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FARADAY EFFECT STUDIES OF CdS AND CdIn₂S_L

by

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ABSTRACT

The Faraday effect is used to study the properties of donor and conduction electrons in CdS and $CdIn_2S_1$.

The experiments on CdS give additional information to that obtained from previous ESR measurements which showed possible 'impurity banding' at concentrations much less than $2\times10^{18}/cc$. The electrons are shown to behave at high frequencies as if they were free and at low frequencies as if they were localized.

The concentration dependence of the conduction band electronic effective mass was measured using the free carrier Faraday effect and found to be constant to within the experimental error of 7% over the concentration range $3x10^{17}$ to $7.6x10^{18}/cc$. The uncertainty is much less than presently reported in the literature but too large to verify the increase of 2% over the concentration range predicted by a $\vec{k}.\vec{p}$ calculation.

A larger Faraday rotation than anticipated was observed at 2°K and an explanation is presented in terms of additional electric-dipole magneto-absorption entering through the spin-orbit interaction. This is interpreted as the observation of the so-called 'combined resonance' effect in CdS.

The conduction band electronic effective mass of $CdIn_2S_4$ was determined from Faraday effect measurements and found to be $m^*/m_{\bar{s}}0.17 \pm .02$. To obtain this value it

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was necessary to measure the index of refraction in the near infrared spectral region between 0.6 and 1.6μ . A value of 2.57 was found at 1.6μ .

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CHAPTER I

INTRODUCTION AND PURPOSE

Faraday effect measurements in semiconductors have yielded important information about their band structure and the effective mass of the majority carriers. Several review articles have appeared over the past few years¹ which deal mainly with such measurements and the important information which may be calculated from them. The motivation for applying the Faraday effect to the present investigation stems from the results of electron spin resonance (ESR) studies of donor electrons in CdS² and CdIn₂S_L³.

The ESR spectrum of electrons in shallow donor states of n-type CdS consists of a single absorption line which is observed only at low temperatures. The g-value of the line is independent of the dopant and is the same as that measured for the conduction electrons through optical Zeeman effect studies.⁴ The absence of hyperfine structure has been explained⁵ by considering that the electrons are in a band of delocalized states resulting in motional averaging of the hyperfine interactions. This would be consistent with the explanation given for the single ESR line observed in moderately doped n-type silicon except for the fact

that it occurs at a lower donor concentration, for example $\sim 10^{17}$ chlorine atoms/cc⁶. Upon increasing the concentration the intensity of the ESR line first increases and then decreases, finally disappearing at N $\simeq 2 \times 10^{18}$ /cc free carriers. This has been interpreted as a merging of the impurity states with the conduction band where spin relaxation effects broaden the resonance to the point of unobservability. In all cases the number of uncompensated shallow donors quoted as being present in the sample was based on a room temperature Hall effect measurement and was approximately an order of magnitude greater than that calculated from the intensity of the ESR signal.

The suggestion of delocalized states or that an 'impurity band' is formed is supported by the work of Mott and Twose (1961)⁷who predicted that the onset of banding should occur at a donor concentration such that the average interdonor separation is approximately three effective Bohr radii. For CdS, this concentration is ~2.5xl0¹⁷/cc. Mott⁸ has argued that at 0°K the onset of banding should be sharp, i.e. the activation energy should fall discontinuously to zero as the donor concentration is increased.

The present work on CdS was undertaken to determine the characteristics of electrons in the donor levels for concentrations of donors which are $\geq 2.5 \times 10^{17}/cc$. The characteristics considered were the electronic effective mass and the mechanism of conduction. The study was made

as a function of concentration between $3x10^{17}/cc$ and $7.6x10^{18}/cc$. Room temperature Hall effect measurements were made to determine the concentrations.

The near infrared Faraday effect was chosen to measure the effective mass for the following reasons: a) it measures a bare mass for the frequencies used, b) the measurements can be performed with equal facility at room and liquid helium temperatures, c) the mass measured is that of electrons near the Fermi level and d) the equipment was readily assembled.

Previous Faraday measurements on CdS were made by Balkanski and Hopfield (1962)⁹ at room temperature for 'pure' and gallium doped (N= $6 \times 10^{18}/cc$) samples only; the latter indicating a free carrier effective mass of (0.20±.01)me. Other optical determinations of m* to date have yielded values close to 0.20m, but the measurements at different concentrations have shown more than a 35% scatter. The theoretical \vec{k} of formulation of Cardona (1961) predicts a 2% increase in m^* over the concentration range $3x10^{17}$ to 8x10¹⁸ /cc. Since the Faraday measurements yield m* at the Fermi level for degenerate materials, these results present a check to the concentration dependence of the effective mass and hence to the possible non-parabolicity of the conduction band.

For the conduction mechanism, two possibilities were considered: a) normal band conduction via the drift velocity

of the electrons and b) a hopping conduction. The first is frequency independent for frequencies which are low compared to the phonon and other scattering frequencies. Hopping conduction may be frequency dependent at low frequencies if the hopping times are sufficiently long. Pollak and Geballe¹²(1961) observed a frequency dependent conductivity from 10^2 to 10^5 Hz in silicon which they attributed to hopping. The presence of conduction via hopping implies that the electrons are localized for times which are at least comparable to the hopping times. Frequency dependent resistivity measurements over the range 10 to 10^5 Hz were made at low temperatures on the CdS samples to identify the conduction mechanism.

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The interest in $CdIn_2S_4$ resulted from the recent ESR work of R. Kerr³ in which further analysis of the results required the knowledge of the conduction band effective mass and the spin-orbit splitting of the valence band. A recent work by Endo et al.¹³ (1970) reported a mass of $0.2m_0$ deduced from Seebeck coefficient data but they gave neither the details of the measurements nor an estimate of the error. Using that value of the effective mass and the magnetoresistance anisotropy which they observed, Endo et al.¹³ (1970) made four suggestions for the transverse and longitudinal effective masses. Since the Faraday effect yields a different average of longitudinal and transverse masses, it should determine which of the suggestions of Endo et al. is correct.

The mass reported by Endo et al.³ would be that of an electron in equilibrium with the phonon field or a polaron mass but the size of this correction should be smaller for the less polar $CdIn_2S_4$ than for CdS where it is ~10%⁹. Neglecting this correction and using the longitudinal and transverse masses suggested by Endo et al.³ one predicts a Faraday effective mass in the range 0.06 to 0.09m_o.

CHAPTER II

THEORY

A-Faraday Effect

The Faraday effect is the rotation of the plane of polarization of plane polarized light propagating through a medium in the direction of an applied magnetic field. For low fields, this rotation is directly proportional to the magnetic field strength.

A simple explanation of this effect is obtained by considering the plane polarized wave as being composed of right and left circularly polarized components which propagate at different phase velocities, c/n_+ and $c/n_$ respectively, where n_+/n_- are the indices of refraction of right/left circularly polarized light and c is the speed of light in vacuo. The result is a rotation of the plane of polarization by an amount θ given by

$$\theta = \frac{\omega l}{2c} (n_{-} - n_{+}) \qquad (II.1)$$

where ω is the angular frequency and $\{$ is the distance traversed. Equation II.1 defines the sense of the rotation as positive for clockwise rotations about the magnetic field direction as viewed by one looking along the field.

At frequencies where the absorption is negligible and

for propagation of light along an axis of at least threefold symmetry, the rotation may be expressed in terms of the conductivity tensor $\sigma_{KL} = \sigma_{KL}^{\prime} + i \sigma_{KL}^{\prime}$ as

$$\partial = \frac{\sigma_{xy}^{r} l}{2nc} \qquad (II.2)$$

where n is the average of n_ and n₊ and is usually taken to be the zero field refractive index.

The Faraday rotation results from the magnetodispersion which is causally related to the magnetoabsorption. The Faraday rotation is labelled by the magnetoabsorption mechanism on which it depends. For the present work there are several mechanisms which contribute to the measured rotation. They are:

1) free carrier Faraday rotation which results from magneto-absorption between Landau levels in a single band. 2) interband Faraday rotation which results from magnetoabsorption between two bands. This includes the Faraday rotation due to donor level to conduction band magnetoabsorption.

3) Faraday rotation due to combined resonance magnetoabsorption.

4) other factors affecting the Faraday rotation.

1-Free Carrier Faraday Effect

The free carrier Faraday rotation has been treated by Mitchell¹⁴(1955) among others using a classical Drude-

Zener approach yielding a Faraday rotation given by

$$\frac{\theta}{LH} = \frac{Nq_{\star}^{3}}{2\pi\pi c^{4}} \frac{\lambda^{2}}{m_{\star}^{*2}}$$
(II.3)

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where N is the free carrier concentration, q is the magnitude of the electronic charge, H is the external magnetic field, and m_{op}^{*} is an average electronic effective mass.

The mass in equation II.3 depends on the energymomentum relation and the appropriate statistics and can be calculated explicitly by using the Boltzmann transport equation modified for the presence of an external magnetic field to calculate the conductivity tensor component σ_{xy}^{r} . A general expression has been given by Stephen and Lidiard¹⁵ (1958) based on the work of Abeles and Meiboom¹⁶(1954). For low fields (ω_{0} <1; $\omega_{z} = \frac{q H}{m^{*}c}$ is the cyclotron frequency), high frequencies (ω_{0} >1) and for a single energy surface with the z-axis being an axis of at least three fold symmetry, they obtained

$$\sigma_{xy}^{F} = \frac{q^{5} H}{4\pi^{3} t^{4} \omega^{2}} \int_{\overline{\partial E}} \frac{\partial f_{0}}{\partial k_{x}} \left[\frac{\partial E}{\partial k_{y}} \frac{\partial^{2} E}{\partial k_{x} \partial k_{y}} - \frac{\partial E}{\partial k_{y}} \frac{\partial^{2} E}{\partial k_{y}^{2}} \right] d\vec{k} \qquad (II.4)$$
which upon comparison with II.3 yields

$$\frac{N}{m_{op}^{*2}} = \frac{c}{(2\pi k)^4} \int \frac{\partial f_o}{\partial E} \frac{\partial E}{\partial k_x} \left[\frac{\partial E}{\partial k_y} \frac{\partial^2 E}{\partial k_x \partial k_y} - \frac{\partial E}{\partial k_x} \frac{\partial^2 E}{\partial k_y^2} \right] d\vec{k} \qquad (II.5)$$

Equation II.5 indicates that the mass measured by the Faraday effect is an average over all electrons weighted by $\partial f \leq E$ or effectively an average of those electrons within ~2kT of the Fermi level E_F .

a-Degenerate Statistics

For degenerate statistics ($E_{\rm F}$ >> kT), the measured mass

is essentially the mass at the Fermi level and for this case case the free carrier Faraday effect can be used to map out the $E(\vec{k})$ relationship.

For spherical energy surfaces though not necessarily parabolic, and for a Fermi level E_F in the band such that $\frac{\partial f}{\partial E}$ is non-zero only at E_F , the Faraday rotation is given by $\frac{\partial}{\partial E} = \frac{N q^3}{2\pi n c^4} \lambda^2 \left[\frac{1}{k^2 k} \frac{\partial E}{\partial k}\right]_F^2$ (II.6) where $k_F = (3\pi^2 N)^{1/3}$. Comparison of II.3 and II.6 gives

$$\frac{1}{m_{op}^{*}} = \frac{1}{k^{2}k_{F}} \left(\frac{\partial E}{\partial k}\right)_{k_{F}}$$
(II.7)

If the band is parabolic, m_{op}^{\star} is equivalent to

$$\frac{1}{m_{op}^*} = \frac{1}{k^2} \frac{\lambda^2 E}{\partial k^2} = \text{constant} \quad (II.8)$$

As will be indicated in chapter IV, the conduction band of CdS is only slightly non-parabolic. b-Non-degenerate Statistics

For this case $E_F/kT \ll 1$ and $\stackrel{1}{\not\sim} E$ is significantly different from zero over the conduction band. Now for a non-parabolic band, electrons at different energies have different masses and the m_{op}^{\star} measured is then an average over the pertinent energy range. The integrals in equation II.5 must be evaluated and hence an explicit $E(\vec{k})$ relation must be known. The first terms for CdS are a small linear term and a slightly anisotropic quadratic term.¹⁷ For CdIn₂S_L, very little is known about the band

structure. Recent measurements indicated that there are 3 or 6 ellipsoids of energy along the [100] directions. Assuming a quadratic dependence of E on \vec{k} in the vicinity of the minima, the Faraday rotation for free carriers can be calculated by generalizing the results of Abeles and ¹⁶Meiboom as outlined by Stephen and Lidiard.¹⁵ The effective mass measured by the Faraday effect for ellipsoids along the [100] directions is then given by

$$m_{op}^{\star} = \left[\frac{3 m_{\ell} m_{t}^{2}}{m_{\ell} + 2 m_{t}}\right]^{1/2}$$
 (II.10)

where m_{χ} and m_{\pm} are the longitudinal and transverse masses respectively. For the frequencies used and for cubic symmetry this expression is independent of the field direction.¹⁵

The free carrier Faraday rotation in all of the above cases varies as ω^2 or λ^2 and is given analytically by (II.6)

2- Interband Faraday Effect

The interband Faraday effect has been treated by several authors . The present section uses the derivation of Boswarva et al., as reformulated by Balkanski and Amzallag¹(1968) in terms of the conductivity tensor.

The total Hamiltonian for this case is given by

$$\mathcal{H} = \sum_{i} \left(\mathcal{H}_{o_i} + \mathcal{H}_{int} \right) \qquad (II.11)$$

the sum over i is over all electrons and \mathcal{H}_{o_i} is given by the one-electron Hamiltonian in the absence of the radiation field but with the presence of the static

magnetic field:

$$\mathcal{H}_{o_{2}} = \frac{\Pi^{2}}{2m} + U(\vec{r}) + \frac{1}{2m^{2}c^{2}} \left(S \times \nabla U\right) \cdot \vec{n} + \frac{q}{mc} \left(S \cdot \vec{H}\right) (II.12)$$

where $\vec{n} = \vec{p} + \frac{q}{c}\vec{A}$ and $\mathcal{U}(\vec{r})$ is the periodic potential, S the spin operator, \vec{H} the external field with \vec{A} its vector potential. \mathcal{H}_{int} represents the interaction of the radiation field as a perturbation

$$\mathcal{H}_{int} = \frac{\mathcal{L}}{c} \sum_{i}^{\prime} \vec{\nabla} \cdot \vec{A}^{\prime} \qquad (II.13)$$

where $\vec{A}' = \frac{ic}{\omega} \vec{E}_{a} \exp \left[i(\omega t - \vec{k} \cdot \vec{r})\right] + c.c.$ is the vector potential of the radiation field, and $\vec{v} = \frac{\vec{1}\vec{l}}{m} + \frac{i}{2m^{2}c^{2}}(S \times \nabla U)$ is a generalized velocity operator. The conductivity tensor is then calculated from the mean value of the current and for frequencies far from resonant absorption is given by

$$\sigma_{ij}^{t} = -\frac{iq^{2}}{\hbar} \sum_{k'} \sum_{k} \frac{1}{\omega_{k'k}} \left[\frac{v_{kk'}^{i} v_{k'k}^{j}}{\omega_{k'k} - \omega} - \frac{v_{kk'}^{i} v_{k'k}^{j}}{\omega_{k'k} - \omega} \right] \quad (II.14)$$

where k is the sum over occupied states and k' the sum over unoccupied states with $\hbar \omega_{ik}$ being the energy difference between states k and k'. $v_{kk'}$ is the matrix element of the velocity operator and is given by

$$kk' = \langle k' | \vec{a} \vee | k \rangle$$

where \vec{a} is a unit vector along the electric field of the radiation.

Boswarva, Howard and Lidiard (1962) calculated the high and low frequency dependence of the rotation. At high

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(II.15)

frequencies they obtained

$$\theta = \frac{Nq^3 \ell H}{2\pi nc^4} \frac{\lambda^2}{m^2}$$
(II.16)

which is the same expression as for free electrons and gives a λ^2 dependence ($\partial \pounds \lambda^2$). This limit is appropriate for the rotation due to donor level to conduction band magneto-absorption and in the effective mass treatment of the donor levels, the mass in equation (II.16) is the effective mass at the bottom of the conduction band.

The low frequency limit applies to transitions between valence and conduction bands and is given by

$$\theta = -\frac{M q^2 l}{n c \hbar m^2} \sum_{k'} \sum_{k'} \frac{\omega^2}{\omega_{k'k'}^2} \left[\frac{|P_{k'k'}^+|^2 - |P_{k'k'}^-|^2}{\omega_{k'k}^2 - \omega^2} \right] \quad (II.17)$$

where the sums are the same as for equation (II.14) and the momentum matrix elements are defined as

$$P_{k'k}^{\pm} = m V_{k'k}^{\pm}$$
 with $V_{k'k}^{\pm} = V_{k'k}^{\times} \pm i V_{k'k}^{\times}$ (II.18)

For wavelengths appropriate to the present work the interband rotation varies as λ^{-2} . The final rotation is thus described by

$$\theta = A \lambda^2 + B \lambda^{-2}$$
 (II.19)

3- Combined Resonance Effect

Free electrons in CdS at $\vec{k}=0$ are doubly degenerate (spin). The application of a magnetic field removes this degeneracy and causes the conduction band states to coalesce into Landau levels [n,ms] where n labels Landau level and m_s is the spin index. the Spinorbit interaction causes a mixing of the states so that the state $|o,+\rangle$ would become admixed as $\alpha|o,+\rangle + \beta|-\rangle + \cdots$ where $\ll >> \delta'$ and states farther away are mixed to a still smaller extent, and represent the breakdown of the $\Delta n = \pm 1$ selection rule for cyclotron absorption. Analogously the state $|0,-\rangle$ admixes as $\alpha |0,-\rangle - \delta |1,+\rangle + \dots$ This means that cyclotron resonance (CR) electric dipole transitions $(\Delta n = \pm 1, \Delta m_s = 0)$ at the same energy as the magnetic dipole spin flip transitions ($\Delta n = 0$, $\Delta m_s = \pm 1$) may occur. These are the so called combined resonance (KR) transitions. Rashba and Sheka (1962) calculated the velocity matrix elements for cyclotron resonance, and for combined resonance which depends on the existence of a linear term in the conduction band energy momentum relation. For light propagating along the c-axis they are

Combined Resonance $\langle + | \vee | - \rangle = \frac{-2i\beta^{*}}{1-\beta^{*}} \left[\frac{\Delta}{m^{*}} \right]^{1/2}$ (II.20) Cyclotron Resonance $\langle n+i | \vee | n \rangle = \left[\hbar \omega_{c} / m^{*} \right]^{1/2}$ (II.21) where Δ is the energy depth of the extremum loop of the conduction band and

$$\beta^* = \frac{g m^*}{2 m_0} \simeq 0.18$$
 (II.22)

The relative absorption intensities vary as the square of the matrix element and this ratio is given by

$$CR/_{KR} \simeq \frac{\hbar \omega_c (1-\beta^*)^2}{4 \Delta \beta^{*2}}$$
 (II.23)

taking $\hbar \omega_c \simeq 3 \times 10^{-4}$ eV and $\Delta = 5.6 \times 10^{-5}$ eV yields

$$CR_{KR} \simeq 20$$
 (II.24)

or the combined resonance absorption is $\sim 5\%$ of the cyclotron resonance absorption.

The Faraday effect associated with KR absorption should also be $\sim 5\%$ of that associated with CR absorption since the combined resonance absorption is electric dipole absorption at the spin-flip energy.

The Faraday effect associated with combined resonance should also be of the same sign as that associated with cyclotron resonance since the absorption for both effects is predominately of the left circularly polarized component.

Since the transition frequency of combined resonance effects are in the microwave region for the fields used and since the Faraday effect is observed at near infrared frequencies ($\omega >> \omega_{kk'}$) the rotation should vary as λ^2 . 4-Other Factors

For completeness two other mechanisms should be

mentioned although they contribute negligibly to the present investigation.

a) Spin-orbit interaction: Bennett and Stern²¹(1965) included the effect of spin-orbit interaction on the velocity matrix elements. For frequencies which are not close to the transition frequency this effect increases the Faraday rotation by E_{SO}/E_g where E_{SO} is the spin-orbit splitting of the valence band and E_g is the band gap energy. This contribution takes on a λ^{-2} dependence for the present measurements and is impossible to separate from the normal interband rotation.

b) Spin level population effects: Mitchell, Palik and Wallis²²(1965) observed that a frequency independent negative rotation of ~10 deg/kG-cm was added to the Faraday rotation of PbS at 100°K. The effect was found to be proportional to 1/T. They explained the result by proposing that the absorption of one circularly polarized component of the plane polarized beam was selectively blocked by the electron population difference of the conduction band Zeeman levels. From their analysis, this becomes significant only if the signs of the gyromagnetic ratios of the valence and conduction bands are different. For CdS they are of the same sign and the CdIn₂S₄ measurements were performed at room temperature where the effect is negligible.

B-Electrical Properties

1 Conductivity

a-D.C. Conductivity

An n-type semiconductor having a concentration of N electrons per unit volume of average mobility μ and charge -q has a D.C. conductivity σ' given by

$$\sigma_{\rm v} = Nq_{\rm A} (11.25)$$

The inverse of the conductivity $1/\sigma$ is called the resistivity f .

The mobility μ depends upon the temperature and scattering mechanism and is given by

$$\mu = q T/m^*$$
 (II.26)

where τ is the average relaxation time and m^{r} is the electronic effective mass.

b-A.C. Conductivity

i-Conduction via the Group Velocity

The A.C. conductivity $\sigma'(\omega)$ for normal band conduction equals the D.C. conductivity at low frequencies for most materials since the scattering times are much shorter than the period of the applied voltage. The A.C. conductivity is given by

$$\sigma(\omega) = \sigma_{b,c.} \left[\frac{1 + i\omega r}{1 + \omega^2 r^2} \right]$$
(II.27)

As the frequency $\omega/_2\pi$ becomes of the order of $1/\tau$ the A.C. conductivity becomes complex -that is, the current response is out of phase with the applied voltage.

ii-Conduction via Hopping

In compensated semiconductors with a small concentration of donors the thermal energy alone is usually insufficient at low temperatures to excite carriers to obtain a steady state current upon application of a D.C. field. A change of potential however is affected implying new equilibrium conditions, i.e. a polarization of the electron distribution. The polarization is obtained by electrons shifting from one donor site to another and has been termed hopping. The first suggestion of a conduction mechanism of this type was made by Hung and Gleiseman²³(1950)

Pollak and Geballe¹²(1961) made A.C. conductivity studies on n-type silicon to obtain information about the characteristic hopping times. They found that the conductivity increased as a function of frequency in their samples according to the relation

$$\sigma_{A.c.} = \sigma - \sigma_{b.c.} = \text{constant } x \, \omega^{0.8} \qquad (II.28)$$

and that $\sigma_{A,C}$ was proportional to the product of donor and acceptor concentrations. They analysed their results assuming low compensation and hopping exclusively between pairs of majority sites. Under the further assumption that the results could be expressed as a superposition of responses corresponding to various hopping times τ they wrote

$$\mathcal{R}e\left(\sigma_{A,c}\right) = \int_{0}^{\infty} G(\tau) \frac{\omega^{2} \tau^{2}}{1 + \omega^{2} \tau^{2}} d\tau \qquad (II.29)$$

which they applied to their experimental data (equation II.28) to find a value of the weighting function $G(\tau)$ yielding

$$G(T) \propto \tau^{-1.8} \qquad (II.30)$$

This was then compared with theoretical calculations.

For the present investigation the relevant fact is that at low frequencies the donor electrons may behave as though they were localized, i.e. they contribute negligibly to the conductivity since the system can readjust itself in a time short compared to the period of the applied frequency, whereas at high frequencies the same electrons may respond as if they were non-localized.

2-Conductivity Temperature Dependence

There are two sources of the temperature dependence of the conductivity. The first is the variation of the carrier concentration N and the second enters through the mobility temperature dependence which in turn reflects changes in the scattering time.

a-Carrier Concentration

At high temperatures, virtually all donor electrons, not in acceptor states, are in the conduction band. This is called the exhaustion temperature range. Decreasing the temperature causes the number of electrons in the conduction band to decrease as $e^{-E_{\rm D}/2{\rm kT}}$ provided N_A<N << N_D²⁴ where E_b is the donor binding energy measured from the conduction band. N_A is the concentration of acceptors,

+Optical absorption by hopping has been treated and possibly indicates photon activated hopping.

то

N is the concentration of conduction electrons and N_D is the concentration of donor centers. As the temperature is decreased further, N decreases to a value much less than N_A. The number of electrons in the conduction band, N, then varies as $e^{-E_{b}/kT}$ ²⁴. At an intermediate temperature the number of conduction band carriers is equal to the acceptor concentration and this temperature can be estimated from the change in the temperature dependence of the Hall effect. An estimate of the acceptor concentration can thus be obtained and hence the compensation ratio.

If the donor concentration is sufficient, the donor electron states overlap and merge with the conduction band implying that $E_{\rm D}$ goes to zero. At these concentrations the semiconductor resembles a very dilute metal and the number of electrons contributing to the electrical conductivity is almost independent of temperature. The conductivity is then limited by impurity scattering associated with the non-periodicity of the lattice. b- Mobility

The temperature dependence of the scattering time is more complex. It depends on the dominant scattering mechanism and the degeneracy. For non-degenerate CdS the mobility for T>150°K is governed by polar optical phonon scattering²⁵ while at lower temperatures piezoelectric scattering dominates²⁵ Little is known about the temperature dependent mobility of CdIn₂S, but the work of Sudo et al.³⁹ (1970)

indicates that acoustic phonon scattering dominates at high temperatures.

Frohlich²⁶(1954) estimated the contribution to the mobility owing to optical phonon scattering. He found

$$\mu_{op} = \text{constant } x \left\{ \exp \left[\frac{\hbar \omega_l}{kT} \right] - 1 \right\}$$
 (II.31)

where $\hbar \omega_i$ is the approximate optical phonon energy $(\hbar \omega_i \simeq 1.5 \text{kT} \text{ at room temperature for CdS})$. The constant also contains a slowly varying temperature dependence for $\hbar \omega_i / \kappa \tau > 1$.

The piezoelectric scattering contribution to the mobility exhibits a temperature dependence given approximately by ²⁵

$$\mu_{\rm P} \simeq {\rm constant} \times {\rm T}^{-\frac{1}{2}}$$
 (II.32)

The temperature dependence of the mobility which is limited by acoustic phonon scattering is given for non-degenerate statistics by ²⁷

$$\mu_A \simeq \text{constant x } T^{-3/2}$$
 (II.33)

3- Hall Effect

If a current density J_x is passed through a semiconductor in the presence of a magnetic field H_z a potential gradient E_y is generated. This is called the Hall effect. For low fields the Hall electric field is proportional to the current density and the magnetic field as

$$\mathbf{E}_{\mathbf{y}} = \mathbf{R} \ \mathbf{J}_{\mathbf{x}} \mathbf{H}_{\mathbf{z}} \tag{II.34}$$

The constant R is called the Hall constant. A simple

classical analysis of the current in a magnetic field leads to

$$R = 1/Ne$$
 (II.35)

where N is the carrier concentration in the specimen and e is the charge of the carriers. Equation (II.35) is derived on the assumption that all carrier velocities are the same. It can be corrected to allow for a distribution of carrier velocities by

$$R = r/Ne$$
(II.36)

where r is the Hall scattering factor and is given by

$$\mathbf{r} = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \tag{II.37}$$

where $\boldsymbol{\tau}$ is the electron relaxation time.

The scattering factor r is a number of the order of unity which depends on the magnetic field, the scattering mechanism and the degeneracy of the carriers. r becomes equal to unity at high magnetic field ($H \gg m^2/e\tau$) and/or for highly degenerate carriers.

The low field value of r for acoustic phonon scattering is r = 3N/8 and for ionized impurity scattering is $r=1.93^{27}$ in the non-degenerate limit.

Devlin²⁵(1967) treated the case of optical phonon scattering by solving the Boltzmann transport equation using a variational technique. He pointed out that the energy of the optical phonon is not negligible. His calculated scattering factor varies from 1.0 to 1.23 as a function of the temperature and is in qualitative agreement with the measurements of Stillman, Wolfe, and Dimmock ²⁸(1970) on polar n-type GaAs. Quantitative agreement is reached at room temperature. Devlin's calculations predict a low field scattering factor of 1.16 for CdS at room temperature.

Lewis and Sondhiemer²⁹(1954) carried a similar analysis to the first approximation only and obtained qualitative agreement with the temperature dependence of the scattering factor found by Stillman et al.²⁸ Lewis and Sondhiemer's²⁹ calculation yields a scattering factor of 1.06 for CdS. Balkanski and Hopfield⁹ interpreted their CdS Hall data using a scattering factor of 1.0 and Kroger, Vink and Volger³⁰(1955) used $3\pi/8 = 1.18$.

The present measurements (300° K) were interpreted using

$$r = 1.10 \pm .10$$
 (II.38)

The uncertainty in the scattering factor is the largest source of error in the present experiment.

For $CdIn_2S_4$ a further correction to account for the non-spherical character of the equal energy surfaces of the conduction band may be necessary, but it is impossible to predict the form of this correction since the exact nature of the band is not established.

The measurements of Sudo et al.³⁹ (1970) on $CdIn_2S_4$ indicate that acoustic phonon scattering limits the electron mobility and therefore the scattering factor

would be 1.18 for non-degenerate samples and for the present measurements with $\chi = E_F/kT \simeq 1$ the appropriate value would be 1.10 ±.10 -the same as used for the CdS data.

There are three additional sources of error in making Hall measurements if temperature gradients are created. These are the Ettingshausen, Nernst, and Righi-Leduc effects. Jones³¹(1961) gave a brief discussion of these three which involve the creation of a temperature gradient (Ettingshausen effect) or a voltage resulting from one.

The Ettingshausen temperature gradient causes an electric field parallel to the Hall electric field, the strength of which is determined by the thermo-electric power coefficient (Seebeck effect). This increment in the true Hall constant is negligible compared to the Hall constants measured in the present work.

The effects of these contributions can be minimized further by maintaining the samples in good thermal contact with a bath or by making the measurements at frequencies such that $\omega \tau_{\tau} > 1$ where τ_{τ} is the thermal relaxation time and is of the order of seconds for the present materials.

Magneto-resistive effects can be neglected if the Hall probes are directly opposite one another and if the measurement draws negligible current.

CHAPTER III

EXPERIMENTAL ARRANGEMENT

The equipment necessary to preform the experiments was assembled during the course of the present work. Since the apparatus for the Faraday effect measurements was different from that used for the electrical measurements it will be discussed separately. The apparatus for determining the index of refraction at infrared frequencies is discussed in section C.

A-Apparatus for Faraday Effect Measurements

The experiment consisted of measuring the rotation of the plane of polarization of plane polarized light as a function of the magnetic field. The light was obtained from the infrared spectral lines of a mercury arc and was dispersed by a triple prism monochromator. Individual spectral lines were plane polarized and transmitted through the sample in the direction of the applied magnetic field.

A block diagram of the experimental apparatus is shown in figure III-1.

1-Source

The source was a PEK-500 mercury arc. Its near infrared emission spectrum was measured on an Ebert



Figure III-1 Block diagram of Faraday experimental arrangement.

spectrometer (resolution ~10A) and consists in part of six lines of halfwidth approximately 50A superimposed on a constant background. The peak intensity varied from 2 to 3 times the background intensity. The source housing contained a focusing arrangement ensuring that most of the light was directed into the monochromator.

2-Monochromator

The output of the PEK-500 arc was focused on the entrance slit (1.5 mm) of an infrared triple prism monochromator built by G. Brealey³²(1951). In order to obtain a parallel beam output, the monochromator was modified so that light from the prism was incident on a plane mirror instead of the off axis paraboloid focusing mirror as the initial construction required. Although this modification reduced the resolving power from $\frac{\lambda}{\Delta\lambda} \approx 1500$ to $\frac{\lambda}{\Delta\lambda} \approx 40$, this was sufficient to resolve the lines emitted by the source. Figure III-2 shows the modified monochromator and the light path. The motor scan was only used to obtain scans of the spectrum as shown in Figure III-3.

3-Initial Polarizer

After being reflected from the plane mirror the quasi-monochromatic light leaves the monochromator and is incident upon the initial Glan-Thompson polarizer oriented such that the electric vector of the transmitted plane polarized beam is vertical. This orientation was



27

Figure III-2 Layout of the monochromator


Figure III-3 Infrared spectrum of source: as measured by the spectrometer with no sample in the path.

chosen to ensure maximum reflected intensity from the small plane mirrors in the cryostat. The polarizer was mounted in the housing shown in figure III-4 which permitted it to be rotated for alignment purposes. 4-Cryostat

The linearly polarized infrared beam enters the cryostat, shown in figure III-5, through a fused quartz window (transmission range 0.2-4.5/4), and is reflected at 45° angle of incidence from a gold plated mirror making the direction of propagation parallel to the magnetic field. The radiation passes through a 3/4 inch diameter hole in the copper nitrogen temperature shield into the glass helium dewar, and follows a similar path leaving the cryostat.

5-Detection System

After leaving the cryostat, the light was incident upon another Glan-Thompson polarizer rotating at 14 rev/sec about an axis parallel to the direction of light propagation. The rotating polarizer modulated the transmitted light intensity at 28 Hertz.

The modulated beam was incident upon a B3-SA19M lead sulphide cell from Infrared Industries generating a 28 Hertz signal. Figure III-6 contains a schematic of the detection electronics. Two 45 volt batteries in parallel were used to bias the lead sulphide cell.

A 28 Hertz reference signal was generated by chopping



Figure III-4 Initial polarizer housing. The gear drive is also shown.





Figure III-6 Schematic of Faraday electronics.

light from an Armaco PLB6 light incident on a Philips OCP71 phototransistor. The light was chopped by two blades attached to the rotating polarizer as in figure III-7. Figure III-6 also contains a schematic of the reference electronics. A 6 volt car battery provided the power for phototransistor and the PLB6 bulb.

The signal and reference were fed into a Princeton Applied Reasearch Lockin #121 amplifier set to measure the phase difference between the input and reference signals. The output voltage, proportional to the phase difference, was recorded on a Bristol 590 recorder.

6-Temperature Determination

The temperature of the liquid helium bath was decreased from its boiling point (4.17~K) to 2°K by pumping on the bath with a large Stokes pump. The pressure in the helium dewar was measured with a mercury manometer and the temperature inferred using the 1958 temperature data of the National Bureau of Standards. The temperature was maintained to within 0.1°K of 2°K by adjusting a small valve in the pumping line to keep the pressure between 1.7 cm and 3.1 cm of mercury. A careful adjustment at the beginning of an experiment was found to be sufficient. A Cartesian diver pressure regulator installed in the pumping line was found to be unnecessary.

7-Magnet

A Pacific Electric Motor Company water cooled magnet

Explanation of Figure III-7

The reference electronics (1) and the reference gear (3) rotate in the housing (2) by means of the worm gear drive (4). The modulating Glan-Thompson polarizer (7) was mounted inside the chopper (5) which was rotated at 14 rev/sec in housing (6) by means of a 3/8 th horse sychronous motor suspended below. The chopper blades (5) spin inside the groove shown in (3) chopping the light from the PLB6 bulb incident upon the phototransistor The light and phototransistor were mounted on either side of the chopper groove.



model 12V-AT-Ll was used with a 2.97 inch pole gap. The pole face diameters were 4 inches. The magnet was powered by a 100 horsepower motor driven 300 Amp, 250 volt generator which was located ~ 100 feet from the magnet to eliminate vibrations. The maximum magnetic field obtained was 20.2 kG.

8-Magnetic Field Determinations

A Rawson-Lush rotating coil type 820/B gaussmeter was placed next to the pole tip about $l_4^{\frac{1}{4}}$ " from the sample. Using the null technique, the field was determined to $\pm 2\%$. Initial calibration showed that fields at the rotating coil and the sample were the same to within this uncertainty.

The gradient in the field near the sample was $\frac{1}{H} \left| \frac{\Delta H}{\Delta x} \right| \simeq 1\%$ /cm parallel to \overline{H} and $\frac{1}{H} \left| \frac{\Delta H}{\Delta y} \right| \simeq 0.5\%$ /cm normal to \overline{H} . Typical sample thicknesses were 0.4 cm.

9-Sample Preparation

The n-type CdS was purchased from Eagle Picher (samples #2 and #3) and from Clevite Corporation (samples Cl, C2-A, C2-B, and C3). The CdIn₂S₄ samples were generously donated by Dr. W. Czaja of RCA Laboratories in Zurich.

The c-axis of the CdS single crystals and a principal axis of the $CdIn_2S_4$ single crystals were located by the back reflection Laue x-ray pattern, and slices were cut normal to these axes with a wire saw. The orientation of the crystals was checked after each cut to ensure that the faces of the samples were within 2 degrees of being normal

to the chosen axes. The slices varied in thickness from 0.60 cm for samples #2 and #3 to 0.22 cm for sample C2-A.

Surface damage due to sample cutting was removed by grinding and polishing. The samples were ground to a flat finish with #600 carborundum on glass and then polished with #600 carborundum on Astromat cloth to a mirror finish. Both faces of the crystal were treated in this manner.

After polishing, the samples were mounted in a sample holder and the mounted sample was x-rayed to determine the relevant axis orientation relative to the crystal face to within $\frac{1}{2}$ degree. The sample in its holder was then mounted on the end of the thin wall nonmagnetic stainless steel probe extending into the pole gap of the magnet.

10-Alignment

With the detector and rotating polarizer removed, a laser beam was used to trace out the optical path. The laser was located 113 inches from the sample. The beam, back reflected from the sample face was used to align the sample such that the orientation of the polished face positioned the desired axis along the optic axis. The orientation could be checked accurately since one degree of rotation moved the reflected image 2 inches.

The final adjustment to the sample alignment was made with the detector and rotating polarizer in place. The sample orientation was changed slightly so that the relative

phase of the reference and signal was the same with and without the sample in place. This adjustment was done to the CdS samples only since $CdIn_2S_4$ is not birefringent. 11-Measurement of the Faraday Angle

The Faraday angle was detected as the change of the relative phase of the output of the PbS cell and the reference signal.

The wavelength was selected by manually adjusting the prism orientation while monitoring the output of the PbS cell. By starting at either end of the spectrum and counting the output maxima the wavelenth was identified.

The voltage output of the Lockin (phase mode) was internally biased to near zero millivolts with only the residual magnetic field (~40 Gauss) acting on the sample. The applied field was then raised in six steps of ~1 kG to ~6 kG while noting the field settings and the output voltage. The applied field was then reduced to zero and the procedure repeated. The same sequence was followed for each of the other five wavelengths. Each set of six data points was least squares fitted to obtain the change in output voltage per unit magnetic field change.

The specific rotation was finally obtained by comparing the least square results.

12-Mirror Correction

The exit mirror of the cryostat affects the plane of

polarization of the reflected beam. This was accounted for by calibrating the phase change as measured against actual rotations in the plane of polarization.

A disc of polaroid was mounted in the probe shown in figure III-8 and lowered into the dewar to intersect the optic axis. The polaroid could be rotated 20 degrees about the optic axis by means of the handle (item A in figure III-8). One complete revolution of the handle produced a 2.54 degree rotation of the polaroid.

The calibration was made by comparing the PAR #121 output voltage (Lockin set to measure phase differences) as the polaroid was rotated and as the reference was adjusted. The comparison procedure was analagous to the procedure for obtaining the Faraday angle.



Figure III-8 Calibrating apparatus.

B-Apparatus for Electrical Measurements

The electrical measurements were made using the same dewar, Lockin amplifier, and magnet as used for the optical studies. They are discussed in part A of this chapter. The PAR #121 Lockin amplifier was used as a tunable frequency voltmeter.

1-Electrical Probe

The samples were mounted on a bakelite probe as shown in figure III-9 which was designed to give minimum capacitance between the sample leads. This capacitance was kept to ~9 pF by using #37 copper wire (0.005 inch diameter) and maintaining a lead separation of 1 inch. An eight inch piece of coax joined the leads to the Lockin providing a total of ~25 pF capacitance between the resistivity leads. At 10^5 Hz this is equivalent to a 70 km resistance in parallel with the sample and serves to limit the sample resistance that can be measured without appreciable (10%) corrections to <16 km.

2-Temperature Measurements

Two thermometers were used to cover the temperature range from 300° K to 2° K.

A copper resistance thermometer, wound with #37copper wire from Canadian Wire and Cable Co., was calibrated at liquid nitrogen temperature using the data of Dauphinee and Preston-Thomas³³(1954). The results were reproducible and permitted the determination of the temperature to within



Figure III-9 Sample Holder for electrical studies: The dimensions of the bakelite were 31 inches long, 1 inch wide and 1/8 inch thick.

 $\pm 2^{\circ}$ K over the range 300°K to 65°K. The resistance was measured with a Gray Instruments Co. Wheatstone Bridge model #E3107. The 77°K resistance was 17.88 ohms.

A Solitron #1753 germanium resistance thermometer was used below 45°K. The recommended measurement circuit shown in figure III-10 was assembled using 1% metal film resistors and a Hewlett Packard model 419A D.C. null voltmeter. Temperatures accurate to the larger of $\pm 1\%$ or 0.1°K were obtained with this four point measurement.

Approximately one half pound of molecular sieve was packed around the sample chamber to slow the warm up time from liquid helium temperatures. With this amount it was necessary to heat the chamber to avoid excessively longs runs.

3-Sample Preparation

For the Hall effect measurements, dumbbell shaped samples were spark cut from slices of the Faraday effect samples as shown in figure III-11. It was necessary to spark cut them since both CdS and CdIn₂S₄ are too brittle for ultrasonic impact cutting.

The low temperature measurements on all CdS samples except #2 and C2-B were made with such samples. In order to keep the resistance at low temperatures to <16 ks. for samples #2 and C2-B it was necessary to use a different geometry and match the low temperature results to the higher temperature results on the dumbbell shaped samples.



Figure III-10 Germanium thermometer electronics

:



length = 4.59 mm
width = 2.53 mm
typical thickness = 2.50 mm
overall length = 10.70 mm

Figure III-11 Hall Sample: The shape and dimensions are shown.

4-Electrical Contacts

The entire sample area on which a contact was <u>not</u> to be made was painted with polystyrene dissolved in toluene. After this hardened (~15 minutes under heat) the samples were etched in a near boiling solution of chromic acid (see Appendix A) for 10 minutes and quickly transferred to a warmed indium plating solution (Appendix B). Two pressure contacts were made to the etched samples and a current of ~3 mA was passed for 2-3 hours. Pure indium (99.999%) was used as the anode. The contacts were rotated periodically so that all the etched surface was indium plated. The polystyrene served to limit the contact area.

Pretinned (with indium) gold leads were soldered to the samples using pure indium as solder, as soon as they were removed from the plating solution. The soldering iron temperature was kept just above the indium melting point of 156°C. This was found to be very important for good contacts. Ohmic contacts were made in this manner. 5-Resistivity Measurement Procedure

The procedure for determining the A.C. and D.C. resistivities was the same.

The voltage V between leads 3 and 4, (figure II-12) was measured with a Hewlett Packard D.C. null voltmeter for D.C. measurements and with a PAR #121 Lockin amplifier for A.C. measurements.

The voltage V across the sample was compared to the



Figure III-12 Schematic of Hall electronics: For D.C. measurements the audio oscillator was replaced with a battery and a current limiting resistor.

voltage V_s across the 1% metal film resistor R_s and the resistance R between the sample leads determined using

$$R = R_s \times V/V_s \qquad (III.1)$$

This was repeated 2-3 times at different voltage levels. up to ~ 50 mV and the average resistance calculated. A typical value was 0.5 ohms at room temperature.

The sample dimensions were measured on a travelling microscope with resolution ~1 micron and the resistivity calculated using

$$\rho = R \times A/1$$
 (III.2)

where A is the cross sectional area and 1 is the length between the leads. The latter was chosen as indicated in figure III-11 and was the major source of error in the resistivity determinations.

6-Hall Effect

The Hall effect apparatus is shown schematically in figure III-12.

The resistance pot R_{pot} was adjusted to give a zero transverse voltage V_B with minimum magnetic field. The transverse voltage was recorded as a function of the magnetic field strength as the latter was increased to 12-13 kG. Four or five determinations were made and the average Hall voltage per kilogauss was obtained. The current I was determined by measuring the voltage across a 1% precision resistor in series with the Hall samples.

The number of carriers N per cubic centimeter was obtained from the Hall voltage per kilogauss V_B and the current I using the relation

$$N = 2.75 \times 10^{14} \frac{I(amps)}{V_{B}(volts/kG)}$$
(III.3)

where the thickness of the samples was 2.50 mm and the scattering factor was taken to be 1.10 .

C-Apparatus for Index of Refraction Measurements

The apparatus consisted of a tungsten source $(3500^{\circ}K)$ a chopper, Bausch and Lomb monochromator (catalogue #33-86-25) and a CdIn₂S₄ prism mounted at the center of a calibrated turntable. A fixed telescope focused on the exit slits of the monochromator provide a parallel beam of quasimonochromatic light incident on a prism and a PbS cell detector (same detector used for the Faraday study). The cell was mounted on a rotatable arm and detected the refracted beam. The output of the PbS cell was sent to the input of the PAR #121 Lockin amplifier operating as a tuned frequency voltmeter.

The monochromator slits were set to give a resolving power of $\frac{\lambda}{\Delta\lambda} \simeq 100$ ($\Delta\lambda$ =75Å) and the angular width of the refracted beam at this setting was 44 minutes of arc. The angles of minimum deviation varied from 49° 51' at λ =1.60 μ to 54° 46' at λ =0.60 μ . The apex angle of the prism was 28° 31'.

In order to prevent interference from overlapping orders from the monochromator a filter was used to eliminate the radiation with $\lambda < 0.9$ while the angles of minimum deviation were determined for $0.90 \le \lambda \le 1.60 \mu$. The filter was removed for the $0.70 \le \lambda \le 1.00 \mu$ measurements. The results for the region of overlap were the same to within 5 minutes of arc. A visual check was also made in the optical region and the results extended to 0.60μ by observing the visible radiation in the second order.

The prism apex angle was determined by reflecting a laser beam from the prism faces and measuring the rotation of the prism necessary to give the same reflection from both faces of the prism which define the prism apex angle.

CHAPTER IV

RESULTS AND ANALYSIS

The results for CdS and CdIn₂S₄ are presented separately in sections A and B respectively.

A- CdS

1-Faraday Effect Results

Since it has been shown in chapter II that the major contributing effects to the Faraday rotation in the present investigation exhibit either a λ^{-2} or a λ^2 wavelength dependence, the data were least squares fit to

$$\frac{\partial}{\ell H} = \sqrt{\lambda^2 + \xi \lambda^{-2}} \qquad (IV.1)$$

The coefficients $\sqrt{3}$ and $\frac{6}{5}$ are tabulated in Table IV-1 and IV-2. The rotation observed for the sample with lowest (#2) and highest (C3) free carrier concentration is shown in figure IV-1.

2-Discussion of 300°K Results

The terms important to the Faraday rotation at room temperature are i) free carrier contribution and ii) interband contributions. Spin effects are negligible at room temperature since $kT \gg g \beta H$.

At room temperature the donor electrons not in acceptor states will be thermally excited into the conduction band where they will contribute to the free







Figure TV-1 Observed Fareday notation

carrier rotation. Those in acceptor levels will contribute to the interband term.

For $1.0l_{\mu} \leq \lambda \leq 1.70\mu$ the Faraday rotation is composed of a free carrier term ($\ll \lambda^2$) and an interband term ($\ll \lambda^{-2}$). <u>a- λ^2 Component</u>

The coefficient \checkmark of the λ^2 term of (IV.1) represents the contribution of free carriers. The results of six n-type CdS samples were obtained and analysed in this manner and the coefficient \checkmark interpreted with

$$v = \frac{q^{3}N}{2\pi nc4m^{\star}2} \qquad (IV.2)$$

using the free carrier concentration N determined from Hall effect measurements. The conduction band effective mass values are summarized in Table IV-3.

Table IV-3	: Conduction Band	Effective Mass
Sample	Free Carrier Concentration	m [*] ∕m₀
#2 C2-B #3 C2-A C1 C3	3.0x10 ¹⁷ /cc 5.0x10 ¹⁷ /cc 1.4x10 ¹⁸ /cc 2.1x10 ¹⁶ /cc 6.0x10 ¹⁰ /cc 7.6x10 ¹⁶ /cc	$0.196 \pm .040 \\ 0.181 \pm .016 \\ 0.190 \pm .011 \\ 0.181 \pm .010 \\ 0.210 \pm .013 \\ 0.202 \pm .015$

The average value of $m/m_s = 0.193 \pm .023$ is in good agreement with that calculated from the effective mass approximation of $m/m_s = 0.19$.

Following the method of Cardona (1961), a k.p

perturbation calculation for the conduction band yields an effective mass as a function of the concentration given by $\int_{-\infty}^{\infty} x^{\frac{3}{2}} f(x-y) dx$

$$\frac{1}{m^{*}} = \frac{1}{m^{*}(k=o)} \left[1 - \frac{10kT}{3(E_{o_{c}} - E_{o_{v}})} \frac{o}{\int_{0}^{\infty} x^{4/2} f(x-n) dx} \right] (IV.3)$$

where f is the Fermi function and $\eta = E_F / kT$ is the degeneracy factor. This predicts a 2% increase in m^{*} for the concentration range 3.0x10¹⁷cm⁻³ to 7.6x10¹⁸cm⁻³. The results in Table IV-3 have a 7% scatter though increasing for the higher doped samples. However, since the assigned error is 7%, no firm conclusion can be drawn about this prediction. The higest doped sample has a degeneracy factor $\eta \simeq 3$ implying that the m^{*} measured is an average of the masses up to E≈125 meV above the bottom of the conduction band but strongly weighted by $\frac{\partial f}{\partial z}$ to give the mass characteristic of electrons with energy $E \simeq E_F$. Since the errors of m^{*} overlap for the various concentrations and thus yield a constant m^{*}, the data will be analysed by

$$\frac{1}{m_{op}^{*}} = \frac{1}{\hbar^{2}} \frac{\partial^{2}E}{\partial k^{2}} = \text{constant} \qquad (IV.4)$$

Thus to within experimental error the effective mass is constant up to a Fermi level of ~73 meV above the bottom of the conduction band.

Other measurements of m/m_{c} have been made for free carriers in CdS but the only other measurements as a function

of the concentration is the reflectivity study by Piper and Marple³⁴(1961). Their results show a considerable scatter ($m/m_o = 0.14 \pm .05$ to $0.235 \pm .02$) or a 35% variation and their average value of $m/m_o = 0.22 \pm .01$ is larger than later investigations. Their study was made at near infrared frequencies and yields a bare mass as does the Faraday effect used in the present experiments.

Since then a number of different techniques have been applied to measure m^{*} on selected samples but the results also vary considerably. Most of these measurements are sensitive to the LO phonon-electron coupling and hence yield a modified mass called a polaron mass.

b- λ^{-2} Component

The coefficient \S of the λ^{-2} component of (IV.1) is(2.00±.08)xl0⁻⁸ deg-cm/kG at room temperature. This value may be compared with the results of Ebina et al.³⁵ (1965) as shown in figure IV-2. The analysis of Ebina et al.³⁵ is based on the high frequency fit to the interband rotation. They find a discrepancy between the extension of the high frequency fit and their experimental results at lower frequencies where the interband effect varies less rapidly. The present value of \S can be considered an extension of their work and is also shown in figure IV-2. It is evident that the experimental values are in agreement and both ~30% larger than the theoretical fit. The present work indicates this discrepancy is not due to free carriers



Figure IV-2 Comparison with the results of Ebina et al. The results above 1.7eV indicated as (----) are as taken from their figure 2. The results indicated by (***) are those obtained in the present study. The line (---) is the fit of the prediction of Boswarva, Howard and Lidiard¹⁶ as indicated by Ebina et al. in their figure 4.

since that contribution was subtracted.

CdS samples from the same source as that used here were mass spectrographically analysed and the results showed large amounts of acceptor and deep donor elements (e.g. Li, Cr, Fe). The extra rotation may be due to electrons occuping acceptor and deep donor states.

3-Discussion of the 2°K Results

The rotation observed at 2°K was larger than that observed at room temperature. The least squares analysis of this rotation to (IV.1) consistently gave a larger λ^2 component, and a λ^2 component which was approximately equal to the room temperature λ^2 component.

The magnitude of the extra rotation observed at 2°K is given in table IV-4

Table IV-4 Extra Rotation at 2°K		
Sample	Average of $\left[\frac{\theta(2^{\circ}K) - \theta(300^{\circ}K)}{\theta(2^{\circ}K)}\right]$	
#2 C2-B #3 C2-A C1 C3	8% 10% 4% 5% 4% 8%	

a- λ^{-2} Component

The coefficient § of the λ^{-2} component of (IV.1) is (1.99±.08)x10⁻⁸ deg-cm/kG which is the same as the room temperature value. A decrease in the interband rotation with temperature from 300°K to 100°K for CdS was observed

by Ebina et al. (1965) near the band gap frequencies. Similar measurements by Balkanski, Amzallag and Langer ³⁶ (1965) show a temperature insensitive interband rotation down to 77°K in the frequency range used for the present study.

This term contains an estimated 3% extra rotation associated with the change in the velocity matrix elements due to spin-orbit interaction.

b- λ^2 Component -Samples C2-A, Cl and C3

Since the donor levels have merged with the conduction band, the Faraday dispersion due to donor electrons was associated with two electric dipole absorption processes: i) free carrier absorption and ii)combined resonance absorption.

The first contribution should increase by 1% from 300° K to 2° K since the three temperature dependent parameters of equation (II.16) N, n and m^{*} change in the following manner: i) all N carriers remain in the conduction band 37 ii) n decreases by 2% from 300° K to 2° K and iii) m^{*} is the conduction band effective mass which varies by an 11 estimated +0.5% from 300° K to 2° K.

The remainder of the λ^2 rotation should be due to combined resonance effects. From the data it is seen that it is 4-8% of the total rotation or ~10% of the free carrier Faraday rotation. The estimate based on the relative absorption strengths is 5%.

c- λ^2 Component -Samples #2 and C2-B

The Faraday dispersion owing to donor electrons was associated with three electric-dipole absorption processes i) free carrier absorption by electrons in donor states, ii) electric-dipole spin flip absorption and iii) donor state to conduction band absorption. The first is the contribution of interest while the second is estimated to be only ~ 5% of it.

The third contribution to the Faraday dispersion was approximately equal to the conduction band free carrier Faraday dispersion since the appropriate expression for the rotation is (II.16) and all N carriers 'freeze' into shallow donor states and the other parameters change in the manner outlined above. This implies that the Faraday dispersion associated with donor to conduction band absorption should be approximately 1% greater than the 300°K free carrier Faraday dispersion which is less than the uncertainty in the least squares analysis.

The 2°K data was analysed by subtracting the 300° K free carrier Faraday rotation and interpreting the rest as donor free carrier Faraday rotation. The estimated ~ 5% rotation due to combined resonance effects contributed to the error.

The result was that the ratio N/m*2 associated with the donor free carrier Faraday effect was the same to within a factor of 2 as the value expected if all N carriers were

in the conduction band. Thus, the high frequency behaviour of electrons in donor states is indistinguishable from that of electrons in the conduction band.

4-Results of Electrical Experiments

Room temperature resistivity and free carrier concentrations are given in table IV-5. The resistivity temperature dependence is shown in figure IV-3.

Hall effect measurements at temperatures down to 45° K shown in figure IV-4 for sample #2 indicate the transition from the number of free carriers varying as $\exp(-E_D/2kT)$ to $\exp(-E_D/kT)$ at liquid nitrogen temperatures. A compensation ratio $N_A/N_D \le 1/3$ is indicated from this change in the Hall effect temperature dependence.

The Hall activation energy for sample #2, $E_D^{\pm}12.0 \text{ meV}$ is in good agreement with the resistivity activation energy of 11.8 meV for $40 \le T \le 15^{\circ}$ K. Thus, the resistivity activation energy E_1 of table IV-6 may be interpreted as the binding energy of the donor electrons relative to the conduction band. Li and Huang³⁸(1970) suggested that the small activation energy E_2 of table IV-6 for T< 4.2° K was associated with hopping conduction. Their conclusion appears to be based on the absence of any other satisfactory explanation rather than any firm identification of hopping.



Figure IV-3 Temperature dependent resistivity data.




The radio frequency resistivity measurements are shown in figure IV-5 for sample #2. All such measurements exhibited a frequency independent resistivity up to 10^5 Hz implying that the maximum hopping time was less than 10^{-5} seconds.

The large resistivity of samples #2 and C2-A at helium temperatures implies that most of the free carriers determined at 300°K are 'frozen' into localized states. At low frequencies the number of free carriers at 2°K is at most 10⁻⁴ times the number at 300°K.





Table IV-5	Resistivity and Free C	Carrier Concentration
Sample	Resistivity (<i>Ω</i> -cm) (300 [°] K)	Free Carriers (300°K)
#2 C2-B #3 C2-A C1 C3	0.080 0.043 0.020 0.014 0.007 0.002	$\begin{array}{rcrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

Table	IV-6 Resistivity Act	ivation Energies
Sample	Temperature Range	Activation Energy
#2	40>T>12 4.2 T	$E_1 = 11.8 \text{ meV}$ $E_2 = 0.7 \text{ meV}$
C2-B	40>T>12 4.2 > T	$E_{1} = 6.9 \text{ meV}$ $E_{2} = 1.0 \text{ meV}$
#3	40>T>12 4.2 > T	$E_1 = 5.3 \text{ meV}$ $E_2 = 0.4 \text{ meV}$

B-CdIn_S,

1-Faraday Effect Results

The Faraday effect was observed for three samples of $CdIn_2S_4$ at room temperature and the results were analysed using equation IV.1

$$\frac{\theta}{\ell H} = \sqrt{\lambda^2 + \xi \lambda^{-2}} \qquad (IV.1)$$

The coefficients \checkmark and ξ are tabulated in table IV-7.

	Table IV-7 Faraday Rotation	1 at 300°K
Sample	√ (x10 ⁸)deg	g (x10 ⁻⁸) <u>deg-cm</u>
	kG-cm ³	. KG
1	$0.22 \pm .02$	$1.58 \pm .07$
3	$0.13 \pm .01$ $0.07 \pm .02$	$1.56 \pm .03$ $1.55 \pm .05$

2-Index of Refraction

The index of refraction of $CdIn_2S_4$ (sample 3) is shown in figure IV-6. It varies slowly from 2.70 at 1.60 μ to 2.57 at 0.60 μ .

The longwavelength index of refraction is approximately 2.55 which is close to the value of 2.43 predicted from the empirical Moss relation.

$$n^4 E_g = constant = 77 eV$$
 (IV.5)

where n is the index of refraction and E_g is the band gap energy. The value of E_g = 2.2 eV was used.



Figure IV-6 Refractive index of CdIn₂S₄

3-Electrical Results

The Hall effect and resistivity were measured for samples 1 and 2. The results are given in table IV-8 and are in agreement with previously reported electrical measurements of Sudo et al. (1970).

	Table IV-8 CdI	In ₂ S ₄ Electr	ical Results	
Sample	$N(cm^{-3})$	ያ (Ω- cm)	Mobility]
l	1.1x10 ¹⁸	0.078	80	1
2	6.9x10 ¹⁷	0.090	110	

4-Analysis of Results

By combining the above data and analysing the λ^2 component of the Faraday rotation with (IV.2)

$$V = \frac{q^{3} N}{2 \pi n c^{4} m_{op}^{*2}}$$
(IV.2)

the conduction band electronic effective mass of $CdIn_2S_4$ at room temperature was determined to be $(0.17 \pm .02)m_o$ for both samples 1 and 2. Using the effective mass and the average mobility of 95 cm²/volt-sec the electron relaxation time of 9.3x10⁻¹⁵ seconds was determined.

From the Faraday data on sample 3 and assuming a parabolic conduction band, a free carrier concentration of $\sim 3.3 \times 10^{17}$ cm⁻³ can be inferred.

The effective mass obtained here can be compared with the effective mass deduced from Seebeck coefficient data. The

Seebeck effective mass is given by

$$m^* = (m_1 m_t^2)^{1/3} s^{1/3}$$
 (IV.6)

where & is the number of minima in the conduction band. Using (IV.6) and (II-10) which is the appropriate expression for the Faraday effective mass yields a negative m_t for either &=3 or 6 as suggested by Endo et al.¹³ (1970). A negative effective mass is unrealistic for the present results. Also, substituting the combinations of m_1 and m_t quoted by Endo et al.¹³ into (II.10) gives $0.06 \le m \le 0.09$ where m^* is the Faraday effective mass. These values are far from the measured value of $m/m_c = 0.17 \pm .02$.

The fact that the Faraday effective mass is markedly different from that predicted by the anisotropic masses quoted by Endo et al.¹³ (1970) indicates that one or both of their assumptions namely:

a) the scattering factor is approximately isotropic
b) the conduction band consists of either three or six
equivalent minima
may be incorrect.

CHAPTER V

CONCLUZIONS

A-General Conclusions

When a donor impurity is added to CdS its electronic ground state lies ~30 meV below the conduction band energy minimum. As more donors are added these donor states broaden due to electronic interaction, forming a relatively narrow set of energy levels. At low frequencies of excitation, electrons in these levels respond as if they were localized --i.e., they contribute negligibly to the conductivity.

At microwave frequencies (10¹⁰ Hz) a fraction of the electrons behave as if they were free --i.e., they exhibit a single line ESR spectrum characteristic of conduction electrons with a g value of 1.76.

At near infrared frequencies, the donor electrons behave the same as free conduction band electrons in CdS.

The apparent mobility of the electrons at high frequencies may be due to electrons hopping from occupied localized states to vacant states. In this way the electrons could interact with a large number of nuclear spins resulting in only a single ESR absorption line. Although the effective mass concept as usually applied would have no meaning in this model, the fact that the ratio N/m*² is equal to the value observed at room temperature for N electrons in the conduction band suggests that at sufficiently high frequencies hopping conduction is indistinguishable from band conduction. B-Specific Conclusions

The Faraday effect provides a useful tool for a band parameter study, but the effect must be measured over an extended frequency range to accurately assess the various contributions. Although the frequency range was limited for the present experiment, some specific conclusions are possible.

a) The room temperature value of the conduction band electronic effective mass is (0.193±.023)m_o for CdS. The main sources of error are i) the uncertainty in the Hall scattering factor taken to be 1.10±.10 and ii) the error involved in the least squares analysis of the data. The free carrier Faraday effect measurement of Balkanski and Hopfield at one concentration yielded (0.20±.01)m_o but didn't include any uncertainty associated with the scattering factor.

b) The curvature of the E vs \vec{k} relationship of the conduction band of CdS is constant to within 7% to a Fermi level of 73 meV above the conduction band energy minimum.

c) The observed interband rotation for CdS was larger than expected in the λ^2 region but in agreement with previous work quoted in the literature. The

this extra present analysis shows \mathtt{that} rotation carriers. The temperature is not due to free independence of the component disputes the suggestion of Ebina et al. 35 (1965) that the larger interband rotation is due to phonon assisted transitions. It is probably due to the large number of acceptors and deep donors shown to be present in CdS by mass spectrographic analysis.

d) The additional magneto-dispersion observed at 2°K for CdS is a consequence of the so-called combined resonance absorption. This explanation correctly predicts the wavelength dependence and gives a good estimate of its magnitude.

e) The room temperature value of the conduction band electronic effective mass in $CdIn_2S_4$ is $m^{*}/m_{o^{=}}0.17 \pm .02$. The major source of error is the uncertainty in the Hall scattering factor which was taken to be $1.10 \pm .10$ -based on the theoretical value of acoustic phonon scattering (1.18) and considering that the degeneracy factor was approximately unity.

f) The index of refraction of $CdIn_2S_4$ from 0.6 μ to 1.6 μ is given in figure (IV-6).

g) The proposed mobility of the electrons at microwave frequencies would explain the lack of hyperfine structure in the ESR absorption spectrum of shallow donors in CdS.

APPENDIX

SOLUTIONS

A- Chromic Acid Etch

The etch was made in one liter quantities and remade when the colour changed from reddish brown to a light green.

A saturated water solution of potassium dichromate ($K_2C_{r_2}O_1$) was prepared using approximately 7 grams $K_2Cr_2O_1$. One liter of concentrated sulphuric acid was then slowly added to 35 cc saturated solution thus forming the etch.

A piece of cadmium sulphide examined under a microscope after being in the near boiling etch for ten minutes showed a fresh surface with triangular etch pits.

B-Indium Plating Solution 41

Five and one half grams of 99.999% pure indium wire were cut into small pieces to increase the surface area and dissolved in a boiling solution of 4 cc concentrated sulphuric acid diluted to 75 cc with distilled water. The volume was maintained at approximately 75 cc by adding distilled water periodically. The resulting solution was filtered and diluted to 250 cc with distilled water and finally 2.5 grams of hydrated sodium sulphate $(N_{o_2}So_4 \cdot \log H_2O)$ was added. This indium plating solution was reusable but some indium precipitated out as an indium salt in time and the solution had to be replaced.

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