THE ELECTRICAL AND OPTICAL PROPERTIES
OF ORTHORHOMBIC SULPHUR CRYSTALS

A Thesis submitted to the
University of Leicester

by

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ABSTRACT

The orthorhombic form of sulphur is a typical molecular crystal and is composed of a structure of $S_3$ rings. Specimens have been grown from solution in $CS_2$ both in a thin platelet habit and in the form of thicker double pyramids. Drift mobility techniques have been used to study the charge transport between $180^\circ K$ and $370^\circ K$. The results show that the charge is carried by the generated holes having a room temperature lattice mobility of about $10^2 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$ and a lifetime of $10^{-5} \text{ sec}$. At the lower temperatures the hole drift mobility is an activated process, and during transit the generated holes interact with a level of centres $0.19 \text{ ev}$ above the valence band. With increasing temperature a transition to a lattice controlled transport takes place. On the basis of the infra-red transmission spectrum it is suggested that the above centres are associated with solvent molecules. The range of generated electrons is estimated to be less than $10^{-3} \text{ cm}^2 / \text{ volt}$; a predominant electron trap is situated $0.9 \text{ ev}$ below the conduction band.

Measurements on the photoconductivity in orthorhombic sulphur revealed for the first time a response in the ultra-violet. The photocurrent reaches a peak at $2,550 \text{ A.U.}$ with unit quantum efficiency and it is likely that this is an intrinsic photo-conductive effect. The photoconductivity in the visible region, which has been reported before, $(15,16)$ has a maximum at $4,600 \text{ A.U.}$
with a quantum efficiency several orders of magnitude less than that in the ultra-violet. It is suggested that this photocurrent is generated by the interaction between molecular excitons.

The absorption spectrum has a sharply rising edge at 4,500 Å.U. reaching an absorption coefficient of $2 \times 10^3$ cm$^{-1}$ at 3,600 Å.U. There is a slight window in the ultra-violet with a minimum at 2,700 Å.U. The absorption edge shows distinct dichroism, moving to longer wavelengths as the E-vector becomes parallel to the c-axis. The total shift of the edge corresponds to an energy difference of 0.05 ev.
Chapter 1

Introduction

1.(a) The Aim and Scope of the Work Presented

A considerable amount of interest has been shown recently in the electrical and optical properties of both organic and inorganic molecular crystals. The question is how much the properties of a free molecule will be retained when it is incorporated into the weakly bound crystal lattice. This is particularly pertinent in the case of charge transport. Will the overlap of wave functions between molecules be sufficient to form a band to which the normal semiconductor theory can be applied, or will the carriers move through the crystal by a series of "hops" from one molecular site to the next?

Attempts to answer such questions have been generally based on the study of the temperature dependence of the electrical conductivity. In the interpretation of these results the fundamental difficulty lies in distinguishing between parameters connected with the process of carrier generation and those connected with the transport of the charge carriers. As Hall effect measurements are not normally possible with highly insulating solids, the application of drift mobility techniques appears to be a promising approach to the problem of isolating meaningful parameters associated with the charge transport.
Methods of this kind, based on fast pulse techniques, have been developed in this laboratory during the last few years and applied to both evaporated films and single crystal specimens.\(^{(1)-(4)}\)

The bulk of the work presented here is concerned with the application of drift mobility techniques to orthorhombic sulphur, a typical molecular crystal.

Sulphur is of particular interest because so little fundamental information is available on its electrical and optical properties. Therefore, after investigating the carrier transport, measurements were made on the spectral dependence of the photoconductivity and absorption to examine the problem of carrier generation.

The following two chapters briefly survey the previous work on sulphur and the theories which appear applicable to its electrical properties. Chapters 4 and 5 describe in detail the preparation of single crystal specimens and the techniques and apparatus used for their investigation. The next chapters give the results obtained on the drift mobility of generated holes, and the properties of the deep traps which restrict the participation of electrons in the conduction process. Chapter 8 deals with both the experimental apparatus and the results of the photoconductivity measurements. In the last chapter all the results are discussed and, where possible, correlated with previous work. Finally, suggested extensions of the present investigation are briefly discussed.
1. (b) Some General Physical and Chemical Properties of Sulphur

Sulphur is an element which occurs in several allotropic forms which have received considerable attention mainly from the chemical point of view. Orthorhombic sulphur ($S_{\infty}$) is the stable crystalline form below 96°C. The pale yellow crystals are soft, brittle, and difficult to cleave. They consist of puckered rings of 8 sulphur atoms as illustrated in fig. 1:1. In the crystal the rings are held together by van der Waals forces and fig. 1:2 illustrates their arrangement in the unit cell. (5)

Sulphur is extremely insoluble in most of the normal solvents except $CS_2$, which dissolves 30% by weight at room temperature. Crystals can be grown quite easily from solution and this has been studied in some detail by Wiggins. (6) Large natural specimens can also be obtained, and much of the earlier work was done on samples of Sicilian sulphur. The solid has a high vapour pressure (7) ($10^{-6}$ mm Hg. at room temperature) and the vapour, which consists predominantly of $S_8$ molecules, reacts with most metals to form the sulphide.

If heated quickly, orthorhombic sulphur melts at 113°C. However, above 96°C the structure changes slowly from orthorhombic to monoclinic ($S_\gamma$), the stable crystalline form above this temperature.

Monoclinic sulphur melts at 119°C forming a straw coloured liquid. The liquid's viscosity at first drops and then increases to a maximum at 194°C due to the breaking up of the $S_8$ rings to form
long chain molecules ($S_\mu$). Sudden quenching of the viscous liquid results in plastic sulphur which slowly reverts to the orthorhombic form at room temperature.

The liquid boils at 444°C, the vapour consisting of $S_8$, $S_6$, and $S_2$ molecules. Condensation onto a cold substrate produces a layer of amorphous sulphur which is partly insoluble in CS$_2$. 
Chapter 2

Survey of Previous Experimental work on the Electrical
and Optical Properties of Sulphur

Sulphur is one of the best natural insulators and as such was once used extensively in scientific instruments. To measure its dark conductivity accurately requires modern vacuum and guard ring techniques. Values given in the literature range from $G = 10^{-14} \text{ (ohm cm)}^{-1}$ to $5 \times 10^{-24} \text{ (ohm cm)}^{-1}$, and it is probable that many of the earlier measurements were unreliable due to surface leakage currents. However, a study of the temperature dependence of conductivity was made by Foussereau and his results show an activation energy of 2.6 ev which is in quite close agreement with the photon energy at the absorption edge usually associated with the intrinsic band gap.

In the last few decades the electrical properties of sulphur have been surprisingly neglected, and so far very little fundamental information is available in terms of the modern theory of solids. In this chapter a few papers most directly related to the present work will be briefly discussed.

2. (a) Charge Transport and Photoconductivity

Dean, Royce and Champion investigated the bombardment conductivity and photoconductivity of orthorhombic sulphur. The crystals used were grown by slow evaporation of a saturated solution in CS$_2$. The specimens had a rather high dark conductivity of
about $10^{-14}$ (ohm cm)$^{-1}$.

Electrical contact was made by gold electrodes pressed against the surface of the specimen. A steady field was applied, and if this was above some critical threshold value, between 5 and 10kV/cm, $\alpha$-particle counting was observed. The counting rate decreased rapidly with time and was not very reproducible, depending critically on the position of the electrodes. Only $\alpha$-particles landing in a sensitive region within $2 \times 10^{-2}$ cm of the negative electrode were detected and it was concluded that electrons were the mobile carrier responsible for the observed conduction pulses.

The delay before counting started could be as long as half a minute after the beginning of irradiation and decreased as the applied field was increased. This was explained in terms of the time taken to build up a space charge barrier in the region of the negative electrode, which was regarded to be essential for the observation of counting pulses. It was, however, more difficult to explain the subsequent decrease in the counting rate. The crystal could be reactivated either by leaving it in the dark for about 12 hours, or by irradiating it with $\alpha$-particles or with light in the absence of an applied field. For the latter, wavelengths shorter than 4,400 A.U. were the most effective.

It is obvious that Dean et al worked under pronounced space charge conditions. They attempted therefore to interpret their observations in terms of a theory developed by von Hippel et al. (14)
for alkali halides containing a large space charge of trapped electrons at F-centre sites.

The above experiments and their interpretation will be discussed further in chapter 9 in the light of the present work.

When studying photoconductivity Dean et al. irradiated the crystal through a hole in one electrode with light containing the full spectral range between 4,400 A.U. and 9,000 A.U. They first restricted their observations to the primary current by placing a glass sheet between the electrode and the crystal surface. The photocurrent was then established in less than $3 \times 10^{-5}$ sec and decayed to zero in about 60 seconds. Similar results were obtained for both polarities of the applied field. If the crystal was re-irradiated after the electrodes had been earthed, a reverse discharge current was observed having the same time dependence as the charging current. From the initial value of the charging current Dean et al. obtained a value for the quantum efficiency of carrier generation. With the full spectral range of the lamp between 4,400 A.U. and 9,000 A.U. this was $5.5 \times 10^{-6}$ for a field of 30 kv/cm.

The thermal release of the space charge barrier was investigated as follows. The crystal was first polarized with light until the photocurrent had fallen to practically zero. The specimen was then left in the dark for a known time in the absence of an applied field. The initial value of the reverse current on re-illumination was then taken as a measure of the remaining
polarization. A plot of this against the time of storage showed that the space charge decayed exponentially and gave a measure of its release time \( t \).

On the assumption that

\[ t = \frac{S}{\varepsilon} \exp\left(\frac{\varepsilon}{kT}\right) \]

where \( S \) is an infra-red vibrational frequency, a trap depth of \( \varepsilon = 0.92\text{ev} \) was obtained. The authors considered the traps to be due to defects or impurities and pointed out that crystals grown under less strict conditions of purity showed poorer counting properties and lower photoconductive gains.

When the glass plate was removed and the top electrode pressed directly against the crystal face continuous photocurrents were observed. These were in some respects similar to the currents induced by \( \alpha \)-particle bombardment. Firstly, a threshold field greater than 5\( \text{kv/cm} \) was required before any measurable current was obtained. Secondly, after switching on the illumination, a delay occurred before any photocurrent was observed. Also the currents produced were both noisy and erratic.

2.(b) Spectral Dependence of Photoconductivity

The spectral sensitivity of the photocurrents in single orthorhombic sulphur crystals has been studied by Kurrelneyer\(^{(15)}\) and by Tartakovsky and Rekalova.\(^{(16)}\) The results of both are shown in fig. 2:1.

Kurrelneyer worked mainly with large natural crystals whose
dark conductivity was less than $10^{-18}$ (ohm cm)$^{-1}$. He made electrical contact with cells of tap water enclosed in thin glass and stuck with wax to the crystal faces. His measurements were made between 4,200 Å and 6,500 Å. He showed a smooth response curve which began to rise at 6,500 Å.U., reaching a maximum at 4,700 Å.U., and then decreased steeply towards the shorter wavelengths.

The photocurrent established itself in less than 0.1 sec. and then dropped away to an equilibrium at about one third of the initial value. This he attributed to the build up of a reverse space charge field. The photocurrent increased linearly with applied fields between 20 volts/cm and 15,000 volts/cm and was directly proportional to the intensity of illumination.

The results of Tartakovsky and Rekolova on the spectral sensitivity are very similar except that they observed a shoulder on the long wavelength side of the curve. When the specimen was cooled to liquid air temperatures the curve moved to shorter wavelengths and the shoulder resolved into a peak at 5,500 Å.U. The energy separation between this and the main peak represented an energy difference of 0.38 ev.

2.(c) Absorption

When sulphur is warmed its colour darkens considerably, changing from a pale yellow at room temperature to a deep orange at its boiling point. The corresponding movement of the
absorption edge with temperature has been studied in some detail by Fukuda,\(^{(17)}\) Mondain-Monval et al\(^{(18)}\) and Bass.\(^{(19)}\) Bass obtained a shift of about 6.2 A.U./°C. The main absorption appears to start at about 4,500 A.U. at room temperature but no measurements on orthorhombic sulphur crystals at shorter wavelengths seem to have been carried out.

In the violet and near ultra-violet the absorption coefficient becomes very large (\(\geq 10^5\) cm\(^{-1}\)). Bass was able to extend his measurements only by using the vapour or a solution of sulphur in alcohol. He observed a double absorption peak in the 2600 A.U.-2,800 A.U. region which agrees with the results of Baer and Carnack\(^{(20)}\) who showed a further maximum near 2250 A.U.
Chapter 3

Survey of the Theoretical Treatment of Carrier Mobility

In this chapter the mechanisms controlling carrier drift mobility will be discussed with particular reference to molecular crystals.

If one assumes that a band picture is applicable for the description of electrical transport in sulphur, then, in a crystal relatively free from defects or impurity centres, one would expect the mobility to be governed by the interaction of the carriers with the acoustic modes of the lattice vibrations. The calculation of such an interaction for sulphur is a formidable task; however, the treatments of electron-lattice interactions in a simple non-polar lattice given by Seitz\(^{(21)}\) and by Bardeen and Shockley\(^{(22)}\) should be applicable to a first approximation, and are briefly summarised in the first section.

Section (b) deals more specifically with transport in a molecular lattice, and the conditions under which the alternative mechanism of hopping transport is to be expected.

If the density of imperfections in the crystal is large, they may considerably alter its transport properties, and the last two sections discuss the effects of shallow and deep trapping centres.

3.(a) Lattice Controlled Mobility

Seitz\(^{(21)}\) considered the case of electrons moving in an isotropic lattice and their interaction with the acoustic node...
vibrations.

To calculate the transition probability for the electrons, first-order time-dependent perturbation theory was applied. This approach is shown to be valid provided the relaxation time \( \tau \) is sufficient to give a mobility

\[
\mu > \frac{e\hbar}{mk} \quad (3:1)
\]

The righthand side of (3:1) corresponds to about 30 cm\(^2\) volt\(^{-1}\) sec\(^{-1}\) at room temperature. Considering only interactions with single phonons the selection rules governing the transitions are

\[
E' = E \pm h\nu
\]

and

\[
h' = k + \frac{q}{k}
\]

where \( E, E' \) and \( k, k' \) are the initial and final values respectively of the electron energy and the wave vector. \( h\nu \) and \( q \) represent the phonon energy and the wave vector. \( K \) is a vector in the reciprocal lattice which is zero for the normal scattering process.

Under these conditions Seitz found that the scattering is isotropic, and that the mean free path is velocity independent and inversely proportional to the temperature down to \( \sim 10^0\)K.

The mobility is given by

\[
\mu = \frac{0.2 N^{\frac{1}{3}} e \hbar^2 k^2 M}{\eta^2 + \frac{5}{2} C^2 k^2 / \tau} \cdot T^{-\frac{3}{2}} \quad (3:2)
\]

where \( N \) is the number of atoms per unit volume and \( M \) is their mass.
Bardeen and Shockley\(^{(22)}\) approached the problem by considering the potential deformation which occurs during the passage of an elastic wave through the lattice. The vibration causes a dilatation of the band gap spread over many lattice spacings and this was treated as a slowly varying potential. The full electron wave function was obtained by multiplying the wave function at the band edge by the wave function of an electron moving in the deformation potential alone.

Because the vibration is spread over many lattice spacings Shockley and Bardeen were able to express the deformation potential, and hence the transition probability, in terms of the macroscopic elastic constants of the crystal. The mobility relation obtained was of a similar form to that of Seitz, namely

\[
\mu = \frac{8 \pi \hbar^2}{3 \bar{E}_1^2 \frac{\sqrt{3}}{2} \frac{C_{11}}{m^* \frac{\sqrt{3}}{2} \frac{1}{2}}} \frac{T^{-3/2}}{3:3}
\]

\(C_{11}\) is the longitudinal elastic constant and \(\bar{E}_1\) is the shift of the conduction band edge per unit dilation.

From the point of view of the present investigation the significant result of both the above treatments is that in a non-polar isotropic lattice the temperature dependence of the mobility is given by

\[
\mu = AT^{-3/2}
\]
5.(b) Hopping Transport

In a recent paper S.H. Glarum (23) examined the transition between band conduction and hopping transport in molecular crystals. He considered first the "delocalised" case, where the overlap of wave functions between neighbouring molecules is sufficient to create a band in which the mobility is comparatively high. Here a carrier will move through the lattice interacting with, and adjusting itself to, the slower moving lattice deformations.

To calculate the electron-lattice interaction terms, Glarum considered a lattice of translationally equivalent molecules. Using the tight-binding approach the wave functions were described by a Bloch sum of localized molecular orbitals. The lattice vibrations were represented independently by the product of 3N harmonic oscillator functions. Assuming an isotropic lattice, Glarum was then able to obtain the relaxation time $\tau$ using first-order time-dependent perturbation theory.

The mobility is generally given by

$$\mu = \frac{e}{kT} \langle v^2 \tau \rangle \quad (3.5)$$

where $v$ is the carrier velocity in the band.

Using an analytical value for $v$, based on the assumption of spherical energy surfaces, together with the calculated relaxation time $\tau$, equation (3.5) leads to a mobility of the conventional form

$$\mu = \frac{e\alpha^2}{k} \cdot \frac{1}{4\pi^2} \cdot \frac{\sqrt{J}}{\hbar \omega_0} \left( \frac{2\pi J}{kT} \right)^{3/2} \quad (3.6)$$
where \( \alpha \) is the lattice spacing, \( \mathcal{J} \) is the band width, \( \omega_0 \) is the Debye frequency, and \( \gamma \) is a dimensionless electron-lattice interaction parameter.

For expression (3.6) to be valid it is necessary that

\[
\mu > \frac{e \alpha^2}{\hbar} \frac{k \omega_0}{\hbar T} \quad (3.7)
\]

\( e \alpha^2 / \hbar \) has the dimensions of mobility and, for typical intermolecular distances, corresponds to 1 to 2 cm\(^2\) v\(^{-1}\) sec\(^{-1}\). Therefore, since \( k \omega_0 \) and \( k T \) are usually of the same order of magnitude, one finds the band theory to be appropriate only when the mobility

\[
\mu > 1 \text{ cm}^2 \text{ v}^{-1} \text{ sec}^{-1}
\]

Glarum suggests that the effect of lattice anisotropy could be taken into account, as a first approximation, by replacing the factor \( \left( \frac{2 \pi \mathcal{J}}{k T} \right)^{3/2} \) in equation (3.6) by \( \left( \frac{2 \pi \mathcal{J}}{k T} \right)^n \) where \( n < 2 \). This may be of significance in the sulphur lattice as indicated by some of the experimental results in chapter 6.

In the above analysis the electron and lattice movements are considered as separable. However, with a low mobility carrier the lattice has time to distort about the charge and trap it at a local site. In this case the electron and lattice waves must be replaced by an electron-phonon wave packet. The relaxation time is then the time a carrier resides at a site before hopping to an adjacent molecule, and equation (3.5) becomes

\[
\mu = \frac{e \alpha^2}{k T \gamma}
\]
To calculate $\tau$, Glarum used the method of Yamashita and Kurosawa\(^{(24)}\) which leads to the probability of an electron being transferred from one site to the next. The drift mobility expected from this type of "hopping" transport is then found to be

$$\mu = \frac{e\alpha^2}{\hbar} \left( \frac{\pi}{8} \right)^{\frac{1}{2}} \frac{\beta^2}{(\hbar \omega_0)^{\frac{1}{2}} (\hbar T)^{\frac{3}{2}}} \cdot \exp \left( \frac{-\gamma \hbar \omega_0}{4 \hbar T} \right)$$

where $\beta$ is an intermolecular resonance energy.

The temperature dependence of the mobility is now more complicated. If $\gamma$, the electron lattice interaction, is large ($\gamma > 10$) then the mobility increases rapidly with temperature. However, for smaller values of $\gamma$ the mobility may be either insensitive to thermal changes, or even decrease with increasing temperature.

A condition for the validity of equation (3:8) is

$$\mu < < \frac{e\alpha^2}{\hbar} \frac{\hbar \omega_0}{\hbar T}$$

This is complementary to equation (3:7) and one would not expect hopping transport for mobilities greater than about $1 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$.

3.(c) Shallow Traps

Imperfection centres produced by structural defects or impurity centres can lead to discrete energy levels within the forbidden band, which may trap a free carrier until it is released by optical or thermal excitation.
The effect of "shallow" traps is illustrated in Fig. 3.1 and can be analysed as follows.

Consider a cloud of holes moving in an electric field and interacting with a single trapping level \( E \) ev above the valence band.

The drift mobility of the carriers is given by

\[
\mu = \frac{d}{E(t_0 + \sum t_{tr})}
\]

where \( \sum t_{tr} \) is the total time spent in traps, \( t_0 \) is the total free time, and \( d \) is the total distance travelled.

It is assumed that the velocity of the drifting carriers is sufficiently slow to allow thermal equilibrium to be established between free and trapped carriers. Therefore, if the Fermi level lies several \( kT \) above the trap level, the ratio of the number of carriers trapped to the number free is

\[
\frac{N_t}{N_v} = \frac{N_t}{N_v} e^{\frac{E}{kT}}
\]

where \( N_t \) is the density of traps and \( N_v \) is the density of states at the edge of the valence band.

This is also the ratio of the average release time \( \tau_R \) to the average free lifetime \( \tau_f \).

i.e.

\[
\frac{N_t}{N_v} = \frac{\tau_R}{\tau_f} = \frac{N_t}{N_v} e^{\frac{E}{kT}}
\]

The number of times the carrier is trapped during a transit
is on the average \( \frac{t_0}{c} \)

\[
\sum t_{tr} = \frac{t_0}{c} \cdot \tau_R
\]

\[
= t_0 \frac{N_t}{N_v} e^{E_{tr}/kT}
\]

\[
\therefore \quad \mu = \frac{d}{t_0 \left( \frac{N_t}{N_v} e^{E_{tr}/kT} \right)}
\]

However, \( \frac{d}{t_0} \) equals \( \mu_L \Phi \), where \( \mu_L \) is the lattice

mobility in the absence of the trapping level

\[
\therefore \quad \mu = \frac{\mu_L}{1 + \frac{N_t}{N_v} e^{E_{tr}/kT}} \quad (3.11)
\]

For temperatures and trap densities such that \( \frac{N_t}{N_v} e^{E_{tr}/kT} > 1 \)

the expression for the mobility becomes

\[
\mu = \mu_L \frac{N_v}{N_t} e^{-E_{tr}/kT}
\]

\( N_v \) is given by \( 2.5 \times 10^{19} \left( \frac{T}{T_R} \right)^{3/2} \left( \frac{m^*}{m} \right)^{3/2} \) where \( T_R \) is room
temperature (290°K). If therefore the lattice mobility is
controlled by acoustic node scattering, (equation (3.4))

then \( \mu = \frac{B}{N_t} e^{-E_{tr}/kT} \quad (3.12) \)
where \( B \) is independent of temperature.

Thus under these conditions a plot of \( \log \mu \) against \( \frac{1}{T} \) should give a straight line of gradient \( -\frac{e}{k_B} \).

On the other hand, if \( N_t \frac{e}{k_B T} \) is small compared with unity \( \mu \ll \mu_c \ll T^{-3/2} \). With increasing temperature the observed drift mobility will therefore go through a maximum which marks a transition from the trap controlled to the lattice controlled transport mechanisms. The position of the maximum will be determined by the density of traps \( N_t \) of the specimen.

3. (a) Deep Traps

The free lifetime of a carrier before trapping can be written in the form

\[
\tau = \frac{1}{N_t \nu_{tk} \sigma}
\]

where \( \nu_{tk} \) is the thermal velocity of the carrier and \( \sigma \) is the capture cross-section of the trap for that type of carrier.

Therefore, from equation (3:10), the release time for holes is

\[
\tau_R = \frac{1}{N_v \nu_{tk} \sigma} e^{e/k_B T}
\]

If this release time is greater than the transit time, the traps will be termed "deep" traps in the present investigation.

Two important effects of such traps are

1. They will cause a continual loss of free carriers during the type of pulse experiment described in section 4.(a).

2. The trapped charges may radically alter the field.
configuration within the crystal.

The theory in the last two sections can of course be applied equally well to electrons interacting with a trapping level below the conduction band. \( N_v \) then becomes \( N_c \), the density of states at the edge of the conduction band.

Chapters 6 and 7 will show that both deep and shallow traps are important in the interpretation of the observed electrical transport properties of sulphur. These centres, as well as the carrier lattice interaction, will be discussed further in chapter 9.
Chapter 4

Experimental Method and Apparatus for
Drift Mobility Measurements

4. (a) Experimental Principle

Drift mobilities were measured directly by timing the transit of carriers across a crystal of known thickness. The technique used was that developed by Spear\(^1\) for measurements on the selenium allotropes and the II-VI compounds.

Single crystal platelets of sulphur were prepared with conducting electrodes on both faces. Electron-hole pairs were generated in the crystal surface beneath the top electrode by a short pulse of light or of energetic electrons. Depending on the polarity of the applied field either generated electrons or holes could be drawn into the crystal bulk. The displacement current of the moving sheet of charge was integrated at the bottom electrode and displayed on a wide band oscilloscope.

The principle of this method is illustrated in fig. 4:1. Suppose that \( N_e \) electron-hole pairs are generated below the top electrode \( T \) of a crystal of thickness \( d \). Rapid recombination will normally take place in the region of generation, but let \( N \) carriers be drawn into the crystal volume by the field \( E \). These will induce a charge on the bottom electrode \( B \) proportional to the distance moved by the carrier cloud. The corresponding rise in voltage across the resistance \( R \) is given by

\[
\Delta V(t) = \frac{N_e}{Cd} \chi(t) = \frac{N_e}{Cd} \mu E t \quad (4.1)
\]
$X(t)$ represents the displacement of the charge sheet from the top electrode at any time $t$, and $C$ is the total capacity across $R$. It is assumed that the integrating time $CR$ is much longer than the time during which the charge displacement takes place.

Under ideal conditions the integrated signal would be as shown in fig. 4:2(a). At $t \gg t$, $X(t) = d$ and $\Delta V$ of equation (4:1) becomes constant. The time between the two discontinuities gives the transit time $t_t = \frac{d}{\mu E}$.

On the assumption that the field is substantially uniform, $E = \frac{V}{d}$

$$\frac{1}{t_t} = \frac{\mu}{d^2} \frac{V}{\rho} \quad (4:2)$$

Therefore plot of $\frac{1}{t_t}$ against $V$ should give a straight line, the gradient of which should lead to the drift mobility $\mu$.

For the observation of the type of oscilloscope trace illustrated in fig. 4:2(a), several conditions must be satisfied.

1. The relaxation time of the crystal must be much longer than $t_t$ or the charge cloud, which represents a deviation from charge neutrality, will tend to become compensated by carrier injection. For a highly insulating crystal such as sulphur this condition is obviously satisfied.

2. The accuracy to which $\mu$ can be determined depends largely on the sharpness of the discontinuity at $t = t_t$. To work under optimum conditions it is essential that $t_t \gg t_p$, where $t_p$
is the duration of the excitation pulse, and that \( d_p \ll d \), where \( d_p \) is the average depth of penetration of the incident electrons or light.

(3) \( t_t < \tau \), the lifetime of the carriers with respect to deep traps as defined in the previous chapter.

(4) Experience has shown that with sulphur crystals, the number of carriers \( N \) drawn across the specimen must be less than about \( 10^7 \) to avoid space charge effects.

(5) \( t_t \) must be greater than the rise time of the detection equipment.

An additional difficulty arises from carrier diffusion and the statistical nature of trapping and release. These cause the cloud to broaden during transit and it may become too diffuse for accurate measurements to be made.

Although it is evident from condition (4) that difficulties with this technique will arise if \( \tau < t_t \), it has been found possible to study drift mobilities and lifetimes when \( \tau \sim t_t \). Under this condition the pulse shape shown in fig. 4.2(b) is observed. Here it is convenient to introduce a time \( t' \), defined by the intersection of the tangents to the pulse at \( t = 0 \) and \( t \geq t_t \). In the presence of a uniform volume distribution of deep traps the charge displacement is given by the well-known Hecht formula

\[
q(t) = (Ne \mu E \tau / d) \left[ 1 - \exp \left( -\frac{t \tau}{\mu E} \right) \right]
\]

for \( t \leq \frac{d}{\mu E} \).
It can then be shown that

\[ \frac{1}{t'} = \frac{1}{\tau} \left[ 1 - \exp\left( \frac{-d}{\mu \bar{E} \tau} \right) \right]^{-1} \quad (4:3) \]

This equation is plotted in fig. 4:5. At \( E = 0 \), \( t' = \tau \), so that \( \tau \) can be obtained by extrapolation. A value of \( \tau \), corresponding to each observed value of \( t' \) can then be calculated from equation (4:3). As indicated in fig. 4:5, it is normally found that in the range of field values employed, the calculated \( \frac{1}{t'} \) curve will pass through the origin and run parallel to the \( \frac{1}{\tau} \) curve.

4.(b) General Description of the Apparatus

In this section the complete experimental arrangement is briefly presented, while a more detailed description of various parts of the equipment is left to the following sections.

Most of the measurements were made with electron excitation which has the advantage that the length, intensity, and shape of the generating pulse can easily be adjusted. In addition, the depth of penetration may be varied to some extent by altering the energy of the incident electrons.

The design of the electron bombardment gear was similar to that described by Spear, Lanyon and Mort, except that the mercury wetted relay was replaced by an avalanche transistor unit which could be triggered more accurately.

The complete apparatus is shown schematically in fig. 4:4. The electron gun, which was normally cut off by the bias circuit B,
was switched on by a short positive pulse to the grid G from the pulse generator P.G. B and P.G., together with the filament heater batteries, were set on an insulated platform which was raised to E.H.T. negative, and the circuit controls were operated by ebonite rods from earth potential. The pulse of electrons produced was focussed onto the specimen S.

For maximum sensitivity, c.f. equation (4:1), it is necessary to keep the specimen capacity and input capacity of the detecting apparatus as small as possible. The integrated charge was therefore fed directly onto the grid of the cathode follower C.F. The output signal was sent to a Tektronix type 541A oscilloscope via a wide-band, low noise, pre-amplifier P.A.

In order to reduce the build-up of space charge in the crystal, the applied field was pulsed at 50 cycles/sec. and the bombardment beam at 100 cycles/sec. The electron pulse in the off field period regenerated trapped carriers, and the size of the discharge pulse served to indicate the presence of a space charge field. Normally during mobility measurements the number of incident electrons was kept sufficiently low that no discharge pulse was observed.

To prevent paralysis of the sensitive wide-band amplifiers by the switching of the large field pulses, the input to the cathode-follower was gated with a mercury wetted relay. This was only open during the bombardment pulses and shorted out the field transients. The timing of the gate and bombardment pulse, which
was adjusted by the phase shift network P.S., is illustrated in fig. 4:5. The electron pulse generator P.G. received its trigger through a high voltage coupling condenser from the signal generator S.G. at earth potential. (Solartron GO 1101.) This in turn was triggered from P.S. at a repetition rate of 100 cycles/sec.

4.(c) The Electron Gun

This has already been described in detail (26) and only the illustration in fig. 4:4 will be given here.

A tungsten filament F, heated by two accumulators in series, provided the source of electrons. The filament holder was mounted in 'O' ring seals in such a way that it could be moved vertically and horizontally with respect to the rest of the gun. The electron beam current was controlled by the filament-grid bias circuit B which will be described later. The 75 Ω termination of the connecting line C.L. was built into the gun housing.

The first anode A, was set near the grid and had a positive bias of 300 volts. This kept the beam current independent of the E.H.T. voltage, which was supplied by a Brandenburg generator capable of giving 1 m.a. at 100 kv.

The focussing of the electron beam was achieved by the electrostatic two cylinder lens L₂, and one of the magnetic lenses L₃ or L₄. The energising current through L₂ or L₃ was adjusted for each value of the accelerating potential.

The specimen holder could be quickly and accurately located beneath the electron gun and was clamped against an 'O' ring seal.
The whole system was evacuated by an oil diffusion pump and a rotary backing pump that gave a normal working pressure of about $10^{-5}$ mm. Hg.

A perspex window enabled the top of the specimen holder to be observed during operation.

4.(d) The Electron Pulse Generator

Short pulses were obtained from the generator shown in fig. 4.6. The delay line D.L. was charged through the 22k $\Omega$ limiting resistor from a 48 volt battery and, when the transistor became conducting, discharged along the connecting line C.L. to the gun. The transistor, a Philco 2N502 operating in the avalanche mode, was triggered from the Solartron pulse generator. The trigger pulses were fed to the transistor base via a low frequency filter circuit which filtered out the 0.1%, 7 kHz ripple of the Brandenburg E.H.T. generator. The diode shorted any faster positive pulses which would cause destructive breakdown in the base-emitter junction.

It was found that the sudden application of the full collector voltage tended to shorten the life of the avalanche transistor. The 1 M $\Omega$ potentiometer was therefore incorporated to allow the collector potential to be increased more gradually. A sudden rise in the collector current indicated the onset of avalanching. A 14 volt positive output pulse was obtained with a rise time of 10 nsec. Normally a 10 metre delay line was used and this gave a pulse length of 100 nsec.

Although the shape of the incident electron pulse does not
affect the mobility measurements provided the condition $t_p \ll t_c$ is fulfilled, the definite length and cut-off of a square pulse was found to be very useful when interpreting more unusual response shapes. Also, as will be described shortly, it enabled the number of electrons per pulse to be easily determined.

Because the pulse height from the delay line was fixed, the electron beam intensity was controlled by the variable voltage from the potentiometer $P$ of the filament-grid bias circuit shown in fig. 4:7. The filament-grid bias for the two positions of the switch $J$ is illustrated in fig. 4:8.

When a steady electron beam current was required $J$ was set in position 1. This automatically disconnected the trigger pulse to the electron pulse generator $P.G.$ $V_f$ could be increased from zero to the full voltage $V_c$ across $P$ which was just sufficient to cut off the electron beam. In position 2, $P.G.$ was triggered, but the filament-grid bias was increased by a pre-set potential adjusted to be equal to the positive pulse height $V_p$. Now, by altering $P$ the filament-grid potential during the pulse was varied between zero and $V_c$.

When the switch was in position 1 the steady filament-grid voltage was equal to that during the pulse. Thus the number of electrons per pulse at a particular setting of $P$ could be determined by measuring the steady beam current and multiplying this by the pulse length.
4.(c) Specimen Holder

Fig. 4:9 shows the specimen holder which was used in all the drift mobility experiments, both with electron and light excitation.

The specimen was mounted on the top of a copper rod \( R \) and its temperature changed by conduction as \( R \) was heated or cooled. Tube \( T \), which connected \( R \) with the base plate \( B \), was made of thin stainless steel and this, together with the evacuated gap between \( R \) and \( T \), provided adequate thermal insulation between \( R \) and \( B \).

Fig. 4:10 is a plan of the specimen holder. B.E. and T.E. are two glass-metal seals which carried the leads to the specimen electrodes. C, a small Faraday cup, was also connected through a glass-metal seal and could be used to measure the beam current or display the electron pulse independently of the specimen. The two magnetic lenses \( L_2 \) and \( L_3 \) of the electron bombardment apparatus were normally adjusted so that switching from one to the other flicked the beam from the specimen to the cup. The remaining seal \( D \) carried the leads T.C. of the Chromel-Alumel thermocouple which measured the specimen temperature.

The specimen and leads were screened by the brass box \( M \). The lid \( L \), which was interchangeable, was selected to have apertures \( A \) just smaller than the specimen's top electrode. A ring of calcium tungstate around each aperture served for focussing.

The screened box \( S.B. \) contained the cathode follower and gate which are shown in fig. 4:11. Switch \( W \), which normally connected
the top electrode T.E. to the field input pulse, could join the two specimen electrodes so that the beam pulse incident on the top electrode could be observed directly. The charge from the bottom electrode B.E. was fed directly to the cathode follower. This has an input capacity of 8 p.f. and an output impedance of 100 Ω.

The input was gated by a polarized mercury wetted relay which had a capacity of about 3 p.f. when open. C_s was a 1.8 p.f. condenser through which a pulse of known height could be fed to calibrate the amplifier system and determine its charge sensitivity.

4.(f) Gate and Phase Shift Circuit

The gate was normally held closed by a permanent magnet mounted outside the capsule of the mercury wetted relay. It could be opened for about 2 milliseconds during each cycle of the output signal from the phase shift circuit P.S. shown in fig. 4:12.

By feeding the shifted signal from the centre-tapped transformer circuit to the grid of an output valve, the loading of the network was kept low and a variable phase over almost 180° was obtained. The primary of a transformer formed the anode load of the valve and the output of the secondary was full wave rectified by a bridge of OA 81 germanium diodes.

4.(g) Pre-Amplifier

The output signal from the cathode-follower was fed through a short length of coaxial cable to the amplifier illustrated in fig. 4:13. This was a wide band, low noise amplifier designed by J. Hartke(27) and consisted of a double triode in cascode followed
by a bootstrap output. Various condensers at the output enabled the signals to be clipped, the largest giving an integrating time constant of 300μsec.

The overall gain of the cathode follower and preamplifier was 8.5 and the rise time was 12 n.sec. The low noise characteristics of the amplifier were of particular value in this investigation.

4.(h) Field Pulse Unit

Figure 4:14 shows a circuit diagram of the field pulse generator. The voltage was provided by a bank of 9, 90 and 300 volt batteries. Four selector switches connected to the battery tappings covered the range between ±1,200 volts in 3 volt steps. The output was pulsed by an unpolarized mercury wetted relay run from the half rectified mains supply through a variac and transformer. The pulse length could be varied from 3 to 7 milliseconds by the variac setting.

During switching, the mercury droplet adheres to the armature and shorts out contacts 1 and 2 for a fraction of a n sec. Resistors \( R_1 \) or \( R_2 \) were therefore necessary to limit the current from the voltage source. With \( R_1 = 0, R_2 = 4.7 \text{ MΩ} \) and the output pulse connected to a low capacity probe, the pulse rises in a few n.secs, but the falling edge has a time constant of 70μsec. Oscillations tend to occur on top of the pulse near the rising edge. These are damped out completely with \( R_1 = 1k\Omega \), which leads
to a rise time of less than 15 n.sec.

Another switch, not shown in fig. 4:14, enabled a change from pulsed to steady fields to be made.

4.(i) Light Pulses

Because of its high vapour pressure sulphur sublimes in the vacuum of the electron bombardment apparatus when warmed above 50°C. For measurements at higher temperatures, the specimen was kept at atmospheric pressure and carrier excitation produced by light flashes. These were obtained from a 2 mm. adjustable spark gap in air. The breakdown discharged a 1000 pf condenser wired in parallel with the gap as shown in fig. 4:15.

The condenser was charged from a 10 k.v. transformer, and a variac connected to the primary controlled the rate of sparking.

The shape of the light output depended to some extent on R, the damping resistance in series with the spark gap. Decreasing R reduced the pulse rise time but increased the time of decay. 70 Ω was found to be the optimum for the gap width used. Fig. 4:16 illustrates the pulse observed using an R.C.A. 951A photomultiplier and Tektronix oscilloscope.

The transformer and spark gap were completely enclosed in the metal box B except for a ½" diameter hole about 2" from the gap. The light passing through this aperture was focussed by a quartz lens and deflected onto the crystal by a surface silvered mirror. The electrodes were kept clean and somewhat pointed to prevent wandering of the discharge.
4. (j) Experimental Procedure

The field, gate and bombardment pulses were first synchronised. The gun was then raised to the required E.H.T. voltage and the filament-grid bias reduced until the incident electrons just caused a glow of the calcium tungstate. After focussing the beam into the lid aperture, the gun was switched immediately to pulsed operation. Final adjustments to focus and synchronization were made under working conditions.

The specimen was normally cooled by immersing the copper rod R in a vacuum flask containing a mixture of dry-ice and alcohol raised into position beneath the specimen holder. For temperatures down to -76°C this would cool the specimen to within one or two degrees of the temperature of the mixture in about a minute. Also, the thermal capacity of the system was sufficient to prevent a change in temperature of more than one or two degrees in the time required to take a mobility measurement.

The normal procedure for a mobility-temperature run was to measure the mobility first at room temperature, and then at -76°C. Intermediate temperatures were quickly obtained by adding room temperature alcohol to the mixture. A final point was obtained with melting ice, and then the room temperature mobility checked. A similar method up to 50°C was used with hot water.

For measurements with spark excitation R was immersed in a thermostatically controlled oil bath which gave a continuous selection of temperatures up to 110°C and was stable within ±1°C.
Over the complete range the specimen's temperature was accurately measured by means of the Chromel-Alumel thermocouple.
Chapter 5
Crystal Growth and Specimen Preparation

5.(a) Methods of Crystal Growing

Most of the crystals for this investigation were grown from a solution of sulphur in CS₂. About half were grown from Infra-Red or anaalar grade CS₂ and Lights' ultra-pure sulphur, (99.999% pure; maximum impurity Ca 2 p.p.m.), the others from ordinary laboratory grade reagents.

Slow evaporation of a saturated solution in a glass trough or beaker gave crystals of the bi-pyramid form shown in fig. 5:1(a). This is a well known habit of orthorhombic sulphur and the crystalline axes could easily be recognised. The crystals were about 2 cm across and thin plate specimens could be cut from them in the direction required.

A method was also developed for growing platelets directly. As shown in fig. 5:2, a pool of nearly saturated solution was spread onto a horizontal glass plate about 8" in diameter. This was kept in a constant temperature enclosure and the rate of evaporation restricted by a glass plate laid partly across the hole in the perspex lid.

By allowing complete evaporation of the pool in one day, about 40 platelets of approximately 5 mm. sidelength were obtained. They ranged in thickness between 200 μ and 500 μ, and their typical shape is shown in fig. 5:1(b). By means of a polarizing
microscope with a universal stage it was found that the c-axis of the platelet crystals makes an angle of 18°20' with the platelet face. This therefore corresponds to a (|||) plane similar to face A of fig. 5:1(a). This conclusion has been confirmed by a number of Lane and Oscillation X-ray photographs (taken by Dr. H. Ehrenberg at University College London).

A number of attempts have been made to grow crystals from the vapour phase. However, in order to keep the pressure below the triple point (3.7 x 10^-3 mm of Hg) the sublimation rate had to be kept very low, and the crystals obtained were too small for use.

5.(b) Crystal Grinding

In order to prepare specimens from the bi-pyramid habit, and occasionally to reduce the thickness of platelet specimens, it was necessary to grind the crystals.

Two of the simple grinding jigs are shown in figs. 5:3 and 5:4. The first, which was used to thin some platelet specimens and to cut plates parallel to a natural face, was recessed to a depth equal to the required specimen thickness. The crystal face was stuck in position by pressing it into a pool of molten salol (Phenyl Salicylate) which bound the crystal as it solidified. Using a slurry of 4f carborundum powder and water on a glass plate, the crystal protruding from the recess was ground away slowly by hand. The specimen was removed from the jig by remelting the salol, and then washed in ethyl acetate. Owing to the brittle nature and large expansion coefficient of sulphur care was always taken not to
heat the specimen unevenly.

For platelets not parallel to the natural crystal face the jig shown in fig. 5:4 was used. The face of the brass bar B, which can slide in the tube T, was milled to the angle between the required platelet face and a natural face. Grinding flush with the tube end formed one specimen face and then the first jig was used as before.

5.(c) The Optical Lever

For both optical and electrical measurements it was important to know accurately the value and the uniformity of the crystal thickness. An optical lever thickness gauge(28) was developed from the moving coil system of a normal pointer milliammeter. This could measure thicknesses of 10 μ to 500 μ to an accuracy of 0.5 μ.

The complete gauge is illustrated in fig. 5:5. In the construction of the optical lever the soft iron cylinder of the meter movement was first removed and a small steel pin P of about 5 mm length was soldered in place of the pointer counterweight. A galvanometer mirror M with its silvered face uppermost was stuck on a thin metal foil which was inserted into the coil frame and secured by a drop of adhesive. By careful adjustment of the foil position the balance of the movement could be restored, so that the pressure exerted by the pin on the crystal surface was determined by the hairspring and could therefore be varied by the zero adjustment
lever L. The pointer of the novenent was bent vertically downwards and conveniently served to lower the pin on to the crystal in a gentle and controlled manner. A retaining bar B could be rotated into position to keep the pin raised when manipulating the crystal. The pin rested on a fixed lower rod R which was made from $\frac{5}{8}$ in. diameter hardened steel. Its upper end was conically shaped with a carefully ground horizontal flat of about 0.1 mm diameter. The optical lever and the steel rod were held in a machined brass pillar and the position of the pin was adjusted to lie exactly in the centre of the small flat.

A second brass pillar held a small table T which carried the crystal. Machined dovetailed slides were used to provide both vertical and horizontal movement of the table. Each slide was fixed with an adjustable gib strip to compensate for wear. The movement was controlled by two steel screws having threads of $\frac{1}{5}$ in. pitch. The screw heads $H_1$ and $H_2$ were calibrated at 10$\mu$ intervals.

A slot S of 0.5 mm width and 2 cm length was cut into the table parallel to the direction of the horizontal movement. It allowed the small flat on the lower rod to protrude by a maximum distance of 0.25 mm when the table was lowered. The brass pillar supporting the table and that holding the lever were both screwed to a $\frac{3}{4}$ in. base plate.

A small laboratory telescope fitted with a horizontal crosswire was mounted rigidly close to the mirror of the gauge. It was focussed on the reflection of a vertically held translucent
galvanometer scale. This was placed at about 5 m from the mirror and was illuminated with a fluorescent tube.

In a thickness measurement the table was first slightly raised above the lower rod and the crystal position adjusted so that the section to be probed was resting over the slot S in the table. The pin P was then placed on to the crystal surface and the table gradually lowered by means of $H_1$ whilst at the same time the scale was observed through the telescope. When the lower rod $R$ made contact, the reading reached a steady value and the difference from the zero reading leads to the local thickness. The table was then displaced through a known horizontal distance using $H_2$, and the process repeated.

The system was calibrated with feeler gauges and foils of accurately known thickness. Alternatively, a calibration graph could be obtained in terms of the vertical table movement $H_1$. The sensitivity of the arrangement was about $1 \mu$ per mm scale division which corresponds to an optical magnification of $10^3$. As the zero position was extremely stable, the accuracy is essentially determined by the precision to which the scale could be read with the telescope. Thickness measurements could therefore be made to within $0.5 \mu$.

5.(d) Electrodes

For the purposes of electron bombardment experiments, electrical contact was made to the crystal by painting opposite faces with a thin film of colloidal graphite in alcohol. The
choice of metal contacts is rather restricted because of the chemical activity of sulphur. However, evaporated gold electrodes proved stable on the sulphur surface and were used in some of the experiments, where they led to the same results as graphite.

For optical excitation, either with spark or steady illumination, the crystal was mounted with a gold top, and a graphite bottom electrode. If the crystal had a good natural face it was possible to evaporate a semi-transparent gold layer which was sufficiently conducting. The amount of gold deposited on the crystal was monitored by measuring the resistance between two graphite electrodes painted as strips on the crystal face. After the evaporation the two strips were joined by two others painted across the gold to complete the square.

In some cases an electrode of thin gold strips was tried. This was produced by masking the crystal surface with a grid of fine parallel wires of about 100 μ thickness. The strips were later joined together at each end by graphite. The mask was mounted directly against the crystal to avoid penumbra effects. The amount of light absorbed by the crystal could therefore be determined more easily than in the case of the thin gold electrode, but the grid introduced field inhomogeneity in the surface region.

Particular care had to be taken to ensure that no short circuit could occur across the edges of the platelet. Normally a ½ mm wide border was left at the crystal edges.
Evaporated gold electrodes showed no signs of deterioration under normal use, even when heated in air to 100°C. However, when the specimen was raised to these temperatures in an atmosphere of nitrogen, intended to prevent oxidation of the sulphur, the gold broke up and peeled away from the crystal surface. It is known that gold electrodes are more stable in an oxidising atmosphere than under inert or reducing conditions. (29)

5.(e) Specimen Mounting

The specimen and leads were mounted on a thin cleaved mica sheet which insulated them electrically from the copper bar of the specimen holder. The arrangement is shown in fig. 5:6.

The leads, thin copper wires, were connected to the electrodes with silver paste. To ensure good thermal contact with the specimen holder, the bottom blob was pressed out until it nearly covered the bottom electrode, and a drop of silicone oil was smeared over the top of the copper bar before the mica sheet was screwed in position.

The specimen was positioned centrally by observing concentric rings lightly scribed on the top of the bar. The thermocouple, which was sprung onto the mica sheet, was stuck in position with silver paste and then the leads soldered to their terminals. The arrangement is shown in fig. 5:7.

It was noted that after a day or two the exposed surface of the silver paste and of the copper wire was covered in a black layer of
sulphide. However, this did not appear to alter the measured properties in any way.
Chapter 6

Experimental Results for Holes

It was found that in practically all of the specimens the lifetime of generated holes with respect to deep traps was in excess of $10^{-5}$ sec. The holes could thus be drawn across the specimen by moderate applied fields.

A typical set of photographed oscilloscope traces is shown in fig. 6:1. They represent hole transits at four values of the applied field. The linear rising edge implies a uniform hole drift mobility $\mu_h$, showing that the internal field must be substantially uniform, and also that the loss of carriers during transit is small. The levelling off of the trace as the holes reach the bottom electrode defines clearly the transit time $t_t$, and the change in $t_t$ with applied field can easily be measured.

When working with light excitation the full spectral range of the spark was normally used. However, as will be shown in chapter 8, the wavelengths most efficient in carrier generation are strongly absorbed and so the condition $d_p \ll d$ (section 4(a)) was adequately fulfilled. The traces observed were similar to those shown in fig. 6:1 and led to the same results as electron excitation.

6.(a) Room Temperature Drift Mobility and Free Lifetime

Fig. 6:2, line 'a', shows a set of results obtained at room temperature for a platelet grown by the shallow pool method.
(section 5(a)). The reciprocal of the transit time is plotted against applied voltage, and according to equation 4.2, the hole drift mobility $\mu_h$ can be obtained from the gradient. The results indicate that $\mu_h$ is independent of applied field up to $2 \times 10^4$ volts/cm.

The specimen used grew to a thickness of 420 $\mu$m and points (a) were obtained with the electrodes on natural faces. After grinding one face the thickness was reduced to 330 $\mu$m and subsequent measurements gave points (b). In both cases the gradient corresponds to a mobility of 2.0 cms$^2$sec$^{-1}$volt$^{-1}$, showing that the transport measurements are not affected by the state of the crystal surface.

Fig. 6.2 shows the effect of reducing the field across a specimen until the transit time $t_t$ approaches the hole lifetime $\tau_h$. At this low field the integrated pulse levels out due to the capture of the moving charge by deep traps before it can reach the bottom electrode. Under these conditions, $t_t \sim \tau_h$ and equation (4.3) is applicable. In the specimen shown the hole free lifetime $\tau_h$ is $\approx 40 \mu$sec. For mobility measurements, fields giving transit times of less than 10 $\mu$sec would normally be used for such a crystal.

6.(b) Temperature Dependence of Hole Mobility

As shown in chapter 3 the temperature dependence of mobility can give information as to mechanism of carrier transport. Hole mobility measurements as a function of temperature were made on
about 30 specimens grown from ultra-pure as well as laboratory reagents. Fig. 6:4 gives the results for 12 typical specimens, plotted as \( \log \mu_h \) against \( \frac{10^3}{T} (^\circ K)^{-1} \). All the specimens had natural or ground \((\overline{111})\) faces and, with the exception of those represented by \( \triangle \), \( \circ \), and \( + \), were grown from ultra-pure reagents.

It can be seen that at the lower temperatures the hole mobility in all the specimens is an activated process,

i.e. \( \mu_h \propto \exp \left( -\frac{\varepsilon}{kT} \right) \)

The range of the low temperature measurements was limited by straggling in the carrier cloud and accurate measurements were not possible below 200\(^\circ\)K.

With increasing temperature the results for the higher mobility specimens go through a maximum and tend towards the lattice mobility curve \( \mu_L \).

At 96\(^\circ\)C, the transition temperature between the orthorhombic \((S_{\alpha})\) and monoclinic \((S_{\gamma})\) allotropes, a drop in hole mobility by a factor of 30 takes place. Measurements in the transition range between the two forms require careful temperature control if the change is to be completely reversible.

Monoclinic sulphur melts at 119\(^\circ\)C, but so far no measurements have been attempted in the transition range to the liquid state.

The most consistent interpretation of the results shown in fig. 6:4 appears to be in terms of a transition from a trap
controlled to a lattice controlled mechanism as described by equation (3:11) with \( \mu_L = \mu T^{-3/2} \).
The solid lines on fig. 6:4 represent curves calculated from this equation.

A value of \( \epsilon = 0.19 \text{eV} \) was obtained from the lowest mobility specimens where clearly equation (3:12) can be applied. The results in the lattice controlled range for the highest mobility specimen gave a value of \( A = 4 \times 10^4 \text{cm}^2 \text{sec}^{-1} \text{volt}^{-1} \alpha^{-3/2} \). \( N_t \) was then fitted for each crystal and is shown adjacent to the corresponding curve. For the specimens investigated \( N_t \) varies between \( 10^{17} \text{cm}^{-3} \) and \( 4 \times 10^{14} \text{cm}^{-3} \). The curve \( \mu_L \) leads to a lattice mobility of about \( 10 \text{cm}^2 \text{volt}^{-1} \text{sec}^{-1} \) at room temperature.

Shallow trapping, rather than hopping, was considered to be the cause of the activated mobility dependence at low temperatures for reasons which will be discussed in chapter 9.
Chapter 7
Experimental Results for Electrons

When the electric field applied to the specimen was reversed so as to draw generated electrons into the crystal volume, no signal that could be associated with electron transport could be observed in any of the laboratory grown specimens.

7.(a) Electron Free Lifetime

The typical oscilloscope trace is illustrated in fig. 7.1. The duration of the initial sharply rising part of the negative pulse is exactly equal to the incident pulse length $t_p$, and is due to the primary electrons. The subsequent slow component of the response is connected with the movement of holes towards the top electrode. This charge displacement decreases rapidly in amplitude as the depth of penetration of the incident electrons is made smaller by reducing their energy; it can therefore be distinguished from any displacement associated with the generated electrons.

The absence of an observable electron transport indicates a very small value of the electron range $\mu_e \tau_e \mu_e$ with respect to deep traps. From the sensitivity of the apparatus it was estimated that $\mu_e \tau_e \mu_e \approx \frac{1}{5} \mu_e$ with the maximum field of $5 \times 10^4$ volts/cm. Thus $\mu_e \tau_e \approx 10^{-3}$ cm$^2$/volt. It is therefore likely that the electron lifetime with respect to deep traps is several orders of magnitude smaller than that of the holes.
7. (b) Space Charge Probing

To obtain some information about the deep electron-trapping centres the following experiment was carried out.

The crystal was first irradiated with electron pulses for about 10 seconds, a steady negative potential being applied to the top electrode. Both electrodes were then earthed and the trapped negative space charge was probed after a time $t$ by another short electron pulse of small amplitude. A response was observed due to the movement of generated holes in the space charge field. The height $h_t$ of the signal was taken as an approximate measure of the number of trapped electrons remaining after a time $t$. Irradiating the crystal for longer than 10 seconds did not increase $h_t$ at a given $t$ and it was assumed that the traps were substantially saturated.

It was found that the results could be represented by the relation $h_t = h_0 \exp \left( \frac{-t}{\tau_K} \right)$ where $h_0$ denotes the pulse height at $t = 0$ and $\tau_K$ is the thermal release time. At room temperature $\tau_K \approx 30$ minutes, as shown in fig. 7:2 and decreases rapidly with temperature. From the observed temperature dependence of $\tau_K$ and equation 3:14 the position of the predominant centre was found to be $\sim 0.9$ eV below the conduction band; with $n^0 = n$ the value of $\sigma^-$ was $10^{-15}$ cm$^2$. One would expect such a comparatively high value of $\sigma^-$ to be associated with a charge centre exerting a coulomb attraction on the free electron.
Both the trap depth and release time are in good agreement with the results of Dean, Royce and Champion for the decay of space charge and this will be discussed further in chapter 9.
Although the experiments described in the previous chapters have given information on the properties of the free carriers and the trapping centres with which they interact, little can be learned about the process of carrier generation and its relation to the band structure. From this point of view measurements of optical properties are more informative. In this chapter an investigation of the spectral dependence of photoconductivity and absorption will be described. The experiments were extended over the visible and ultra-violet regions and brought out for the first time the rather remarkable photoconductive properties of sulphur in the ultra violet.

8.(a) Experimental Details

The dark resistivity of the specimens, which were grown as described in chapter 5, was greater than $10^{-18} \Omega \cdot \text{cm}$. The steady photocurrents were therefore measured with a vibrating reed electrometer (Ecke N616B). This had a full scale deflection of $3 \times 10^{-15}$ amp. on the most sensitive range and, to prevent comparable leakage currents, the sulphur platelet was mounted on a highly insulating vacuum specimen holder which was attached directly to the electrometer head. This is illustrated in fig. 8:1.

D was a polythene disc, 1" thick and 4" in diameter, carefully turned to a smooth finish and recessed to fit firmly over the
electronometer socket. P, a brass rod of \( \frac{\frac{1}{2}}{\text{diameter passing}} \) through the centre of D and cemented with Araldite into position, was drilled out and split so that it clipped over the socket core. The high voltage terminal T was a length of 2BA brass studding also cemented into a hole tapped through D. The bottom electrode of specimen S was attached with silver paste directly to P, and the semitransparent gold top electrode was connected to T by a thin copper wire.

The brass enclosure G was placed over the specimen and evacuated through a port in its side. The specimen was then illuminated through the quartz window W.

The nonochromatic radiation was normally obtained from a C.F.A. Optica grating spectrometer. This had a spectral range from 10,000 A.U. to 1,800 A.U. and a spectral band width of 16 A.U./mm slit width. For all of the photoconductivity measurements a slit width of 3.6 mm was used. The light sources, a hydrogen discharge lamp and a tungsten lamp, which were interchanged at 4,000 A.U., were both run from stabilised power-packs.

A Rank Cintel VD59 photocell, which had been calibrated at the N.P.L. for absolute sensitivity between 2,800 A.U. and 8,000 A.U., was used to determine the photon flux at the nonochromator output. Intensity measurements during the experiment were carried out with an E.M.I. 9592B photomultiplier. In the range between 1,800 A.U. and 2,800 A.U., a fluorescent layer of sodium salicylate was
placed in front of the photomultiplier. Since the wavelength of the fluorescent emission was constant, the measurements were independent of the spectral response of the photomultiplier.

To produce a fluorescent layer, a glass microscope slide was covered in a film of methyl alcohol saturated with ground sodium salicylate crystals. When the alcohol evaporated it left a uniform adherent layer. It has been shown [10] that such a layer fluoresces under ultra-violet irradiation, and that the quantum efficiency of conversion is constant between 800 A.U. and 3,800 A.U. The fluorescence has a maximum at 4,200 A.U. (\(\lambda_{\text{max}}\)) and a No. 1A Kodak Wratten filter was placed between the microscope slide and the photomultiplier. This had an edge at 4,100 A.U. and ensured that no directly transmitted ultra-violet radiation was received by the photomultiplier.

The absolute sensitivity of the fluorescent detecting system was obtained by calibrating its output against the standard photocell between 2,800 A.U. and 3,800 A.U. This also confirmed that the salicylate's quantum efficiency remained constant within the above range. The spectral distribution of the monochromator output using the hydrogen discharge lamp is shown in fig. 8:2.

Unfortunately the light intensity from the monochromator was insufficient to produce photocurrents in the visible region that could be measured with reasonable accuracy. For detailed measurements in this spectral range, a simple monochromator employing a Schott 25 cm wedge interference filter was used together with a
50 watt microscope lamp. The filter gave approximately 30% transmission and, with a slit width of 2 mm., the half width of the transmitted light was about 150 A.U. The wavelength transmitted varied linearly with distance along the wedge and was calibrated using the emission lines of the mercury spectrum. The intensity calibration of the light output was carried out by means of a Hilger thermopile and is shown in fig. 8.3.

With both the monochromator and the wedge filter the emitted light was focussed onto the specimen by surface silvered mirrors.

The steady voltage across the crystal was supplied from a bank of H.T. batteries and adjusted by a 100 k.ohm potentiometer.

8.(b) Results of the Photoconductivity Measurements

The purpose of these measurements was to study the quantum efficiency of carrier generation and its spectral dependence.

In the present experiments it was not found possible to observe saturation of photocurrent with applied field under steady illumination. However, with pulsed excitation a fairly well defined saturation of the photogenerated holes was obtained.

A typical steady photocurrent vs. applied voltage curve taken at the wavelength $\lambda = 2550$ A.U. is shown in fig. 8.4. In this, as in all the photoconductive experiments, the illuminated top electrode was made positive, so that generated holes were drawn towards the bottom electrode. Below about 200 volts the photocurrent is non-ohmic, presumably due to space charge effects connected with the trapped electrons in the absorption region. Above this
voltage the curve becomes linear but in the region of 800 volts the photoresponse is too unsteady for reliable measurements. It was therefore decided to confine the work on steady photocurrents to lower voltages and the results on the spectral sensitivity given below all refer to an applied potential of 560 volts.

The problem now arises how to correct such measurements to saturation conditions. Fig. 8:5 shows the saturation observed under conditions of pulsed illumination. The light pulses were obtained from the spark light source described in chapter 4. The integrated pulse height of the holes drawn across the specimen is plotted against applied potential. It can be seen that (a) space charge effects at the lower voltages are absent, and (b) saturation sets in at about 1,000 volts.

Figure 8:6 compares the response observed with slow and fast pulse rates. Curve A was taken at about one pulse per second and curve B at ten pulses per second. Evidently space charge effects similar to those obtained under steady conditions begin to appear at the faster pulse rate. Comparison of curves A and B indicates that, to a first approximation, space charge effects can be taken into account by defining an effective applied voltage \( V-V' \), where \( V' \) is the intercept of the extended linear region with the voltage axis.

Ideally, therefore, the study of quantum efficiency should be carried out under pulsed conditions. Unfortunately, this is not only a small possibility over the complete spectral range because of the far lower
detection sensitivity of the oscilloscope and wide band amplifiers as compared with the vibrating reed electrometer used for the steady photocurrent measurements. The following procedure, illustrated by fig. 8:7 was therefore adopted to correct the results of the steady photoconductivity measurements to saturation conditions.

It is assumed that the curve of figure 8:4 (solid line A) can be extended according to the curve of fig. 8:5 (dotted line B). B now has its origin at $V'$ and reaches saturation at about 1,200 volts. The ratio of the current at 1,200 volts to the current at 360 volts then gives the factor required to correct the steady photocurrent at 360 volts to saturation.

Although this procedure must be regarded as a first approximation, an independent measurement under pulsed conditions at one wavelength was carried out, and led to very reasonable agreement with the corrected steady photoconductivity curves.

The complete photoconductive response of sulphur between 2,000 A.U. and 5,600 A.U. is shown in fig. 8:8. As mentioned above, this curve was obtained from steady photoconductivity measurements and the following corrections were applied:

(a) an area correction to allow for the transmission ratio through the grid which formed the top electrode;

(b) correction for saturation;

(c) conversion to a constant incident photon flux using the source intensity calibrations of fig. 8:2 and fig. 8:3 together
with independently determined photocurrent-intensity curves which will be described later.

The quantum efficiency plotted as the ordinate in fig. 8:8 is defined as the number of carriers generated per photon incident on the crystal and does not allow for the reflection or transmission of light.

The curve is split into two parts. In the optical region the response was similar to that observed by Kurrelmeyer, with a maximum at about 4,600 Å. The photocurrent fell more quickly on the short wavelength side of the peak and was less than the dark current at 4,000 Å. At 3,400 Å, the ultra-violet photoconductivity rose extremely steeply reaching another peak at 2,550 Å, five orders of magnitude larger than the optical response.

The dotted curve represents the absorption edge which will be discussed later.

As a check of the correcting procedure for saturation, the quantum efficiency of the pulse response was measured at the maximum of the spectral sensitivity curve at \( \lambda = 2,550 \) Å. The hydrogen source of the monochromator was replaced by the spark generator and the number of holes transported across the specimen per pulse was measured at saturation. By determining the number of photons per pulse the point in fig. 8:8 denoted by P was obtained. It can be seen that this is in reasonable agreement with the corresponding result deduced from steady illumination and supports the validity of the correcting procedure.

* THE BROKEN LINE HAS BEEN CORRECTED FOR TRANSMITTED LIGHT.
The intensity dependence of the steady photocurrent was investigated at $\lambda = 2,550$ A.U. and at 4,600 A.U. corresponding to the maxima in the ultra-violet and visible regions respectively. The results are shown in figs. 8:9 and 8:10. Whereas in the visible region the relation is strictly linear, in the ultra-violet non-linearity at small intensities is observed. This may possibly be due to space charge effects, but no further experiments have as yet been carried out to clarify this point. As mentioned above, the shape of the curve has been taken into account under (c) to correct the measured photocurrent to constant flux throughout the spectral range, although the non-linearity of fig. 8:9 hardly affects the results shown in fig. 8:8.

8.(c) Absorption

The optical and ultra-violet absorption spectrum of orthorhombic sulphur has received very little attention in the past. As it should be of importance in the interpretation of the photoconductivity results, absorption measurements have been carried out in this investigation.

The results in the visible region for five non-crystalline specimens are shown in fig. 8:11. The points do not include any reflectivity correction.

The absorption coefficient rises slowly from 5,000 A.U. to 4,500 A.U. where it begins to increase exponentially with decreasing wavelength. With a 75 $\mu$m specimen, the thinnest single crystal used so far, no transmitted light was observed beyond 3,800 A.U.
It was, however, found possible to extend the measurements to 2,000 A.U. using a thin microcrystalline layer. This was produced by subliming ultra pure sulphur onto a thin quartz slide. The results obtained are shown in fig. 8:12. The absorption coefficient, which was fitted to the results on single crystals at longer wavelengths, rises to a maximum of $2 \times 10^3/\text{cm}$ at 3,600 A.U. It decreases slowly at shorter wavelengths, forming a shallow window with a minimum at about 2,700 A.U. The absorption coefficient then rises again steadily, reaching about $2 \times 10^3/\text{cm}$ again at 2,000 A.U. This window and its relation to the ultra-violet photoconductive peak will be discussed further in chapter 9.

The sudden increase in absorption at about 4,500 A.U., which has normally been identified with the fundamental edge, was investigated further using polarized light. It was found that the edge showed pronounced dichroism. Its position depended on the orientation of the E-vector with respect to the c-axis, moving to longer wavelengths as the two became parallel.

Fig. 8:13 shows a typical set of results. The separation of these two extreme edges corresponds to 0.05 ev. A crystal plate cut perpendicular to the c-axis showed no dichroism.
Chapter 9

Discussion

In the first part of this chapter the interpretation of the hole mobility experiments will be discussed. The second section deals with the results for electrons presented in chapter 7, and finally an attempt is made to explain the results of the photoconductivity and absorption measurements. A brief summary of general conclusions and of suggestions for further experiments has been added.

9. (a) Interpretation of the Temperature Dependence of the Hole Mobility

As mentioned in chapter 6, the most consistent interpretation of the hole drift mobility appears to be in terms of a mechanism involving the interaction of carriers with acoustic node lattice vibrations and with a single level of shallow traps 0.19 ev above the valence band. The solid lines shown in fig. 6:4, which were calculated using equation (3:11), indicate the reasonable correlation of this theory with the experimental points.

The divergence between the theoretical curves and the experimental points which occurs in the lattice controlled region, may be due to the creation of additional defects as the transition temperature is approached. In addition, the exponent in equation (3:4), which from the experimental points appears to be greater than \( \frac{1}{2} \), could have been increased by a more fundamental effect connected with the anisotropy of the sulphur lattice as mentioned in section 3(b).
A lattice mobility of 10 cm$^2$ sec$^{-1}$ volt$^{-1}$ is consistent with the work of Glamn (section 3(b)), who predicted that in molecular crystals mobilities above 1 cm$^2$ sec$^{-1}$ volt$^{-1}$ would most likely be controlled by acoustic mode scattering. Also, the value $A = 4 \times 10^4$ cm$^2$ sec$^{-1}$ volt$^{-1}$ deg K$^{3/2}$ obtained from the dotted curve can be shown to agree approximately with that predicted by the deformation potential theory, equation (3:3). The value of $E_1$ can be estimated from the linear thermal expansion coefficient $(6 \times 10^{-5}$ deg$^{-1})$ (32) and the temperature coefficient of the energy gap $(1.1 \times 10^{-3}$ ev deg$^{-1}$). With an elastic modulus of $G \approx 10^{11}$ dynes cm$^{-2}$, a value of $A = 9 \times 10^4$ cm$^2$ sec$^{-1}$ volt$^{-1}$ deg K$^{3/2}$ is found. In view of the approximate nature of this estimate, it would be unreasonable to draw any conclusions regarding the effective hole mass.

For several reasons, shallow trapping rather than hopping was considered to be the cause of the activated mobility dependence at low temperatures.

Firstly, the wide variation of mobility from specimen to specimen made it unlikely that a fundamental hopping from molecule to molecule, as envisaged by Glamn, took place. On the other hand, if hopping occurred between impurity sites, one would expect a decrease in activation energy as the impurity concentration and mobility increased. However, the activation energy remains constant for a change in mobility of nearly two orders of magnitude.
Secondly, in their general characteristics, the results shown in fig. 6:4 are very similar to those obtained from drift mobility measurements on CdS\(^{(4)}\) and ZnS, where the interpretation in terms of a trap controlled mechanism also led to consistent results. In such high mobility substances hopping transport is most unlikely.

The nature of the .19 ev hole trapping centres represents an interesting problem. Impurities in the starting materials are unlikely to be the cause, because no systematic difference seems to exist between specimens grown from ultra-pure, and those grown from rather impure reagents (see fig. 6:4). In fact, a batch of crystals grown from the same solution may contain both high and low mobility crystals.

It would seem, therefore, that the centres are connected either with a characteristic structural defect, or with solvent molecules incorporated in some way into the sulphur lattice.

Careful annealing has so far failed to reduce the concentration of shallow traps in any way. However, the infra-red absorption spectrum shown in fig. 9:1 may be significant in connection with the second possibility. The solid line is the spectrum of a typical crystal used in this work. It shows the predominant absorption peak in the 12\(\mu\) region, which has been assigned to a stretching mode of the S\(_{6}\) ring.\(^{(34)}\) However, the second large peak at 6.5\(\mu\) (0.192 ev) does not appear to be part of the sulphur spectrum, and is absent in natural crystals.\(^{(35)}\) As shown by the dotted line obtained with
laboratory grade CS$_2$, the 6.5 $\mu$ peak is most likely associated with solvent molecules. The close agreement between the value of $\epsilon$ and the energy of this molecular transition may be significant. It is not impossible that up to $10^{17}$ cm$^{-3}$ solvent molecules may be incorporated into the crystals during growth and for these to form hole traps.

In an attempt to support this explanation, measurements were made on a number of natural Sicilian sulphur crystals which did not show the 6.5 $\mu$ peak. All the specimens led to hole mobilities smaller by a factor of ten or more than the lowest values obtained from laboratory grown crystals. The temperature dependence of $\mu_h$ indicated a hole transport controlled by a considerable density of deeper centres (about 0.3 ev above the valence band), which were absent in the grown specimens. The experiment proved therefore inconclusive, because these centres would tend to completely mask the effect on the hole transport of any 0.19 ev centres that might be present.

Efforts made to remove the solvent molecules from laboratory grown specimens by heating them in a vacuum for several days, failed to affect the 6.5 $\mu$ peak in any way. A similar technique had been used successfully by MacNeil, (38) who did not obtain the 6.5 $\mu$ peak in crystals grown from solution in CS$_2$.

9.(b) Discussion of Experimental Results for Electrons

The small range of generated electrons, which was estimated in chapter 7 to be less than $10^{-8}$ cm$^2$/volt, prevented the observation of
electron movement in all the sulphur crystals investigated. This result is in complete disagreement with the work of Dean, Royce and Champion,\(^{(15)}\) who associated the conduction pulses obtained under \(\alpha\)-particle bombardment with the movement of generated electrons.

However, there can be no doubt as to the sign of the transit pulse observed in the present investigation. The possibility that this might represent the movement of electrons towards the top electrode has been excluded by experiments with incident energies from 50 kev to as low as 5 kev, which led to the same transit time.

On the other hand, the results of Dean et al on the depth of the centre responsible for trapped space charge in sulphur is in good agreement with the results of chapter 7 on the deep electron traps. If these traps did exist in the crystals used by Dean et al, it seems very unlikely that the predominant carrier could be electrons.

As pointed out in chapter 2, Dean et al worked under conditions predominantly controlled by space charge. The interpretation of charge displacements in a strong barrier region is undoubtedly a complicated problem, and it might be possible that they observed in fact the drift of holes towards the negative electrode.

It is of interest to note that the lifetime of electrons in the specimens of Sicilian sulphur was also very low, and again the .9 ev centre may have been present, although no measurements were made to confirm this.

\(9.(c)\) Photoconductivity

From the remarkable difference in magnitude between the
visible and ultra-violet response, and from the wide spectral separation of the two peaks, it would appear that the photocurrents are due to different mechanisms of carrier generation or of carrier transport.

The position of the visible photoconductive peak is in quite good agreement with the results reported by Kurrelmeyer\textsuperscript{(15)} and by Tartakovsky and Rekolova\textsuperscript{(16)} (Fig. 2:1). The maximum occurs near the beginning of the absorption edge which has generally been associated with the intrinsic band gap. The quantum efficiency of about $10^{-5}$ electrons/photon, which agrees approximately with the results of Dean et al, is remarkably low for an intrinsic photoconductive process. Also, the decrease in the response at shorter wavelengths occurs at unusually low optical densities.

At first sight the most remarkable characteristic of the photoconductivity curves is the comparatively enormous response in the ultra-violet, which does not seem to have been reported previously. However, the rise of this peak to about unit quantum efficiency is far more in keeping with an intrinsic photoconductive effect than the small quantum efficiency in the visible. The most unusual feature of the ultra-violet response is its position with respect to the absorption edge which lies near 4,500 Å. If in fact the rise in photocurrent in the ultra-violet marks the beginning of transitions between the edges of a fundamental band gap, it is left to explain the strong absorption which occurs at longer wavelengths.
Any explanation of the photoconductivity results should therefore be consistent with the following experimental facts:

(a) A quantum efficiency of unity in the ultra-violet region where the absorption coefficient is high.

(b) An apparent quantum efficiency (not allowing for transmitted radiation) of about $10^{-5}$ electrons/photon in the weakly absorbed visible region.

(c) A definite decrease in the photoconductive response associated with a rapid increase in absorption at the short wavelength side of the visible response peak.

The last point shows clearly that not all the transitions produced by the absorbed radiation lead to the generation of free carriers, since it has already been demonstrated that a free hole can easily be drawn across the crystal.

There appear essentially three possible explanations.

(1) Sulphur may possess a double valence band with widely different hole mobilities. This model would require that the comparatively high drift mobility of holes described in chapter 6 occurs in the lower band. Transitions from this band would then be responsible for the ultra-violet photoconductivity.

Holes generated in the upper band, which give rise to the small visible photoconductive response, must have a very low mobility or, more likely, a transport by the hopping process described in chapter 3 may occur. Alternatively, it is possible that if the holes are completely bound, the small photocurrent in the visible
may represent the movement of generated electrons.

There are two main objections to the above explanation in terms of a double valence band. Firstly, it is rather difficult to understand the experimental result (c) and secondly, one would not expect the long hole lifetime observed in the fast band, as generated holes would tend to be trapped easily in the upper band.

(2) Assuming again that the ultra-violet photoconductivity is due to excitations across the fundamental band gap, the visible response may be explained by transitions from the valence band into discrete states caused by imperfections in the lattice. The comparatively low density of such states could explain the small photoconductive response in the region of weak absorption. This theory, however, again fails to explain result (c).

(3) It is well known that the absorption of light by a molecule in a molecular crystal leads to a state in which the excitation can migrate from molecule to molecule. Northrop and Simpson, studying the photoconductivity and fluorescence in anthracene, concluded that interactions between these molecular excitons were responsible for the generation of electron-hole pairs. It was suggested that the incident radiation was first absorbed with the production of excitons. Molecules were therefore put into an excited state, but the energy was insufficient for the production of free carriers. The transfer of an exciton from one molecule to a neighbouring one already in the excited state could then lead to a molecule in the ground state and a molecule with twice the exciton
energy. This may well be sufficient to produce an electron-hole pair.

Recently, Silver\(^{(39)}\) has shown fairly convincingly that such a mechanism occurs in anthracene for weakly absorbed light. He found the efficiency of free carrier generation was about \(10^{-6}\) electrons/photon. Theoretical work by Choi and Rice\(^{(40)}\) on the probability of exciton transfer between two molecules leads to a probability of interaction consistent with Silver's results. This mechanism could therefore explain result (b).

The relative positions of the two photoconductive peaks gives another strong indication that the response in the visible involves exciton-exciton interactions. These peaks are at 4,600 Å and 2,550 Å and correspond to photon energies of 2.6 ev and 4.9 ev respectively. If therefore the ultra-violet photoconductivity is connected with direct transitions between the fundamental bands, it is clear that interaction between two excitons produced by the weakly absorbed light will provide just sufficient energy to create an electron-hole pair.

The recombination kinetics of carriers generated by exciton-exciton interaction has also been studied by Choi and Rice.\(^{(40)}\) These authors concluded that the photocurrent for weakly absorbed light would increase linearly with the intensity of incident radiation. This is again in agreement with the results on sulphur as shown by fig. 8:10.

It now remains to explain result (c), why the response
decreases in the visible with rising absorption which should lead to an increase in the number of excitons generated. Silver showed experimentally that carrier generation by exciton-exciton interactions could only be observed as a volume effect in very weakly absorbed light. Obviously, from the low efficiency of carrier generation observed, exciton-exciton interactions play a very small part in determining the exciton lifetime. There exists a considerable amount of evidence, particularly from work on anthracene, that the exciton lifetime is critically determined by interaction with imperfection centres. This causes a rapid decrease in the lifetime of excitons generated near the crystal surface. The probability of exciton-exciton interaction may therefore decrease quite sharply as the light becomes more strongly absorbed.

9.(d) Absorption

The detailed investigation of the absorption, which was intended primarily to help in the interpretation of the photoconductivity results, is still incomplete.

The dichroism in the absorption edge shown in fig. 8:13 is well established, and may possibly be associated with the valence band structure as observed in CdS and ZnS, although other explanations are possible. However, the energy separation of the two edges (0.05 ev) is too small to be directly related to the effects mentioned in (1) of the previous section.

The structure in the absorption curve at shorter wavelengths,
which was observed using the microcrystalline layer, (fig. 8:12) might be related to the ultra-violet photoconductivity, particularly as the minimum in the absorption window corresponds to the peak of the photoconductive response.

The structure in the absorption is probably far more pronounced for a single crystal, and it would be of considerable interest to extend the study of the dichroism to this region.

9.(e) Conclusions

(1) The charge in orthorhombic sulphur crystals is carried predominantly by generated holes. Their lattice mobility, which is controlled by acoustic mode vibrations, is about $10 \text{ cm}^2 \text{sec}^{-1} \text{v}^{-1}$ at room temperature and they possess a lifetime longer than $10^{-5} \text{sec}$.

(2) At lower temperatures the hole drift mobility is trap controlled and the free carriers interact with a shallow level of centres $0.19 \text{ ev}$ above the valence band with densities between $10^{12}$ and $10^{17} \text{cm}^{-3}$.

(3) The $0.19 \text{ ev}$ hole trapping centre may possibly be associated with solvent (CS$_2$) molecules incorporated into the lattice.

(4) The range of generated electrons is very short ($<10^{-3} \text{cm}^2/\text{volt}$). A predominant electron trapping level with a large capture cross-section is situated about $0.9 \text{ ev}$ below the conduction band.

(5) The visible photoconductivity reaches maximum at 4,600 A.U.
where the apparent quantum efficiency, not allowing for transmitted light, is about $10^{-5}$ electrons/photon. It is likely that this response is due to exciton-exciton interactions.

(6) The ultra-violet photoconductivity reaches a peak at 2,550 A.U. with unit quantum efficiency.

(7) The absorption coefficient begins to rise exponentially at 4,500 A.U. reaching a maximum of $2 \times 10^3$/cm at 3,600 A.U. There is a slight window in the absorption at shorter wavelengths with a minimum at about 2,700 A.U.

(8) The edge at 4,500 A.U., which may not be due to transitions across the intrinsic band gap, shows distinct dichroism. It moves to shorter wavelengths when the E-vector is perpendicular to the c-axis. This shift corresponds to an energy difference of 0.05 ev.

(f) Suggestions for Future Work

The work on sulphur presented in the previous chapters has been very useful in the understanding of molecular crystals. Although the study of charge transport in the orthorhombic solid is essentially complete, the mechanism of carrier generation still presents a number of unsolved problems of considerable general interest.

The conclusion that the photoconductive response in the visible region is caused by exciton-exciton interactions could be supported by measurements on the mobility of holes generated by visible radiation only. If these could easily be drawn across the crystal, the low photoconductive response must be due to a poor quantum
efficiency of carrier generation as in the exciton-exciton theory. This experiment would require the production of a far more intense light flash than has so far been used.

Another approach to the problem, is the more detailed study of the band structure. Absorption measurements on a very thin single crystal should give more precise information on the window or other details which occur at shorter wavelengths and also allow the extension of the investigation of dichroism. On the other hand, absorption measurements on a very thick crystal may show some structure in the weakly absorbing visible range.

A study of the reflection coefficient of sulphur in the visible and ultra-violet regions would also give complementary information to the absorption measurements.

There are two possible lines of investigation which would do much to complete the understanding of hole transport in orthorhombic sulphur. Firstly, it may be possible to grow pure single crystals from the melt or from the vapour phase. These would be free from CS₂ and therefore might not contain the .19 ev trapping level. This would enable the lattice controlled mobility to be studied over a greater range and the temperature dependence obtained more accurately. Secondly, all the hole mobility measurements so far have been made along an axis perpendicular to the (111) directions. A systematic study along different crystallographic directions may give some indication of the variation of mobility with different intermolecular orientations.
Spark excitation has proved a very satisfactory method of producing carriers for drift mobility measurements in sulphur. Work has been carried out successfully at atmospheric pressure with temperatures near the melting point. There appears, therefore, some possibility of extending the measurements to the liquid state. It would be extremely interesting to investigate whether the mobility in the liquid is in any way related to the lattice controlled or hopping mechanisms mentioned in chapter 3.

It is possible to grow mixed crystals of sulphur and selenium in all proportions. The drift mobility of carriers in selenium has already been studied in some detail, and preliminary measurements have been made on the mixed crystal system with low selenium content. These show that the hole drift mobility is about two orders of magnitude less than in the pure crystal, but there are definite indications of an electron response. This could be associated with the selenium centres only, but may be connected with the intrinsic electron conduction mechanism in sulphur.
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Figure 1 : 1 Illustration of the puckered ring of 8 sulphur atoms forming the sulphur molecule

Figure 1 : 2 The arrangement of sulphur molecules in a unit cell of orthorhombic sulphur seen looking along the c-axis. The open circles represent the atoms in the first layer of molecules. The molecules represented by the closed circles illustrate the orientation of the second layer, of which only half is shown. Two further layers complete the unit cell. (after Warren and Burwell).
Figure 2.1 Spectral sensitivity of photocurrent (after Kurrelmeyer (A) and Tartakovsky and Rekalova (B, C)).
The effect of a single level of shallow trapping centres on the hole drift mobility.

\[ \mu_{\text{drift}} = \mu_L \cdot \frac{1}{1 + \frac{N_L e \epsilon}{N_V kT}} \]
Figure 4: 1 Illustration of the principle of the transit time method for determining the carrier mobility.

Figure 4: 2 Observed charge displacement of holes drifting in
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(after J. Hartke)
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Figure 8: Variation in photocurrent with intensity of irradiation at a wavelength of 4,600 A.U.
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