ELECTRON AND HOLE TRANSPORT

IN CdS CRYSTALS

A Thesis submitted to the

University of Leicester

by

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For the degree of

Doctor of Philosophy.

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ACKNOWLEDGEMENTS

The author would like to express his thanks to Professor E.A. Stewardson for the opportunity to work in his department. He is greatly indebted to Dr. W.E. Spear for suggesting the problem and the generous help and guidance given continually throughout the investigation.

This work would not have been possible without the supply of crystals kindly given by: Dr. J. Franks, A.E.I., Harlow, Dr. R.W. Smith, R.C.A., Princeton, N.J. and Mr. McGill, E.M.I., Hayes. The author is grateful to Dr. J.J. Hopfield, University of California, for supplying effective mass data in a private communication.

The author would like to pay a tribute to the late Mr. N.A. Hunt for his skilful building of the electron bombardment gear. Thanks are also due to Mr. D.J. Watson for help in building some of the equipment, in particular the nanosecond pulse generator. The author acknowledges with thanks the research scholarship awarded by the University of Leicester during most of this work.

He wishes to thank Mrs. M.E. Beck and Mr. E. Singer for their help in the preparation of this thesis.

ABSTRACT

Fast pulse methods have been used to study the drift mobility of both electrons and holes in pure CdS crystals, obtained from different sources, over the temperature range 500°K - 77°K. An electron pulse of 5 nsec. duration generates free carriers near the top electrode, and measurements of the transit time in a pulsed applied field lead to a value for the drift mobility. The method is sensitive to the injection of additional carriers and the choice of electrodes is discussed.

The experimental method provides the first definite evidence for hole transport in CdS. The hole drift mobility μ_h at room temperature has a mean value of 15 cm²/v/sec and the hole lifetime lies between 1×10^{-7} and 3×10^{-7} sec. An attempt is made to explain the temperature dependence of μ_h by a model involving transport in the upper two valence bands of CdS. The mobility and effective mass ratios in these bands are estimated to be 50 and 3 respectively. The presence of about 10^{18} cm⁻³ charged defects has to be assumed. The model is used to interpret some optical properties of CdS.

At room temperature the electron drift mobility μ_e is 275 cm²/v/sec in agreement with recent Hall mobility and other measurements. Below about 220°K the temperature dependence of μ_e begins to differ significantly from that of the Hall mobility and the charge transport is predominantly controlled by shallow trapping states which may be connected with non-stoichiometric defects.

In the temperature range where both μ_e and μ_h are largely controlled by lattice scattering, none of the known theories can predict the experimental curves. It is concluded, however, that non-

polar scattering by the acoustic modes must be considered to be predominant over most of this temperature range.

CHAPTER 1

INTRODUCTION

1 : 1 Properties of CdS and Scope of the Present Work.

Cadmium sulphide can crystallise with either the zinc blend structure or the wurtzite structure. The former ~~is unstable and~~ is only obtained by 'wet' chemical means. Single crystals of the stable wurtzite modification, which can grow by the vapour phase techniques briefly described in section 5:2, are ideally suited for the study of the electrical and optical properties of CdS. This is because the crystals produced are large in size, have a useful range of thicknesses and, more important, can be grown relatively free from impurities and defects.

Crystals of pure CdS, at room temperature, are light yellow in colour since the fundamental absorption edge lies at a wavelength of about $5100 \text{ \AA}$. The bonding of CdS is predominantly covalent, although there is a significant ionic contribution. Pure, perfect crystals ^{available at present} have a dark conductivity of $\sim 10^{-12} \Omega^{-1} \text{ cm}$ and possess a relatively low photo-sensitivity. However, by introducing donor impurities such as chlorine, indium or gallium, the conductivity may be increased by twelve orders of magnitude or more. In this case CdS should really be considered as an extrinsic semi-conductor.

The remarkable feature of CdS is its high photo-sensitivity, which can lead to secondary photocurrent gain $\sim 10^4$. This high photo-sensitivity is associated with the presence of compensated acceptors. These acceptors are negatively charged so that they have a much larger cross-section for the capture of a free hole than they subsequently have for the capture

of a free electron. In this way the recombination lifetime for the free electrons, which determines the photoconductive gain, is greatly increased. With increasing concentration of donor impurities, both the dark and light conductivity increases but there exists a certain concentration of incorporated donors for which the ratio of light to dark conductivity is a maximum. The addition of an acceptor impurity such as copper causes a decrease in the light and dark conductivities. A versatile method for producing crystals of different sensitivities is to prepare highly conducting material by heavy donor doping and then to add sufficient acceptors until the required sensitivity results. These properties have led to many practical applications and CdS is now widely used as a detector of X-rays, high energy particles and in numerous other devices such as relays and light amplifiers.

Both theoretical and experimental investigations of the fundamental mechanisms occurring in this material have been carried out in recent years. A survey and detailed discussion of this work will be given in chapter 3. It is of considerable interest that none of the many studies of CdS have revealed direct evidence for the presence of mobile holes. The main reason for this appears to be that so far most of the work on the transport properties has been based on Hall effect measurements from which it is extremely difficult to obtain information about a less mobile minority carrier. The results have therefore always been interpreted in terms of mobile electrons only. Several investigations of the temperature dependence of the electron Hall mobility have been reported. As shown in chapter 3, considerable confusion still exists about the explanation of these results in terms of the theories of scattering

mechanisms.

The aim of the work described in this thesis was to provide more information concerning the transport of electrons and holes in CdS. It seemed that a completely new experimental approach to this problem was needed; the experimental techniques developed in the course of this work were able to overcome some of the limitations inherent in the Hall effect and led to results which allowed a deeper insight into the basic processes involved in the charge transport in CdS. A particular merit of the method is that it is best suited to highly insulating crystals, so that pure and perfect crystals could be investigated. This makes it possible to first gain a better understanding of the transport in the pure material before investigating the effect of the deliberate addition of impurity atoms.

In the present work it was possible to measure, in a very direct way, the drift mobility for electrons and its dependence on temperature (chapter 7). These measurements gave information concerning defect levels, lying very close to the conduction band in the crystals used. It is of particular interest that in the course of this work the drift mobility and life-time of generated holes have been measured, for the first time, in a very direct and unambiguous way. The study of the temperature dependence of the hole mobility and its interpretation in terms of the valence band structure of CdS seems to go some way towards explaining some of the recently reported optical properties of these crystals.

CHAPTER 2

SURVEY OF THE THEORETICAL TREATMENT OF CARRIER MOBILITY

In this chapter the interaction of the free carriers with the lattice vibrations, and defect centres will be discussed with particular reference to the extent to which they may be expected to determine the carrier mobilities in CdS. The detailed correlation of the experimental results with the theories will be given in chapters 6 and 7.

2 : 1 Lattice Vibrations.

The theory of elastic waves, in a lattice containing two atoms per unit cell, predicts that the frequency spectrum for the allowed modes of vibration is made up of two branches (e.g. Born and Huang 1954). A graph of the angular frequency ω versus the wave vector q_x , ($q_x = 2\pi/\lambda$), of the displacement waves in the x direction, is given in Fig. 2:1. The upper branch O is called the optical branch and the lower the acoustical branch; in general there will be one longitudinal and two transverse dispersion curves for each branch. The longitudinal modes Q_l and A_l correspond to the compression waves whilst the transverse modes O_t and A_t are associated with the propagation of a shear strain. In an isotropic crystal the two transverse dispersion curves degenerate into one for each branch. The optical modes correspond to the movement of the two types of atoms in opposite directions such that their centre of mass remains at rest. The acoustical branch represents modes in which the two atoms move in the same direction. It can be seen from Fig. 2:1 that for the acoustical modes the group velocity, for small q_x

values, is independent of the wavelength λ , whereas for the optical modes it is the frequency which is approximately independent of λ . The CdS lattice, which contains two atoms per unit cell, will therefore give rise to both optical and acoustical modes of vibrations and the interaction of free carriers with these two types of lattice vibration will now be considered.

In a compound, such as CdS, the bonding possesses an appreciable amount of ionic character (e.g. Bube 1960) and both the acoustical and optical modes will produce polarization waves. It can be seen from Fig. 2:1 that the optical modes of vibration, as the wave vector $q_x \rightarrow 0$ (i.e. for long wavelengths), have a group velocity equal to zero. This is the condition for a standing wave and corresponds to an oscillation in which all the atoms of the crystal of type 1 in the unit cell move in phase and all the atoms of type 2 move in phase. Clearly this will produce a strong polarization of the lattice. For the acoustical modes, the group velocity, as q_x approaches zero, tends to the velocity of sound in the crystal, and the displacements of both atoms will be in phase throughout a considerable volume. Hence no polarization waves are possible. However, as q_x tends to $\pi/2a$, the wavelength of the displacement waves λ will tend to $4a$ and the displacements of the atoms will be in opposite directions in neighbouring cells. Such a motion causes local polarization of the lattice which, however, will be far less effective in scattering a free carrier than the polarization caused by the optical modes. This is because the polarization waves are only in phase over a few unit cells.

The frequency of the polarization waves, produced by the optical

vibrations, is different for the longitudinal and transverse modes, The angular frequency of the long transverse waves (i.e. $q_x = 0$), $(\omega_t)_0$, is equal to that of the residual rays, (the 'restrahlen'), which is the characteristic frequency excited optically. It was pointed out, by Fröhlich and Mott (1939), that the angular frequency of the long longitudinal waves $(\omega_l)_0$ is higher than that of the residual rays.

It now remains to consider the relative importance of polar scattering by the longitudinal and transverse optical modes. If $\underline{P}$ is the average electrical polarization vector, it can be shown that for the transverse optical modes $\text{div } \underline{P} = 0$ ^(Fröhlich and Mott, 1939) and that for the longitudinal optical modes $\text{div } \underline{P} \neq 0$. Further, if $W(r)$ is the interaction energy between an electron at a position r and a polarization wave with a wave vector $\underline{q}$, it can be shown from electrodynamics that

$$W(r) = 4\pi e \text{div } \underline{P}_q(r)$$

Thus it can be seen that only the longitudinal optical modes interact with the electron. Therefore for temperatures near and above the characteristic temperature Θ , $\left(\Theta = \frac{\hbar(\omega_l)_0}{k}\right)$, at which the optical modes are excited, the polar scattering is predominantly due to the longitudinal optical modes of the lattice vibrations.

As a result of such scattering by the lattice, an electron with a wave vector $\underline{k}$ and energy E , can acquire a wave vector $\underline{k}'$ and an energy E' by the emission or absorption of a quantum of lattice energy $\hbar\nu$ viz. a phonon. The selection rules governing the transition are,

$$\begin{aligned} E' &= E \pm \hbar\nu \\ \underline{k}' &= \underline{k} + \underline{q} + \underline{K}_n \end{aligned}$$

$\underline{K}_n$ is ^a ~~the~~ ^{the} ~~lattice~~ vector in reciprocal lattice ~~space~~. If the vector difference between the two electron states is such that the electron remains within the first Brillouin zone then $\underline{K}_n = 0$; this is normal scattering. If the vector difference lies outside the first zone then $\underline{K}_n \neq 0$ and the scattering is an Umklapp process.

2 : 2 Polar Scattering.

It has been pointed out that at temperatures where the optical modes can be excited, the polar scattering is dominated by the longitudinal optical modes. The scattering of carriers by these modes was first treated theoretically by Fröhlich and Mott (1939) and by Davydov and Smushkevitch (1940), using a quantum mechanical perturbation method, and by Seeger and Teller (1938, 1939) who used a classical approach. Although the two results agreed, Seeger and Teller did not discuss the temperature dependence of the scattering. A solution for the mobility determined by the scattering as a function of temperature is obtained in two stages. First, an expression for the scattering cross-section for an electron of fixed energy is derived and then, a statistical average of the thermal distribution of electron energies is determined by the solution of the Boltzmann transport equation. Although Fröhlich and Mott evaluated the scattering cross-sections, they made assumptions under which the Boltzmann equation need not be solved.

Howarth and Sondheimer (1953), using the scattering cross-sections of Fröhlich and Mott, went further and solved the Boltzmann equation by a variational method. The solution of the Boltzmann equation for a non-degenerate polar semiconductor is complicated by the fact that the energy of interaction in a collision is so large compared with the electron energy.

However, as pointed out earlier, to a good approximation the longitudinal optical modes can be considered to have a single frequency so that no integration over lattice frequencies is necessary. Howarth and Sondheimer obtained a solution which is approximately valid over the complete temperature range $0 \leq T \leq \infty$, and more accurately so over more limited temperature ranges. Petritz and Scanlon (1955) made a correction to the Howarth and Sondheimer result to allow for the polarization of the atoms by the movement of free carriers. The corrected formula is

$$\mu = \frac{8\pi a_0 e}{3} \cdot \frac{1}{(2\pi m_e k \Theta)^{1/2}} \cdot \left(\frac{\epsilon \epsilon_\infty}{\epsilon - \epsilon_\infty} \right) \cdot \left(\frac{m_e}{m_e^*} \right)^{3/2} \cdot \frac{X(z)(e^z - 1)}{z^{1/2}} \quad (2:1)$$

$$z = \frac{\Theta}{T}, \quad \Theta = \frac{\hbar(\omega_l)_0}{k}, \quad a_0 = \frac{\hbar^2}{m_e e^2}$$

where ϵ is the static dielectric constant, ϵ_∞ the high frequency or electronic dielectric constant, $(\omega_l)_0$ the angular frequency of the longitudinal optical modes, e the electronic charge, m_e the free electronic mass, m_e^* the effective electron mass, $\hbar$ Planck's constant, k Boltzmann's constant, and $X(z)$ is a slowly varying function of z ; $(\omega_l)_0 = \left(\frac{\epsilon}{\epsilon_\infty} \right)^{1/2} (\omega_t)_0$ where $(\omega_t)_0$ is the 'reststrahlen' angular frequency.

The perturbation method, as used by Fröhlich and Mott, was based on a power series expansion of a parameter α which is a measure of the strength of the interaction between the carrier and the polar modes, where

$$\alpha = \frac{e^2}{\hbar} \left(\frac{m_e}{2\hbar(\omega_l)_0} \right)^{1/2} \left(\frac{\epsilon - \epsilon_\infty}{\epsilon \epsilon_\infty} \right) \left(\frac{m_e^*}{m_e} \right)^{1/2}$$

In order that the perturbation method may be used α must be less than unity. For cases in which α exceeds unity, Low and Pines (1953) developed the polaron theory of mobility. In this theory the scattering process is presumed to occur between the polar modes and the motion of the polaron, i.e. the electron together with the polarization it causes in the lattice. An effective mass m_p can be assigned to the polaron for $\alpha < 6$ (Lee, Low and Pines 1953), where

$$m_p = m_e^* (1 + \alpha/6)$$

Low and Pines (1953) derived the variation of mobility with temperature for temperatures less than the characteristic temperature Θ . They showed that

$$\mu = \left(\frac{m_e^*}{m_p} \right)^2 \cdot f(\alpha) \cdot \frac{ea_0}{(2\hbar(\omega_l)_0 m_e)^{1/2}} \cdot \left(\frac{m_e}{m_e^*} \right)^{3/2} \cdot \left(\frac{\epsilon\epsilon_\infty}{\epsilon - \epsilon_\infty} \right) e^Z \quad (2.2)$$

$$Z = \frac{\Theta}{T} ; \quad \Theta = \frac{\hbar(\omega_l)_0}{k}$$

$f(\alpha)$ is a slowly varying function of α which equals $5/4$ for $3 < \alpha < 6$ and $f(\alpha) = 1$ as $\alpha \rightarrow 0$. For small α good agreement exists between the polaron theory and the formula of Howarth and Sondheimer. The polaron theory has not yet been extended for temperatures greater than Θ .

Meijer and Polder (1953) showed that piezo-electrically active acoustic modes causing significant polar scattering can occur in crystals such as CdS, which have a lower symmetry than the alkali halides. This so-called piezo-electric scattering causes the mobility to vary as $T^{1/2}$.

For this type of scattering to become significant compared with that due to the optical modes the temperature must normally be low ($\sim 150^\circ\text{K}$) in order that the optical modes are frozen out. Using the elastic constants for CdS, Hutson (1961) has given the mobility determined by this scattering alone as,

$$\mu \simeq 400 \left(\frac{m_e}{m^*} \right)^{3/2} \left(\frac{300}{T} \right)^{1/2} \quad (2:3)$$

2 : 3 Non-Polar Scattering.

Seitz (1948) considered the interaction of free carriers with the acoustic modes of vibration in non-polar substances. Several assumptions were made:

- 1) the temperature is sufficiently low that the inelastic collisions involve only one phonon,
- 2) only the acoustic modes are excited,
- 3) the electron temperature is sufficiently high that its mean energy is large compared with $m^* C^2$ where C is the acoustical velocity and m^* the carrier effective mass.

Under these conditions, Seitz showed that the scattering is isotropic, and that the mean free path is velocity independent and inversely proportional to the temperature down to $\sim 10^\circ\text{K}$. The mobility is given by

$$\mu = \frac{2^{1/2} \times 6^{1/3}}{4\pi^{5/6}} \cdot \frac{N^{1/3} e \hbar^2 k^2 \Theta^2 M}{m^{*5/2} C^2 (kT)^{3/2}} = \text{constant} \times T^{-3/2} \quad (2:4)$$

where N is the number of atoms per unit volume and M is their mass.

Bardeen and Shockley (1950) used a theory based on the potential deformation which occurs during the passage of an elastic wave through the lattice, to arrive at a result very close to that of Seitz, namely,

$$\mu = \frac{(8\pi)^{1/2} \hbar^4 C_{\ell\ell}}{3 E_c^2 m^{*5/2} (kT)^{3/2}} = \text{constant} \times T^{-3/2} \quad (2:5)$$

$C_{\ell\ell}$ is the average longitudinal elastic constant and E_c is the shift of the conduction or valence band edge per unit dilation.

All these lattice scattering mechanisms cause the mobility to decrease with increase in temperature. In polar compounds, near or above the characteristic temperature, polar scattering by the longitudinal optical modes predominates. As the crystal becomes less ionic in character, the non polar scattering by the acoustical modes grows in importance, particularly at temperatures below the temperature necessary to excite the optical modes.

In CdS, which is only partially ionic, one would therefore expect that the lattice scattering would be neither purely polar or non-polar but a combination of the two. Also, since the characteristic temperature of CdS is $\sim 440^\circ\text{K}$, a mixture of these two types of scattering would be expected up to temperatures in the region of $\sim 500^\circ\text{K}$. The calculation of carrier mobility, in the presence of several scattering processes, will be discussed at the end of the next section.

2 : 4 Impurity Scattering.

Experiments on the electrical properties of germanium yielded curves,

for the resistivity as a function of temperature, which could not be explained on the basis of lattice scattering alone. The temperature variation of the mobility indicated the influence of another scattering mechanism, particularly at low temperatures. Lark-Horovitz pointed out that the scattering by ionised impurities at low temperatures ought to be considered.

Conwell and Weisskopf (1950) worked out the theory of charged impurity scattering in a non-degenerate semi-conductor using Maxwell-Boltzmann statistics. The problem was one of Rutherford scattering of free carriers by an assumed uniform distribution of impurities in which the electric field of the charged centre is modified by the neighbouring impurities. The result obtained gave

$$\mu_I = \frac{8/\pi \sqrt{2} \epsilon^2 (kT)^{3/2}}{N_I e^3 m_e^{*1/2}} \left[\log \left[1 + \left(\frac{3\epsilon kT}{e^2 N_I^{1/3}} \right)^2 \right] \right]^{-1} \quad (2.6)$$

where N_I is the density of scattering impurities, m_e^* is the electron effective mass and ϵ is the static dielectric constant. Neglecting the contribution of the slowly varying logarithmic term, this leads to a mobility approximately proportional to $T^{+3/2}$.

This form of scattering can be caused by the presence of charged defects in a crystal completely free from impurities. Deviations from stoichiometry, which are very likely to occur in a compound crystal such as CdS, may lead to comparatively large densities of charged defects.

At room temperature the relaxation time τ_I for charged impurity or defect scattering is normally much longer than the relaxation time τ_L for lattice scattering. At lower temperatures, and particularly for large

densities, τ_I can become comparable and even less than τ_L . In certain temperature ranges, therefore, both scattering mechanisms may be important and it becomes necessary to consider the combined effect of charged impurity and lattice scattering. For free carriers of one particular energy, the two relaxation processes will be additive. Hence a perturbation of the equilibrium will decay in a time dt by a fraction

$$\frac{dt}{\tau_I} + \frac{dt}{\tau_L} = \left[\frac{1}{\tau_I} + \frac{1}{\tau_L} \right] dt = \frac{dt}{\tau}$$

where

$$\tau = \frac{\tau_I \tau_L}{\tau_I + \tau_L}$$

This quantity should now replace τ in the averages used in computing τ_μ

If τ_I and τ_L depended on the carrier velocity v in the same way this would lead to

$$\tau_\mu = \frac{\tau_{\mu I} \tau_{\mu L}}{\tau_{\mu I} + \tau_{\mu L}} \quad \text{where } \tau_{\mu I} = \tau_\mu \text{ determined by impurity scattering}$$

$\tau_{\mu L} = \tau_\mu \text{ determined by lattice scattering}$

The errors introduced by this method, due to the fact that τ_I and τ_L depend differently on v , may be quite large. The approximation leads to the result

$$\frac{1}{\mu} = \frac{1}{\mu_I} + \frac{1}{\mu_L} \quad (2:7)$$

where μ_I and μ_L are the mobilities determined by charged impurity and lattice vibrations respectively. Such an approximation is widely used in comparing theory and experiment.

2 : 5 Impurity Conduction.

At very low temperatures a phenomenon known as impurity conduction has

been detected by Hall effect measurements. The idea of impurity conduction was first suggested by Gudden and Schottky (1935). They put forward the idea that conduction might occur because a carrier has a finite probability of tunneling from an occupied impurity centre to an equivalent unoccupied impurity centre.

The effect was first observed by Hung and Gliessman (1950) in the course of Hall effect studies of doped germanium. The conductivity, instead of falling rapidly with decrease in temperature as would be expected for an extrinsic semi-conductor, was found to tend to a constant value. Moreover, the Hall constant R_H which is $\propto \frac{1}{n}$, where n is the density of free carriers, did not continue to increase with fall in temperature, but passed through a maximum and became a constant. The position of the maximum in R_H depended on the impurity content and occurred at higher temperatures as the impurity content was increased. The conclusion is that, at low temperatures, a transport of charge is associated with the impurity centres, but without thermal excitation into the conduction band.

Two quite different types of impurity conduction are possible, one of which occurs only in a compensated semi-conductor, when the concentration of impurities is relatively small ($\sim 10^{16}/\text{cc.}$). In this case impurity conduction is impossible unless compensating impurities produce empty majority centres (i.e. empty donors in an n-type semi-conductor). An interaction between occupied impurity centres, which are separated by more than a few 'radii' of the ground state wave functions of an impurity, can only result in the exchange of carriers, but not in charge transport. As the number of compensators is increased, the

conductivity first increases because there are more empty centres into which carriers can jump. At higher degrees of compensation, however, the conductivity decreases because there will be a decreasing number of carriers in the majority centres. In the case of complete compensation there will be no impurity conduction at all because all the donor levels are empty and all the acceptor states are full.

For large impurity densities the impurities lose their localised character because of their proximity to each other. Their mutual interaction results in the formation of an impurity band in which the carriers have a mobility different from the mobility they would have in the conduction band at the same temperature. Under these conditions compensators are not necessary. In fact in this type of impurity conduction the addition of any compensators immediately results in the decrease of the conductivity when free carriers in the impurity band become trapped at these compensating states.

2 : 6 Trap Controlled Charge Transport.

A trap controlled mobility, which leads to a drift mobility smaller than the microscopic mobility, can occur under special circumstances. It can only be observed if the time spent by a carrier in a trap is appreciably smaller than the transit time. For such traps the release time t_e is less than the transit time t_{tr} i.e. there exists a large probability of a carrier being released by thermal activation in a time less than t_{tr} . Such traps are called shallow traps, since the probability of thermal release is $\propto e^{-\epsilon/kT}$ where ϵ is the depth of the trap above the valence band or below the conduction band. If the carrier release time is greater than t_{tr} then this is termed deep

trapping and results in the loss of a carrier as it traverses the crystal. In severe cases of deep trapping a space charge field is set up which makes the field distribution within the crystal non-uniform. The extent to which space charge build-up occurs depends on the rate at which deep traps are being filled compared with the rate at which they are emptying, i.e. on the ratio of the average thermal release time to the time between the generating pulses which produce the free carriers. If the repetition rate of the pulses is small enough, then the majority of carriers will be thermally released before the next pulse occurs and space charge build-up will be negligible.

An investigation of the drift mobility as a function of temperature will indicate the presence of a trap-controlled mobility if it exists. Such a mobility will only be observed when the mean free path before a trapping event becomes comparable or less than the mean free path between the occurrence of any of the scattering mechanisms previously discussed, and therefore normally a trap-controlled mobility only occurs at low temperatures.

Spear (1957, 1960), showed that electron and hole mobilities in amorphous selenium films were controlled by shallow states even at temperatures up to 320°K . In single crystals of monoclinic selenium, Spear (1961) found that above about 273°K the electron mobility was determined by interaction with the non-polar acoustical modes of the lattice vibrations. This transition, from a trap-controlled mobility to a lattice controlled mobility, is shown in Fig. 2:2, and was formulated in the following way: assume that the transit time t_{tr} is sufficiently long for an equilibrium to be established between the free and trapped

charge; the measured mobility μ is then given by

$$\mu = \frac{d}{[(t_0 + \sum t_e) E]} \quad (i)$$

where t_0 denotes the transit time in the absence of trapping and is determined by the lattice mobility $\mu_L = d/Et_0$ and t_e is the release time for a carrier trapped at a depth E . The release time can be found by equating the rate of thermal release with the rate of trapping. This leads to $t_e = \tau(n_t/n)$ where τ is the free carrier lifetime and n_t/n is the ratio of trapped to free carriers and it is assumed that $n_t \ll N_t$ i.e. the traps are only partially full. Since the average number of trapping events in a transit is t_0/τ then $\sum t_e = t_0(n_t/n)$ and if the Fermi level lies below E by more than a few kT

$$\sum t_e = \frac{N_t}{N_{c \text{ or } v}} \cdot t_0 e^{E/kT} \quad (ii)$$

The effective density states at the bottom of the conduction band or at the top of the valence band $N_{c \text{ or } v}$ equals

$$2.5 \times 10^{19} \left(\frac{T}{T_r}\right)^{3/2} \left(\frac{m^*}{m}\right)^{3/2}$$

from (i) and (ii) and with

$$\left(\frac{\mu_L}{\mu_r}\right) = \left(\frac{T}{T_r}\right)^{-3/2} \quad \text{subscript 'r' refers to room temperature}$$

i.e. assuming only non-polar scattering by acoustic phonons, it can be seen from Fig 2:2

$$\frac{\mu}{\mu_r} = \left[\left(\frac{T}{T_r}\right)^{3/2} + 0.4 \times 10^{-19} N_t \left(\frac{m^*}{m}\right)^{-3/2} e^{E/kT} \right]^{-1}$$

From the position of the maximum

$$N_t = T_r^{-3/2} \times \frac{3}{2} T_{\max}^{5/2} \times 2.5 \times 10^{19} \times \left(\frac{m^*}{m}\right)^{3/2} \times \frac{k}{e} \times e^{-E/k T_{\max}} \quad (2.8)$$

Therefore a plot of $\log \left(\frac{\mu}{\mu_r} \right)$ versus $1/T$ will be a straight line of slope E/k , and from the temperature at which the transition from trap-controlled to lattice controlled mobility takes place it is possible to estimate the density of trapping centres N_t . The larger the density the higher the temperatures at which the transition occurs (see Fig. 2:2). It will be seen in chapter 6 that the electron mobility in CdS shows such a mobility dependence on temperature and that this is consistent with a shallow trap level near the conduction band.

CHAPTER 3

SURVEY OF LITERATURE ON CHARGE TRANSPORT IN CdS.

3 : 1 Electron Transport.

Values for the mobility of electrons in CdS were first computed by Fassbender and Lehmann (1949), Bosser and Warminsky (1950) and Gildart and Ewald (1951) from the quantum yield and the time constant of the rise or decay of photocurrents. A range of value between 5-40 $\text{cm}^2/\text{v}/\text{sec}$ was reported. Smith (1951) measured the Hall mobility for electrons and obtained mobilities ranging from 1-200 $\text{cm}^2/\text{v}/\text{sec}$. The explanations given for such a large spread in values were that, a) it represented a true variation of electron mobility from specimen to specimen, b) it was due to a combination of electron and hole mobilities or c) it was caused by effects not taken into account. Attempts by Smith to provide some evidence for hole conduction were negative.

An extensive study of the Hall effect in CdS single crystals was carried out by Kröger, Vink and Volger (1955). Some of the crystals used were pure and others deliberately doped with Cl, Ga and, or Ag. Depending upon the conditions of preparation, the crystals were either insulating or conducting in the dark at and below room temperature. Photo-induced Hall effect measurements were carried out on the insulating specimens.

For the insulating type of crystal, Kröger et al found that the resistivity and Hall constant increased towards high and low temperatures. This was explained in terms of the reduction in the concentration of free carriers. At the higher temperatures this was due to the liberation of trapped holes, leading to an increased recombination. The low temperature

variation appeared to result from the trapping of electrons in levels ~ 0.01 to 0.04 ev below the conduction band. The Hall mobility, which was ascribed solely to electrons, increased in these crystals from $210 \text{ cm}^2/\text{v}/\text{sec.}$ at room temperature to $\sim 1,000 - 3,000 \text{ cm}^2/\text{v}/\text{sec}$ at 40°K . Below this temperature it decreased again due to charged defect scattering, but more steeply than predicted by the theory of Conwell and Weisskopf (equation 2:6).

In the dark conductive CdS crystals, Kröger et al could best explain their measurements in terms of impurity band conduction (section 2:5). Analysis of the results led to the depth of the donor levels below the conduction band. This varied from 0.02 ev for a donor concentration of 10^{17} cm^{-3} to zero for a donor concentration in excess of 10^{18} cm^{-3} .

By combining the mobility data for the insulating CdS crystals, in the range where the mobility was determined by lattice scattering ($100-300^\circ\text{K}$), with those of the dark conductive crystals above room temperature, (where the mobility was also lattice controlled), Kröger et al were able to compare their experimental results with a theoretical curve of mobility versus temperature from $80-700^\circ\text{K}$. This is shown in Fig 3:1. For the theoretical curve a combination of the mobility determined by non-polar scattering by the acoustical modes of the lattice vibrations and the mobility determined by polar scattering by the longitudinal optical modes was used. With a characteristic temperature of $250-300^\circ\text{K}$ and an electron effective mass of $0.2m_e$, the theoretical and experimental curves in Fig. 3:1 are in satisfactory agreement above 200°K . Below this temperature the mobility increases more slowly than predicted by the theoretical

curve, presumably because of the influence of charged defect scattering.

Similar experiments by Miyazawa, Maeda and Tomishima (1959), were undertaken to investigate the effect of lattice vibrations on the electron mobility, but in this case corrections were made to the results for the effect of charged defect scattering. After correction the experimental results could be explained in terms of polar scattering by the optical modes of lattice vibration alone. In order to reach this result, Miyazawa et al had to assume the presence of deep trapping centres for electrons with a density $\sim 10^{17}$ - 10^{18} cm⁻³. This interpretation differs considerably therefore from that of Kröger et al who assumed the presence of non-polar as well as polar scattering.

Piper and Halstead (1960) also made a study of the Hall effect in CdS over the temperature range 20-700°K. In these experiments pure and gallium doped crystals were used; ohmic indium contacts ensured the presence of a sufficiently high density of free carriers for the measurement of the Hall constant even in the pure samples. The effect of impurity banding became evident at low temperatures (<60°K) and high concentrations of gallium, as can be seen in Fig. 3:2. From the gradient of the linear portion of the $\log R_H$ versus $1/T$ graph the depth of the donor levels was found to be 0.032 eV for the purest samples. Their results also indicated that the activation energy associated with the donors decreases with increasing concentration of gallium; at a concentration of 2×10^{17} cm⁻³ the activation energy was 0.02 eV. Fig. 3:3 is a plot of electron Hall mobility versus temperature with both parameters plotted on logarithmic scales. As shown, Piper and Halstead found that the mobility passed through a maximum which shifted to higher

temperatures and decreased in value as the gallium concentration was increased.

Fig. 3:3 shows a comparison of the experimental data with the theoretical mobility curves. In the range where the mobility was determined by lattice scattering, a combination of polar scattering by the longitudinal optical modes (equation 2:1) and polar scattering by the piezo-electrically active acoustic modes (equation 2:3) was used to explain the results. With $(H) = 450^{\circ}\text{K}$, (Collins (1959)), the only adjustable parameter was the electron effective mass m_e^* and the best fit was obtained with $m_e^* = 0.16m_e$. The fit at temperatures above 350°K became progressively worse. In this temperature range the measured mobility decreased more rapidly than the theoretical curve. Piper and Halstead suggested that this was due to the diffusion of the indium electrode into the crystal. The interpretation of these results again differs from that of both Kröger et al and Miyazawa et al and it must be concluded that a satisfactory explanation of the lattice scattering of conduction electrons in CdS has yet to be given.

An interesting method of measuring the drift mobility for electrons in CdS has been reported by Hutson, McFee and White (1961). They observed amplification of ultrasonic waves in photo-conductive crystals of CdS by applying a D.C. electric field in the direction of wave propagation. This effect is caused by the interaction of the mobile carriers with the longitudinal piezoelectric fields which are associated with certain acoustic modes. Acoustic gain is achieved by applying a large enough D.C. electric field to make the free carriers drift in the direction of wave propagation with a velocity greater than the velocity

of sound in CdS. Free carriers were produced uniformly throughout the sample by illuminating it with weakly absorbed light. Fig. 3:4 shows the observed attenuation as a function of drift field for a wave with a frequency of 15 Mc/s. As can be seen, the attenuation, which occurred at low fields, decreased with increasing field until it became zero. Further increase in drift field produced amplification of the ultrasonic wave. Zero attenuation occurred when the drift velocity of the mobile carriers just equalled the velocity of sound in CdS and, from the field strength at which this occurred, a value of the drift mobility for electrons of $285 \text{ cm}^2/\text{v}/\text{sec.}$ was obtained.

3 : 2 Evidence for Hole Transport in CdS.

It might be expected, that by heating CdS with sulphur, the Cd⁺⁺ ion vacancies so produced would lead to p-type conductivity. Similarly, the substitution of Ag⁺ ions for Cd⁺⁺ ions might also be expected to produce p-type conductivity, as observed in the case of CdTe (Kröger, Vink and Boomgaard 1954). Experimentally however, it is found that such treatments merely result in the increase of the resistivity of CdS, presumably due to the compensation of the donor levels by the added acceptors. The absence of p-type conductivity has been attributed to the very high activation energy for acceptor levels in CdS (Jenny and Bube 1954; Kröger, Vink and Boomgaard 1954).

Van Heerden (1957) investigated the properties of primary photo-currents in CdS crystals using pulsed excitation with short light flashes or ^{with} 15.3 Mev α -particles, which generated free electrons and holes close to the top surface of the crystals. Pulses resulting from the displacement of carriers were observed for either polarity of the applied field

and Van Heerden interpreted these results in terms of the drift of both free electrons and holes. The photocurrent versus applied voltage curves for electrons were found to saturate, but no saturation was observed for holes. From the initial slope of the curves Van Heerden estimated the Schubweg to be $2 - 8 \times 10^{-7} \text{ cm}^2/\text{v}$ for electrons and $10^{-8} - 10^{-7} \text{ cm}^2/\text{v}$ for holes.

Smith (1957) observed low-field electroluminescence, the emission being in the green, in CdS. In these experiments gallium electrodes, spaced 1 mm. apart, were applied to one face of the crystal. With a voltage of 1,000 volts an abrupt increase in current and drop in voltage across the crystal was observed. The electroluminescence, which could be seen through a low power microscope, occurred simultaneously with the increase in current; first as a few yellow spots near the anode and then as streams of green light originating at the yellow spots. As the current through the crystal was further increased, the yellow spots and associated green beams grew in number and size until the entire crystal was filled with green light.

These experiments were interpreted in terms of two processes:

- 1) the injection of electrons and holes from the contacts,
- 2) electroluminescence produced by radiative recombination of these carriers.

The potential distribution along the surface of the crystal was measured and it was found that the field in the body of the crystal, where the green emission occurred, was relatively low ($\sim 1,000 \text{ v/cm}$). This low field, in the central part of the crystal, precludes the internal generation of free carriers by impact ionisation. The importance of these observations in connection with the present work lies in the fact that recombination

radiation, extending over 1 mm. in the crystal, is consistent with a free hole lifetime $\sim 10^{-6} - 10^{-7}$ sec.

Measurements of the P.E.M. effect, which can only be observed if ambipolar diffusion takes place, have been published by Sommers, Berry and Sochard (1956). A value of $\mu^{*3} \tau_a \sim 1 \text{ cm}^6/\text{v}^3/\text{sec}^2$ was obtained, where μ^* is the ambipolar or group mobility as defined by Van Roosebroek (1953) and τ_a is the ambipolar diffusion lifetime. Under the conditions of the experiment Sommers et al concluded that μ^* was the hole mobility and with $\mu^* \sim 200 \text{ cm}^2/\text{v}/\text{sec}$ the hole lifetime would be about 10^{-7} sec. Diemer and Hoogenstraaten (1956) inferred from studies of space charge limited currents that holes are mobile in CdS, although no quantitative data of the hole transport was given.

To summarize, therefore, some indirect evidence has been reported for the existence of appreciable hole conduction in CdS but so far no direct and unequivocal measurements have been made.

CHAPTER 4

EXPERIMENTAL METHOD AND APPARATUS

4 : 1 Principle of Experimental Method.

Drift mobilities can be measured in several ways, either by the direct timing of the transit of carriers over a known distance, or by other, more indirect methods.

The first method was used by Haynes and Shockley (1951), who timed the transit of minority carriers injected into germanium crystals by a voltage pulse. Light pulses were used by Lawrance and Gibson (1952), and ^{by} Ludwig and Watters (1956) to measure the drift mobility of minority carriers in germanium. In semi-conductors, such as silicon and germanium, which have an appreciable conductivity, the dielectric relaxation time t_r is extremely short $\sim 10^{-12}$ second. In this case, therefore, the transit time t_{tr} will be $> t_r$ and the minority carriers will drift towards the appropriate electrode carrying with them an equal number of majority carriers to maintain neutrality.

In insulators, however, since t_{tr} will be $\ll t_r$, it is possible for charge neutrality to be disturbed for times much greater than t_{tr} and the drift mobility of both carriers can in principle be measured. Haynes and Shockley (1951) and Brown (1953) measured the carrier drift in AgCl using a method which allowed the macroscopic observation of the carrier drift. Light freed electrons which drifted in the material and produced visible specks of metallic silver. As mentioned in Chapter 3, Hutson and White (1961) determined the electron drift mobility in CdS by propagating an acoustic wave through a CdS single crystal.

The method used in the present investigations was developed by Spear (1957) to study the drift mobilities of electrons and holes in thin evaporated selenium layers. Electron bombardment pulses were used to produce free electrons and holes near to the top surface of the layer. Electron and hole transits through the bulk of the specimen were examined separately by choice of the polarity of the applied electric field. The advantages of this technique as a method of excitation are the easy control of the duration and intensity of the exciting pulse and the possibility of varying the depth of penetration by adjustment of the accelerating potential.

The principle of the method is illustrated in Fig. 4:1. Suppose that the energy of the incident electrons is such that the depth of penetration p is negligible compared with the crystal thickness d . At $t=0$, N_0 electron-hole pairs will be generated, and in this region rapid recombination will take place, so that on application of a field only $N(t_p)$ carriers will pass out of this recombination region into the crystal volume. After a time t if $N(t)$ carriers have drifted a distance $z(t)$ from T in the field E , assuming diffusion to be negligible, the charge $q(t)$ induced (see appendix 1) on the bottom electrode B is

$$q(t) = \frac{N(t) e z(t)}{d}$$

If no carriers are lost during the transit, due to capture by deep traps in the crystal bulk, then $N(t_{tr}) = N(t_p)$. and when $z(t)$ equals d the sheet of drifting charge reaches B and charge neutrality is restored. With a specimen of capacity C , R can be chosen so that the time constant RC is much longer than the transit time t_{tr} and the charge displacement

is integrated.

Fig. 4:2 shows the time dependence of the integrated charge displacement. In Fig. 4:2(a) it is assumed that (1) $N(t) = N(t_p)$ i.e. all the carriers leaving the recombination region reach B , and (2) that $z(t) = vt$ where v is the constant drift velocity of the carriers. The linear increase of charge terminates sharply at $t = t_{tr}$. As $d \gg p$, $v = d/t_{tr}$ and on the assumption that the carrier mobility is field independent $v = \mu E$ which leads to

$$\mu = \frac{d}{t_{tr} E}$$

The observation of a transit, as illustrated in Fig. 4:2(a), is only possible if

1. The duration of the electron pulse generating the electron-hole pairs $t_p \ll t_{tr}$, otherwise the excitation pulse obscures the transit of carriers.
2. t_{tr} is less than the lifetime of carriers with respect to deep traps τ_D , for if this is not so, then $N(t)$ cannot be assumed to equal $N(t_p)$. Capture of generated carriers by such traps, will result in the establishment of a volume space charge which will make E non-uniform within the crystal.

The effects of non-uniform fields upon the pulse shape are shown in Fig. 4:2(b), (c) together with the corresponding potential distributions. Even in the absence of deep trapping, the edge of the pulse at $t = t_{tr}$ may be rounded due to the straggling of carriers produced by either diffusion or random shallow trapping.

4 : 2 General Description of Apparatus.

A general description of apparatus and the requirements affecting its

design will now be given, whilst detailed descriptions of the various components will be presented in the subsequent sections of this chapter.

Since single crystals, particularly those of compounds, even when extremely pure, may still have large densities of defects, τ_D may be $\ll 10^{-7}$ second. Avoidance of deep trapping made it essential therefore to have $t_{tr} < 10^{-7}$ second, and this in turn required the use of very short excitation pulses $t_p \sim 5$ nanoseconds (see section 4 : 4). However, even if deep trapping of generated carriers did not occur, it would still be possible for a space charge field to be established due to the trapping of additional carriers injected by the applied field. To reduce injection to a minimum, a pulsed rather than a steady field was used (4 : 5). The use of pulsed fields brought the problem of amplifier paralysis, and to surmount this difficulty a method was devised for gating the input to the amplifiers. (4 : 5). Finally, it was essential to ensure that the timing of the bombardment pulses, field pulse and the gate operation was correct. To do this, all these units were driven from independent phase shift networks. A description of the pulse techniques developed for this work has recently been given. (Spear, Lanyon and Mort (1962)).

A schematic diagram of the apparatus is given in Fig. 4:3. The bombardment pulse was obtained from a tetrode gun which was normally biased beyond its cut-off point by the bias battery B . The gun produced a burst of electrons of short duration when a positive voltage pulse was applied to the control grid C . The voltage pulse was derived from the nanosecond pulse generator M , which was run from half-wave (either phase) or full-wave rectified A.C., so that the pulses occurred at 50c.s. or 100c.s. The phase of this signal was adjusted by the phase

shift network P.S. After electrostatic and magnetic focussing by L and L', the electron pulse struck the specimen S. The field pulses V, which had a repetition frequency of 50c.s., could ^{be} phase shifted with respect to the bombardment pulses. The transit pulse was fed, via the cathode follower C.F. and the pre-amplifier P.A., whose input was gated, ^{by} G, to the oscilloscope. The duration for which G was opened, and its phase, were adjustable. Fig. 4:4 shows the typical phase relations between the operations. The flexibility of the arrangement lay in the adjustment, provided by the phase shift networks, which allowed the correct conditions to be attained. Condenser C_s was provided for determining the charge sensitivity of the system (see section 4:9).

4 : 3 Electron Gun.

A comprehensive diagram of the construction of the electron gun is given in Fig. 4:5(a).

The design was a logical development of the apparatus used by Spear (1955, 1957), but several improvements on the earlier model were made. It was aimed to build a gun which was comparatively simple to dismantle for maintenance purposes and yet possessed several degrees of freedom in the movement of the filament to allow the adjustment of the gun under running conditions.

The fine tungsten filament F was spot-welded onto two glass-metal seals soldered in the brass tube G. Attached to G was a threaded brass shoulder S on which the knurled knob K was screwed. K was clamped onto the plate P by screws and held in position. The O-ring seals allowed the filament to be pulled up or pushed down with a minimum of

lateral movement, by the rotation of K . This arrangement gave a very fine adjustment of the height of F above the control grid C and allowed a critical approach to the cut-off condition, which was very difficult to achieve by the mere adjustment of the bias potential. Horizontal adjustment of F was achieved by the movement of the 4 diametrically opposite screws indicated at H in the diagram. This was essential, to ensure that the tip of F was on the electron-optical axis of the system.

The nanosecond voltage pulses were fed into the gun through the disc seal Y which enabled the delay line to be matched up to the gun wall. A glass-metal seal X was used to apply the first accelerating potential of +300v to the anode A_1 , which made the beam current independent of the final accelerating voltage. The field between A_1 and A_2 formed the electrostatic lens L . ^{main point of the} The design of the control grid and first anode, shown in Fig. 4:5(b), was to ensure a low capacity to the wall thus preserving the pulse risetime. C was made of stainless steel which, being non-magnetic, did not interfere with the magnetic focussing. C and A_1 were insulated from each other and from the wall of the gun by mica discs M , and clamped together by the threaded brass rings R . ^{(Fig. 4:5(c)),} Pumping holes were provided in the grid, first anode and mica discs. A 1 inch perspex plate I insulated the electron gun, which was maintained at a high negative potential (upto 45 k.v.), from earth. Magnetic lenses L' and L'' were mounted outside the gun on 3 screws, so that their height and orientation could be varied.

4 : 4 Production of Nanosecond Electron Pulses.

Details of the nanosecond pulse generator, which used the well known delay line technique (e.g. Lewis and Wells 1954), ~~is~~ ^{are} shown in Fig. 4:6. The pulse unit was constructed from two pieces of brass tubing (0.375 in. diam.), hard-soldered together to form a T-piece. The vertical part housed a polarized mercury wetted contact relay capsule **M. S.** and carried at its upper end a 75 Ω B.N.C. socket for connection to the delay line **D. L.** The horizontal tube carried two pulse output sockets. Selected $\frac{1}{2}$ w. composite carbon resistors (25 Ω) were incorporated in each section of the inner conductor (0.110 in.) to give the correct output impedance. The dimensions were chosen to give as far as possible a 75 Ω match throughout the generator.

The normally open relay contact carried a small steel socket **H** which, together with the permanent magnet **M**, provided the necessary polarization, (see also Fig. 4:9). The switching solenoid consisted of 5000 turns of 38 s.w.g. wire and required an operating current of 3-4 m.a. The delay line was charged to the desired voltage through a 50 k Ω resistor mounted in a screened side tube close to the delay line socket. For a normal type of co-axial cable with polyethylene insulation ($\epsilon = 2.3$) the duration of the voltage pulse was very nearly 10 n.sec. for each metre of open-ended delay line.

Since both the gun and pulse generator were kept at a high potential, the relay was switched through a coupling condenser and a small amplifier; the indicated voltage levels are referred to the negative high tension line. The circuit of the relay driving unit, shown in Fig. 4:7, consisted essentially of a phase shift network, (see appendix 2),

connected to full-wave rectifying unit. Selector switches S_1, S_2 allowed a half-wave rectified, either phase, (50 c.s.) or full-wave rectified (100 c.s.) signal to be applied to the relay. The jack switch

J was used to switch the rectifier out and a few electron pulses at a time to be produced by closing the micro-switch M . A separate transformer was used to heat the rectifier valve, so that it operated immediately M was closed.

4 : 5 Production of Field Pulses.

The field pulses of 3-7 m.sec. in duration, were produced using a commercially available unpolarized mercury-wetted contact relay. The details of this unit are shown in Fig. 4:8. Alternating voltage from a centre-tapped transformer again passed through a variable phase shift network, and was half-wave rectified, before application to the relay solenoid. The repetition rate was 50 c.s., but a few pulses at a time could be obtained using the jack switch and micro-switch. The voltage source B was built up from small 90 and 300v layer type batteries and with tapping points, a whole range of voltages up to 1800v were switched without any deterioration in the relay. During the switching of the relay however, the mercury droplet adheres to the armature and shorts out contacts 1 and 2 for a fraction of a millisecond. Resistors R_1 and R_2 were necessary therefore to limit the current drawn from the voltage source. With $R_1 = 0$ and $R_2 = 4.7 M\Omega$ and the output connected to a low capacity probe, the pulse rose in a few n.secs., but the falling edge decayed in about 70 μ .secs. Oscillations of small amplitude, tended to occur at the leading edge of the pulse. These were completely damped

out with $R_1 = 1k\Omega$ and although the risetime suffered as a result, it was still better than 15 n.secs. The selector switch S allowed the top electrode either to be earthed or connected to the voltage pulses. Another switch, not shown, enabled the change from pulsed to steady fields to be made.

4 : 6 Gating Unit.

A modified mercury relay provided a simple, yet effective means of gating the input to the amplifiers. This gate was developed during some work on MgO, since in order to get appreciable response it was necessary to apply voltage pulses upto 1800v. An insulating crystal behaves as a condenser, and the rise of such large pulses applied to the top electrode is faithfully reproduced at the bottom electrode, and therefore at the input to the amplifiers. Such large ^{ients}transients, which received further amplification, rendered the amplifiers inoperative during the occurrence of any transit of carriers. The gating unit is shown in Fig. 4:9 and the details given in 4:4 apply in this case also. In this application the steel socket and the polarizing magnet were placed on the side of the normally closed relay contact. With the relay in the open position the capacity of the gate is less than 3pf., and its effect on the input capacity to the amplifiers was negligible.

The full wave rectified signal, derived from the circuit shown in Fig. 4:10, had a fixed phase shift but the duration of the open period of the gate could be varied between 1m.sec. and 5 m.sec; the repetition rate being 100 c.s. Referring to Fig. 4:4, the gate opened for 2 m.sec after the application of a 4 m.sec. voltage pulse to the crystal.

During the open period a pulse of generated carriers, produced by the electron bombardment pulse, was displayed with a sensitivity of 0.3 mv/cm. This was done in the case of MgO, even when a pulse of 1800v was applied. It was observed that the switching transients, produced by the gate, were negligibly small, but this was, at least partly due to the limited low frequency response of the amplifiers.

4 : 7 Specimen Holders.

Most of the measurements were made with the specimen holder illustrated in Fig. 4:11(a), which was designed to permit the specimen temperature to be varied in the range 80°K to 500°K. In order to reach the lowest temperatures, it was essential to have good thermal contact to the specimen and yet reduce the heat conduction, to the specimen from the base plate to a minimum. As can be seen in the diagram, the copper rod R was tapered as it passed through the base plate B , and the upper end of R formed the actual specimen platform. To reduce the heat conduction, a silver steel tube T , having a small thermal conductivity at low temperatures, was silver soldered to R and B . An evacuated jacket therefore separated R from B . Disc seals D were soft-soldered in B for the thermocouple leads, ^{the} connections to the specimen and the Faraday cup C (4:9).

Fig. 4:11(b) shows a plan view of the specimen holder. The specimens were mounted on the mica base M in a manner described in chapter 5, and the thermocouple, which was spot welded onto a nickel strip, was clamped onto M . A shield S , which slotted into B , was provided with a detachable lid L and prevented electrons striking the mica and

the specimen area ~~was~~ not covered with the metal electrode. Apertures **A** allowed the electron beam to strike the specimen or enter the Faraday cup. For low temperatures, **R** was immersed in a flask of liquid nitrogen which was mounted in a holder which could be raised or lowered in a controllable manner, thus enabling intermediate temperatures to be reached. For temperatures above room temperature a heater coil was used. This consisted of a heater element embedded in a cylinder of refractory cement which fitted snugly around **R**.

The screened box **S.B.** mounted under the base plate contained the cathode follower, the gating unit and a switching arrangement. Fig. 4:11(c) indicates the circuit schematically. The switch **S** allowed the top electrode **T** to be connected either to the pulsed voltage source or directly to the input of the cathode follower **C.F.**, if the incident pulse was to be observed. The standard condenser **C_s** was provided in order that the charge sensitivity of the system could be measured. The experimental method will be discussed in section 4 : 9.

For temperatures exceeding 500°K, this specimen holder became impracticable because of appreciable heat conduction to the base plate which resulted in the O-ring rubber seals becoming hot. To overcome this, water cooling of the O-rings was necessary, and the holder shown in Fig. 4:12 provided this. It consisted of a vacuum tested alumina tube **T** which fitted into the two base plates **B**. O-ring seals between the base plates and **T** made the assembly vacuum tight. The copper tubing **C** was soft soldered in grooves cut in the base plates and provided the means for water cooling. The brass rods **R** prevented any possible strain

on **T** which might have led to its fracture. The heater coil **H** was wound in grooves cut in the alumina tube and secured by refractory cement. The nickel tube **N** was held centrally by its brass top which slotted into the base plate and passed down **T** to a point just above the specimen. This prevented stray electrons from striking the walls of the ceramic tube and charging it up.

Temperatures up to 1100°K were achieved without any difficulties being encountered due to the overheating of the O-rings. Problems associated with the stability of specimen electrodes at these high temperatures were not, however, overcome.

4 : 8 Amplifiers.

A schematic diagram of the amplification and display of the signals is shown in Fig. 4: 3. The output from the cathode-follower **C.F** was led via the pre-amplifier **P.A** to the distributed amplifier of a Tektronix type 541A oscilloscope. The gating unit described in 4:6 was connected directly to the glass-metal seal **B**, as was the grid of the cathode follower.

Since the charge displacement was integrated it was essential to keep the input capacity to the amplifiers as small as possible to obtain the maximum charge sensitivity. The input capacity was the sum of the specimen capacity and stray capacities and whilst, for a given crystal the specimen capacity was fixed, the stray capacities were kept as low as possible by the careful positioning of the components. A further reduction in the total input capacity was achieved by the use of the cathode follower, the circuit of which is given in Fig. 4:13. Particular care was taken

with the decoupling of all the supply leads in order to eliminate spurious pick-up emanating from the mains supply. The cathode follower had an input impedance of $7\text{ M}\Omega$ and an output impedance of 100Ω . From the cathode follower the output was fed via a short length of screened co-axial cable to the wide-band pre-amplifier (see Fig. 4:14). An amplification of 10 was obtained at a bandwidth of 27 Mc/s , whilst an amplification of 80 was available, at a reduced bandwidth of 12 Mc/s , with the switches S_1 and S_2 in position 2. The input time constant of the pre-amplifier was $10\text{ }\mu\text{secs.}$, and this eliminated any low frequency noise. The low frequency response could be reduced still further by making the input time constant to the oscilloscope amplifiers even smaller and switch S_3 permitted the variation of this time constant. This resulted in a much steadier signal display on the oscilloscope.

The system possessed an overall risetime of about 15 nanoseconds, and with a typical specimen, 1 cm. of vertical deflection represented about 10^5 charge carriers.

4 : 9 Experimental Method.

The electron beam was focussed by operating the gun at very low D.C. currents and observing the blue fluorescence produced by the electrons striking the calciumtungstate painted around the aperture in the specimen holder lid. The gun was switched to D.C. by applying to the filament a negative voltage, equal to that used to charge the delay line. The current through the magnetic lens was adjusted by a variable resistance until the fluorescent spot just passed into the aperture and the gun was then switched to pulsed working. The integrated transit pulse was displayed

on the oscilloscope by connecting the top electrode of the specimen to the pulsed voltage source by means of the switch described in 4:7. It was usually necessary to slightly adjust the focussing to obtain the maximum signal height from the crystal. Since many of the crystals were not very uniform in thickness, it was often found that the transit pulse was not sharply defined. By adjusting the path of the electron beam, so that it struck the crystal at different points on the electrode surface, the spot at which the transit pulse had its sharpest edge was found. This was easily done by varying the orientation of the magnetic lens by the adjustment of the three screws on which it rested. The incident pulse height was adjusted, by the variation of the output of the potentiometer charging the delay line, until the transit pulse represented the movement of about 10^6 carriers.

Measurements of the transit time were then made as a function of the voltage applied to the crystal. Consistent results were achieved by measuring the transit time as the voltage was increased and decreased. A check on space charge build up was conveniently carried out by the operating of the gun, using the single-shot arrangement, so that the crystal was bombarded with a few of the pulses out of phase with the field pulse.

For gain measurements the system had to be calibrated in terms of the number of carriers represented by 1 cm. deflection on the oscilloscope at maximum sensitivity. To do this, a fast voltage pulse of known value V was applied to the standard condenser C_S (see Fig. 4:3), and the amplified signal was displayed on the oscilloscope. If the amplified signal height

was χ cms. on the highest sensitivity range, then the charge sensitivity S_q of the system in terms of the number of charge carriers represented by 1 cm., S_q equals

$$S_q = \frac{V \times C_s}{e \times \chi} \text{ carriers/cm}$$

where e is the electronic charge in coulombs. The crystals were sufficiently thick that their capacity was negligible, compared with stray capacities, as was seen by the fact that S_q was the same whether the specimen was shorted out or not.

With a high gain material, such as CdS, this value of the charge sensitivity was of no value for measuring the number of incident carriers. This was because with the top electrode connected directly to the cathode follower input, the incident number was so small that no signal was seen on the oscilloscope. In this case the following method was used. A potential divider connected across the delay line, provided a potential equal to the pulse amplitude. This was reversed and switched in series with the bias battery, so that the steady beam-current then flowing was equal to that during the pulse. The second magnetic lens L'' (see Fig. 4:5(a)) was then switched in and the beam was deflected into the Faraday cup which was connected to a sensitive galvanometer. If the current sensitivity of the galvanometer was S_g amperes/cm., then the number of carriers represented by 1 cm. of deflection on the galvanometer scale was

$$\frac{S_g}{e} \times t_p$$

where t_p was the pulse length. In this way as few as 300 incident electrons could be measured.

CHAPTER 5

SPECIMEN PREPARATION AND CONTACT PROPERTIES

5 : 1 Survey of Methods of Growing CdS Single Crystals.

CdS single crystals are usually grown from the vapour phase. This can be done either by the interaction of cadmium vapour with sulphur vapour or H_2S gas, or by the sublimation of CdS powder followed by recrystallisation.

The first method was used by Frerichs (1947) to produce crystals of CdS by the high-temperature reaction of cadmium vapour and H_2S . A schematic diagram of a modified Frerichs technique is given in Fig. 5:1. The apparatus is divided into five sections in which, (1) the sulphur is vapourised, (2) the cadmium is vapourised, (3) any impurity to be incorporated, such as gallium, copper etc., is vapourised, (4) ~~where~~ the reaction between the cadmium and sulphur takes place, and (5) a buffer zone ~~to~~ provides the required temperature gradient. Usually H_2S gas is used rather than sulphur vapour and the first section is not needed. Quartz rods or plates are used to provide the surface on which the crystals grow. The vapours are moved through the apparatus by passing a carrier gas, commonly argon, through the system. Such a method, or modifications of it, has been used by Bishop and Liebson (1953) and Bube and Thomsen (1955). Single crystals of CdS have also been obtained by Miller and Bachman (1958) by directing beams of evaporated cadmium and sulphur onto a common substrate in vacuum.

In the sublimation method CdS powder is heated to a temperature high enough to obtain an appreciable vapour pressure. The vapour is

then carried by the flow of an inert gas to a rod or plate held at a lower temperature, where growth occurs. Using this technique, Hollander (1957) produced a single crystal 6 X 10 X 20 mm. CdS powder was placed in a quartz tube which, after evacuation, was filled with argon at atmospheric pressure. The tube was held at $900^{\circ}\text{C} \pm 5^{\circ}\text{C}$ for about 80 hours before being cooled slowly in a controlled manner. By using H_2S in place of the argon, Reynolds and Czyzak (1955) also obtained large single crystals.

The crystals used in the present work were grown using vapour phase techniques at R.C.A. laboratories, Princeton N.J., A.E.I. laboratories, Harlow, and E.M.I. laboratories, Hayes. Unless stated to the contrary all the crystals were undoped. The R.C.A. crystals were from the batch grown by Bube and Thomson (1955), in which Smith (1957) observed low-field electro-luminescence (section 3:2), and were used only for hole mobility measurements, since they were ~~typically~~ of the order of $50\ \mu$ thick. The crystals from A.E.I. and E.M.I. ranged in thickness from 20-300 μ .

5 : 2 Preparation and Mounting of Specimens.

Before the evaporating of electrodes and the mounting of a crystal, its thickness was determined. Because of the small size and fragile nature of most of the CdS crystals this proved a rather difficult problem. Also few of the crystals were plane parallel over the complete surface, so that the thickness was uniform only across restricted regions. The problem was overcome by the use of an optical lever built by Mr. A.R. Adams, a diagram of which is given in Fig. 5:2.

It consisted of a miniature optical lever which was made from the well balanced moving coil system of a D.C. meter. A small mirror M was stuck to the moving coil and reflected the image of a horizontal wire onto a scale at a distance of about 5 m. The vertical part of the lever L consisted of a small steel needle carefully rounded off at its lower end. The arrangement was screwed onto the table of a microscope, and the microscope condenser replaced by a similar needle L' . The crystal rested on the slide traverse so that its position in an horizontal plane could be adjusted with respect to L and L' . L was lowered onto the crystal, the coil spring of the meter movement applying a gentle pressure.

L' was then moved upwards until it touched the crystal, which occurred when the light spot began to move from its initial position. The crystal was then removed and the difference in the scale reading gave the local thickness. In this way the electrode region was tested for uniformity and the average thickness over the area to be bombarded was obtained. The system was calibrated with feeler gauges and possessed a sensitivity of about $1\ \mu$ per mm. of scale deflection.

The method of mounting a specimen is shown schematically in Fig. 5:3(a)(b). The specimen was mounted on a mica base M and attached to it by a film of silver paste. In the case of crystals intended for the study of hole mobility, the silver paste also formed the bottom electrode B (see section 5:3). In addition, the silver gave good thermal contact between the crystal and the copper platform of the specimen holder. For electron mobility measurements the same method of mounting the crystal was used, but in this case the bottom electrode was indium (section 5:3). A thin copper wire W was sandwiched in the silver paste

to provide contact to the bottom electrode.

In both electron and hole experiments the top electrode was made of a thin pyrex film 0.5μ thick on one side of which a gold layer was evaporated. The top face of the specimen also had an evaporated gold layer to ensure that it was an equi-potential surface. The pyrex film **P**, conducting face upwards, was pressed onto the specimen by a flat ring **R**. The ring was attached to a simple spring lever and was gently lowered by turning the screw **S**. In this way, **P** made intimate contact with the specimen and did not buckle. The mica base was secured to the specimen platform by four screws (see also Fig. 4:11(b)); the slots in the mica allowed the positioning of the specimen, so that the centre of the area of overlap of the top and bottom electrodes was on the electron-optical axis of the bombardment gear. To further improve the thermal contact between the copper rod and specimen at low temperatures, a spot of diffusion pump oil was placed between the mica base and the specimen platform. Finally, a chromel alumel thermocouple was clamped by a small nickel bracket **N**, as near to the specimen as practicable. To simulate the thermal environment of the specimen as closely as possible, the thermocouple was separated from the nickel bracket by a mica strip.

5 : 3 Investigation of Contacts to CdS Crystals.

The study of the charge transport in a material requires the use of electrodes, usually metals, to make electrical contact to it. A contact which plays no role in the electrical measurements, i.e. it is experimentally invisible, is termed a neutral contact. Although electrical contacts to some materials can approach the character of a neutral contact,

in most cases the contact is certainly not experimentally invisible and can drastically modify the electrical properties of a material.

The different kinds of contacts a metal can make to the conduction band of an n-type material such as CdS, are illustrated by the schematic energy band diagrams of Fig. 5:4(a),(b). The diagrams in Fig. 5:4(a) correspond to thermal equilibrium, whilst those of Fig 5:4(b) are the energy diagrams for an applied negative voltage to the contact. E_c , E_v refer to the bottom and top of the conduction and valence bands respectively, whilst F indicates the position of the Fermi level. ϕ_m and ϕ_{cds} are the work functions of the metal and CdS.

From the usual considerations of work functions, the ohmic contact would be expected to be formed by metals for which $\phi_m < \phi_{cds}$, the neutral contact would occur for $\phi_m = \phi_{cds}$, and the blocking contact would be produced by a metal for which $\phi_m > \phi_{cds}$. For the ohmic or injecting contact a reservoir of free electrons, present at the contact, is available for injection into the bulk when a negative voltage is applied. When an electron leaves the CdS at the anode contact, (not shown in the diagram) an electron will automatically enter at the cathode contact. It is this fact which makes high photoconductive gains possible. The middle diagrams show the neutral type of contact which is very difficult to obtain experimentally. The bottom diagrams indicate the rectifying or blocking contact. In this case an electron leaving at the anode cannot be replenished by another entering at the cathode contact because of the blocking action of this contact. Under these conditions the photoconductive gain is confined to unity at the most. It is important to realise that these properties are idealised, and under experimental

conditions divergences from these may be encountered. Smith (1955) showed that for metals with lower work functions than CdS, such as gallium and indium, the metal-CdS contact was ohmic for electrons. On the other hand, metals with a larger work function e.g. gold, silver and copper, made rectifying contacts to CdS. In other experiments with CdS Smith (1957) showed that gallium may be 'formed' so that it becomes an injecting contact for holes.

In the course of preliminary experiments on the carrier transport in CdS, using the fast pulse techniques described in chapter 4, it soon became apparent that the observation of the generated carriers was complicated by the presence of secondary effects. These were due to the injection of excess carriers through the electrodes. The choice of electrode material was therefore extremely critical and a series of experiments were carried out in order to determine the most suitable electrodes for the observation of the transit of generated carriers.

A number of 'pure', i.e. undoped CdS crystals, ranging in thickness between 50-250 μ , were prepared with top and bottom electrodes of indium and gold. The response of these specimens to fast excitation pulses, during the application of the pulsed field was examined. It was found that for specimens with indium electrodes the primary photocurrent was masked by electron injection. However, specimens with gold electrodes, which should show little injection, did not give pulses corresponding to electron transits. A possible reason for this may have been a reduced hole lifetime near the surface which would lead to a large density of trapped holes. The resultant strong positive space charge established in the excited region near the top electrode would tend to decrease and eventually annul the

the applied field in the crystal bulk.

These results suggested that the top electrode should be blocking for the carrier making the transit in order to prevent any injection current from swamping the transit of the generated carriers. In addition, if the bottom electrode were injecting for the carrier making the transit, then in the off period of the field, the trapped charge near the top electrode should draw carriers through the injecting bottom electrode, so that self-neutralisation would occur. (see Fig. 5:5 (a),(b)) In order to test whether a transit of generated electrons could be observed under these conditions, a specimen was prepared with a thin pyrex blocking electrode mounted on the top crystal face (section 5:2), and ^{with} an evaporated indium bottom electrode. With a negative voltage applied to the top electrode, a well-defined transit of generated electrons was detected using a 5 n.sec. excitation pulse. This seems to indicate that self-neutralisation does occur under these conditions. A similar self-neutralisation effect has recently been reported by Freeman, Kallman, and Silver (1961). During the transit of the electrons a positive space charge is established near to the top electrode since no holes can leave the crystal. In appendix 3 the effect that such a space charge produces on the applied field is discussed. For the incident carrier densities used in the present work it is shown that the effect is negligible.

Since the preliminary results showed that the gold also formed a blocking contact for electrons, a specimen, with an evaporated gold top electrode and indium bottom electrode was made. Again a well-defined transit of electrons was observed. Further experiments showed, however, that gold electrodes tended to become electron injecting after prolonged

bombardment and application of pulsed fields. Fig. 5:6 shows the results of measurements of the current voltage characteristics for a specimen with gold-indium electrodes under D.C. applied voltage, pulsed applied voltage, and pulsed applied voltage with pulsed bombardment. For the D.C. fields, the typical rectifier characteristics were obtained, but the pulsed field and pulsed bombardment resulted in the decrease in the rectification properties of the gold electrode. In this case the process was reversible but if the crystal was heated to about 200°C under bombardment the gold electrode became permanently electron injecting. Similar effects have been reported by Buttler and Muscheid (1954) and Davis (1958). For these reasons the pyrex blocking electrodes were used in all subsequent experiments.

In the case of the experiments on the drift mobility of holes in CdS (see chapter 6) similar considerations held, but for these investigations the bottom electrode had to be hole injecting and it was found that silver paste was admirably suitable for this purpose.

Chapter 6

EXPERIMENTAL RESULTS FOR HOLES

6 : 1 Room Temperature Drift Mobility and Lifetime Measurements.

At low applied fields ($E \approx 4 \times 10^3 \text{ v/cm}$), the observed pulse, corresponding to the movement of about 10^6 carriers, had the shape shown in Fig. 6:1(a). With larger fields, the rising edge of the pulse became practically linear (Fig. 6:1(b)). The intersection of the tangents at $t=0$ and $t \geq t_{tr}$ defined t' , which was measured as a function of the applied field E . Fig 6:2 shows experimental curves of $1/t'$ versus E/d for three specimens. It is seen that the curves have a linear portion at the higher field values, which, when extrapolated, does not pass through the origin of co-ordinates. Further, the experimental points, at low fields, do not lie on the extrapolated straight line, but tend to a constant $1/t'$ value. This behaviour has been explained in the following way (Mort and Spear (1962)).

For excitation restricted to a region, close to the top electrode, small compared with the crystal thickness, the Hecht formula (Hecht (1932)), has the form,

$$q(t) = \frac{Ne\mu E\tau_h}{d} (1 - e^{-t/\tau_h}) \quad \text{for } t \leq t_{tr} \quad (6:1)$$

and

$$q(t) = Q \quad \text{for } t > t_{tr}$$

N is the number of free carriers generated at $t=0$, $q(t)$ is the measured charge displacement after a time t and τ_h is the lifetime of a free hole with respect to deep traps (section 2:6).

Differentiating with respect to time, one obtains for the slope of the

$q(t)$ versus t curve at $t=0$,

$$\left(\frac{dq(t)}{dt} \right)_{t=0} = \frac{Ne\mu E}{d}$$

At $t=t'$, the intersection with the line $q(t) = Q$ is given by

$$\left(\frac{dq(t)}{dt} \right)_{t=0} \times t' = \frac{Ne\mu E}{d} t' = Q \quad (6:2)$$

Similarly, at $t = t_{tr}$, $q(t_{tr}) = Q$ and we therefore have

$$Q = \frac{Ne\mu E \tau_h}{d} (1 - e^{-t_{tr}/\tau_h})$$

which leads to

$$t' = \tau_h (1 - e^{-t_{tr}/\tau_h})$$

or

$$1/t' = 1/\tau_h [1 - \exp.(-t_{tr}/\tau_h)]^{-1}, \quad t_{tr} = d/\mu E \quad (6:3)$$

Curve (a) in Fig. 6:3 is a plot of τ_h/t' versus τ_h/t_{tr} . At low applied fields, as τ_h/t_{tr} approaches zero, t' tends towards τ_h . This means that measurements of t' , extrapolated to zero applied field, can lead directly to a value for the lifetime of a free hole. As the applied field increases, the curve becomes practically linear and runs almost exactly parallel to the line (b), obtained when $t' = t_{tr}$. For large ratios of τ_h/t' , ~ 100 , the two lines approach each other asymptotically. In the range of the present experiments, the difference in the gradients was only about 1%.

Seven crystals, ranging in thickness from 50μ to 165μ , from the three sources indicated earlier, were investigated. Curves of $1/t'$ versus E/d , for one specimen from each source, are given in Fig. 6:2 (a), (b) and (c), together with the corresponding curves of $1/t_{tr}$ versus E/d , which were obtained in the following way: a value for τ_h was

deduced from the intercept on the $1/t'$ axis, and with this, the experimental values of τ_h/t' were obtained. The corresponding values for τ_h/t_{tr} were then read off from Fig. 6:3. The linearity of the calculated $1/t_{tr}$ versus E_d curves indicates that the interpretation of the observed pulses in terms of deep trapping effects, is justified. The lifetimes for free holes in the seven specimens lay between 1×10^{-7} sec. and 3×10^{-7} sec., and the mean hole drift mobility was $15.0 \text{ cm}^2/\text{v}/\text{sec.}$

It is also possible to predict the shape of the experimentally observed pulses. From equations 6:1 and 6:2 one obtains

$$\frac{q(t)}{Q} = \frac{(1 - e^{-t/\tau_h})}{(1 - e^{-t_{tr}/\tau_h})} \quad \text{for } t \leq t_{tr} \quad (6:4)$$

Fig 6:4(a) is a photograph of a pulse due to the drift of holes, under an applied field of $3 \times 10^3 \text{ v/cm}$, in a crystal with a hole lifetime of 2×10^{-7} sec. Fig. 6:4(b) shows the predicted pulse shape for the ratio t_{tr}/τ_h , which equals 1.15. Superimposing Fig. 6:4(b) onto the photograph, it can be seen that the agreement between predicted and observed pulses is satisfactory.

6 : 2 Temperature Dependence of the Hole Drift Mobility and Interpretation.

The dependence of the hole drift mobility on the specimen temperature, over the range 500°K to 80°K , was investigated for five of the crystals. The crystal orientation was such that the holes drifted perpendicular to the c-axis of the crystals.

In these experiments, great care was necessary if consistent results were to be obtained. Particular attention was given to allowing the

specimen time to reach the temperature indicated by the thermocouple, before a measurement was made. This was particularly important at low temperatures where a few degrees error causes a large variation in $1/T$. Periodic checks on the room temperature mobility were also made, although the value never varied by more than 10%.

A plot of $\log(\mu_h/\mu_{RT})$ versus $1/T$, which correlates the results for all five specimens, is given in Fig. 6:5 and has several interesting features. Above room temperature, the mobility decreases as the temperature increases; this would be expected for a lattice controlled mobility. At about 220°K, however, $\log(\mu_h/\mu_{RT})$ passes through a maximum and then decreases linearly with $1/T$ down to the lowest temperature attained, 77°K. Another striking feature of the graph is the fact that the results for all the specimens lie closely on a common curve.

From the discussion given in section 2:6 (see also Fig. 2:2), a possible explanation for the results would be in terms of a transition from a lattice to a trap controlled mobility. The slope of the linear part of the graph would indicate a level of traps lying within 0.020 ± 0.002 ev of the top of the valence band. N_t , the density of these trapping levels, can be computed from the position of the maximum. Under the assumption that the lattice scattering is purely non polar involving only the acoustic modes, N_t would be $8 \times 10^{18} \text{ cm}^{-3}$ for $m_h^* = m_e$.

The possibility of such a trapping level has been tentatively suggested by Pedrotti and Reynolds (1960) to explain some features of the edge emission in CdS. Edge emission is the fluorescence which

occurs just to the long wavelength side of the fundamental absorption edge. It is characterised, at low temperatures, by two series of peaks equally spaced by 0.04 eV and displaced from one another by 0.025 eV (Furlong 1954). Much work has been done on edge emission and several models presented to explain its mechanism. Some workers have suggested that edge emission results from the luminescent decay of excitons (Kröger and Meijer 1954), whereas others have argued that the luminescence is due to the recombination of free and trapped carriers. Lambe, Klick and Dexter (1956) showed that the decay of the photocurrent was always more rapid than that of the luminescence. This could only be explained in terms of the recombination of a trapped electron with a free hole; the assumption of excitons was not necessary in this interpretation. In order to explain some of their results on the edge emission in CdS, Pedrotti and Reynolds (1960), used a band model involving a trap level 0.023 eV from the conduction band and a level 0.14 eV from the valence band. However, a mirror reflection of these centres about the middle of the forbidden energy gap would explain their data equally well. Insufficient experimental evidence prevented them from distinguishing between the two alternatives. In either case, however, the edge emission at 4.2°K was assumed to be caused by the recombination between two trapped carriers, whilst at higher temperatures the recombination between trapped and free carriers was postulated.

Several objections may be levelled against the possibility of a shallow level of acceptor states. The consistent failure to produce p-type CdS has always been attributed to the fact that the activation energy for p-type impurities in CdS is comparatively high (Kröger, Vink

and Boomgaard, 1954; Jenny and Bube, 1954). Also, if the activation energy obtained from Fig. 6:5 were associated with a level of traps, then it would be remarkable if the density of these traps did not vary from specimen to specimen, particularly as these were obtained from different sources. Such a variation of trap density should lead on a $\log(\mu_n/\mu_{nT})$ versus $\frac{1}{T}$ curve, to different positions of the mobility maximum and widely different μ_n values in the lower temperature range. The results for the temperature dependence of the electron drift mobility in CdS (see Fig. 7:1) are a typical example. It can, however, be seen that the present experimental results for the five specimens show an identical position of the mobility maximum and agree closely in the low temperature range. This suggests the possibility that the activation energy is not associated with a trapping level, but may be due to a more fundamental property of CdS crystals.

It was first observed by Gobrecht and Bartschat (1953) that a dichroism existed in the fundamental absorption of CdS. Two absorption edges were obtained, see Fig. 6:6, depending on whether the light was polarized with its E vector parallel or perpendicular to the c-axis of the crystal. According to Balkanski, the separation in energy between the two absorption edges was 0.02 eV at room temperature and decreased to about 0.016 eV at 4.3°K. Such a phenomenon can only be explained in terms of a knowledge of the band structure of CdS. The band structure for CdS near the centre of the Brillouin zone has been deduced from group theory considerations by Balkanski and des Cloizeaux (1960). Introduction of spin orbit coupling led to three complex valence bands originating from the sulphur 3p levels (Fig. 6:7).

On the basis of this band structure it is possible to explain the dichroism in the absorption edge. Balkanski and des Cloiseaux showed that transition (1), corresponding to the direct transition of an electron from the upper valence band to the conduction band, is only possible if the absorbed light is polarized with its $\vec{E}$ vector perpendicular to the c-axis. Transition (2), corresponding to a direct electron transition from the second valence band to the conduction band, however, may take place whether the light absorbed is polarized with its $\vec{E}$ vector perpendicular or parallel to the c-axis of the crystal. Thus the dichroism is explained in terms of transitions from the two valence bands which, at ordinary temperatures, have an energy separation of 0.02 ev.

It is therefore possible that the activation energy of 0.020 ± 0.002 ev, found in the present work to be associated with the hole drift mobility in CdS, is due to interband transitions of free holes between the upper two valence bands. Similar mechanisms have been suggested by Caldwell and Fan (1958) to explain the optical properties of tellurium, and by Ehrenreich (1960) to interpret Hall effect measurements on GaAs at higher temperatures. An analysis of the experimental results will now be presented in terms of such a model, and it will be seen that a mechanism of this type can go some way to explaining the puzzling behaviour of the edge emission in CdS. It must be stressed, however, that insufficient evidence makes a difficult interpretation even harder and until more substantial data is available the model must be regarded as a tentative attempt to explain the experimental observations.

A schematic representation of the model is given in Fig. 6:8, which

shows the two valence bands s and f separated by an energy ϵ . Assume a hole is created in band f , and that on the average it moves in this band for a time t_f with a mobility μ_f ; ~~and~~ ^{it} then drops into band s where it moves with a mobility μ_s for an average time t_s before being thermally excited back into band f . In this cycle the carrier has moved a distance $\mu_s t_s + \mu_f t_f$ in unit applied field. The number of such cycles during the transit time t_{tr} of the crystal of thickness d is

$$\frac{t_{tr}}{t_s + t_f} = \frac{d}{\mu_h} \left(\frac{1}{t_s + t_f} \right)$$

μ_h is the measured drift mobility.

The total distance travelled

$$d = \frac{d}{\mu_h} \left(\frac{1}{t_s + t_f} \right) \cdot (\mu_s t_s + \mu_f t_f)$$

Therefore re-arranging

$$\mu_h = \frac{\mu_f \left(1 + \frac{\mu_s}{\mu_f} \cdot \frac{t_s}{t_f} \right)}{\left(1 + \frac{t_s}{t_f} \right)} \quad (6:5)$$

The ratio of the times spent in the two bands t_s/t_f can be obtained by considering the probabilities of thermal release.

If the probability of a free hole being thermally excited from the s band into the f band is P_s , then the number per unit volume n'_s making the transition is

$$P_s n_s$$

where n_s is the density of free holes present in the s band.

Suppose that the bottom of the s valence band and the Fermi level lie at energies E_s and $\{$, and, if $\}$ lies more than a few kT from the bottom of the s valence band, one can use Maxwell-Boltzmann

statistics, giving

$$n_s = N_s e^{-(\zeta - E_s)/kT}$$

where N_s is the effective density of states at the bottom of the s band. Similarly, the number of free holes per unit volume falling from the f into the s band is

$$P_f n_f$$

where

$$n_f = N_f e^{-(\zeta - E_f)/kT}$$

N_f is the effective density of states at the top of the f band and E_f is the energy of the top of the f band.

The condition for thermal equilibrium to occur is that

$$P_s n_s = P_f n_f$$

and

$$\frac{P_f}{P_s} = \frac{n_s}{n_f} = \frac{N_s e^{-(\zeta - E_s)/kT}}{N_f e^{-(\zeta - E_f)/kT}} = \frac{N_s}{N_f} e^{E_f - E_s/kT}$$

$$\frac{n_s}{n_f} = \frac{N_s}{N_f} e^{E/kT} \quad (6:6)$$

and since $1/p_f = t_f$ the average time a free hole spends in the f valence band, we finally have

$$\frac{t_s}{t_f} = \frac{N_s}{N_f} e^{E/kT} \quad (6:7)$$

From equation 6:6 it can be seen therefore that, as the temperature is lowered, more holes will populate band s than band f in thermal equilibrium. Since the observed mobility μ_h was found to decrease with decreasing temperature, the mobility μ_s in the s

band must be smaller than the mobility μ_f in band f . The S band will therefore be called the slow band and band f the fast band. Substituting for t_s/t_f from 6:7 in 6:5, we finally obtain that the measured drift mobility

$$\mu_h = \frac{\mu_f \left[1 + \frac{\mu_s}{\mu_f} \frac{N_s}{N_f} e^{\epsilon/kT} \right]}{\left[1 + \frac{N_s}{N_f} e^{\epsilon/kT} \right]} \quad (6:8)$$

This substitution involves the assumption that a thermal equilibrium distribution of free holes occurs at any time and position of the drifting charge during the transit. The quantitative explanation of the experimental results in terms of equation 6:8 is complicated by the fact that the exact ratio of the mobilities and the effective density of states in the two upper valence bands in CdS are not known. Indeed, it will be seen that the present results suggest that to acquire such data may prove extremely difficult.

It is possible, however, from Fig. 6:5, to arrive at a fairly limited range of values for these ratios. The line of reasoning is as follows :-

1. Making the initial assumption that $\mu_s/\mu_f \ll 1$, it is possible to write 6:8 in the form

$$\mu_h = \frac{\mu_f}{1 + M e^{\epsilon/kT}} \quad ; \quad M = \frac{N_s}{N_f}$$

Referring to Fig. 6:5 it will be seen that the experimental curve follows an equation of the form

$$\mu_h = \frac{\mu_f}{M} e^{-\epsilon/kT} \quad (6:9)$$

to within 10% up to a temperature $\sim 220^\circ\text{K}$. This immediately requires that M must be ≥ 5 . Hopfield (private communication) has estimated that the effective masses of holes, in a direction perpendicular to the c-axis, are 0.7 for the slow band and ~ 1.0 for the fast band. In the absence of any other criteria, a value of $M=5$ was chosen to give as close agreement as possible to this effective mass data.

2, A value of $M=5$ implies an effective mass ratio of $\frac{m_s^*}{m_f^*} \sim 3$ and an estimate of the mobility ratio μ_f/μ_s can be obtained only on the assumption of spherical energy surfaces, since

$$\frac{\mu_f}{\mu_s} = \left(\frac{m_s}{m_f} \right)^n$$

where $n = 3/2$ for optical scattering
and $n = 5/2$ for acoustical scattering

Thus $\frac{\mu_f}{\mu_s} \sim 5$ for optical scattering and ~ 15 for acoustical scattering.

Substitution of these values for μ_f/μ_s , and the chosen value of $M=5$, into equation 6:8 allows a determination of μ_f as a function of temperature. However, these values do not result in the numerator in equation 6:8 remaining constant over the experimental temperature range. This constancy is essential if the experimental curve is to be described by an equation of the form of 6:9. Since larger values of M increase the divergence, the smallest value of the ratio μ_f/μ_s was chosen which ensured that the numerator was constant to within 10%. This value was found to be 50, and gave a room temperature value of

$$\mu_f = 165 \text{ cm}^2/\text{v}/\text{sec}, \text{ and } \mu_s = 3.3 \text{ cm}^2/\text{v}/\text{sec}.$$

Fig. 6:9 shows a plot of $\log \mu_f$ versus $1/T$. In the higher temperature range, neither the mobility μ_A , predicted for the

scattering by acoustic modes (equation 2:4,2:5), nor μ_o , the mobility determined by polar scattering by the optical modes, followed the experimental curve exactly. The formula of Howarth and Sondheimer, corrected by Petritz and Scanlon (equation 2:1), was used for μ_o with a characteristic temperature of 440°K, and both μ_A and μ_o were fitted to the value for μ_f at room temperature. The closest agreement with the experimental curve was provided by the acoustic mode scattering, $\mu_A = b T^{-3/2}$, if b was assumed to equal $9 \times 10^5 \text{ cm}^2 \text{K}^{3/2} / \text{v}/\text{sec}$, and since both μ_A and μ_o lay above the curve for μ_f no combination of the two gave a better fit.

At about 220°K the curve for μ_f begins to deviate appreciably from both lattice scattering curves and μ_f decreases with further decrease in temperature. The only scattering mechanism known to lead to this is that due to charged impurities or defects (section 2:4). Equation 2:6, which has the form $\mu_I = \frac{\text{constant}}{N_I} T^{3/2}$, was used with N_I , the density of charged defects, being the adjustable parameter. N_I was chosen so that a combination of μ_I with μ_A given by

$$\frac{1}{\mu_f} = \frac{1}{\mu_I} + \frac{1}{\mu_A}$$

fitted the curve for the fast mobility. The presence of about $8 \times 10^{17} \text{ cm}^{-3}$ defects had to be assumed and the dashed line in Fig. 6:9 shows this fitted curve. Assuming that the scattering mechanisms in the two valence bands were identical, the curve for μ_s would be as shown.

It appears therefore, that an interpretation of the results is

possible in terms of interband transitions between the upper two valence bands. For such an interpretation to be acceptable the experimental data requires:

1. The ratio of the effective masses in the two valence bands to be at least 3 and the ratio of the mobilities in the two bands to be equal to or greater than 50. These two ratios are inconsistent with a simple spherical energy band picture. If the mechanism suggested is correct, then one might question the validity of the assumption that the valence bands in CdS are parabolic in k-space. Hopfield (private communication) has pointed out that, above 100°K, the upper two valence bands cannot be regarded as quadratic, since kT is comparable with the valence band gap.
2. The mobility, below room temperature, in both bands is determined predominantly by a combination of acoustic and charged defect scattering. A comparatively high density of charged defects of $8 \times 10^{17} \text{ cm}^{-3}$ has to be assumed to fit the results. The possible nature of these defects is discussed in chapter 7.

It is also of interest to note that, in Fig. 6:9, the mobility at higher temperatures decreases more rapidly than predicted by either of the known lattice scattering mechanisms. A similar disagreement was observed with the electron mobility (see chapter 7) and the possible reasons for this disagreement will be discussed in chapter 8.

The transport of holes is envisaged in terms of their movement in the two valence bands with an associated activation energy of 0.02 ev. The decrease of the hole drift mobility with decreasing temperature occurs as a result of the increasing population of the upper valence

band by the holes, The ~~hole~~ mobility in this band being 50 times smaller than in the lower valence band.

Further evidence, which indicates that the above model is essentially correct, is contained in the work of Thomas and Hopfield (1959) and others. They observed that the green edge emission in CdS shifted to longer wavelengths as the crystal was cooled from 77°K to 4.2°K, whereas the band gap shift is in the opposite direction. When the shift in the direct gap was subtracted, the edge emission was found to have shifted by 0.023 ev to lower energies. This is exactly what would be expected from the transport model outlined above, since the present results indicate that with decreasing temperature the holes will move into the upper valence band which is 0.020 ev nearer the conduction band. Also one would expect that, since the graph of $\log \mu_n$ versus $1/T$ is still linear at 77°K, an appreciable number of holes still exist in the lower valence band. It would be expected, however, that a reduction in temperature below 77°K would eventually lead to an almost complete occupancy of the upper valence band and therefore to a shift in the edge emission of 0.02 ev. From equation 6:6, the ratio, of the density of holes in the slow valence band to the density of holes in the fast valence band would be 100 at 77°K and 10^{10} at 10°K.

Thomas and Hopfield (1959), in measuring the edge emission at 77°K, observed two peaks which they designated A and B. Peak A was found to be completely polarised with its E vector perpendicular to the c-axis of the crystal. The other peak had its E vector perpendicular and parallel to the c-axis. They found that the intensity ratio A/B was approximately that to be expected from a Boltzmann

distribution of holes between the upper two valence bands. At 4.2°K it was found that the edge emission was completely polarized with its $\mathbf{E}$ vector perpendicular to c . This would be expected if the holes were entirely concentrated in the A valence band. From Balkanski's results, Fig. 6:7, it can be seen that the A valence band is the upper or slow band as it is described in the present model.

It is suggested that the mechanism of edge emission may be the recombination between trapped electrons and free holes, as suggested by the work of Lambe, Klick and Dexter (1956), and that at temperatures exceeding 77°K , the holes are distributed between the two valence bands. The results of Pedrotti and Reynolds (1960), which can be explained in terms of a trap level 0.02 eV from the valence band, also seem to be consistent with the proposed model.

Chapter 7

EXPERIMENTAL RESULTS FOR ELECTRONS

7 : 1 Room Temperature Drift Mobility.

Five pure, i.e. undoped crystals were investigated at room temperature. The crystals, from A.E.I. and E.M.I., were 170μ to 300μ thick. No measurements were possible on the crystals from R.C.A., because of insufficient thickness. Crystals, thinner than about 170μ , were unsuitable since, with the fields required to give reasonable response, the transit times became comparable with the amplifier risetime. This restriction, and the limited supply of thick crystals, meant that the work on the electron mobility was necessarily less comprehensive than that for the hole mobility.

For the reasons discussed in chapter 5, the crystals for these investigations were prepared with indium bottom electrodes. Quite sharp, well defined electron transits were observed and the mobility values at room temperature ranged from $246\text{ cm}^2/\text{v}/\text{sec.}$ to $300\text{ cm}^2/\text{v}/\text{sec}$ with a mean value of $275\text{ cm}^2/\text{v}/\text{sec.}$

7 : 2 Temperature Dependence of the Electron Drift Mobility and Interpretation.

Measurements on three crystals were made over the temperature range $500 - 85^\circ\text{K.}$ A correlation graph for the specimens of $\log(\mu_e/\mu_{HT})$ versus $\frac{1}{T}$ is given in Fig. 7:1. At temperatures above 300°K the results for the three crystals fall closely on a common curve. Over this temperature range the mobility is determined by the scattering of free electrons by the lattice vibrations. It can be seen that for

each crystal the mobility goes through a maximum below room temperature. The main feature which distinguishes these results from the temperature dependence of the hole mobility (Fig. 6:6), is that the position of the maximum and the low temperature mobility values are dependent on the specimen itself. For specimen C8 the maximum occurs at 220°K, whilst for C23 it lies at 190°K and for C26 at 133°K. After passing through the maximum $\log \mu_e$ for C8 and C23 decreases linearly with $1/T$, although with slightly different slopes. The maximum for C26 is quite broad, and the linear decrease is only apparent below 95°K. This behaviour strongly suggests that the mobility undergoes a transition from a lattice controlled to a trap-controlled mobility, as discussed in section 2:6.

The attempts to fit the theoretical lattice scattering curves to the experimental results are shown in Fig. 7:2. At temperatures in excess of 400°K, neither the mobility curve predicted for non-polar scattering by the acoustic modes $\mu_a = b T^{-3/2}$ (equations 2:4, 2:5), nor that for polar scattering by the optical modes μ_o (equation 2:1) gave a satisfactory fit. The value of the b required to fit μ_a to the experimental curve was $1.5 \times 10^6 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1} \text{ K}^{3/2}$. For μ_o the characteristic temperature was taken to be 440°K and $m^*e = 0.2 m_e$. For temperatures greater than about 400°K it would be expected that optical mode scattering would become important, because these modes are excited in this temperature range. The observed disagreement has previously been reported by Piper and Halstead (1960) for CdS, by Petritz and Scanlon (1955) for PbS, and by Ehrenreich (1957) for InSb. Possible reasons for this discrepancy

will be given in chapter 8.

Since the mobility for specimen C26 does not pass through a maximum until a temperature of 133°K , it was assumed that it would follow one of the lattice scattering curves down to about 165°K . It can be seen that, apart from the disagreement at higher temperatures, the experimental curve for C26 lies on the curve for non-polar scattering by the acoustic modes down to this temperature. Such a behaviour may be expected since CdS is predominantly covalent and most of the experimental temperature range lies below the characteristic temperature of 440°K necessary to excite the optical modes.

An interpretation of the electron drift mobility results in the low temperature range in terms of a trap-controlled mobility will now be given. It will be seen, however, that the analysis is complicated by the shallow depth of the traps involved.

The relation between the drift mobility μ_e and lattice-controlled mobility μ_L , in the presence of a shallow discrete trapping level, is given by

$$\mu_e = \frac{\mu_L}{1 + \frac{N_t}{N_c} e^{\epsilon/kT}} \quad (7.1)$$

where N_t is the density of traps, N_c is the effective density of states in the conduction band and ϵ is the activation energy associated with this level. For $\log \mu_e$ versus $1/T$ to be linear then $\frac{N_t}{N_c} e^{\epsilon/kT}$ must be much greater than unity. Under this condition it is possible to write

$$\mu_e = \mu_L \frac{N_c}{N_t} e^{-\epsilon/kT} \quad (7.2)$$

and from the linear portions of the experimental curves for the specimens the activation energy ϵ for each was computed. Using equation 2:8, an estimate of the density of traps was made from the position of the maximum. The values are summarised in table 1.

TABLE 1

CRYSTAL SOURCE	ACTIVATION ENERGY ϵ	DENSITY OF TRAPS N_t
C 26 A.E.I	$\sim 0.027 \text{ eV}$	$4 \times 10^{16} \text{ cm}^{-3}$
C 23 E.M.I	$0.020 \pm 0.002 \text{ eV}$	$4 \times 10^{17} \text{ cm}^{-3}$
C 8 A.E.I	$0.018 \pm 0.002 \text{ eV}$	$7 \times 10^{17} \text{ cm}^{-3}$

The small values for the activation energies provide a further indication that the predominant lattice interaction with the free electrons, at least below room temperature, is that due to the non-polar acoustic modes. If $\log \mu_e$ versus $1/T$ is to be linear, then it can be seen from equation 7:2, that the product $\mu_e N_c$ must remain essentially constant or its temperature dependence must be negligible compared with the change in the exponential term. Since the value of ϵ is so small, the variation of the exponential term

is not large enough to allow any temperature dependence of $\mu_c N_c$.

N_c , which does not depend on the scattering mechanisms, is $\propto T^{+3/2}$ and the only possible scattering mechanisms which will make $\mu_c N_c$ temperature independent is that by non-polar acoustic modes, since $\mu_a \propto T^{-3/2}$. The relatively low value of N_t for specimen C26 explains the broad mobility maximum observed for this crystal, since $\frac{N_t}{N_c} \cdot e^{E/kT}$ cannot be assumed to be $\gg 1$. At a temperature of 110°K, $\frac{N_t}{N_c} \cdot e^{E/kT}$ is about 1.2, whilst at 86°K it is about 5.

Although the explanation of these results, in terms of a trap-controlled mobility at low temperatures, is made difficult by the small activation energies or trap depths involved, there seems to be sufficient experimental evidence to justify such an attempt. Since the density of the traps is different for each crystal, the results further suggest that the origin of these levels is either impurities or lattice defects. In either case it is assumed that these shallow traps are due to compensated donors. The identification of these levels with particular physical defects is a difficult problem, but some possibilities as to their nature will be discussed. The origin of the donor levels will be treated first and throughout the discussion it will be assumed that compensating acceptors are present which convert the donor levels into electron traps.

An obvious explanation of the donor levels would be the presence of an impurity such as chlorine. In this case a divalent sulphur ion S^{--} is replaced by the monovalent chlorine ion Cl^- to produce a net positive charge at this site. An electron trapped there could re-enter the conduction band on receiving the necessary activation energy.

This energy has been measured by Kröger, Vink and Boomgaard (1954) and for low chlorine concentration was found to be 0.03 ev. However, an explanation of this kind seems unlikely in the present experiments. The crystals investigated were grown from highly purified starting materials, and considerable care was taken to exclude impurities during growth. This seems to rule out the required impurity concentration of the order of 10^{18}cm^{-3} .

A more likely explanation of these levels is in terms of a non-stoichiometric composition of the crystals used. This possibility cannot be excluded with a compound crystal such as CdS even under careful control of growth. It is known that the introduction of an excess of cadmium can result in increased n-type conductivity in CdS. The mechanism can be understood by considering the extreme case of heating a CdS crystal in an atmosphere of cadmium vapour. This treatment gives rise to new layers of material formed on the crystal surface. Sulphur ions diffuse to the surface ~~ions~~ leaving anion vacancies behind; cadmium atoms combine with these ions and give up two electrons to the crystal, thus balancing the effective charge of the negative ion vacancies. The region around the sulphur ion vacancy is positively charged and can be expected to trap these extra electrons, so that a thermal activation energy is required to release them into the conduction band. It is likely that the sulphur ion vacancy has a relatively large binding energy for one electron and a substantially weaker binding for a second electron. The activation energy ϵ_1 , for the first electron to be released can be roughly estimated, using the hydrogen orbit approximation, as 0.04 ev. The activation energy ϵ_2 , for the

second electron can also be found approximately by using a model resembling a helium atom. According to this model, $\epsilon_2 > 4\epsilon_1$, giving a value for ϵ_2 of about 0.16 ev. Activation energies in such n-type CdS have been measured by Kröger, Vink and Boomgaard (1954) who found a value of 0.03 ev.

A third possibility is that the crystals used were of stoichiometric composition and free from impurities but contained a large density of defects. Such defects, including vacancies and interstitials, could be formed during the crystal growth, particularly as this takes place at high temperatures (see section 5:1). Again, sulphur vacancies could occur and act as a trap for two electrons, as explained above.

A similar line of reasoning can be followed in considering the origin of the required acceptor states. Again, a monovalent positive impurity ion such as silver, which produces acceptor levels, is excluded from purity considerations. The more likely possibility is the presence of cadmium ion vacancies resulting from non-stoichiometric or stoichiometric defects. Bube (1955) has found the ionisation energy of these defects to be 1.0 ev. Such levels, lying in the middle of the band gap, would form excellent compensators. Nickisch (1961) has observed these levels in undoped crystals and estimated their density to be greater than 10^{16}cm^{-3} .

Each of the possible explanations for the existence of both donor and acceptor defects has so far been considered separately. This is certainly unrealistic, and it appears more reasonable to suppose that they occur together in a real crystal. However, the experimental evidence suggests that the contribution from impurities is negligible compared with that of defects.

Chapter 8

DISCUSSION OF RESULTS.

In this chapter, the experimental results will be discussed and compared with previous work on charge transport in CdS. Suggestions for further experiments, using the technique described in this thesis, will also be made.

The room temperature value for the electron drift mobility μ_e of $275 \text{ cm}^2/\text{v}/\text{sec}$ agrees well with values of the electron Hall mobility obtained by Piper and Halstead (1960) and Kröger et al (1955). This indicates that shallow trapping is insignificant at these temperatures, as verified by the present work (see Fig. 7:1). μ_e has recently been measured by Hutson, McFee and White (1961) who used an independent method (see section 3:1). They found $\mu_e = 285 \text{ cm}^2/\text{v}/\text{sec}$ in good agreement with the above value.

The temperature dependence of μ_e , below 220°K , has been interpreted here in terms of a trap-controlled mobility. This explanation differs from that given by Piper and Halstead (1960), since they measured the temperature dependence of the electron Hall mobility, which should be unaffected by multiple shallow trapping. The results of these authors (section 3:1) can be explained by the presence of incompletely compensated donors, since even their pure specimens have a conductivity of $\sim 1 \Omega^{-1} \text{ cm}^{-1}$. The observed mobility maximum and subsequent decrease with decreasing temperature is assumed to be caused by charged impurity scattering. Since the mobility maximum shifts to higher temperatures with increase in gallium concentration, (see Fig. 3:2, 3:3), this indicates that the gallium itself causes scattering ^{that} or ^{or} its incorporation into the

lattice produces other charged defects. The present results (see Fig. 7:2) do not reveal the presence of charge defect scattering, probably because the mean free path before a trapping event is less than that for charged defect scattering to occur.

It has been assumed that the traps are associated with donor levels completely compensated by an equal or greater density of acceptor levels. It would appear, therefore, that a difference, in the degree of compensation, existed between the crystals used by Piper and Halstead (1960) and those investigated in the present work.

More information concerning the nature of both donor and acceptor defects in undoped CdS could be obtained by further drift mobility experiments. It would be of interest to investigate crystals of non-stoichiometric composition, produced by heating pure crystals in atmospheres of Cd and S vapour. Experiments on crystals before and after careful annealing might also give further indications as to the origin of the defects. Further, it would be of interest to study the effects of deliberate doping by the addition of different impurities. An extension of these experiments to lower temperatures would also be useful.

Since the electron and hole drift mobilities and hole lifetimes are now known, it is possible to predict values of the ambipolar diffusion constant and ambipolar diffusion length and compare them with values estimated from the P.E.M. effect.

In section 3:2 it was pointed out that Sommers et al (1956) had obtained a value for $\mu^* \tau_a \sim 1 \text{ cm}^6/\text{v}^3/\text{sec}^2$ at room temperature, where μ^* is the ambipolar mobility defined by Van Roosebroek (1953)

and τ_a is the ambipolar diffusion lifetime. μ^* , as defined by Van Rosebroek is only applicable to cases where the density of free photo-excited carriers is very much less than the dark density of free carriers. This would not be the case for the insulating CdS crystals used by Sommers et al. It can also be shown (Diemer and Hoogenstraaten (1957)) that for an insulator μ^{*3} must be replaced by

$$\mu^{*3} = [2\mu_e\mu_h(\mu_e + \mu_h)]$$

where μ_e and μ_h are the electron and hole drift mobilities.

Inserting the value $\mu_e = 275 \text{ cm}^2/\text{v}/\text{sec}$, $\mu_h = 15 \text{ cm}^2/\text{v}/\text{sec}$ at room temperature and assuming $\tau_a = \tau_h = 2 \times 10^{-7} \text{ sec}$. it is found that $\mu^{*3}\tau_a = 0.5 \text{ cm}^6/\text{v}^3/\text{sec}^2$. An estimate of the ambipolar diffusion length l_a is readily made since

$$l_a = \sqrt{D_a \tau_a}$$

where D_a is the ambipolar diffusion constant. (Diemer and Hoogenstraaten (1957))

and

$$D_a = \frac{2\mu_e\mu_h}{\mu_e + \mu_h} \cdot \frac{kT}{e}$$

using the same experimental values as above $l_a = 3.7 \times 10^{-4} \text{ cm}$. Auth (1961) has estimated the ambipolar diffusion length in CdS using the P.E.M. effect and obtained values ranging from $0.4 - 3.7 \times 10^{-4} \text{ cm}$. The agreement between the calculated values of l_a , D_a and $\mu^{*3}\tau_a$ and those estimated from the P.E.M. effect is therefore satisfactory.

The interpretation of the temperature dependence of the hole drift mobility, given here in terms of a transport mechanism involving the upper two valence bands in CdS, is consistent with the observed dichroism of the absorption edge and with some of the polarization effects

associated with the edge emission in CdS. A conclusive verification, or otherwise, of the model might be obtained by an extension of the hole drift mobility measurements to lower temperatures. At temperatures below 77°K, the model indicates that the population of holes in the slow mobility band should rapidly increase. Referring to Fig. 6:9, if the model is correct, the experimental curve ought to merge with the μ_s curve at some temperature below 77°K. Under such circumstances the plot of $\log \mu_h$ versus $1/T$ would lose its linear shape and μ_h would then follow a $T^{+3/2}$ curve. Such an experiment would, however, present serious difficulties. In the first place, the hole lifetime would tend to decrease because of the increased capture cross-section at lower temperatures. As explained previously (section 4:2), this could be overcome, in principle at least, by an improvement in the amplifier risetime. A more serious complication would be the increase in the equilibrium level of space charge caused by the extremely slow thermal release of trapped holes at these temperatures.

Further experiments on the hole drift mobility could be carried out on crystals with orientations such that the holes drift along the c-axis of the crystal. It would be interesting to attempt a verification of the predicted anisotropy of the hole mobility in the slow mobility band (Hopfield and Thomas (1961)).

It is remarkable that in previous attempts to explain the temperature dependence of the electron mobility in the range where it is determined by lattice scattering, the polar optical modes have been assumed to predominate. Piper and Halstead (1960) and Miyazawa et al (1959), made this assumption. In view of the predominant covalent

nature of the bonding in CdS and the relatively high characteristic temperature $\Theta = 440^{\circ}\text{K}$, at which the optical modes are excited, it seemed more reasonable to assume that, up to about 400°K , acoustical modes dominated the lattice scattering. Some experimental evidence for this view has been given in chapters 6 and 7.

At temperatures greater than about 350°K , however, both electron and hole mobilities decreased more rapidly with temperature than predicted by either type of scattering. This observation seems to apply to all the previous work on the electron Hall mobility in CdS. In order to explain a similar disagreement in PbS, Petritz and Scanlon (1955) suggested that a possible source of error lay in the perturbation theory expressions, for the scattering cross-sections of the polar optical modes, for temperatures greater than Θ . Ehrenreich (1957) extended the theory of Howarth and Sondheimer (1953) to cover the case of non-parabolic energy bands and found that the revised formula resolved a similar discrepancy between theory and experiment in InSb. There is some evidence, particularly for the valence bands (see chapter 6), that the energy bands in CdS cannot be regarded as being parabolic in k-space.

APPENDIX 1 (see page 27)

Assume at $t=0$, N_0 electron-hole pairs are generated. Under the action of the applied field, $N(t_p)$ holes move out of the excited region between $x=0$ and $x=p$, ($p \ll d$) and after a time t reach a depth $z(t)$. Diffusion is assumed to be negligible. This thin sheet of charge slightly perturbs the applied field $E_0 = V/d$ so that $E_1 < E_0$ and $E_2 > E_0$.

By Gauss's Law

$$E_2 - E_1 = \frac{4\pi N(t)e}{K}$$

and from the continuity of potential

$$V = E_1 z(t) + E_2 (d - z(t)).$$

Solving for E_1 and E_2

$$E_1 = E_0 - \frac{4\pi N(t)e}{K} \left(1 - \frac{z(t)}{d}\right)$$

$$E_2 = E_0 + \frac{4\pi N(t)e}{K} \frac{z(t)}{d}$$

The charge induced on the electrodes is given by $E = \frac{4\pi q(t)}{K}$

so that

$$q_B(t) = -\left(\frac{KE_0}{4\pi} + \frac{N(t)z(t)e}{d}\right) ; \quad q_T(t) = \frac{KE_0}{4\pi} - eN(t)\left(1 - \frac{z(t)}{d}\right)$$

at $t=0$

$$q_B(0) = -\frac{KE_0}{4\pi} \quad ; \quad q_T(0) = \frac{KE_0}{4\pi} - N_0 e \quad (i)$$

at $t=t_r$

$$q_B(t_r) = -\frac{KE_0}{4\pi} - N(t_r) e \quad ; \quad q_T(t_r) = \frac{KE_0}{4\pi} \quad (ii)$$

Equations (i) and (ii) indicate that a charge $-N(t_r)e$ has moved from T to B and a charge $+N(t_r)e$ has moved from B to T through the external circuit.

At times between $t=0$ and $t=t_r$

$$\Delta q_B(t) = \frac{N(t) e z(t)}{d}$$

APPENDIX 2 (see page 32)

From the vector diagram

$$V_{out} = \frac{V_{app}}{2} - V_c = \overline{OA} - V_c = \overline{AB} = \overline{AD} = \frac{V_{app}}{2}$$

Thus, the output from the phase shift network is constant, at $\frac{V_{app}}{2}$

and for a condenser V_{out} leads V_{app} by ϕ

where

$$\phi = 180^\circ - \delta$$

but since

$$V_{out} = \frac{V_{app}}{2} \quad \delta = 180^\circ - 2\theta$$

$$\therefore \phi = 2\theta$$

Now

$$\tan \theta = \frac{Z}{R} = \frac{1/\omega C}{R} = \frac{1}{\omega C R}$$

and when

$$R = 0, \quad \theta = 90^\circ \quad \text{and the phase angle } \phi = 180^\circ$$

$$R = \infty, \quad \theta = 0 \quad \text{and the phase angle } \phi = 0$$

The lower value of ϕ is determined by the actual values of R and C used.

The same discussion holds, where an inductance is used in place of the condenser, except that V_{out} lags behind the applied voltage.

APPENDIX 3 (see page 47)

Assume a uniform density of positive carriers N is distributed throughout the excited region. The applied field E_0 is such that electrons are drawn out of the excited region into the crystal bulk, which is assumed to remain free from space charge.

Poisson's equation for the excited region, in one dimension, is

$$\frac{dE}{dx} = \frac{4\pi Ne}{\kappa}$$

$$E_1 = \frac{4\pi Nex}{\kappa} + C_1$$

$$V_1 = -\frac{2\pi Nex^2}{\kappa} - C_1 x + C_2$$

at $x = p$, let $E_1 = E_p$

$$E_p = \frac{4\pi Nep}{\kappa} + C_1$$

therefore

$$C_1 = E_p - \frac{4\pi Nep}{\kappa}$$

and

$$E_1 = \frac{4\pi Nex}{\kappa} + E_p - \frac{4\pi Nep}{\kappa} \quad (1)$$

integrating

$$V_1 = -\frac{2\pi Nex^2}{\kappa} - E_p x + \frac{4\pi Nepx}{\kappa} + C_2 \quad (2)$$

since at $x=0$, $V=0$ then $C_2=0$

For the remaining region $N=0$ so that $E_2 = \text{constant} = E_p$

$$V_2 = -E_p x + C_3$$

so that

$$V_2 = E_p (d-x) + V_d$$

at $x=p$, V_1 must equal V_2 i.e. from (1) and (2)

$$-\frac{2\pi N e p^2}{\kappa} - E_p p + \frac{4\pi N e p^2}{\kappa} = E_p (d-p) + V_d$$

solving for E_p

$$E_2 = E_p = \frac{-V_d}{d} + \frac{2\pi N e p^2}{\kappa d} = E_0 + \frac{2\pi N e p^2}{\kappa d}$$

$$\text{or } |E_2| = |E_0| - \frac{2\pi N e p^2}{\kappa d}$$

from (1)

$$E_1 = \frac{4\pi N e (x-p)}{\kappa} + E_2$$

or

$$|E_1| = \frac{4\pi N e (p-x)}{\kappa} + |E_2|$$

From these solutions it can be seen (see diagram below) that in the crystal bulk the field E_2 is decreased by a constant amount whilst, in the excited region, the field E_1 increases linearly from E_2 at $x=p$

Taking a value of $N = 10^{13} \text{ cm}^{-3}$ for the density of generated carriers,

$$\rho = 5 \times 10^{-4} \text{ cm}, \quad d = 10^{-2} \text{ cm}, \quad K = 10, \quad E_{\text{omin}} \sim 1000 \text{ v/cm}$$

$$|\Delta E_2| = 30 \text{ v/cm}$$

$$\therefore \frac{\Delta E_2}{E_{\text{omin}}} \sim 3\% \quad \text{maximum}$$

$$|\Delta E_1|_{\text{max}} \sim 900 \text{ v/cm}$$

$$\therefore \frac{\Delta E_1}{E_{\text{omin}}} \sim 90\% \quad \text{maximum}$$

The fact that the space charge reduces the applied field by a constant amount justifies the assumption of the existence of a uniform field in the crystal bulk made throughout the mobility measurements. The above estimate of $\Delta E_1/E_{\text{omin}}$ has been made only for one incident pulse. The space charge presumably accumulates during several pulses until ΔE_1 becomes sufficiently large to produce injection. An equilibrium density of space charge probably exists, producing a field just less than that required for injection to occur.

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Fig. 2:1 Dispersion curves for a diatomic linear lattice.

Fig. 2:2 Transition from lattice controlled to trap controlled mobility in monoclinic selenium (after Spear 1961).

Fig 31

Fig. 3:1 Calculated and experimental values of the electron Hall mobility for the temperature range where it is limited by lattice vibrations (after Kröger, Vink and Volger 1954).

Fig 32
33

Fig. 3:2 Temperature dependence of the Hall constant for n-type CdS. In order of increasing magnitude the concentration of added Ga was $6 \times 10^{17} \text{ cm}^{-3}$, $2 \times 10^{17} \text{ cm}^{-3}$, $2 \times 10^{16} \text{ cm}^{-3}$ and none added to the top three curves.

Fig. 3:3 Temperature dependence of the Hall mobility. Points refer to the same samples as shown in Fig. 3:2. The solid curve is the theoretical mobility $\mu = (\mu_0^{-1} + \mu_p^{-1})^{-1}$ for $\frac{m_e^*}{m_e} = 0.16$ (after Piper and Halstead 1960).

Fig. 3:4 Observed attenuation as a function of the drift field. Zero db represents attenuation with sample unilluminated (after Hutson, McFee and White 1961).

Fig. 4:1
4:2

Fig. 4:1 Illustration of the principle of the transit time method for determining the carrier mobility.

Fig. 4:2 Integrated charge displacement of electrons generated in the surface region by an electron bombardment pulse; (a) in the absence of space charge, (b) with a negative space charge due to the capture of electrons by deep traps, (c) with a positive space charge due to the deep trapping of holes.

Fig. 4:3
4:4

Fig. 4:3 Schematic diagram of the apparatus.

Fig. 4:4 Phase relationships between, bombardment pulse, field pulse, and operation of gate.

Fig. 4:5

Fig. 4:5 (b)
Details of control grid
and first anode.

Fig. 4:5 (c)
Plan view of control grid

Fig. 4:5 (a) Electron gun.

Fig. 4:6 Nanosecond pulse generator.

Fig. 4:7 Driving unit for relay used in nanosecond pulse generator.

Fig. 4:6
4:7

Fig. 4:8 Milli-second field pulse generator.

Fig. 4 :9 Gating unit.

Fig 4:10 Driving unit for gate.

Fig. 4:8
4:9
4:10

Fig. 4:11 (a) Specimen holder used in the experiments.

Fig. 4:11 (b) Plan view of top of the specimen holder.

Fig. 4:11 (c) Schematic diagram of switching arrangement underneath the specimen holder.

Fig. 4:12 Specimen holder built for experiments at temperatures in excess of 500°K.

Fig. 4:11
4:12

Fig. 4:13 Cathode follower circuit.

Fig. 4:14 Circuit of the wide-band pre-amplifier.

Fig. 4:13
4:14

Fig. 5:1 Schematic diagram of the modified Frerichs technique for growing CdS from the vapour phase.

Fig. 5:2 Optical lever for accurate measurement of crystal thickness.

Fig. 5:1
5:2

Fig. 5:3(a) Specimen mounting arrangement.

Fig. 5:3(b) Side view of a mounted specimen.

Fig. 5:4(b) Energy diagrams for the same contacts with an applied negative voltage.

Fig. 5:4(a) Energy band diagrams of metal- CdS contact, under thermal equilibrium.
 $\phi_m < \phi_{cds}$, $\phi_m = \phi_{cds}$, $\phi_m > \phi_{cds}$

Fig. 5:3
5:4

Fig. 5:5(a)

Establishment of strong positive space charge by generated holes unable to leave the crystal. Bottom electrode injecting for electrons which make the transit.

Fig. 5:5(b)

Self-neutralization due to the injection of electrons through the indium bottom electrode.

Fig. 5:6 Current - voltage characteristics for CdS crystal with the indicated electrodes. Voltage applied to the gold top electrodes.

Fig. 5:5
5:6

Fig. 6:1 (a) Observed charge displacement due to holes drifting in a low applied field so that $t_{tr} > \tau_h$

Fig. 6:1 (b) Observed charge displacement due to holes drifting in a larger applied field so that $t_{tr} < \tau_h$

Fig. 6:1

FIG. 6:2 Plot of $1/\tau$ versus E/d for one crystal from each source. The hole lifetime τ_h was directly obtained from the intercept indicated. The curve $1/\tau_{tr}$ versus E/d was calculated from the experimental points using Fig. 6:5.

Fig. 6:3 The calculated curve (a) is a plot of τ_h/t' versus τ_h/t_{rr} obtained from equation 6:3. Curve (b) results when $t' = t_{rr}$.

Fig. 6:4 (a) Photograph of charge displacement due to holes drifting in an applied field of 3×10^7 v/cm. The hole lifetime in the crystal $\tau_h = 2 \times 10^{-7}$ second and $t_{rr}/\tau_h = 1.15$

(b) Predicted pulse shape calculated from equation 6:4.

A comparison between predicted and observed pulse shapes can be made by superimposing (b) on (a).

Fig. 6:3
6:4

Fig. 6:5 Plot of $\log(\mu_h/\mu_{RT})$ versus $1/T$ for five specimens from the sources indicated. μ_{RT} , the mean hole drift mobility at room temperature, = $15 \text{ cm}^2/\text{V}/\text{sec.}$

Fig. 6:6

Absorption edge in CdS, at room temperature, for light polarised with its E vector $\perp$ to the c axis of the crystal and $\parallel$ to c . (After Balkanski and Waldron (unpublished)).

Fig. 6:7

Schematic representation of the allowed direct optical transitions for light polarised with its E vector $\perp$ to c and $\parallel$ to c . (After Balkanski and des Cloiseaux (1960)).

Fig 6:6
6:7

Fig. 6:8

Proposed model for interpreting the observed temperature dependence of the hole mobility in CdS.

Fig. 6:9 Plot of $\log \mu_h$ versus $1/T$

μ_f is the mobility in the fast band calculated from equation 6:8 using the experimental data from curve $\mu_{\text{exp.}}$.
 $\mu_f(\text{calc.})$ is the fitted mobility curve given by $\mu_f(\text{calc.}) = (\mu_A^{-1} + \mu_I^{-1})^{-1}$.
 μ_s is the mobility in the slow band obtained from curve μ_f using the chosen mobility ratio $\mu_f/\mu_s = 50$.

Fig. 7.1 Plot of $\log(\mu_e/\mu_{RT})$ versus $1/T$ for the electron drift mobility. μ_{RT} , the mean value of the drift mobility at room temperature, = $275 \text{ cm}^2/\text{v}/\text{sec}$.

Fig. 7:2

Temperature dependence of the electron drift mobility. Points refer to same specimens as in Fig. 7:1.

μ_A is the predicted mobility determined by the non-polar acoustic modes; μ_0 is the mobility determined by the polar optical modes. Both curves were fitted at room temperature.

HOLE DRIFT MOBILITY AND LIFETIME IN CdS CRYSTALS*

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(Received March 5, 1962)

In view of the considerable interest in the properties and applications of CdS, it is surprising to find that hardly any information is available on the transport properties of holes in these crystals. Low-field electroluminescence experiments, photoelectromagnetic effect,² and other measurements^{3,4} have led to the conclusion that holes must be mobile. A hole lifetime τ_h between 10^{-7} and 10^{-6} sec has generally been estimated.

By the use of fast-pulse techniques it has been found possible to study the drift mobility of holes in a very direct way and to obtain consistent values for both μ_h and τ_h . In the experiments a 40-keV electron pulse of a few nsec duration⁵ generates free carriers to within a depth of about $5\ \mu$ below the top electrode. Holes are drawn out of this region by a pulsed applied field and drift across the specimen. The resulting charge displacement is integrated and displayed on wide-band electronic equipment. The success of the experiment depends largely on the choice of suitable electrodes. Work on the electron drift mobility in CdS⁶ suggested the use of a noninjecting top electrode and an injecting bottom electrode for the type of carrier drifting across the specimen. In the present investigation a thin blocking top electrode (transparent to the electron beam) and a Au or Ag bottom electrode were therefore used. The blocking electrode consisted of a $0.5\ \mu$ blown Pyrex film gently pressed against the crystal.

The observed pulse shape gives the integrated charge displacement q as a function of time. It is shown in Fig. 1(a) for a low applied field ($E \approx 4 \times 10^3$ v/cm). The deviation from linearity of the rising edge indicates the loss of holes during transit into deep traps, possibly recombination centers, for which the thermal release time is far longer than the transit time t_t . The pulse shape corresponds to point A on curve (c), ($t_t \approx 2\tau_h$). With a large field ($\approx 13 \times 10^3$ v/cm), point B) the rising edge of the pulse tends to become practically linear, as shown in Fig. 1(b) which was observed for $t_t \approx \frac{1}{2}\tau_h$. The intersection of the tangents at $t=0$ and $t \geq t_t$ defines t' which was measured as a function of E . It can be shown that

$$1/t' = (1/\tau_h)[1 - \exp(-t_t/\tau_h)]^{-1}. \quad (1)$$

If d is the specimen thickness, $t_t = d/(\mu_h E)$.

Seven pure (i.e., undoped) high-resistivity crystals were investigated. They were obtained from three different sources: RCA, Princeton; AEI, Harlow; EMI, Hayes. Curves (c) and (d) show typical experimental results of $1/t'$ vs E/d for two of the specimens. The crystal orientation is such that the holes drift in a direction perpendicular to the c axis. At low E , t' tends towards τ_h and the experimental values of τ_h obtained all lie between 1×10^{-7} and 3×10^{-7} sec, in agreement with the above estimates. With the known value of τ_h , t_t can now be calculated from Eq. (1) for each value of E/d . This leads to curves (c') and (d') from which μ_h is obtained. The room-tem-

FIG. 1. (a) Typical pulse shape at low E when $t_t \approx 2\tau_h$, corresponding to point A on curve (c). (b) Pulse shape at high E when $t_t \approx \frac{1}{2}\tau_h$, corresponding to point B on curve (c). (c) $1/t'$ measured for EMI crystal, $d = 165\ \mu$, $\tau_h = 1.4 \times 10^{-7}$ sec. (d) $1/t'$ measured for RCA crystal, $d = 40\ \mu$, $\tau_h = 1.0 \times 10^{-7}$ sec. (c') and (d') $1/t_t$ curves calculated from Eq. (1).

perature values of μ_h for the seven crystals lie in a range between 10 and 18 cm² v⁻¹ sec⁻¹ with a mean value of about 15 cm² v⁻¹ sec⁻¹. The good linearity of the calculated curves supports the validity of the assumptions made in deriving Eq. (1).

The temperature dependence of μ_h has been investigated between 500°K and 77°K for five of the specimens. The agreement between different curves is very satisfactory. The interesting feature of the results is a mobility maximum at about 210°K after which all log μ_h vs $1/T$ curves decrease linearly towards the lower temperatures with an activation energy of 0.019 ± 0.002 ev. It may be possible that this energy is associated with transitions of free holes between the upper two valence bands of CdS. Such an interpretation appears to be supported by recent work on the band structure of CdS,⁷ in which the dichroism of absorption edge is explained in terms of transitions from the upper two valence bands to the conduction bands. From the optical data it is concluded that the energy separation between these

bands is 0.02 ev at room temperature and 0.016 ev at 4.3°K, which agrees with the above activation energy, measured between 200°K and 77°K.

Further work on the possible interpretation of these results in terms of the valence band structure is in progress.

The authors wish to thank Dr. R. W. Smith of RCA, Dr. J. Franks of AEI, and Mr. McGill of EMI for kindly supplying the crystals.

*This work was supported by the European Research Office of the U. S. Army.

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Some applications of mercury wetted contact relays

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Within the limitations inherent in mechanical switching devices, mercury wetted contact relays can provide a simple and effective solution to a number of experimental problems. Details of the following applications are given and their limitations are discussed: the generation of nanosecond electron pulses with energies up to 50 keV; the production of fast rising millisecond voltage pulses of up to ± 1800 V; a compact, low capacity gating unit which allows the application of high voltage pulses to crystal specimens, or other apparatus, coupled capacitatively to the input of sensitive amplifying equipment; a technique employing two relays which has been used to study the decay of excess carriers injected in an insulating solid by a fast rising voltage step.

1. Introduction

Mercury wetted switching devices, which were developed by Brown and Pollard (1947), successfully eliminate the disturbing effects caused by contact bounce. The relays are therefore suitable for high speed switching and have been mainly applied in nanosecond pulse generators (Garwin 1950) and in the production of fast rising voltage steps.

The attraction of using mechanical switching devices lies in their comparative simplicity, but their range of application is severely limited by the low repetition rates that can be obtained and the fluctuations in the time interval between successive operations. In cases where this can be tolerated, the relays often provide a simple and effective solution to experimental problems.

This paper describes a number of applications of mercury switches which do not appear to be in general use and also discusses the limitations of the suggested methods.

2. The production of nanosecond electron pulses

The method described in this section has been used for the generation of electron-hole pairs in insulating solids but should be applicable to other problems where fast electron pulses of high energy are required. Figure 1 shows the arrangement which consists essentially of a fast voltage pulse generator modulating an electron gun. The pulse unit, which employs the well-known delay line technique (e.g. Lewis and Wells 1954), has been constructed from two pieces of brass tubing (0.375 in. i.d.) hard-soldered together to form a T-piece. The vertical part houses the polarized mercury switch capsule MS* and carries at its upper end a 75 Ω type BNC socket for connection to the delay line DL. The horizontal tube carries the two pulse output sockets. Selected $\frac{1}{2}$ W composite carbon resistors (25 Ω) are incorporated in each section of the inner conductor (0.110 in.) to give the correct output impedance. The dimensions have been chosen to provide as far as possible a 75 Ω match throughout the generator.

The normally open relay contact carries a small steel socket H which, together with the permanent magnet M, provides the necessary polarization (see also figure 3). The switching solenoid S consists of 5000 turns of 38 s.w.g. wire and requires an operating current of 3-4 mA. The delay line

Figure 1. Nanosecond electron pulse generator.

MS, mercury switch capsule; DL, delay line; CL, connecting line; M, polarizing magnet; H, steel socket; P, potentiometer; S, solenoid; T, terminating socket; F, hairpin filament; G, glass tube; C, control grid; A, accelerating electrode; L, electrostatic lens; L', magnetic lens; I, insulation.

is charged to the desired potential through the 50 k Ω resistor mounted in a screened side tube close to the delay line socket. For the normal type of coaxial cable with polyethylene insulation ($\epsilon = 2.3$), the duration of the voltage pulse is very nearly 10 nsec for each metre of open-ended delay line.

The inner conductor of the connecting line CL enters the demountable electron gun through a glass-metal seal close to the control grid aperture G. The line may be terminated at the aperture by a carbon resistor, but it is preferable to evaporate a 75 Ω nichrome film on the circular glass disk of the seal. The hairpin filament F is spot welded to tungsten supports sealed into the glass tube G. O-ring seals allow both lateral and vertical adjustment of the filament with respect to the grid aperture under running conditions. The emission is biased off by a positive potential of 20-30 V applied to F. The magnitude of the beam current which flows for the duration of the positive pulse is controlled by the potentiometer P. Electrode A at +300 V makes the beam current practically independent of the main accelerating potential (5-50 kV) which is applied across the electrostatic lens L.

* Available from Elliott Bros.

As both the gun and the pulse generator are kept at high potential, the relay is switched through a coupling condenser and a small amplifier. The indicated voltage levels are referred to the negative high tension line. A rectified sinusoidal voltage is applied to the earthy side of the coupling condenser, which could be replaced with advantage by a simple peaking transformer, preferably with an electrostatic screen. The resulting electron pulses, displayed on a 500 Mc/s sampling oscilloscope, possess a rise time of about 1 nsec. The maximum pulse repetition frequency is 250 sec⁻¹. A number of prepared delay lines provide pulse lengths from 5 to 500 nsec.

If an external trigger signal is required the following simple, but not altogether satisfactory, method has been used. A few turns of wire are connected in series with the termination T of the second pulse output. The signal is picked up at the low potential end and used as a trigger after amplification. However, the mismatch introduced by the inductive component leads to a deterioration of the electron pulse.

3. The production of millisecond voltage pulses of large amplitude

A useful millisecond pulse generator can be constructed with a commercially available unpolarized mercury relay.* Although the pulse length is limited to values between 3 and 7 msec and the maximum repetition frequency is about 150 sec⁻¹, the generator can be used for the production of fast rising positive and negative pulses of high amplitudes. A unit built on the lines indicated in figure 2 has now been used for a considerable length of time for pulse heights up

Figure 2. Millisecond voltage pulse generator.
R, half or full wave rectifier; PS, phase shift network.

to ± 1800 v with no sign of deterioration or damage to the relay. The voltage source has been built up of small size 90 v and 300 v layer-type batteries. With a tapping point at 30 v and at 60 v, the complete voltage range can be covered in 30 v steps by the use of three selector switches.

During switching, the mercury droplet adheres to the armature and shorts out contacts 1 and 2 for a fraction of 1 msec. Resistors R_1 or R_2 are therefore necessary to limit the current from the voltage source. With $R_1 = 0$, $R_2 = 4.7$ M Ω and the output connected to a low capacity probe, the pulse rises in a few nanoseconds, but the falling edge has a time constant of about 70 μ sec. Oscillations of small amplitude tend to occur on top of the pulse near the rising edge. These are damped out completely with $R_1 \approx 1$ k Ω , which leads to a rise time of less than 15 nsec.

The relay solenoid is driven from the a.c. mains; half- or full-wave rectification gives repetition frequencies of 50 or 100 sec⁻¹. A phase shift network is useful when the pulses are being applied in relation to other signals triggered from the mains.

* Type 275 Relay produced by Elliott Bros.

4. Input gating

The mercury switch often provides a simple and effective answer to the problem of input gating which may be essential to prevent the paralysis of sensitive amplifying equipment through overloading. A compact gating unit is shown in figure 3. The details given in § 2 in connection with the

Figure 3. Gating unit.

MS, mercury switch capsule; M, polarizing magnet; H, steel socket; S, solenoid; B, polythene bush.

pulse unit apply equally well to this case. With the relay in the 'open' position, the capacity of the unit is less than 3 pf and its effect on the input capacity is normally negligible.

It should be noted that in this application the steel socket and the polarizing magnet are placed on the side of the normally closed relay contact. With a rectified sinusoidal potential applied to the solenoid, the open gate could be varied between 1 and 5 msec by adjustment of the current or the magnet position. The highest repetition rate was about 270 sec⁻¹.

It was found possible to apply voltage pulses (from the unit described in § 3) of up to 1800 v across a specimen coupled capacitatively to the input of sensitive amplifying equipment (bandwidth 100 kc/s–30 Mc/s). The gate opened for 2 msec, about 1 msec after applying a 4 msec voltage pulse. During the open period the transit of generated charge carriers was displayed with a sensitivity of 0.3 mv cm⁻¹. The switching transients produced by the gate were negligibly small; this may be partly due to the small specimen capacity and the limited low frequency response of the amplifiers.

5. Double relay technique

This method has been used in the study of the decay of additional charge carriers injected in an insulating solid by a voltage pulse. As indicated in figure 4, the polarized mercury switch A produces a fast rising voltage step (up to about 120 v) across the specimen S. Switch B shorts out the load resistor R_L during the application of the potential. The solenoids of A and B are connected in parallel and are energized for a single operation by depressing the micro-switch D. As the speed of response of a relay depends largely on the energizing current, the variable resistance R is used to delay the opening of B by a time Δt with respect to the closing of A. The limiting factor in this method is evidently

SOME APPLICATIONS OF MERCURY WETTED CONTACT RELAYS

Figure 4. Double relay method for the determination of decay time constants.

A, B, polarized mercury relays; D, microswitch; S, specimen; R_L , load resistor.

the reproducibility of individual relay operations. In our experience the useful minimum value of Δt is about 50 μsec . The oscilloscope, preferably with a fairly long persistence tube, is triggered on the closing of the relay A. This provides a common origin for the time-scale and successive sweeps

will superimpose. Fluctuations in Δt merely affect the starting point along the common decay curve in different sweeps. With suitable amplification the 'tail end' of decay curves having time constants as low as 10 μsec could be displayed. It is, of course, essential that the value of R_L is sufficiently small to make the time constant determined by the specimen capacity and the load resistor much smaller than the time constant to be measured.

Acknowledgments

The authors wish to thank Mr. J. A. Garnett of Elliott Bros. for help and advice, and Mr. David Watson of Leicester University for constructing some of the apparatus described. The work was carried out in connection with research supported by the U.S. Department of the Army.

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