction band transition as a function of magnetic field. The points represent the averages for both polarizations; the line is a theoretical fit using the parameters of table InPT2 (present work).
InP-D  Exciton parameters

Although no detailed analysis of the exciton behaviour was done for InP a description of some of the properties of the exciton could be obtained from the data and Landau level analysis.

The exciton position at zero magnetic field is found to be

\[ E_x = 1.4183 \pm 0.0002 \text{ eV} \]

which agrees with the values of 1.4185 eV of Evangelisti et al. (74E1) and of 1.4182 eV of White et al. (72W2).

Using the expression developed by Baldereschi and Lipari (71B1) for the exciton-reduced effective mass, \( \mu_0 \), together with the band parameters of table InPT2 we obtain

\[ \frac{\mu_0}{m_0} = \frac{n_0}{m_c + \gamma_1}^{-1} = 0.056 \]

In turn using

\[ R_{ex}^0 = \frac{\mu_0 e^4}{2m^2 \varepsilon_s^2} = 13.6 \frac{\mu_0}{m_0} \left( \frac{\varepsilon_0}{\varepsilon_s} \right)^2 \text{ eV} \]

gives the exciton binding energy \( R_{ex}^0 = 5.2 \pm 0.1 \text{ meV} \). The binding energy of the exciton and its position at zero magnetic field gives the band gap value of

\[ E_g = E_x + R_{ex}^0 = 1.4235 \text{ eV} \]

essentially the value deduced from the extrapolated Landau levels.
Discussion

The above study of the interband magneto-optical properties of InP has again shown that the photovoltaic effect and its wavelength derivative can be powerful methods for observing very small changes in the optical properties of semiconductors. Considering the high visibility of the exciton structure in the photovoltaic spectrum (peak 1 in figure InPF3) it is indeed regrettable that no theory exists to analyze the excitons behaviour at intermediate magnetic field. Although the experimental resolution had not been preset for research of this specific peak a shift in its energy position as a function of magnetic field was observed and the results are presented in figure InPF7. The energy position of the exciton in the absence of magnetic field could also be followed as a function of temperature as given in figure InPF8.

The analysis of Landau Levels permits a determination of the band parameters of the semiconductors; in addition the analysis of the behaviour of exciton states in a magnetic field would also result in the determination of these same parameters. Since theories exist for both the exciton states and Landau level behaviour in a high magnetic field, the analysis of the structures in the photovoltaic spectrum of InSb, a more suitable material, in that respect, was attempted.
Figure InPF7 - The average position of the 1S exciton line as a function of magnetic field. No attempt was made to fit these points. They are presented as a matter of record since they may prove useful in future work.
Figure InPF8 - The energy position of the 1s exciton peak as a function of temperature.

No fit was attempted and this experimental curve is presented as a matter of record.
INDIUM ANTIMONIDE

Indium antimonide was one of the first semiconductors studied in magneto-optics and has since been often subjected to further investigation. Its low conduction band effective mass has permitted the observation of spectacular magneto-optical structures at moderately high fields. Because of this light effective mass the high magnetic field condition required for the use of Altarelli's and Lipari's theory (74Al) on exciton behaviour could easily be satisfied in the present experiments. As a consequence the band parameters of InSb which best explain both the exciton and Landau level behaviours could be estimated.

The results were obtained on samples cut from a monocrystalline block of n-type InSb with a carrier concentration of $10^{16}$ cm$^{-3}$. The contact barrier depletion width was estimated at $W = 5 \times 10^{-4}$ cm with a maximum electric field of $2 \times 10^3$ V cm$^{-1}$. The polished samples were etched in a solution of HNO$_3$. The back ohmic contact was of diffused indium while the front rectifying contact was again a semitransparent gold film. Some care had to be taken not to overheat the front contact during soldering since this could very well remove the barrier. The photoresponse of these devices could only be checked at low temperatures (see Appendix C). The specimen was mounted in the Faraday configuration with $\mathbf{B} // [111]$. A Nernst filament was used as light source for the infrared and the 400 nmeter blaze grating easily allowed the use of a 0.3 mev resolution at a photon energy of 0.3 eV.
InSb-A Landau level analysis

A typical spectrum of the photoresponse in InSb in the presence of a magnetic field is presented in figure InSbF1. The figure is a reduced version (5) of the actual spectrum. The structures at high energy were assumed to be due to transitions between Landau levels. Spectra were obtained at every 0.5 tesla in the range 0 to 3 tesla and in the wavelength range of 540 nmeters to 380 nmeters. Following the arguments in the previous section on the pertinent positions of Landau level transitions, the energies of the maximum slope on the low energy side of the structures were taken as data and were plotted as functions of the magnetic field in figure InSbF2. By extrapolating the values of the points corresponding to Landau levels to zero magnetic field the band gap was found to be $E_g = 235.5$ meV, in agreement with Zwerdling et al.'s value of 235.7 meV (61Z1). The data of the lines 9 to 19 were considered as Landau levels and compared to the theoretical lines predicted by various sets of parameters for InSb found in the literature (table InSbT1). The Pidgeon and Brown parameters (66PL) gave the best fit to the data and the theoretical lines indicated in figures InSbF1 and InSbF2 are those obtained by this fit and are labelled in table InSbT2. Although the data for Landau levels of high quantum number were very well fitted, the lower energy structures differed in both their shape and position from the structures expected from Landau levels.
Figure InSbF1 - Spectral distribution of the photovoltage in a magnetic field of 3 Tesla. The indicated transitions are those predicted by the Pidgeon and Brown theory as labeled in table InSbT2.
Figure InSbF2 - Energy positions of oscillations as a function of magnetic field.
TABLE I
BAND PARAMETERS OF INDIUM ANTIMONIDE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_c/m_0)</td>
<td>0.0145</td>
<td>0.0145</td>
<td>0.0145</td>
<td>-</td>
<td>0.014</td>
</tr>
<tr>
<td>(\sigma_c)</td>
<td>-48</td>
<td>-48</td>
<td>-48</td>
<td>-</td>
<td>-48.4</td>
</tr>
<tr>
<td>(\lambda_1)</td>
<td>32.5</td>
<td>33.5</td>
<td>36.0</td>
<td>25</td>
<td>35.08</td>
</tr>
<tr>
<td>(\lambda_2)</td>
<td>14.3</td>
<td>14.5</td>
<td>14.5</td>
<td>10.5</td>
<td>15.64</td>
</tr>
<tr>
<td>(\lambda_3)</td>
<td>15.4</td>
<td>15.7</td>
<td>16.2</td>
<td>11.5</td>
<td>16.91</td>
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<tr>
<td>(\lambda_4)</td>
<td>13.4</td>
<td>13.5</td>
<td>-</td>
<td></td>
<td>14.76</td>
</tr>
<tr>
<td>(\sigma_d)</td>
<td>0.4</td>
<td>0.4</td>
<td>-</td>
<td></td>
<td>0.15</td>
</tr>
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</table>

A - Pidgeon and Brown (66Pl)
B - Pidgeon and Groves (69Pl)
C - Zwerdling et al. (6121)
D - Baguley et al. (63Bl)
E - Lawatzi, theory, (71L1)
TABLE InSbT2

Identification of the transitions in InSb (in the Pidgeon and Brown notation)

\[ \text{HH} (n) = \frac{\text{a}^-(n-1) \text{a}^c(n) \text{b}^-(n-1) \text{b}^c(n)}{2} \]

<table>
<thead>
<tr>
<th>No.</th>
<th>transition</th>
<th>No.</th>
<th>transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a^- (1) a^c (0)</td>
<td>11</td>
<td>HH (6)</td>
</tr>
<tr>
<td>2</td>
<td>b^- (1) b^c (0); b^- (-1) b^c (0)</td>
<td>12</td>
<td>HH (7)</td>
</tr>
<tr>
<td>3</td>
<td>a^+ (1) a^c (0); a^- (2) a^c (1)</td>
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<td>HH (8)</td>
</tr>
<tr>
<td>4</td>
<td>b^+ (0) b^c (1); b^- (2) b^c (1)</td>
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<td>HH (9)</td>
</tr>
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<td>5</td>
<td>a^- (3) a^c (2)</td>
<td>15</td>
<td>HH (10)</td>
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<tr>
<td>6</td>
<td>b^- (1) b^c (2)</td>
<td>16</td>
<td>HH (11)</td>
</tr>
<tr>
<td>7</td>
<td>a^- (4) a^c (3)</td>
<td>17</td>
<td>HH (12)</td>
</tr>
<tr>
<td>8</td>
<td>b^- (4) b^c (3); b^- (2) b^c (3)</td>
<td>18</td>
<td>HH (13)</td>
</tr>
<tr>
<td>9</td>
<td>HH (4)</td>
<td>19</td>
<td>HH (14)</td>
</tr>
<tr>
<td>10</td>
<td>HH (5)</td>
<td>20</td>
<td>HH (15)</td>
</tr>
</tbody>
</table>

TABLE InSbT3

Identification of transitions in InSb. Exciton states, following the notation of Altarelli and Lipari.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Spin</th>
<th>'L'</th>
<th>'n'</th>
<th>corresponding Landau edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>up</td>
<td>0</td>
<td>-3</td>
<td>b^- (1) b^c (0)</td>
</tr>
<tr>
<td>C</td>
<td>down</td>
<td>0</td>
<td>-3</td>
<td>b^+ (1) b^c (0)</td>
</tr>
</tbody>
</table>
InSb-B Exciton analysis

An expanded spectrum of the photovoltage in the energy region near the fundamental gap is presented in figure InSbF3. Except for the impurity absorption structure (I) below the gap, the zero magnetic field spectrum has no evident structure. The exciton is not resolved in this spectrum because of its low binding energy (0.45 meV). The photoresponse in a high magnetic field, where $\Theta_c \gg 1$, for example at 3 tesla in the above figure, does show well defined structures (labelled A, B, C). These structures differ from the expected structures for Landau levels in both their line shape (they are strong and sharp) and their positions (they are below the expected energy position). The structures were then taken to be exciton states associated with the lower Landau level edges and following the arguments presented for the case of InP (III section InP-A) the pertinent energies were taken to correspond to the maxima of the structures. The structures could be seen at the various magnetic field values studied and the energy positions of the maxima were plotted as a function of field in figure InSbF4. Using the various sets of band parameters (table InSbT1) the theoretical energies for exciton states were computed following the theory of Altarelli and Lipari (74Al) with the hamiltonian matrix for $\hat{\mathbf{B}} \parallel [11]$ developed in Appendix A. As in the case of the Landau level analysis the Pidgeon and Brown parameters
(66P1) again gave the best fit to the data and the predicted positions are represented in figure InSbF4 by the solid lines. These theoretical lines were seen to correspond to exciton states associated with the Landau level labelled \( b^+(1) b^-(0) \) and are labelled in the Altarelli and Lipari formalism as \( A \rightarrow \ell = 0, n = -3, \text{spin up}; \ C \rightarrow \ell = 0, n = -3, \text{spin down} \) (table InSbT3). The structure B was not yet identified. The structure I was identified as a transition originating from an acceptor impurity of the type reported by Johnson and Fan (65J1).
Figure InSbF3 - Expanded $V_{pv}$ spectrum for energies near the fundamental gap.

The structures are labeled according to table InSbT3. 'I' is a transition associated with an impurity level.
Figure InSbF4 - Fan diagram for the structures observed in fig. InSbF3.
InSb-C Impurity structure

The theory for the behaviour of impurity transitions in a magnetic field has been reviewed by Johnson (67W1). Structures corresponding to these impurity transitions should occur at a photon energy
\[ h\nu = E_g - E_A + \varepsilon_c(H) + \varepsilon_A(H) \]  

where \( E_A \) is the acceptor ionization energy in the absence of magnetic field, \( \varepsilon_c(H) \) is the shift of the lowest Landau level (\( n = 0 \)) of the conduction band, and \( \varepsilon_A(H) \) is the shift of the impurity levels in a magnetic field. For low magnetic field values, when \( \varepsilon(H) \ll E_g \), the shift of the lowest Landau level of the conduction band can be expressed as

\[ \varepsilon_c(H) \approx \left( \frac{m_e}{m_c} \pm \frac{1}{2} g_c \right) B H \left| 1 - \frac{m_e}{m_c} \pm g_c \right| \]

where \( B \) is the Bohr magneton.

The magnetic field induced energy shift of the acceptor state, \( \varepsilon_A(H) \), includes both the Zeeman splitting and diamagnetic shift; but because of the high effective mass of the state, the contribution of \( \varepsilon_A(H) \) should be small and can be neglected. The theoretical line I in figure InSbP4 was computed using equation InSbE1 and InSbE2 with

\[ m_c = 0.0145 \, m_e, \, g_c = -48, \, \text{and} \, E_g = 235.5 \, \text{meV} \] (Table InSbT1). The fit predicts an extrapolated acceptor ionization energy of 5.4 meV.

The above calculation has assumed that the structure observed
is due to a free state of the electron in the conduction band. The curvature of the points at low magnetic field however suggest that Coulomb interaction between the hole in the acceptor state and the electron in the conduction band should not be neglected and that the structure I corresponds to a bound state of the electron-hole pair. In this case the photon energy required for absorption is written as

$$h\nu = E_g + E_C - R(H) - E_A$$  \[\text{InSbE3}\]

where $R(H)$, the exciton binding energy as a function of magnetic field, was estimated following the calculations by Yafet (56Y1) with $R(0) = 0.7$ meV. Using equation InSbE3 the acceptor ionization energy which fits the data is calculated to be $E_A = 2.8$ meV, a value identical to that reported by Vinogradova et al. (64V1). The theoretical line predicted by equation InSbE3 is represented in figure InSbF4 by the dashed line.

\[\text{InSb-D Discussion}\]

The band parameters proposed by Pidgeon and Brown for InSb were seen to give the best fit to both the Landau level behaviour and the exciton states behaviour in a magnetic field. It is indeed pleasing to find that with these parameters most of the structures observed in the spectra can be identified. On the other hand, as previously
pointed out, peak B of figures InSbF3 and InSbF4 has yet to be explained and should be subject to further investigation.

The power of the photovoltaic effect as a method of observing weak variations in the absorption coefficient was again demonstrated in the case of the impurity level absorption. In the light of this and of the previous success of the method with Ge and InP preliminary studies were done on GaAs.

4  GALLIUM ARSENIDE

Gallium arsenide has recently been under extensive research by industry and others for its application in electronic and optical devices. The determination of its band parameters and optical properties is thus of major importance. Interband magneto-optical studies have not as yet proven very successful in this respect because of both experimental and theoretical difficulties. The most recent research and analysis of the Landau levels in GaAs has been done by Ureken (68V1) who had to use an empirical correction to analyse his data. More recently Reine (70R1) had obtained very good spectra of magneto-optical structures in GaAs; he did not however attempt to analyze his results. On the other hand many authors, including Willmann et al. (73W1) and Evangeliste et al. (73El) have recently investigated the properties of exciton states in GaAs. Since the
photovoltaic signal of Au-GaAs Schottky barriers were usually found to be strong and largely noise free, we have made an attempt to observe and analyze magneto-optical structures in GaAs. The following is a report on the preliminary results which were obtained on the few samples we had.

The samples were cut from a monocrystalline block of n-type GaAs with a carrier concentration of $5 \times 10^{15}$ cm$^{-3}$. The specimens were polished with Al$_2$O$_3$ powder and etched in a solution of HF:4HNO$_3$. The back surface ohmic contact was of diffused indium and the front surface rectifying contact was a semitransparent gold film. The sample was mounted, as usual, in the Faraday configuration with $\mathbf{B} // [111]$.

GaAs-A Landau levels and excitons.

Typical spectra of the photovoltage and its wavelength-modulated derivative in the presence of a magnetic field are presented in figure GaAsF1. On the direct $V_{pv}$ spectrum the 1s exciton peak is quite pronounced however the magneto-optical structures above the gap are small in comparison with the background signal. These same structures, on the other hand, are readily visible on the $\Delta V_{pv}$ spectrum. The energies of the maxima of $\Delta V_{pv}$ for high quantum number were plotted as a function of magnetic field in figure GaAsF2. A fit was done of these points which were assumed to correspond to Landau level structures. Because of the
Figure GaAsFl - The spectral distribution of the photovoltage and its wavelength modulated derivative for R.C.P. light. The indicated transitions are labeled according to table GaAsT2.
Figure GaAsF2 - Energy positions of the magneto-optical structures as a function of magnetic field. The full lines are the predicted transitions for Landau level. The dashed lines are the predicted positions for exciton states empirically calculated following Vreven. The transitions are labeled in Table GaAsT2.
small number (50) of points and of their dispersion a method of indirectly estimating the band parameters had to be used. In this method the contours of the r.m.s. deviation between the experimental points and the values predicted by the Pidgeon and Brown theory were plotted as a function of the band parameters $m_c$, $\gamma_3^L$, and $\gamma_1^L$. For example, figure GaAsF3 shows a contour graph for $m_c = 0.067 m_0$ where $\gamma_3^L$ and $\gamma_1^L$ are varied. The final parameters for GaAs were taken to be those parameters which best describe the central position of the contour lines on the accumulated graphs. The parameters in this case were estimated as $m_c = 0.067 \pm 0.002 m_0$, $\gamma_1^L = 7.14 \pm 0.1$, and $\gamma_3^L = 2.7 \pm 0.1$. These parameters and the others necessary for the fit are given in table GaAsT1. The theoretical lines derived by using the parameters in the Pidgeon and Brown theory are shown in figure GaAsF1 and GaAsF2 where the labelling is as in table GaAsT2.

The dashed lines also seen in the above figure were calculated using the method suggested by Vrehen (68V1) explained in section 2 of Chapter 1. The band gap value $E_g = 1.526$ eV was obtained by extrapolating the Landau levels to zero magnetic field. This value agrees with the values of $E_g = 1.521$ eV reported by Sturge (62St1) and $E_g = 1.5205$ reported by Gilleo et al. (68Gl1). The exciton energy $E_x = 1.516$ eV in the absence of magnetic field agrees well with the value of 1.515 eV of Willmann et al. (74Wl1).
Figure GaAsP3 - An example of the contours of the deviation between experimental values and the theoretically predicted values. In this case both $\gamma_3^L$ and $\gamma_3^L$ are varied while $m_c=0.067 M_\odot$ is kept constant. The central position of the contours gives $\gamma_3^L=7.14\pm0.1$ and $\gamma_3^L=2.74\pm0.1$. 
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<th>Parameter</th>
<th>Present work</th>
<th>Others</th>
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<td>$m_e/m_o$</td>
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<td>0.0665</td>
</tr>
<tr>
<td></td>
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<td>0.067</td>
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<td></td>
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</tr>
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<td></td>
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<td>6.8</td>
</tr>
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<td>3.4</td>
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<td></td>
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<td>3.3</td>
</tr>
</tbody>
</table>

a - Stillman et al. (69S2)
b - Vrehen (68V1)
c - Chamberlain and Stradling (69C2)
d - Stradlig (68S1)
### Table GeAsTe2

**Identification of transitions in Gallium arsenide**

**R.C.P.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Landau notation</th>
<th>type of transition</th>
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<td>$a^-(1)a^+(0)+b^-(1)b^+(0)$</td>
<td>Ex.</td>
</tr>
<tr>
<td>2</td>
<td>$a^-(2)a^+(1)+b^-(2)b^+(1)$</td>
<td>Ex.</td>
</tr>
<tr>
<td>3</td>
<td>$a^+(1)a^-(0)$</td>
<td>L.</td>
</tr>
<tr>
<td>4</td>
<td>$b^+(1)b^-(0)$</td>
<td>Ex.</td>
</tr>
<tr>
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<td>$b^+(1)b^-(0)$</td>
<td>L.</td>
</tr>
<tr>
<td>6</td>
<td>$a^+(3)a^-(2)$</td>
<td>L.</td>
</tr>
<tr>
<td>7</td>
<td>$a^-(4)a^+(3)+b^-(4)b^+(3)$</td>
<td>Ex.</td>
</tr>
<tr>
<td>8</td>
<td>$b^+(2)b^-(1)$</td>
<td>L.</td>
</tr>
<tr>
<td>9</td>
<td>$a^+(3)a^-(2)$</td>
<td>L.</td>
</tr>
<tr>
<td>10</td>
<td>$b^+(3)b^-(2)$</td>
<td>L.</td>
</tr>
<tr>
<td>11</td>
<td>$a^+(4)a^-(3)$</td>
<td>L.</td>
</tr>
<tr>
<td>12</td>
<td>$b^+(4)b^-(3)$</td>
<td>L.</td>
</tr>
</tbody>
</table>
GaAs-B Impurity absorption

The photoresponse at room temperature and just below theFundamental edge is shown in figure GaAsP4. The structure peaked at approximately 50 meV below the gap was identified as originating from impurity absorption. This structure corresponds well with the peak observed in emission in Zn-doped GaAs by Nathan and Burns [62NL] and in absorption by Sturges [62SL]. The impurity absorption which originates from an ionized acceptor level did not appear at low temperatures and, as a consequence, its behaviour in the presence of a magnetic field could not be observed with our present equipment.

GaAs-C Optical phonon participation

In photoconductivity and the photoelectromagnetic effect, spectral oscillations originating from longitudinal optical phonon participation to the transport processes have previously been observed (Filion, 73F1, Barbarie 74B1) and explained in terms of a model proposed by Habegger and Fan [64H1].

Because of the high signal-to-noise ratio of the photosignal in GaAs, the signal could be amplified and offset to such an extent that these same oscillations, with an amplitude of 1/50 of the basic signal, could also be observed. A spectrum where this has been done is presented in figure GaAsS5. The energy position of the minima of the
oscillations were plotted as a function of energy in figure GaAsF6. A slope of 40.6 meV/N was calculated and using (6SN1)

\[ E_n = E_g + n\hbar \omega (1 + \frac{m_e}{m_{hh}}) \]

for the energy positions of the minima, with \( m_e/m_{hh} = 0.153 \) (table GaAsTl). The L.O. phonon energy was found to be 35.6 meV. This value agrees with the value of 36.8 meV obtained by Mooradian (66M2) and the value of 36.2 calculated from Barbarie (74B2).

**GaAs-D Discussion**

The analysis of these preliminary results on GaAs indicate that the results obtained here are comparable to those obtained by Vreken (68V1). However, the use of the photovoltaic effect for observing magneto-optical structures in GaAs has not to this point been optimized and further research, with specimens of high purity for example, should indeed be profitable. The present work could also be extended to study the behaviour of the acceptor impurity level with temperature and in a magnetic field.
Figure GaAsP5 $-V_{pv}$ spectrum showing phonon participation. 'A' is the direct $V_{pv}$ signal amplified by 10 and offset. 'B' is the average signal. 'C' is the difference between A and B.
Figure GaAsF6 - Energy positions of the minima of the oscillations as a function of the phonon order number. The slope of the line is of 40.6 meV/N. The intercept gives a band gap value of 1.522 eV.
CONCLUSION

The above study of the interband magneto-optical properties of Ge, InP, InSb, and GaAs has shown that the photovoltaic effect and its wavelength derivative can be powerful methods for observing very small variations in the optical properties of semiconductors. A first indication of the success of the method are the prominent noise free structures observed in the spectra. Secondly, and of greater importance, the band parameters of the semiconductor could be determined with some degree of confidence. Finally the observation of other phenomena such as impurity absorption and excitons shows that the method is comparable to if not better than absorption or reflection techniques.

The main advantages of the photovoltaic effect for studies in magneto-optics are the simplicity of sample preparation, the sample size itself, and finally the fact that it acts as its own detector. The samples can be made quickly and efficiently. The contacts which cover most of the surface of the specimen eliminate the necessity of protecting the samples against oxidation or other reactions with the atmosphere. The sample size reduces the effects of strain and stress, a major problem in the absorption techniques where very thin samples are required. In addition, specimens can be made out of very small chips of the semiconductor when large crystals are difficult to obtain. The actual detection depth, approximately the depletion barrier width, allows the data to be interpreted in a fashion similar to the data obtained in absorption
techniques. Finally the fact that the sample is its own detector excludes the problem of finding other good noise free detectors which could be used in the spectral region of interest.

Germanium served well as a test sample in this study. The high signal to noise ration displayed by the samples and the observation of well defined magneto-optical structures in its photoresponse indicated that the use of the photovoltaic effect would indeed be advantageous. The analysis of the magneto-optical results demonstrated that the maxima of the derivative of the P.V. signal should be considered as pertinent data. Excitonic participation is also seen in the spectra. Further investigation in the magneto-optical effects in germanium could involve combining wavelength modulation with the P.V effect to observe the behaviour of exciton states in a magnetic field as well as the behaviour of Landau levels of very high quantum numbers.

The first analysis of the interband magneto-optical structures observed in InP is reported. Some of the band parameters, \( m_e \) and \( m_h \), compare favourably with those obtained by cyclotron resonance. Exciton participation is very evident in the spectra and the data for Landau levels of lower quantum number are empirically corrected for this effect following Vreken's (68V1) suggestion. The band parameters are confirmed in the behaviour of the split-off transition as a function of magnetic field. The high precision on the position of the 1s exciton peak permits the observation of the excitons behaviours as a function of magnetic field and temperature. Considering the high signal to noise ratio of the signals in both the photovoltaic effect and its wavelength
derivative, future work could be done on the behaviour of the exciton states in low magnetic field or on the Landau levels associated with the split-off transition.

The spectra in InSb clearly showed structures which could be associated with Landau levels and structures which could be associated with exciton states. From the analysis of the behaviour of both these types of structures we concluded that the Pidgeon and Brown (66Pl) parameters for InSb gave the best description of the magneto-optical data. The observation of the behaviour of an impurity peak in a magnetic field again confirms the strength of the method used here. Research on InSb could be extended even further by observing the very high quantum number Landau levels. This would permit a rigorous test of the Pidgeon and Brown theory for the effects of upper bands on the conduction band. In addition more information about exciton states could be obtained by specifically studying the magneto-optical structures near the fundamental edge.

The preliminary results on GaAs show the complexity in the determination of the origins of magneto-optical structures. The analysis of the results was the first attempted since the work done by Vrehen (68Vi). The experimental results are comparable to Vrehen's, however a great improvement of these results can probably be made by finding the correct samples to be used. Finally a great deal of theoretical and experimental work has recently been done to analyze the behaviour of the 1s exciton in a magnetic field, further research of this pheno-
menon would eventually result in a solution for the exciton states at intermediate magnetic fields.

Finally, the recent studies of the photovoltaic effect of other compounds (e.g.: MoS$_2$, WSe$_2$, GaSe, GaS, Cu$_2$O, and HgI$_2$) have shown that a great deal of information can still be obtained by this method. Furthermore, preliminary results have been obtained for the magneto-optical properties of the III-V alloys (e.g.: Ga$_x$In$_{1-x}$Sb) by A. Roth, a member of our group, who has found the photovoltaic effect to be advantageous in this research.
APPENDIX A  EXCITON STATES IN A MAGNETIC FIELD $\vec{B} // [111]$ 

Altarelli and Lipari (74Al) have developed the theory for exciton states of diamond and zinc-blende type semiconductors in high magnetic fields for the cases $\vec{B} // [110]$ and $\vec{B} // [001]$. The hamiltonians are expressed in terms of $4 \times 4$ matrices. The following is the development of the matrix for $\vec{B} // [111]$. This matrix was required to analyze the results in InSb (Chapter III).

The hamiltonian for exciton states in the presence of a magnetic field $\vec{B}$ is written as, using the gauge $A = \frac{1}{2}(\vec{A} \times \vec{F})$,

$$
\mathcal{H} = \mathcal{H}_0 \left( -i \nabla + \frac{e}{2\hbar c} (\vec{H} \times \vec{F}) \right) - \frac{e^2}{\varepsilon \rho}
$$

where $\vec{A}$ is the vector potential describing the field $\vec{H}$, and $\varepsilon$ is the static dielectric constant. The explicit expressions for the conduction and valence band hamiltonians are:

$$
\mathcal{H}_c(\vec{k}') = \frac{\hbar^2}{2m_e} \vec{k}'^2 + \vec{p} \cdot \vec{\sigma} \cdot \vec{H}
$$
and (Dimmock 67W1)

\[- \mathcal{H}_A (k') = \frac{e^2}{m_c} \left( (\gamma_1 + \frac{e}{2} \gamma_2) \frac{\dot{k}^2}{2} - \gamma_3 \left( k_x^2 \vec{J}_x + k_y^2 \vec{J}_y + k_z^2 \vec{J}_z \right) \right) \]

\[- 2 \gamma_3 \left( k_x \vec{J}_x \vec{J}_y + k_y \vec{J}_y \vec{J}_z + k_z \vec{J}_z \vec{J}_x \right) \]

\[- \frac{e}{c} \times \vec{J} \cdot \dot{\vec{H}} - \frac{e}{c} \vec{g} \left( \vec{J}_x \vec{H}_y + \vec{J}_y \vec{H}_z + \vec{J}_z \vec{H}_x \right) \]

where \( \gamma_1, \gamma_2, \gamma_3, k \) and \( q \) are the five valence band parameters introduced by Luttinger (56L1). In equation A12, \( m_c \) is the conduction band effective mass and \( \vec{m}^* \) is the effective magnetic moment of the conduction band; in equation A13 \( m_0 \) is the free-electron mass, \( \vec{J}_x, \vec{J}_y \)

\( \vec{J}_z \) are the 4 x 4 angular momentum matrices corresponding to a spin 3/2 state, and, following Luttinger

\[ \vec{J}_A \equiv \frac{1}{a} \left( k_i \vec{J}_i + k_j \vec{k}_j \right) \]

where \( k_j \) is a pseudo-momentum operator.

The \( x, y, z \) directions above were selected to be the cubic crystal axes [100], [010], [001]. A new cubic coordinate system \( u, v, w \) is defined with the magnetic field in the \( w \) direction. For \( w \) in the [111] direction the new coordinate system can be written in terms of the \( x, y, z \) coordinates as...
\[ \vec{u} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix} \]

\[ \vec{v} = \frac{1}{\sqrt{6}} \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix} \]

\[ \vec{w} = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \]

The pseudo-momentum operators of equation AL2 and AL3 can now be expressed in terms of the pseudo-momentum operators in the new coordinate system as

\[ k_\lambda = \frac{1}{\sqrt{3}} k_u + \frac{1}{\sqrt{2}} k_\sigma + \frac{1}{\sqrt{2}} k_w \]

\[ k_\sigma = \frac{1}{\sqrt{2}} k_u + \frac{1}{\sqrt{2}} k_\sigma + \frac{1}{\sqrt{3}} k_w \]

\[ k_\omega = -\sqrt{\frac{2}{3}} k_\sigma + \frac{1}{\sqrt{3}} k_w \]

For the angular momentum matrix representation \( \vec{J}_u, \vec{J}_v, \vec{J}_w \) we take

\[ \vec{J}_u = \begin{pmatrix} 0 & 0 & \frac{1}{2} \sqrt{3} i & 0 \\ 0 & 0 & -i & \frac{1}{2} \sqrt{3} i \\ -\frac{1}{2} \sqrt{3} i & i & 0 & 0 \\ 0 & -\frac{1}{2} \sqrt{3} i & 0 & 0 \end{pmatrix} \]
The products of the type $k_{ij}^2 J_{ij}$, $k_{ij} J_{ij}$ can now be easily obtained from equation AL6 and AL7. After some lengthy but straightforward calculations we write the Hamiltonian for the hole contribution (AL6) in the $u, v, w$ coordinates as:

$$H_h(k) = \frac{\hbar^2}{m_0} \left( (\gamma + \frac{5}{2} \chi) \frac{p^2}{2} - \nabla \left( k_u J_u + k_v J_v + k_w J_w \right) \right)$$
$$- \frac{2}{3} \left( 3 \nabla - \delta \right) \left( k_u v J_{uw} + k_v w J_{vw} + k_w v J_{vw} \right)$$
\[
\begin{align*}
&+ \frac{5}{3} (-4 \kappa_{\omega} \mathcal{J}_{\omega} + \kappa_{\omega}^2 \mathcal{J}_{\omega}^2 + \kappa_{\omega}^2 \mathcal{J}_{\omega}^3 + \kappa_{\omega}^2 \mathcal{J}_{\omega}^4 + \kappa_{\omega}^2 \mathcal{J}_{\omega}^5 \\
&+ \kappa_{\omega} \mathcal{J}_{\omega}^2 + 2 \kappa_{\omega} \mathcal{J}_{\omega} \mathcal{J}_{\omega}^2 + 2 \kappa_{\omega}^2 \mathcal{J}_{\omega}^3 + 2 \kappa_{\omega}^2 \mathcal{J}_{\omega}^4 \left( \kappa_{\omega} \mathcal{J}_{\omega}^2 - \kappa_{\omega} \mathcal{J}_{\omega} \right) \\
&- \kappa_{\omega} \mathcal{J}_{\omega}^2 - 4 \mathcal{J}_{\omega} \left( \kappa_{\omega} \mathcal{J}_{\omega} - \kappa_{\omega} \mathcal{J}_{\omega} \right) \\
&+ \frac{2 \sqrt{2}}{9} \left( \tilde{Y} - 2 \tilde{\delta} \left( \kappa_{\omega}^2 \mathcal{J}_{\omega} - \kappa_{\omega}^2 \mathcal{J}_{\omega} \right) \right)
\end{align*}
\]

where \( \tilde{Y} = \frac{Y_2 + Y_3}{2} \) and \( \tilde{\delta} = \frac{Y_3 - Y_2}{2} \)

In order to obtain the matrix elements, new operators \( k_+ \) and \( k_- \) are defined as

\[
\begin{align*}
k_+ &= k_0 - i k_\omega \\
\end{align*}
\]

Following Rees (72RL), Altarelli and Lipari wrote the eigenfunctions of the exciton states as

\[
\psi_{\mathbf{k} \ell} (\mathbf{r}, \omega) = \begin{pmatrix}
h_1 (\omega) | m, \ell \rangle \\
h_2 (\omega) | m, \ell \rangle \\
h_3 (\omega) | m, \ell \rangle \\
h_4 (\omega) | m, \ell \rangle
d\end{pmatrix}
\]
which are eigenfunctions similar to those of the Landau problem. These authors also determine the effects of the operators \( k_+ \), \( k_- \), and \((x_u^2 + k_v^2 + 2L_w)\) on the states \(|n, l\rangle\):

\[
\begin{align*}
\hat{k}_+ |n, l\rangle &= (2\gamma)^{1/2} |n\rangle^{1/2} |n-1, l+1\rangle \quad l > 0 \\
\hat{k}_- |n, l\rangle &= (2\gamma)^{1/2} (m-l) |n\rangle^{1/2} |n, l+1\rangle \quad l < 0 \\
\hat{k}_- |n, l\rangle &= (2\gamma)^{1/2} (m-l) |n\rangle^{1/2} |n, l+1\rangle \quad l > 0 \\
\hat{k}_+ |n, l\rangle &= (2\gamma)^{1/2} (m-l) |n\rangle^{1/2} |n, l+1\rangle \quad l \leq 0
\end{align*}
\]

\[
\begin{align*}
\hat{k}_u^2 + \hat{k}_v^2 + 2\gamma \omega \hat{L}_w |m, l\rangle &= \gamma (2m + 2l + 1) |m, l\rangle \quad l > 0 \\
\hat{k}_u^2 + \hat{k}_v^2 + 2\gamma \omega \hat{L}_w |m, l\rangle &= \gamma (2m + 1) \frac{|m\rangle}{m_0} \quad l \leq 0
\end{align*}
\]

where \( \gamma \) is the "reduced field" defined as

\[
\gamma = \frac{\epsilon \mathbf{A}}{2\mu_0 c R_0}
\]

In the following a new set of mass parameters (74A) will be used with

\[
\frac{1}{\mu_0} = \frac{\gamma_1}{m_0} + \frac{1}{m_c}
\]

\[
\frac{1}{\mu_1} = \frac{\gamma_2}{m_0}
\]
\[ \frac{1}{\mu_2} = 2 \sqrt{3} \frac{\gamma_2}{m_0} \]
\[ \frac{1}{\mu_1} = \frac{1}{m_c} \left( \gamma_1 + \gamma_2 \right) \]
\[ \frac{1}{\mu'_1} = \frac{1}{m_c} \left( \gamma_1 - \gamma_2 \right) \]
\[ \frac{1}{\mu'_2} = \frac{1}{m_c} \frac{\gamma_2}{m_0} \]
\[ \frac{1}{\mu_3} = \frac{1}{m_c} \frac{\gamma_2 - \gamma_3}{m_0} \]

and the effective units will be adopted: i.e.

\[ R_0 = \frac{\mu_0 e^4}{2 \hbar^2 \varepsilon^2} \quad \alpha_0 = \frac{\hbar^2 \varepsilon}{\mu_0 e^2} \]

as units of energy and length respectively. We can now calculate the explicit terms for the matrix representation of the Hamiltonian. For example consider the term \((1,1)\) where the numerical values for the J-matrices are computed.

\[ (1,1) = \frac{k^2}{2m_e} \frac{1}{m_0} \left( \gamma_1 + \frac{\gamma_2}{2} \right) \frac{k^2}{2} - \gamma \left( \frac{3}{4} k^2 + \frac{3}{4} k^2 + \frac{3}{4} k^2 + \frac{3}{4} k^2 \right) \]
\[
\frac{5}{3} \left( -\frac{9}{4} k_{\omega}^2 + \frac{3}{4} k_{\gamma}^2 + \frac{3}{4} k_{\mu}^2 + \frac{5}{4} k_{\nu}^2 + \frac{5}{2} k_{\mu}^2 + \frac{1}{2} k_{\nu}^2 \right) + \frac{3 \sqrt{5}}{4} \left( k_{\mu} - k_{\nu} \right) - \frac{e}{\sqrt{\gamma}} \left( \Delta \kappa + 2 \beta \zeta \right)
\]

\[
\frac{1}{2} \left\{ \frac{\mu \times \nu}{\sqrt{\gamma}} - \frac{e}{\sqrt{\gamma}} \right\}
\]

In (1,1) operators like \( k_{\mu}^2, k_{\nu}^2, k_{\mu}, k_{\nu} \), and therefore, \( k_{\mu \nu} = \frac{1}{4i} (k_{\mu}^2 - k_{\nu}^2) \) and \( k_{\mu \nu} = \frac{1}{2}(k_{\mu} - k_{\nu}) \) \( k_{\mu} \), will not contribute to the energy. Therefore,

\[
(1,1) = \frac{\kappa_{\omega}^2}{2m_\omega} \left( \left[ \gamma_\omega + \frac{3}{2} \gamma_\omega \right] \frac{\kappa_{\omega}}{2} - \frac{1}{i} \left( s_{\omega} - \gamma_\omega \right) \left( \kappa_{\omega} + \kappa_{\omega}^* \right) \right)
\]

\[
- \frac{1}{4} \left( s_{\omega} - \gamma_\omega \right) \kappa_{\omega}^2 - \frac{e}{\sqrt{\gamma}} \left( 3 \kappa_{\mu} + 2 \beta \zeta \right) \left( \frac{\mu \times \nu}{\sqrt{\gamma}} - \frac{e}{\sqrt{\gamma}} \right)
\]

and expanding and transforming to effective units with

\[
\kappa_{\omega} = \frac{\kappa_{\omega}}{\Delta \kappa}, \quad \kappa_{\mu} = \frac{\kappa_{\mu}}{\Delta \kappa}, \quad \kappa_{\nu} = \frac{\kappa_{\nu}}{\Delta \kappa}, \quad \kappa_{\omega} = \frac{\kappa_{\omega}}{\Delta \kappa}
\]

we obtain, after some manipulation,

\[
(1,1) = \left( \frac{\mu_{\omega} + 2 \mu_\omega}{\mu_\omega} \right) \left( \kappa_{\mu}^2 + \kappa_{\nu}^2 + 2 \gamma \kappa_{\omega} \right)
\]

\[
- 2 \gamma \left( \frac{\mu_\omega + 2 \mu_\omega}{\mu_\omega} \right) \kappa_{\omega}
\]
\[
\begin{align*}
+ \left( 1 - 2\frac{\mu_a^0}{\mu} - \frac{3\mu_a^0}{\mu^2} \right) \bar{\rho}_i^2 \\
- \frac{\mu_0}{m_0} \left( 3 \gamma + \frac{2 \gamma}{\gamma} \delta \right) \\
\end{align*}
\]

This process is continued for each term of the matrix the final product being given in table ALT1. The solution of this problem now consists of applying the adiabatic method for the degenerate-band case. Altarelli has generously provided us with a copy of his computer program which applies the method to the matrix for the [\(110\)] direction. Our work was greatly simplified from then on since we only had to rewrite the program including the new matrix elements of table ALT1 for the [\(111\)].
TABLE A11

MATRIX ELEMENTS FOR EXCITON STATES \( \bar{E} // [111] \)

\[
\begin{array}{cccc}
A-B-C & Fk^2 & -Gk P_w & 0 \\
+D+E & & & \\
Fk^2 & M-N-P & 0 & Gk P_w \\
+D+E & & & \\
Gk P_w & 0 & M-N-P & Fk^2 \\
+D+E & & & \\
0 & -Gk P_w & Fk^2 & A-B+C \\
+D+E & & & \\
\end{array}
\]

\[
A = \left( \mu \frac{2 \mu_0}{\mu_L} \right) \left[ \frac{K_u^2}{\mu} + \frac{K_v^2}{\mu} + 2 \sqrt{L} \right] \\
B = \left( \mu_0 + \frac{2 \mu_0}{\mu_L} \right) \left( 2 \sqrt{L} \right) \\
D = \left( \frac{1}{2} - \frac{5 \mu_0}{\mu_L} \right) \frac{2}{\mu} \\
C = \frac{\mu_0}{m_0} \left( 3 \sqrt{L} + 23 \right) \\
E = \frac{1}{2} \sqrt{\frac{1}{\mu_L}} - 2 \\
F = \sqrt{\frac{5 \mu_0}{3 \mu_s} + \frac{3 \mu_0}{3 \mu_5}} \\
G = \frac{2 \mu_0}{3} \left( \frac{\mu_0}{\mu_L} - \frac{\mu_0}{\mu_s} \right) \\
M = \frac{\mu_0}{\mu_5} \left( \frac{K_u^2 + K_v^2}{\mu} + 2 \sqrt{L} \right) \\
N = \frac{4 \mu_0}{\mu_5} - \frac{2 \mu_0}{m_0} \sqrt{L} \\
P = \frac{\mu_0}{m_0} \frac{1}{4} (-13 + q) \\
\]

\[
\]

\[
\]
APPENDIX B  THE CORRESPONDENCE BETWEEN STRUCTURES OBSERVED FOR THE
PHOTOVOLTAIC EFFECT AND STRUCTURES IN THE ABSORPTION
COEFFICIENT

We recall that the expression for the photovoltage (in Chapter
I section B) was given as

\[ V_{pv} = \frac{kT}{Q} \ln \left( \frac{Q \cdot \frac{d}{\omega}}{S} \frac{1 - \exp(-\alpha \omega)}{1 + \alpha \cdot \frac{L}{\rho}} \right) \]  \hspace{1cm} (P13)

It can now be easily shown that the maxima (minima, inflection point)
in the absorption coefficient correspond to maxima (minima, inflection
point) in the photovoltage \( V_{pv} \). For example if \( \alpha \) is a maximum at a
photon frequency \( \gamma \), then

\[ \frac{d\alpha}{d\gamma} = 0 \]

and

\[ \frac{d^2\alpha}{d\gamma^2} < 0 \]

For the photovoltage we obtain:

\[ \frac{dV_{pv}}{d\alpha} = \frac{dV_{pv}}{d\gamma} \frac{d\alpha}{d\gamma} = 0 \quad \text{since} \quad \frac{d\alpha}{d\gamma} = 0 \]
and
\[ \frac{d^2 v_{pv}}{d v^2} = \frac{d}{d v} \left( \frac{d v_{pv}}{d \alpha} \frac{d \alpha}{d v} \right) \]

\[ = \frac{d v_{pv}}{d \alpha} \frac{d^2 \alpha}{d v^2} + \frac{d^2 v_{pv}}{d v d \alpha} \frac{d \alpha}{d v} \]

The second term is zero since \( \frac{d \alpha}{d v} = 0 \). To show that \( v_{pv} \) is a maximum, we must show
\[ \frac{d^2 v_{pv}}{d v^2} < 0 \]

or

since \( \frac{d^2 \alpha}{d v^2} < 0 \) we must show \( \frac{d v_{pv}}{d \alpha} > 0 \).

From P13 we get
\[ \frac{d v_{pv}}{d \alpha} = \frac{k_T}{c_0} \left( \frac{\sigma \phi}{c_0} \left( 1 - \frac{\exp(-\alpha w)}{1 + \alpha l_p} \right) \right) \]

\[ \left( \frac{\sigma \phi}{c_0} \left( \frac{w \exp(-\alpha w)}{1 + \alpha l_p} + \frac{l_p \exp(-\alpha w)}{(1 + \alpha l_p)^2} \right) \right) \]

> 0

because all the parameters are positive.

Therefore \( v_{pv} \) is a maximum when \( \alpha \) is a maximum. Similarly

\( v_{pv} \) is a minimum (inflection point) when \( \alpha \) is a minimum (inflection point).
APPENDIX C  THE PHOTOVOLTAGE AS A FUNCTION OF TEMPERATURE
(CASE OF InSb).

In order to get some understanding of the effects of temperature on a P.V. detector one must keep in mind the mechanisms at work. The photovoltaic detector is frequently analyzed in terms of an equivalent circuit including an external load resistance $R_L$ (Sulte 6081) as represented in figure (PT1). The effect of radiation is represented by a constant current generator $i_L$, $Z$ is a non-linear impedance; $R_b$ is the shunt resistance of the barrier layer; $R_s$ is the resistance of the body of the sample, and $V_{PV}$ is the measured photovoltage. Variations in any of the parameters ($i_L$, $Z$, $R_b$, $R_s$) as a function of temperature can play an important role in determining whether or not the detector can be used over a wide temperature range. We have already reported the influence of thermal changes on the P.V. detectors made of CuGaS$_2$ (75R1) and of Cu$_2$O (75F1). In the following development we will consider the behaviour of the photovoltage in InSb as a function of temperature.

For the case of InSb, the bulk resistance $R_b$ will be considered to always be much smaller than the load resistance and its temperature dependence will be neglected. The behaviour of the P.V. detector is determined firstly by the thermal behaviour of the current source $i_L$, and secondly by the thermal behaviour of the impedances $Z$ and $R_b$ which
Figure PTF1 - Equivalent circuit for a photovoltaic detector.

The effect of the light is represented by a current source $i_L$. The impedances $Z$ and $R_b$ shunt the source. The bulk resistance of the sample is $R_s$. $R_L$ is the input impedance of the measuring instrument and $V_{pv}$ is the signal measured.
are in parallel with the load resistance $R_L$. The behaviour of the current source is almost completely determined by the height of the barrier itself. In the following we shall show that the barrier height, and therefore the current source, changes little from 60K to 300K. We shall then show that the behaviours of $Z$ and $R_D$ as a function of temperature are at the origin of the large variation observed in $V_{pv}$.

Let us consider the barrier itself. We recall that the barrier heights of metal-semiconductor contacts are usually determined by both the metal's work function and the presence of surface states on the semiconductor. However, the barrier for a gold-InSb contact, neglecting surface states, is calculated to be very small. This can be seen in equation (4.4) (Chapter I, section B) assuming that the electron affinity of InSb is $\chi = 4.59$ eV (72M1) and that gold's work function is $\phi_m = 4.56$ eV (72M1). In the following development, we shall therefore assume that the barrier is due to the presence of surface states only.

In order to evaluate the barrier height and its associated depletion width, the abrupt junction approximation (69sl) will serve as model. The surface states are considered to have accepted the electrons that were in the conduction band due to the presence of ionized donors near the surface. A space charge is therefore created. Overall charge neutrality is required and this condition can be expressed as

$$\int_0^W \left( n_0 - n(x) \right) - \left( \phi_e - p(x) \right) \, dx = n_s$$
where \( n_0 \) and \( p_0 \) are the electron and hole densities respectively when no barrier is present. The position dependent terms \( n(x) \) and \( p(x) \) are the electron and hole densities respectively near the surface in the presence of the barrier. The electron density in the surface states is given by \( n_s \). The above quantities can also be written as

\[
\begin{align*}
\text{n}(x) &= N_c \chi \psi \left( \frac{E_F(x)}{kT} \right) \quad \text{PT2} \\
\text{p}(x) &= N_v \chi \psi \left( -\frac{E_F(x)}{kT} \right) \quad \text{PT3} \\
\text{and} \\
\frac{n_s}{N_s} &= \frac{N_c}{1 + \frac{1}{2} \chi \psi \left( \frac{E_s - E_{F_S}}{kT} \right)} \quad \text{PT4}
\end{align*}
\]

where \( N_c, N_v \) and \( N_s \) are respectively the conduction band density of states, the valence band density of states, and the density of surface states. \( E_s \) is the energy position of the surface states and \( E_{F_S} \) is the position of the fermi level at the surface. \( E_g \) is the band gap. The position of the fermi level with respect to the bands, \( E_F(x) \), is now a function of position, \( x \), and in the abrupt junction approximation can be expressed as

\[
E_F(x) = E_{F_S} + \frac{2}{\omega^2} \left( E_{F_0} - E_{F_S} \right) \left( \chi \chi - \frac{1}{2} \chi \chi \right) \quad \text{PT5}
\]

where \( E_{F_0} \) is the position of the fermi level in the bulk, \( \omega \) is the barrier depletion width which is expressed as
\[ W = \frac{2\varepsilon_s}{N_d} \left[ \frac{E_{F_0} - E_{F_S}}{q_0} - \frac{kT}{q_0} \right] \]

where again \( \varepsilon_s \) is the static dielectric constant of the semiconductor and \( N_d \) is the donor impurity concentration.

We now proceed to rewrite the charge neutrality equation. The integral containing \( n_0 \) and \( p_0 \) can immediately be written as

\[ \int n_0 (n_0 - p_0) \, dx = q_0 W N_d \]

The integral for \( n(x) \) is

\[ \int n(x) \, dx = \int_{0}^{w} N_c \exp \left( \frac{E_{F_S}}{kT} \right) \, dx \]

\[ = N_c \exp \left( \frac{E_{F_S}}{kT} \right) \int_{0}^{w} \exp \left( \frac{c}{kT} \left( \frac{w_x - \frac{1}{2} x^2}{} \right) \right) \, dx \]

\[ = \frac{N_c W}{z} \exp \left( \frac{E_{F_0}}{kT} \right) \text{ERF}(z) \]

where

\[ c = \frac{2}{\omega^2} \left( E_{F_0} - E_{F_S} \right) \]

and

\[ z = \left( \frac{E_{F_0} - E_{F_S}}{kT} \right) \frac{V_L}{x} \]

\[ \text{ERF}(x) = \int_{0}^{x} \exp \left( -x^2 \right) \, dx \]
Values for this function are generally obtainable either in tabular form or as automatic subroutines in many computer facilities.

The integral for \( p(x) \) is evaluated as

\[
\int_{0}^{\infty} p(x) dx = N_0 \exp(-E_g/kT) \int_{0}^{\infty} \exp\left(-\frac{E_p(x)}{kT}\right) dx
\]

\[
= \frac{N_0}{\pi} \frac{\exp\left(-\frac{(E_{ps} + E_g)/kT}{2}\right)}{\frac{\exp(-E_g/kT)}{kT}} + \int_{0}^{\infty} \exp\left(-\frac{E_p(x)}{kT}\right) dx
\]

where \( I_D(x) \) is the Dawson integral of \( x \), this can be evaluated as

\[
I_D(x) = \int_{0}^{x} \exp(-u^2) du
\]

\[
= x \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n}}{(2n+1)!}
\]

\[
= \sum_{n=1}^{\infty} F(n)
\]

where \( F(n) \) can be expressed in terms of a recursion formula

\[
P(1) = x
\]

\[
P(n) = P(n-1) * \frac{2x^2}{(1 - 2n)}
\]
if \( x > 5.5 \) the above sum cannot be evaluated by most computers and one can then use the asymptotic approximation

\[
I_D(x) \approx \frac{1}{2x}
\]

good to within one percent.

The equation for charge neutrality is now rewritten as

\[
\begin{align*}
W N_d - \frac{N_c}{Z} & \exp \left( \frac{E_{F_0}}{kT} \right) \text{ERF} (Z) \\
+ \frac{N_v}{Z} \exp \left( - \frac{(E_{F_S} + E_s)}{kT} \right) I_D (Z) & = \frac{N_s}{1 + \frac{1}{2} \exp \left( \frac{E_s - E_{F_S}}{kT} \right)}
\end{align*}
\]

This expression can now be solved for values of \( E_{F_S} \) or \( W \) when it is supplied with the following parameters:

\[
-\frac{E_{F_0}}{kT} = \ln \left( \frac{N_d}{N_c} \right), \text{ the fermi level in the bulk of the sample.}
\]

\[-N_d' \text{ the density of donors}
\]

\[-N_c = 2(2\pi m_e kT)^{3/2}, \text{ the density of states for the conduction band.}\]
\[ N_v = 2(2\pi^2 m_d kT/\hbar^2)^{3/2} \] the density of states of the
valence band

\[ \varepsilon_s \] the static dielectric constant.

\[ E_g(T) \] the temperature dependent band gap

\[ E_s(T) \] the temperature dependent energy of the surface
states

\[ N_s \] the density of surface states.

As an example we consider InSb with the following parameters

\[ E_g(I) = 0.27 - 0.003 \times T \text{ eV} \]

\[ m_e = 0.0145 m_0 \]

\[ m_d = (m_{h1}^{3/2} + m_{h2}^{3/2})^{2/3} = 0.51 m_0 \]

\[ \varepsilon_s = 16 \varepsilon_0 \]

\[ E_s(T) = -\frac{2}{3} E_g(T) \]

\[ N_d = 10^{16} \text{ cm}^{-3} \]

\[ N_s = 10^{10} \rightarrow 10^{11} \text{ cm}^{-3} \]

The above quantities are in general the values one can find in
the literature. The value of \( E_s(T) \) was taken to follow the 2/3 criterion
proposed by Mead (66ML). The density of surface states \( N_s \) was selected
such that the fermi level at the surface \( (E_{FS}) \) would fall within a
reasonable range of the gap at low temperatures where a barrier is
expected to exist. From the above parameters the temperature variation
of the barrier height was calculated as presented in figure (PTF2). It can be seen that the barrier changes very little with temperature in the range we have considered and even though the change will have some influence on the magnitude of the photovoltage, this influence will not be very important.

The presence of a barrier at the surface does not however guarantee the production of a photosignal. The impedance of such a barrier in the reverse current direction must be considered since this quantity will determine the photovoltage that can be measured externally.

Once a barrier is established the photovoltage produced by an incident flux of light is represented by

$$v_{pv} = \frac{kT}{e} \ln \left( \frac{\frac{e}{e}}{1 + \frac{e}{e}} \left( 1 - \exp \left( \frac{-\alpha \omega}{1 + \omega} \right) \right) \right)$$

Assuming $\alpha \omega \ll 1$ and low light intensity equation (PT13) can be expressed as

$$v_{pv} = \frac{kT}{e} \left( 1 - \exp \left( -\alpha \omega \right) \right)$$

PT13

The photovoltage that can be built across the junction is not only a function of the depletion width $W$ but is also a function of the reverse bias saturation current density $J_s$. This current density is essentially a measure of the impedance of the barrier and therefore determines the magnitude of the voltage that can be measured. The
Figure PTF2 - The variation of the barrier height ($\phi_B$) in InSb as a function of temperature.

It is noted that the variation of the barrier height is not large and that therefore the contribution of this variation to the total variation in the photovoltaic signal as a function of temperature will not be significant.
reverse bias current density can be thought of as being composed of various parallel current densities, for example

\[ J_s = J_T + J_A + J_D \]

where \( J_T \) is the thermionic emission component as expressed by Sze (69S1).

\[ J_T = A^* T^2 \exp \left(-\frac{q \phi_B}{kT} \right) \]

The thermionic emission current is that produced when an electron is thermally excited over the barrier to recombine with the hole at the surface.

The current density \( J_A \) is dependent on the ionized acceptor concentration. A reverse current can exist due to the presence of holes in the bulk and in the depletion layer. We therefore express \( J_A \) as

\[ J_A = c_1 \exp \left(-\frac{E_A}{kT} \right) \]

where \( c_1 \) is a constant and \( E_A \) is the energy position of the acceptor states above the valence band.

Finally the reverse current can be composed of many other sources which have less influence on the photovoltage than the thermionic emission and acceptor density dependent currents. Therefore \( J_D \) is considered to be a small leakage current density. The origin of such a leakage current may be phenomena such as tunneling or optical
excitation over the barrier. Since this current is small and essentially serves as a lower limit for the reverse current physically obtainable we write

\[ J_{D} = D \]

The curve of the photovoltage for InSb as a function of temperature is presented in figure (PF3). The curve was fitted to expression (PT13) for the photovoltage. In this expression the barrier height and the depletion width which were used were obtained by equation (PT12) using the parameters previously suggested for InSb. The high temperature results are determined by the thermionic emission component and the slope of \( \ln(V_{pv}) \) vs 1/T can be used to obtain the zero degree extrapolated barrier height. From figure (PF3) a barrier height of 0.19 eV was found, this value compares favourably with the value of 0.18 eV determined by Mead (66M1) at 77K. In the intermediate temperature range an acceptor energy of 35 meV fitted the experimental results with some accuracy. This acceptor energy is again a reasonable value for the average energy of various acceptors that can be found in InSb (71N1).
Figure PTP3 - The photovoltage as a function of temperature (InSb).
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Paul L. Rochon was born on May 27, 1949 in Alexandria, Ontario, where he graduated from the Glengarry District High School in 1967. He later obtained his Bachelor of Science degree in 1972 from the University of Ottawa. He then chose to remain at this university to work in solid state physics as a doctoral candidate with Dr. Emery Fortin. During the course of these studies he has had the opportunity to be the author or co-author of the following publications:

- P. Rochon and E. Fortin, "Photovoltaic effect of a Au-Ge barrier in a quantizing magnetic field"
- E. Fortin, P. Rochon and J. P. Zielinger, "Photoconductivity and photovoltaic excitation spectra and their wavelength modulated derivatives in Cu_2O".
- P. Rochon and E. Fortin, "Photovoltaic effect and interband magneto-optical transitions in InP"
Mr. Rochon has also presented papers related to the above work at the following conferences:

- Seconde Conference Internationale sur le Composes Semi-conducteur Ternaires, Strasbourg, France, 1975

and he has presented seminars on his work at the following institutions:

- University of Ottawa, Physics Department, Ottawa, Ontario
- Universite de Louis Pasteur, Physics Department, Strasbourg, France,
- University of Cagliari, Physics Department, Cagliari, Italy
- Royal Military College of Canada, Physics Department, Kingston, Ontario,
- Sir George Williams University, Electrical Engineering Department, Montreal Quebec.