THE PRESSURE DEPENDENCE OF THE ELECTRONIC PROPERTIES OF ORTHORHOMBIC SULPHUR AND VITREOUS SELENIUM

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Friedrich Karsten Dolezalek, Diplom-Physiker,
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ABSTRACT

Drift mobility techniques have been used to measure the transport of excess electrons and holes in orthorhombic S and vitreous Se under hydrostatic pressures $p$ of up to 6 kbar in the temperature range from -50°C to 80°C. In the S crystals, where electrons propagate by an intermolecular hopping mechanism, a strong pressure dependence was found for the electron mobility,

$$\mu_e \propto \exp \left( \frac{p}{3.15 \text{ kbar}} \right)$$

the activation energy, however, remained unchanged.

It is concluded, on the basis of small polaron theory, that the observed effect is caused by an increase of the intermolecular resonance integral $J$. In fact, a LCAO calculation of the intermolecular overlap integral as a function of pressure predicts changes in $J$ of the right order of magnitude.

At low temperatures the hole mobility depends on the pressure as $\mu_h \propto \exp \left( \frac{p}{3.15 \text{ kbar}} \right)$. If the temperature is increased, however, a progressively weaker dependence is found. This can be described phenomenologically by taking the trap density to be dependent on the pressure as $N_t \propto \exp \left( -\frac{P}{5 \text{ kbar}} \right)$.
In vitreous Se no pressure dependence of the mobilities could be detected and the implications of this result on the conduction mechanism are discussed. It is also suggested that the pronounced pressure dependence of the steady state dark- and photo-conductivity in this material is primarily due to the effect of pressure on the injecting properties of the contacts.
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CHAPTER 1

Introduction

"The gods throw stones of sulphur on me"

Cymbeline.

The electronic properties of sulphur and selenium have only recently been studied in some detail. Of the two materials, selenium has received more attention, mainly because of its application in rectifying and photoconductive devices and in electrophotography (e.g. Xerography).

Throughout the ages sulphur has been associated mostly with disagreeable manifestations of human and superhuman powers. According to Homer (-1100), Ulysses used sulphur as a home disinfectant after having most forcibly disposed of his wife's suitors. This purgatory property of sulphur was later confirmed by Plinius (0077) in his monograph "Naturalis Historia," where he also recommends the use of sulphur for the diagnosis of epilepsy, and speculates about its role in lightning discharges. The latter idea was taken up by Shakespeare (1609) who had already connected sulphur to infernal pyrotechnics in an earlier paper (1604).
In his monograph "Inferno" Dante Alighieri (1307) had described the unpleasant smell of that environment, probably referring to \( \text{SO}_2 \).

Since the introduction of gunpowder in the late fourteenth century, sulphur became increasingly involved in the forcible settlement of political arguments. On a well-documented occasion (Casanova, 1788) the Venice lead chambers, meant for the production of sulphuric acid, were used to detain political prisoners.

Up to the present day, sulphur is indispensable for the production of such intoxicants as wine and tobacco, its use in papermaking provides the basis for the publication explosion to which the element selenium also contributes heavily.

Though the chemical reactivity of sulphur has given it a bad reputation, elemental sulphur is a particularly good example of an easily accessible molecular solid and the study of its transport properties has already led to interesting results. Recent work of this group furnished strong evidence for the occurrence of two different types of low mobility transport in sulphur, namely a hopping motion for electrons and a narrow band conduction for holes.

The aim of the present work has been to investigate the electronic properties of some low mobility solids under hydrostatic pressure and to determine whether this variable is useful
in the study of their transport mechanisms. In view of the remarkable and well-established conduction properties of orthorhombic sulphur, it was felt that this material would form a promising starting point for such an investigation. Selenium was chosen as a second material, because a comparison of the effect of pressure on the conduction in a crystalline and amorphous solid appeared to be of considerable interest.

After briefly surveying the general effects of pressure on a solid, Chapter 2 deals with previous measurements of drift mobility in Si and anthracene under pressure; a further subsection treats the conductivity of organic solids under pressure.

In Chapter 3 an account is given of some of the theoretical treatments of low mobility transport and their application to S and Se.

The experimental techniques are outlined in Chapter 4, where the apparatus and the preparation of the samples is described. The next chapter deals with the experimental results on the transport properties of orthorhombic sulphur and vitreous selenium. Preliminary data on trigonal selenium are also included for comparison.

An intermolecular overlap calculation for sulphur is presented in Chapter 6, laying the groundwork for the interpretation of the electron transport results under pressure. In the following discussion chapter it is shown that an intermolecular hopping mechanism
can explain the order of magnitude of the observed pressure effect on the electron mobility in sulphur. For the hole mobility two models are tested, but no definite conclusion as to their applicability can be drawn so far.

Finally some suggestions for the extension of the present work are made.
CHAPTER 2

Survey of the Previous Work on High Pressure

2.1 Effect of High Pressure on Solids

In recent years excellent equipment for the pressure range up to 10 kbar has become available commercially and this has resulted in a somewhat more widespread exploitation of pressure as a readily controlled parameter of solid state research. Pressure has been used as a tool for investigations of almost all aspects of the behaviour of solids and liquids such as lattice structure, phase changes, diffusion, mechanical, electrical, magnetic and optical properties, and others.

In the following brief survey of high-pressure effects on solids, special attention is given to the work on sulphur and selenium.

The primary effect of hydrostatic pressure is the reduction in the equilibrium values of the interatomic or intermolecular distances.
This has an effect on the electronic and the atomic arrangement of the solid, but not on the symmetry. The latter can be altered by the application of uniaxial stress as shown by the extensive work of Fritzsche (1962) and others.

The compressibility of sulphur was repeatedly determined by Bridgman and is summarized in his monograph (1958). As seen from Table 2.1 the compressibility is anisotropic and a function of pressure and temperature. The results on vitreous Se by Weir (1954) are also shown in Table 2.1.

The phase diagram of Se and that of S, both are shown in Fig. 2.2, have been examined in some detail by Deaton and Blum (1965), Ward and Deaton (1967), and many others as reviewed by Tuller (1954) in the Sulphur Data Book. Tammann (1925) found that in sulphur the rhombic to monoclinic phase boundary intersects the melting curve forming a triple point at 1.3 kbar and 135°C. Above that pressure the melting curve is that of rhombic sulphur, it can be represented by a straight line with a slope of +15 deg C/kbar. The corresponding slope for trigonal Se is +20 deg C/kbar, the amorphous phase has no melting point.

The effect of very high pressures on the electronic structure of solids has been studied in great detail by Drickamer and co-workers (1963, 1965) using optical means. Balchan and Drickamer (1960) found that the absorption found in sulphur at 2.9 eV shifted toward
lower energies at a constant rate of 67 μeV/bar. The results of Adams and Spear (1966), however, show clearly, that the absorption edge lies at 3.7 eV, whereas the band gap as derived from transport measurements is 4.2 eV. The results of Suchan and Drickamer (1957) for the 1.7 eV absorption edge in selenium indicate a shift of 130 μeV for the same pressure interval.

If one interprets the energy of the absorption edge as a measure of the width of the forbidden band, one would expect the gap to disappear at the extrapolated pressures of 130 kbar and 400 kbar for selenium and sulphur respectively. For the case of Se this conclusion is supported by the conductivity measurements of Balchan and Drickamer (1961) who found a discontinuous drop in resistance of 2 - 3 orders of magnitude at 130 kbar. The results of Kozyrev and Nasledov (1956) give an activation energy for the conductivity that extrapolates to zero at 118 kbar.

In sulphur Harris and Jura (1965) did not find resistivities below 10^7 Ω cm in the pressure range up to 400 kbar, shockwave experiments reported by Haman (1958), however, appear to reveal metallic conduction above about 230 kbar.

The Hall effect of many substances has been measured as a function of pressure. The interpretation of the results, however, present some difficulties, as the Hall constant not only reflects changes in the carrier density, but of the band structure and transport
properties.

By measuring resistance changes with pressure and temperature in suitably chosen samples of Ge and Si, Holland and Paul (1962 a + b) have determined the pressure dependence of ionization energies of impurities. The coefficients were of the order of $+10^{-8}$ eV/bar for shallow centers and $10^{-6}$ eV/bar for the deeper lying levels, and the band gap. The decrease in the donor ionization energy was explained by the model of a hydrogenic impurity. There the ionization energy is

$$E = \left(\frac{m^*}{m}\right) \frac{1}{\varepsilon^2} \times 13.6 \text{ eV} \quad (2.1)$$

$m^*$ being a suitably chosen average for the effective mass and $\varepsilon$ the permittivity. For a nearly free electron the pressure variation of $m^*$ is small compared to the pressure dependence of $\varepsilon$. For Si

$$\frac{d\varepsilon}{dp} = (4 \pm 1) \times 10^{-7} \text{ bar}^{-1} \quad (2.2)$$
as determined by Cardona, Paul and Brooks (1959). This value gives a shift of $-4 \times 10^{-8}$ eV/bar for the As donor level, the value quoted by Holland and Paul (1962) was $-5.4 \times 10^{-8}$ eV/bar.

In the absence of precise measurements a rough estimate on the pressure dependence of the permittivity can be obtained from the volume dependence of the polarization, as expressed in the Clausius-Mossotti relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{P}{V} \quad (2.3)$$
where $P$ is the over-all polarizability of the crystal and $V$ the volume. Differentiation yields

$$
\frac{d\varepsilon}{\varepsilon d\rho} = \frac{3 \kappa}{\left(\frac{2P}{V}\right)(\frac{V}{P}-1)} 
$$

where $\kappa$ is the compressibility of the medium. The pressure variation found by Cardona et al (1959) was somewhat larger than the shift expected from volume effects alone.

The vibrational spectrum of a crystal has a strong influence on the transport properties of a solid. For band conduction, the scattering of the carriers by phonons controls the mobility, and in very low mobility solids the interaction of the carriers with local modes leads to the formation of the so-called small polaron, discussed in Chapter 3.1.

The pressure dependence of the phonon frequencies, say $f$, can be estimated using the volume dependence of the Debye temperature $\Theta$

$$
\frac{df}{f} = \frac{d\Theta}{\Theta} = \gamma \left(\frac{-dV}{V}\right)
$$

with the Grüneisen constant $\gamma$ ($\gamma \approx 2$).

In a molecular solid such as orthorhombic sulphur the Debye approximation cannot be expected to give good results, the effect of pressure on the internal vibrations of the molecules will be considerably smaller than that on the so-called external lattice vibrations, the phonons.
By means of infrared spectroscopy Sherman (1966) and Field and Sherman (1967) have found pressure-induced shifts of the frequencies of internal and external modes in NaCl of 0.23%/10 kbar and 10%/10 kbar respectively.

Taking \( \gamma = 1.6 \) and the compressibility of 3.1%/10 kbar we would expect from equation (2.5) to find 5% increase in the frequency of external modes of NaCl. The very small pressure coefficient of the internal modes cannot be accounted for by the Debye model.

In Table 2.3 a number of constants relating to S and Se are listed with their values at 0 and 10 kbar. Data were taken from Samsonov's handbook (1968), the Grüneisen constants were calculated from

\[
3\alpha = \gamma \cdot \kappa \cdot \gamma \cdot c_v
\]

with the linear expansion coefficient \( \alpha \), the compressibility \( \kappa \), the specific heat \( c_v \) and the density \( \gamma \).

2.2 The Pressure Dependence of the Drift Mobility in Germanium

The determination of drift mobilities of minority carriers by the method of Haynes and Shockley (1951) is one of the classical
experiments in the field of semiconductor physics. The adaption of that method to the confines of a high pressure vessel with no loss in accuracy, however, is a formidable problem that has been solved by A. C. Smith (1959) and, independently, by Landwehr (1956, 1959).

Both authors found the electron mobility in Ge to decrease with pressure, as shown in Fig. 2.4. The hole mobility increases with pressure at a rate of $1.4\%$ per 10 kbar. Smith concluded that for electrons the drift mobility, as well as the mobility derived from the resistivity, of doped samples, had the same pressure dependence within the experimental error of $2\%$.

A quantitative theory for the pressure dependence of the electron mobility in Ge was given by Nathan et al (1961). The basic assumption in his treatment was that the (111) band is moving away from the valence band under pressure whereas the (100) band does not. This has the consequence that the energy difference between the two sets of minima is decreasing with increasing pressure. At low pressures most of the conduction electrons populate the (111) minima; at a pressure of 20 kbar, however, a substantial proportion of the electrons has been transferred to the (100) minima, which give a lower mobility. Further reduction of the over-all mobility comes from intervalley scattering between the minima.
2.3 The Pressure Dependence of the Drift Mobility in Anthracene

The results on the pressure dependence of the electronic transport properties of anthracene as determined by Kepler (1961) are of particular relevance to this work as they represent the only investigation of that type on a low mobility molecular solid. Fig. 2.5 shows Kepler's results replotted on a semilogarithmic scale, proving that an exponential dependence on the pressure cannot be excluded as was in the case of Ge. The pressure dependence varies for the crystallographic directions and for the type of carrier. At 3 kbar the increase amounts to 45% on the average. For electrons moving perpendicular to the ab plane the effect was very small, it is not shown in the figure.

In a first attempt to explain the observed pressure dependence, Kepler estimated the change in the Debye temperature with pressure and using a band conduction formula, he arrived at a 10% change in mobility for 3 kbar. This value could only be regarded as a rough estimate, as in anthracene the Debye approximation is expected to give particularly bad results because of the molecular vibration spectrum and the anisotropy of the lattice.

The band structure of anthracene under high pressure was calculated by Harada et al. (1964) and Rice and Jortner (1965) using
the tight binding approach. Under the assumption of an isotropic compressibility Harada et al. obtained mobility increases of about 30% at 3 kbar. Rice and Jortner allowed for anisotropic compressibility; their results, however, give on the average only a change of 10% per 3 kbar for the mobilities. Both calculations do not even qualitatively predict the observed typical anisotropies in the pressure dependences of the mobilities.

2.4 Other Organic Solids

It seems very likely that many organic molecular solids are similar to anthracene in their behaviour under pressure. Unfortunately, however, so far only measurements of conductivity have been carried out, some of which were reviewed recently by Rice and Jortner (1965) and are shown in Table 2.6. One finds a rapid drop of the resistivity with pressure, followed by a levelling off of the resistance in the region of 200 kbar, apparently due to the rapid decrease of the volume compressibility. The activation energy of the observed conductivity is found to decrease with pressure at a rate of about $10^{-5}$ eV/bar. On the basis of their estimates for the pressure dependence of the mobilities as well as the experimental
evidence found by Kepler (1961), both Rice and Jortner (1965) and Harada et al. (1964) concluded that the major contribution to the rise in conductivity at high pressure comes from an increase in carrier density rather than from the mobility.

Rice and Jortner suggested that the activation energy observed in the conductivity experiments is interpretable as the difference between the Fermi level of the contact metal and the bottom of the conduction band. The model assumes that the charge carriers are injected into the crystal from the contacts and do not arise from thermal excitation across the band gap as is the case for intrinsic conduction.

The activation energy is expected to change with pressure by an amount equal to the change in the polarisation energy of the lattice in interaction with the excess charge, depending on the inverse fourth power of the intermolecular distance. As Rice and Jortner showed for the case of pentacene, the contact effect can very well account for the observed pressure dependence.

In contrast to the ideas just mentioned, many workers interpret their pressure-resistance measurements in terms of an increase in intrinsic carrier density resulting from the narrowing of the band gap with pressure. This explanation was first put forward by Bardeen (1949) to account for the pressure effect on resistivity in tellurium found by Bridgman; it was also used in the pressure work on Se and S,
as reviewed in section 2.1. of this chapter.

Ironically, pressure work on pentacene appears to be in agreement with both explanations: Shirotani et al. (1966) quoted pressure shifts in pentacene of \(8.5 \times 10^{-6} \text{ eV/bar}\) and \(9.3 \times 10^{-6} \text{ eV/bar}\) for the activation energy and the absorption edge, respectively.
CHAPTER 3

Survey of the Previous Work on Low Mobility Conduction

3.1 Theoretical Work

During the last decade the field of low mobility transport has attracted both theoretical and experimental workers. Many of the theoretical approaches as well as some of the experimental evidence available were reviewed by Appel (1968), by Klinger (1968) and by Austin and Mott (1969).

In this section some of the theoretical work will be briefly outlined and its application to the conduction mechanism in S and Se will be discussed in section 3.2.

One has to distinguish between two fundamentally different mechanisms of low mobility transport. Firstly the wavelike propagation of the carrier in a narrow band, and secondly a diffusive hopping motion of the charge between sites spaced a few atomic distances apart.

In the so-called narrow band conductors the band width is comparable to kT and all states are equally populated. Under these conditions, the well-known relation \( \mu = e \tau / m^* \), applicable to wide
band conduction, is not a valid approximation. Instead, following Fröhlich and Sewell (1959), the mobility is obtained from a statistical average of $\nu^2 \tau$ throughout the band

$$\mu = \frac{e}{kT} \langle \nu^2 \rangle$$

Here $\nu$ is the gradient of the dispersion curve,

$$\nu = \frac{1}{h} \frac{\partial E}{\partial k}.$$  

This lattice (or microscopic) mobility can be reduced by the presence of shallow trapping centers as has been shown for instance by Spear and Mort (1963) for CdS. The carriers are trapped and thermally released during the transit; experimentally one determines the sum of the drift time and the total time spent in traps. The observed resultant drift mobility $\mu_D$ is then according to Rose (1951)

$$\mu_D = \mu_L \left[ 1 + \frac{N_t}{N_c} \exp(\epsilon/kT) \right]^{-1}$$

(3.1)

where $\mu_L$ is the lattice mobility, $N_t$ is the density of the traps, $\epsilon$ their depth, and $N_c$ the effective density of states of the band in question. At high temperatures the exponential term is small and the drift mobility $\mu_D$ is nearly equal to the lattice mobility $\mu_L$. The latter depends on the temperature as $\mu_L \propto T^{-a/2}$, where $a$ is a small positive integer, which depends on the scattering mechanism.
At low temperatures the exponential term in (3.1) dominates, and we have an activated mobility

$$\mu_D = \mu_L \frac{N_c}{N_t} \exp(-\epsilon/kT)$$  \hspace{1cm} (3.2)

An example for a trap controlled drift mobility showing both regimes is given in section 3.2 of this chapter.

As Fröhlich and Sewell (1959) showed there is a lower limit $\mu_*$ to the lattice mobility set by Heisenberg's uncertainty principle

$$\mu_* \approx (J/kT) \text{ cm}^2/\text{Vs}$$  \hspace{1cm} (3.3)

where $2J$ is the band width. Below $\mu_*$ (which is of the order of 1 cm$^2$/Vs at room temperature for many molecular crystals) band-type conduction is no longer possible.

In low mobility materials the charge carrier is likely to polarize its immediate environment, thereby lowering the energy of the total system. This polarization can be described in terms of an interaction of the carrier with the optical modes of the lattice (as is the case in ionic crystals) or of the molecules (in the case of a molecular solid). The carrier and its distorted environment can move through the crystal, thus forming a quasiparticle called the polaron. If the binding energy $E_b$ of the polaron is much larger than the bandwidth $2J$ the distortion is confined to one unit cell, or in some cases (e.g. $S_8$), to the immediate neighbourhood of one
molecule. This case has been given the name "small" polaron by Holstein (1959), who carried out the first detailed treatment of this conduction mechanism.

At low temperatures zero point energy enables the polaron to move in a narrow band in a manner similar to band conduction. As the temperature is raised, however, the polaron band width as well as the scattering time decrease rapidly. As a result, the band model breaks down above a transition temperature which according to Holstein (1959) lies at approximately half the Debye temperature. At higher temperatures the polaron then proceeds by phonon-assisted diffusive hopping from one localization site to another. It should be emphasised that the low temperature polaron-band transport is unlikely to be observable at room temperature, and should not be confused with the narrow band conduction discussed earlier in this section.

In the hopping transport theory the jump probability $P$ between sites spaced a distance $a$ apart, gives a diffusivity of $D = 6^2 a_2 P$. The factor $6$ depends on the lattice investigated; it is 1 for the one-dimensional lattice considered by Holstein, and $1/6$ for a cubic lattice (six nearest neighbours). The Einstein relation then gives

$$
\mu = \frac{ea^2}{kT} P \quad (3.4)
$$
Appel (1968) pointed out that one has to distinguish between two cases of hopping transport which depend on the relative magnitude of the energy resonance integral $J$ and the polaron binding energy $E_b$:

(a) If $J$ is sufficiently large, the carrier can follow adiabatically the motion of its surroundings by tunnelling to and fro between adjacent sites during one period of the vibrational mode. As Appel notes this so-called adiabatic hopping transport requires that $\hbar J$ be larger than the energy $\hbar \omega_0$ of the mode predominantly responsible for the formation of the polaron. According to Emin and Holstein (1969), the hopping probability is in this case

$$ P = \frac{\omega}{2\pi} \exp\left[ -\frac{(E_b - 2J)}{2kT} \right] \quad (3.5) $$

where $\omega/2\pi$ denotes the frequency of the vibrational mode.

(b) If, on the other hand, the probability of the carrier transferring during one vibrational period is small, then we have the case of non-adiabatic hopping. For this transport both Yamashita and Kurosawa (1958) and Holstein (1959) agree for high temperatures

$$ P = \frac{\sqrt{\pi}}{\hbar} \frac{J^2}{\sqrt{2E_b kT}} \exp(-E_b/2kT) \quad (3.6) $$
Substitution of the hopping probability in expression (3.4) for the mobility gives an activated mobility for both cases

(a) adiabatic hopping:

\[ \mu = \delta \frac{ea^2 \omega^*}{2nkT} \exp \left[ -\frac{(E_b - 2J)}{2kT} \right] \] (3.7)

(b) non-adiabatic hopping:

\[ \mu = \delta \frac{ea^2 \sqrt{T/2E_b}}{\hbar (kT)^{3/2}} J^2 \exp \left( -\frac{E_b}{2kT} \right) \] (3.8)

We note that the pre-exponential factor of the mobility depends on \(a^2 T^{-1}\) in the adiabatic and on \(a^2 J^2 T^{-3/2}\) in the non-adiabatic case.

3.2 Electron and Hole Transport Mechanisms in Sulphur

Up to the mid-sixties the electronic transport properties in crystalline sulphur had received comparatively little attention. Since then, however, more than a dozen papers have appeared on the subject; much of the work and its interpretation has been reviewed recently by Spear (1969).

Using the now well-established drift mobility techniques (described in Chapter 4.4) Adams and Spear (1964) observed hole
transits in solution-grown crystals of orthorhombic sulphur, leading to a trap controlled mobility with a trap depth $\varepsilon$ of 0.2 eV and a lattice mobility of

$$\mu_{lh} \approx 10 \text{ cm}^2/\text{Vs}$$

at room temperature. The experimental results as well as their fit to eqn. (3.1) are shown in Fig. 3.1. Later work by Gill et al. (1967) confirmed this result for solution and vapour-grown crystals. However, their activation energy was slightly larger ($\varepsilon = 0.22$ eV).

Thermally stimulated current (TSC) experiments carried out by these authors confirmed the correlation between the density of traps $N_t$ as determined from the temperature dependence of the drift mobility and the area under the corresponding TSC peak.

In contrast to the hole transport, the electron drift mobility

$$\mu_e = 6 \times 10^{-4} \text{ cm}^2/\text{Vs at 21}^\circ \text{C},$$

is considerably smaller than the lower limit set by eqn. (3.3). It was first measured by Adams, Gibbons and Spear (1964) on solution-grown crystals and by Many et al. (1965) on natural crystals. Their results were subsequently confirmed by Gill et al. (1967) and by Watanabe (1968). In addition to the above-mentioned "slow" electrons Thornber and Mead (1965) claimed to have observed at low fields signals corresponding to "fast" electrons. This result,
however, has so far not been reproduced elsewhere, though attempts in that direction have been made by Gill et al. and by the Spear group. Thornber and Mead used evaporated gold dots as the illuminated top electrode T (see Fig. 4.8) and it is now believed that the "fast" signals observed under those conditions are in fact due to holes moving sideways, along the surface, in the strongly inhomogeneous field produced by such an electrode arrangement. The fact that the fast signals could only be observed at low fields follows from a basic property of the electronic circuitry used. Slow electron transits were recorded in the "current mode" (Fig. 4.8b), the superimposed "fast" electron signals, however, were integrated by the network. For a given charge, the current pulse height rises proportional to the field, whereas the integrated pulse height remains constant.

The remarkable similarity of the electron mobilities arrived at by measurement on crystals from different sources, the low value of $\mu_e$ and the absence of any saturation with temperature led Adams, Gibbons and Spear (1964) to interpret the mobility-temperature dependence in terms of the expressions for a non-adiabatic hopping transport. By careful fitting of the experimental results to the Holstein theory, Gibbons and Spear (1966) derived the following limiting values for the polaron binding energy $E_b$ and the energy
of the vibrational modes $\hbar \omega$

$0.44 \text{ eV} < E_b < 0.49 \text{ eV}, \quad \text{mean value } 0.48 \text{ eV}$

$0.009 \text{ eV} < \hbar \omega < 0.033 \text{ eV}, \quad \text{mean value } 0.025 \text{ eV}$.

The fact that the latter interval contains the most prominent fundamental peaks of the vibrational spectrum of $S_6$ supported their conclusions. Taking the above mean values for $E_b$ and $\hbar \omega$, and putting $\delta = 1$, the resonance integral $J$ was found from equ. (3.8), $J \approx 0.05 \text{ eV}$.

Since the binding energy is much larger than $J$ we are dealing with a small polaron. According to Austin and Mott (1969) the condition for non-adiabatic hopping requires that the pre-exponential factor in (3.6) be smaller than the phonon frequency $\omega_p/2\pi$. For electron transport in sulphur, these two quantities are $5.0$ and $5.8 \times 10^{12} \text{ Hz}$ respectively, so that the condition is only marginally satisfied.

Recently Ghosh and Spear (1968) extended electronic transport studies into the liquid phase. On melting the electron mobility drops to $1/25$ of its value in the solid; however, the activation energy and thus the polaron binding energy, remains unchanged in the liquid. This proved that the formation of the small polaron is a molecular property connected with the $S_6$ rings, which remain intact on melting up to a temperature of $160^\circ \text{C}$. The drop in $\mu_e$ was attributed to fluctuations in the exchange integral $J$ in equ. (3.8) caused by the free rotation of the molecules in the liquid. The hole results show that on melting the mobility drops
by a factor $10^{-4}$. The band structure is destroyed in favour of an intermolecular hopping mechanism similar to that for electrons, and the binding energy is almost the same.

The lines of reasoning followed so far were further supported by the molecular orbital calculations on the neutral $S_6$ molecule carried out by Gibbons (1965) and by his suggested band scheme for the crystalline solid. The analysis employed four $3sp^3$ hybrid orbitals per atom. Two hybrids per atom are occupied by lone pairs and the remaining two form the single covalent bonds of the ring molecule. Gibbons calculated the hybridization parameters from the observed bond angles, he obtained:

$$\varphi_{LP} = 0.515s + 0.857p \quad (3.10a)$$

and

$$\varphi_B = 0.478s + 0.875p. \quad (3.10b)$$

The bonding wavefunctions $\varphi_B$ are directed towards the nearest neighbours in the ring, thus forming $\sigma$-type bonds. The lone pair orbitals $\varphi_{LP}$ project outwards from the ring; they interact only weakly to give rise to a system of molecular $\pi$ or $\pi^*$ orbitals; their energies are very close to those of the isolated atom. The overlap between the bonding orbitals gives a $\sigma$ system and the stronger interaction leads to widely separated bonding ($\sigma$) and antibonding ($\sigma^*$) states. Fig. 3.2 shows the energy level diagram for sulphur according to Gibbons (1969). The hole conduction is thought to take
place in the band made up from the overlapping $\pi$ and $\pi^*$ states, the $\sigma^*$ states form the electron band.

Using the muffin-tin approximation, i.e. a constant intermolecular field $V_o$, Gibbons proceeded to estimate the width of the hole bands from the intermolecular exchange integral $J$

$$ J = <\psi, V_o, \psi'> = V_o <\psi, \psi'> = V_o S, \quad (3.11) $$

calculated from the intermolecular overlaps $S$. He arrived at a band width of 0.8 eV and $2 \times 10^{-2}$ eV for electrons and holes respectively.

Recent studies of the UV reflectivity of sulphur by Cook and Spear (1969) together with earlier optical studies by Adams and Spear (1966) lend strong support to the band scheme proposed by Gibbons. An analysis of the imaginary part of the permittivity $\varepsilon$ derived from the reflectivity curve put the band structure model on a more quantitative basis. The most prominent feature in $\varepsilon_2$ is a large, narrow peak at 9.4 eV, which requires for its explanation a transition between two very well-defined levels, namely the $3sp^3\sigma$ and $\sigma^*$ levels.

In conclusion one can say that the electronic conduction in sulphur has many features that can very well be explained by an intermolecular hopping mechanism. It was of interest to investigate the pressure dependence of such a transport mechanism and to compare it to that of a band conductor such as Se. In particular, the
dependence of the hopping mobility on $J^2$ as expressed in equ. (3.8) had already led Paul (1963) to expect an exponential pressure dependence of the mobility, a result fundamentally different from those obtained on high mobility semiconductors discussed in Chapter 2.2.

3.3 Transport Mechanism in Vitreous Selenium

Three Se allotropes have been studied by drift mobility techniques so far: monoclinic Se, consisting of a lattice of puckered Se$_8$ rings, the trigonal form containing Se chains, and vitreous Se, a disordered mixture of the two forms.

The properties of evaporated films of vitreous Se have been investigated extensively by Spear (1957, 1961a), Hartke (1962) and Grunwald and Blakney (1968). The electron mobility,

$$\mu_e = 5.10^3 \text{ cm}^2/\text{Vs at room temperature},$$

was found to be activated, $\varepsilon$ assuming values between 0.33 and 0.25 eV depending on the substrate temperature during evaporation. The underlying transport mechanism is by no means clear, although most authors have suggested an interpretation in terms of a trap controlled conduction in accordance with equ. (3.1). In fact, Grunwald and
Blakney showed that there is a correlation between the substrate temperature and the trap densities. It is possible that the proportion of $\text{Se}_8$ rings in the glass depends on the evaporation temperature.

A similar conclusion is likely to apply to holes, although the magnitude of the lattice mobility is still uncertain. The room temperature hole mobility in vitreous Se is $\mu_h = 0.14 \text{ cm}^2/\text{Vs}$, appreciably lower than that for trigonal Se as measured by Mort (1967), using the acoustoelectronic saturation effect, namely 26 cm$^2$/Vs in the direction of the chains and 7 cm$^2$/Vs perpendicular to it. It is assumed that the hole transport in vitreous Se takes place in a narrow band with a lattice mobility which may not be too different from that of the trigonal form, but is reduced by interaction with defect centers. However, Grunwald and Blakney found that the surprisingly low value of $\mu_{Lh} = 0.36 \text{ cm}^2/\text{Vs}$ was consistent with their results.

The third modification, monoclinic Se, is of particular interest to this work because both orthorhombic S and monoclinic Se are molecular crystals made up from eight-membered puckered rings. Spear (1961b) found the electron mobility to be trap controlled below $250^\circ \text{K}$ with an activation energy of 0.25 eV and a room temperature value of $\mu_{Le} = 2 \text{ cm}^2/\text{Vs}$. 

CHAPTER 4

Experimental Method.

4.1 Specimen Preparation.

4.11 Sulphur Crystals.

Single crystals of orthorhombic sulphur were grown from carbon disulfide solution following the procedure of Adams and Spear with the improvements introduced by Gibbons. Starting material was laboratory grade sulphur crystals and CS$_2$, supplied by BDH. Some solvent was funneled through a 15 cm diameter filter into a Petri dish, 9 cm deep and 19 cm wide, which was covered by a perspex disc bearing a concentric hole of 3 cm diameter. Saturated solution was then poured into the filter till the filtrate level came to about 6 cm. The dish was then carefully lowered into a large dewar container, kept in a room with minimal temperature fluctuations.

As the solvent evaporated through the vent hole in the perspex cover for a period of one or two weeks, one or more small seed crystals could be observed forming at the surface. After some growth these crystals would eventually overcome surface tension, sink to the bottom and develop into crystals of bipyramid habit. Their final size was found to depend on the number of competing seed crystals only. It appeared that supersaturation starting from the middle of the dish and strict temperature control were essential for the growth of larger crystals. The crystals were removed from
the solution, washed immediately in a saturated solution of sulphur in toluene, dried, then "seasoned" at 50°C for several hours. This was done in order to drive out any larger quantities of CS$_2$ enclosed in the crystals during growth, as this would interfere with the grinding procedure.

Using toluene as a coolant, large bulk crystals could be sawed into two or more parts with sizeable natural faces, mostly of (111) orientation. The natural face of the crystal was stuck on a brass jig using phenyl salicylate as the adhesive. The thickness of the resulting platelet could be set by adjusting the threaded collar of the jig. For crystal orientations other than (111) the specimens were mounted on special jigs, the construction of which was such that principal axial sections could be ground by mounting the crystal on a (111) face. After one face had been ground down and polished, the crystal was separated from the special jig and the freshly polished face stuck on the above jig used for (111) faces. It was then ground down to a suitable thickness in the usual way.

Grinding was carried out on an Engis grinding machine, using discs with wet-and-dry emery paper, 240 and 600 mesh SiC, and 14 µm diamond paste. For the final polish the platelets were submerged in toluene to which drops of CS$_2$ were slowly added till the echant proved to be strong enough.

Circular discs of 9 mm diameter were cut from the platelets by carefully scratching the surface along straight lines tangential
with the circumference, using a fine needle; the crystal would eventually cleave along these marks.

The thickness of the specimens was measured with an optical lever gauge at five points; the thickness variation over the width of the platelet was typically below 10%.

4.12 Vitreous Selenium.

Selenium shot of 99.999 99% purity, obtained from Johnson, Matthey and Company, was evaporated in vacuo on to aluminium foil. The mask holding the foil was clamped to a substrate heater, held at 50°C. The aluminium foil was subsequently peeled off yielding self-supporting discs of vitreous Se, 9 mm in diameter and up to 100 µm thick. Circular semitransparent gold electrodes were then evaporated on to both sides of the specimen.

4.2 High Pressure Apparatus.

Two pressure set-ups were used in the course of the experiments and they will now be described.

4.21 First High Pressure Apparatus.

The first high pressure set-up, shown in Fig. 4.1, was a combination of a one-stroke pressure generator with a cross-bore sample cell, kindly lent to us by Dr J. Lees of S.T.L., Harlow.

It was used as a prototype set-up to gain some experience in high pressure techniques and obtain preliminary results on the effects

*Spear et al (1963)*
of pressure on the transport properties of molecular solids.

The principle of the apparatus was as follows:

A 20-ton hydraulic press, \( H \), drove a plunger, \( P_L \), into the bore of the pressure generating cylinder, \( C \). The pressure was then transmitted through the capillary of a double acting sealing piston, \( S_P \), into the specimen chamber of the sample cell, \( S_C \). The specimen, \( S_P E \), and a manganin coil, \( M \), were mounted on the piston, \( P \). Stainless-steel-sheathed thermocouple wires, \( T_H \), of 1.5 mm diameter served as electrical lead-ins. Light could be flashed through the bore of the window piston, \( W_P \), opposite to the specimen. This piston supported a 3 mm sapphire window, \( W \).

With this apparatus first results on the drift mobility in sulphur and selenium were obtained. The measurements proved to be rather difficult because

(a) The hydraulic fluid in the gap between specimen and window tended to absorb too much of the excitation radiation
(b) Small leaks were disastrous as the stroke-volume of the plunger action was too small
(c) Temperature variation affected the pressure measurement as the manganin coil was mounted in the specimen cell.

In order to overcome these difficulties a second, improved, high pressure apparatus was constructed.
4.22 Second High Pressure Apparatus.

Fig. 4.2 gives the layout of system employed. The generation of the final pressure of 7 kbar was achieved by a two-stage process. On the low pressure side a 700 bar (1 bar = 0.98kg/cm$^2$ = 14.5 p.s.i.) hydraulic handpump $H_1$, supplied by Applied Power Industries, Watford, drove a B-2.5 laboratory type intensifier, supplied by Harwood Engineering Company of Walpole, Massachusetts. The intensifier was capable of delivering up to $29 \text{ cm}^3$ hydraulic fluid at 7 kbar into the high pressure stage. The stepping-up of the pressure in the intensifier is achieved by using the force acting on the large-area low pressure piston to drive a second piston of one-tenth that area into the high pressure stage. Standard capillaries and fittings were used on both stages and Aeroshell hydraulic oil was used as the fluid.

For the return of the high pressure piston of the intensifier, and also to drive out a sticking specimen piston, a second handpump, $H_2$, was necessary. During the high pressure cycle it is protected by closing the high pressure valve, $V$, that connects it to the high pressure stage.

The second low pressure port of the intensifier was connected to a graduated expansion cylinder, $E$, which made it possible to monitor the position of the intensifier piston.

The high pressure side of the intensifier was connected to a T-piece leading to the above-mentioned high pressure valve, $V$, and
then to the manganin cell, MC, and the specimen bomb, SB.

4.221 Pressure Measurement.

The manganin gauge cell, MC, Fig. 4.3, designed by Dr. Lees of S.T.L., was constructed from nickel alloy steel EN 30 B, and then heat treated as specified by the makers. The 1000 Ω manganin coil was contacted by means of a 1.5 mm stainless-steel-sheathed thermo-couple wire, obtained from Spembly Technical Products Limited, and soldered into a piston. The increase of the resistance with pressure was measured by the Wheatstone bridge circuit of Fig. 4.4, capable of resolving a change of 50 mΩ, corresponding to 40 bar.

The pressure coefficient of the resistance of manganin varies from batch to batch by maximal ± 6% according to Bridgman (1958). It was felt, however, that such an uncertainty in the absolute value of the pressure was tolerable. The pressure coefficient used for the calibration of the manganin gauge was taken as 2.4 x 10^-6 bar^-1 following Zeto et al. (1969) and Chi-Yuen-Wang (1967). No attempt was made to "season" the coil. With the above value 960 divisions on the Helipot R dial of the pressure gauge corresponded to 8 kbar.

4.222 Specimen Bomb.

The specimen bomb, SB, shown in Fig. 4.5, was made from EN 30 steel and subsequently heat treated. The flange, F, holding the piston, P, with the specimen capsule, SP (see Section 4.3), reaches far into the main body of the bomb in order to keep the zone of
maximum stress well contained in the middle of the bomb. Sealing of the piston against the wall of the bomb is affected by a mitre ring made from Acetal Rod, obtained from Polypenco Limited, and an O-ring for the initial seal at low pressures. The seal was very effective at all temperatures and could be re-used many times. The sapphire window, W, sealed on to the piston in accordance with Bridgman's principle of unsupported area.

4.223 Temperature Control.

The specimen bomb was enclosed by a jacket, J, permitting liquids to be flown around the cell in a sealed-off system. The jacket could be connected to

(a) A temperature controller (Churchill), for temperatures above 20°C

(b) A circulating pump in series with a copper coil immersed in a dewar containing solid CO₂ and acetone, for temperatures from +20°C down to -50°C.

The fluid used was water for (a) and methyl alcohol for (b).

The temperature was measured by a thermocouple mounted on the piston in the specimen bomb cavity; the thermal voltage was read on a Levell D.C. Multimeter and monitored on a recorder.
4.224 Electrical Lead-Ins.

Four 0.5 mm stainless-steel-sheathed thermocouple wires were baked for several hours at 150°C following Cornish et al. (1961). Both ends were filed carefully and with the aid of fine tweezers a few mm of the central Chromel/Alumel wire pair could be exposed. The wires were scraped clear of the insulation, then a thin iron wire was tightly wrapped round the wire pair, serving as a strong and flexible extension of the very fragile thermocouple wires.

The open ends of the lead-in as well as the wrapped contacts were then sealed with Araldite and cured for three hours at 80°C. Excess Araldite was filed off so that the lead-ins could be introduced into the 0.6 mm wide holes of the piston, where they were silver- or soft-soldered. Araldite sealing was found effective, but not very reliable. The thermocouples would eventually be blown out at high pressures.

4.225 Optical Set-Up.

Through a concentric hole of 5 mm width in both piston, P, and flange, F, of Fig. 4.5, one side of the platelet specimen could be illuminated by continuous or pulsed light. In order to increase the light flux in the bore, a hollow light pipe constructed from
aluminium-coated Mylar foil was introduced into the bore hole. The excitation light was focussed on to the light pipe by means of a lens, as indicated in Fig. 4.2. With the exception of the sapphire window quartz optics were used throughout in order to minimize absorption of the shorter UV radiation necessary for efficient carrier generation in sulphur.

Light flashes of 15 μs duration could be obtained from a 15 joule Xe flashtube, operated by a Dawe Transistor Strobotorch 1202D. For shorter flashes a pressurized spark gap was designed, which gave bright UV-rich flashes of 40 ns duration from a well-defined point source and is shown in Fig. 4.6. A 20 kV Brandenburg high voltage supply charged a cylindrical condenser through a 500 MΩ Resistor, R, with a time constant of about a second. The condenser was discharged by the breakdown of the 100 μm spark gap, G, in the nitrogen-filled pressure chamber, producing a well-defined intense spark. The radiation was gathered by a small lens, C, and made parallel by the lens pair, P. The latter also served as a window to the spark chamber which was pressurized to 180 p.s.i. with N₂.

The advantage of running the gap at a pressure is due to the fact that for a given voltage and power rating a much smaller gap can be used, making it easier to focus on the light pipe. The inert gas atmosphere has the added advantage of making the sparking more reproducible and to avoid oxidisation of the contacts.
4.226 Procedure at a High Pressure Run.

The piston, P, shown in Fig. 4.5 with the assembly of window, W, and specimen cell, SP, was fastened to the flange, F, with an Allen screw through the bore hole in the flange.

Using three long threaded studs, screwed into the specimen bomb as guides, the flange was carefully slid towards the bomb. When the specimen cell had just entered the bomb, the handpump, \( H_2 \), shown in Fig. 4.2, was used to bleed air bubbles from the system. The studding was then replaced by Allen screws, six of which were used to secure the flange to the specimen bomb.

The high pressure valve, V, of Fig. 4.2 was then shut and the intensifier operated by the handpump, \( H_1 \), till a pressure of about 0.8 kbar was reached. At this point the fastening screw holding the piston was removed and the bore hole cleared from any trace of hydraulic fluid. This was necessary as the UV radiation used for excitation was readily absorbed by the fluid. The light pipe was introduced, the quartz lens mounted and the spark source aligned.

The pressure dependence at a given temperature was measured at the values 0.8, 1.6, 2.4, 3.2, 4.0, 4.8 kbar going up and 4.4, 3.6, 2.8, etc., going down. Following every step in pressure the system was allowed a few minutes to recover from the slight temperature changes introduced by adiabatic effects.
To release the pressure, the needle valve in the handpump, $H_1$, was slowly opened. At zero pressure the high pressure valve, $V$, was opened and the second handpump was used to return the intensifier piston. The flange screws were slackened, the studdings reintroduced and the piston screwed on to the flange as described before. Slackening the remaining flange screws in rotation, the piston plus flange could be driven out with the handpump, $H_2$.

4.3 Specimen Mounting.

Considerable difficulties were experienced in experiments with the first high pressure set-up described in Section 4.2.1. The reasons were as follows:

For signals of useful magnitude strong excitation by UV light of wavelength shorter than 300 nm was essential. There are only a limited number of hydraulic fluids available which combine a high insulation resistance with a small absorption for UV light. Among them n-Hexane and n-Heptane proved to be the most promising liquids. All fluids with favourable properties, however, tended to dissolve sulphur readily enough to make evaporated contacts come off during
a pressure run. Moreover, the sulphur solution formed absorbed strongly in the critical region, further reducing the signals. High leakage currents around the surface of the specimen often obscured the signals by their fluctuations.

At this stage it was felt that perhaps encapsulation might overcome the effects of the solvent on the specimen. Various encapsulants were tried but without success. Upon application of the pressure the crystals fractured as a result of the different compressibilities of encapsulant and sulphur.

The difficulties were overcome by the development of the specimen capsule shown in Fig. 4.7.

The specimen, SP, is mounted next to the sapphire window, S, for minimum loss of radiation due to absorption in the hydraulic fluid. The capsule is constructed from an easily machinable plastic (Acetal Rod). On the front side the specimen, SP, is contacted by a concentric layer of semiconducting tin oxide (Nesa) deposited on the quartz disc, Q. A small hole filled with indium connects front and back Nesa layers on the quartz disc. The latter makes contact with a Nesa ring, N, on the circumference of the sapphire window, S, which is in turn contacted by indium pressed on to the side face with a worm screw, W. A thin iron wire, I, connects the indium to the field supply thermocouple lead-in.
The back side of the specimen is contacted by an aluminium guard ring configuration, evaporated on to the face of a piston, P, constructed from Acetal Rod. Small indium-filled holes connect front and back side of the piston. The signal contact is led out of the capsule by a thin gold wire, A, screwed into the indium-filled centre hole by a watchmaker screw. The guard ring is connected by means of indium to the spring, SR, which bears against the earthed back plate, B.

The advantages of this somewhat complicated arrangement were the following:

(i) Minimal amounts of hydraulic fluid are in direct contact with the soluble specimen, hence no appreciable dissolving takes place

(ii) As the spring, SR, gently presses the specimen as well as the quartz plate, Q, on to the window, S, the absorption in the remaining films of hydraulic liquid is small.

(iii) As external pressed-on contacts are used evaporated contacts are no longer needed provided the specimen is sufficiently even on the surface

(iv) Leakage currents are not observed as the leakage path is long and the guard ring takes up the remainder of the current.
It should be noted, however, that in spite of the very small amount of liquid surrounding the specimen, hydrostatic conditions are maintained at high pressures as small scratches on the surface of specimen and contact plates are already sufficient to prevent any build-up of pressure gradients.

4.4 Measurement of Electronic Transport Properties.

Electron and hole drift mobilities were measured using the pulse techniques which had been developed in these laboratories in the past few years and had been used in previous work on the selenium allotropes, CdS, on some of the rare gas solids and liquids as well as solid (Adams and Spear, 1964; Gibbons and Spear, 1966) and liquid (Ghosh and Spear, 1968) sulphur.

In the following description of the principle of drift mobility measurements only brief reference is made where the details have already been described in great detail elsewhere, see for instance, the recent survey of Spear (1969).

The platelet specimen is contacted in sandwich-configuration by large-area contacts, T and B of Fig. 4.8.
Free carriers are generated near the top face, T, by a short excitation pulse of strongly absorbed light incident through the semi-transparent top electrode. Carriers of opposite sign are separated in the presence of an applied electric field. Depending on the polarity, either electrons or holes are drawn into the bulk of the crystal towards the bottom electrode, B. In the absence of deep trapping and space-charge effects the steady drift of one sign of carrier gives rise to a constant displacement current which may be readily detected in the external circuit. When the carriers arrive at the bottom electrode, B, the current falls rapidly to zero. The transit time $t_t$ can then be measured and the mobility determined from

$$
\mu = \frac{d^2}{t_t V},
$$

where $V/d$ is the field applied.

The amount of charge generated can be found by taking the initial height of the current pulse, and multiplying it with the transit time.

A limitation on the method for determining drift mobilities arises when the lifetime of drifting carries with respect to deep traps is short compared with the transit time, in this context 'deep' refers to traps from which the thermal release time constant is long compared with the transit time. No discontinuity in the current may be seen at $t = t_t$ if deep trapping is severe, and the mobility can then no longer
be measured by these techniques. In practice, this limitation eventually determines the lowest temperature at which mobilities may be measured since, in general, an increasingly larger number of traps becomes 'deep' as the temperature is lowered.

If the transit time is short, somewhat greater detection sensitivity and noise reduction can be achieved by displaying the charge displacement rather than the current. At high signal levels and long transit times it is possible to increase the accuracy of the transit-time measurement by differentiating the current pulse. The basic circuits used for the measurements are shown in Fig. 4.8 together with the idealized pulse shapes obtained by the three methods.

In all the measurements, particular care was taken to avoid build-up of an internal space charge field due to trapped carriers as this effect tended to reduce signal height as well as to lengthen the transit time. Following every transit the specimen was shorted and discharged by a few light pulses.

4.5 Steady State Current Measurements.

The front electrode of the specimen remained connected to the voltage supply, the back electrode was fed into a Keithley Electrometer
602, working in the ammeter mode. The input resistance was kept more than an order of magnitude smaller than the insulation resistance of the lead-in used for the back contact.

The specimen could be illuminated by a 40 W tungsten lamp focussed into the bore hole of the specimen bomb. Interference filters or Kodak UV bandpass filters 18A and 18B were used to produce excitation in the fundamental absorption region of the samples.
CHAPTER 5

Experimental Results

5.1 Sulphur

5.1.1 Survey of the Transport Properties of the Specimen Used in the Investigation

The sulphur specimen used in the pressure experiments were selected from a total of about 100 crystals, grown from solution and prepared as described in section 4.1.

In an effort to find specimen with high hole mobilities, electron and hole mobilities of more than 100 specimen were determined in a survey, using pressed-on Nesa coated quartz discs contacts. The direction of carrier movement was perpendicular to the (111) face of the crystals.

Fig. 5.1 shows the distribution of the mobilities for both carriers as measured within a few months after their preparation. Standard deviations \( \sigma \) are indicated assuming normal distribution of the mobilities in the logarithmic plot. As is evident from the graphs, electron mobilities scatter much less than hole mobilities.
This lends further support to the conclusion of Gibbons and Spear (1966) (mentioned in Chapter 3) that the electron transport is determined by centers whose density is a fundamental property of the crystal. The hole mobility, however, depends in the majority of the specimen on the density of shallow trapping centers (see Chapter 3), even at room temperature. So far it has not been made possible to control the number of these centers during crystal growth.

No correlation was found between the values for $\mu_h$ and $\mu_e$ of all the specimen investigated.

The position of the maximum of the histogram plotted in Fig. 5.1a indicates an average value of the electron mobility of $4.0 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at $21^\circ\text{C}$, in agreement with the value quoted by Thornber and Mead (1965) and the average value of Street et al. (1967), but somewhat lower than $6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ as found by Gibbons and Spear (1966) and Many et al. (1965).

As the constancy of the electron mobility is one of the arguments put forward in support of a hopping transport in sulphur further investigation of the discrepancy was of interest. Furthermore, Wild and Hogarth (1968) had recently reported a slow decrease with time of the electron mobility of their sulphur crystals. In order to check whether our crystals showed a similar effect the crystals surveyed in Fig. 5.1 were carefully remeasured 480 days later. The
ratio of the mobilities found in the two surveys are plotted in Fig. 5.2b. It can be seen from the histogram that the distribution of ratios strongly favours values below 1. In fact, 73% of the specimen had now a smaller mobility, the decrease amounting to 10% on the average. A similar conclusion cannot be drawn for the case of holes, as can be seen from the histogram for the quantity
\[
\frac{\mu_h(t_2) \times \mu_e(t_1)}{\mu_h(t_1) \times \mu_e(t_2)}
\]
where \((t_2 - t_1) = 480 \text{ d}\). The slight shift to the right by about 10% is probably caused by the decrease in the average electron mobility.

An obvious cause for a slow decrease of the transit time is a deterioration of the crystal surface region. This would result in a non-uniformity of the drift field causing a slowing-up of the transit and thus a reduction in the apparent mobility. In an effort to clarify the influence of the surface and the contacts on the mobility results, three crystals showing electron mobilities of about \(4.5 \times 10^{-4} \text{ cm}^2/\text{Vs}\) were accurately remeasured after ageing and then reduced in thickness by about 50%. Table 5.4 lists the results of the mobility determinations at various stages of the crystal preparation. As can be seen from the table the mobilities remained essentially the same after the reduction in thickness, even when fitted with semitransparent gold electrodes.
Another cause for a low electron mobility might be the interaction of the drifting carriers with the 0.6 eV shallow trap level observed by Gill et al. (1967) on vapour grown sulphur crystals. However, in all the samples that were investigated in temperature runs, no deviation from the 0.17 eV activation energy could be found down to temperatures of -50°C.

5.12 The Pressure Dependence of the Electron Drift Mobility

The pressure dependence of the electron drift mobility in sulphur was measured on 11 specimens. A total of 19 measurements were made at various temperatures. The movement of the carriers was perpendicular to the (111) face of the specimen except for one crystal, S137, where it was in the direction of the c-axis.

The pressure dependence of the electron mobility was reversible, reproducible over a period of days, and largely independent of the individual specimen. The measurements below about 300 bar tended to be less reliable and were not included in the results. A possible explanation is the incomplete wetting of the specimen by the insulating high pressure fluid at low pressures.

At all temperatures and for all specimen the pressure
dependence of the mobility was exponential; Fig. 5.5 gives a typical example.

The results suggest that

\[ \mu(p) = \mu(p = 0) \exp(\alpha p). \]

Experimentally, the exponent \( \alpha \) was determined from the so called doubling pressure \( p_2 \), denoting the pressure at which the mobility \( \mu(p) \) has doubled its value to \( 2\mu(p = 0) \). The exponent \( \alpha \) is obtained from \( p_2 \) by means of

\[ \alpha p_2 = \ln 2. \]

For an accurate determination of the pressure dependence a double logarithmic graph of the transit time \( t_t \) versus the field voltage involving at least four readings was plotted at every value of the pressure giving a value for the drift mobility. The graphs gave no indication of a polarization voltage similar to that observed by Spear (1957) on Se thin films. The value for \( p_2 \) was then found from a plot of the mobility versus pressure. The accuracy of the value so obtained was judged by the maximum deviation \( M \) of the \( N \) points on the graph from the straight line. Table 5.3 gives the results obtained for \( p_2 \) and their weighted mean of \( p_2 = 2.2 \) kbar. The weight \( w_i \) of a measurement was taken as

\[ w_i = 10 \frac{\sqrt{N}}{M} \]

For example, a \( p_2 \) value from a graph with nine points deviating at
most by 10%, would get a weight of 3.

The standard deviation for the mean is 0.05 kbar, corresponding to a (statistical) error of 2.5%, this being already smaller than the systematic error of ± 6% introduced by the manganin coil pressure coefficient. Thus the final result is

\[ p_2 = (2.2 \pm 0.15) \text{ kbar}. \]

The temperature dependence of the electron mobility, shown in Fig. 5.6 for S124 for two pressures, had the same activation energy of 0.17 eV as found by Gibbons and Spear (1964), no variation with pressure could be detected within the experimental uncertainty.

The dependence of the pressure effect on the crystallographic direction of carrier motion was not studied to any extent. The effect is probably very small, or absent, as was found by Gibbons and Spear (1966) at atmospheric pressure. This suggestion is supported by the results on crystal S137 of Table 5.3 giving a doubling pressure of 2.34 kbar in the c-direction. This value deviates from the mean 2.2 kbar by an amount less than the statistical error of a single \( p_2 \) value, namely 0.2 kbar.
5.13 The Pressure Dependence of the Hole Drift Mobility

The pressure dependence of the hole drift mobility was measured perpendicular to the (111) face of the platelet crystals, on eight specimen during a total of 13 runs. In contrast to the results on electrons, the hole pressure dependence varied with temperature, and from specimen to specimen, but was reversible and fully reproducible.

Fig. 5.7 gives a typical example; it shows the pressure dependence for S124 at three temperatures. An exponential dependence is found, as with electrons. The temperature dependence of the effect is plotted in Fig. 5.8a for the same specimen, at high and low pressure, and is shown in Fig. 5.8b for another sample. As can be seen from the graphs the activation energy of 0.2 eV in the low temperature region is not altered by the pressure to any noticeable extent. At higher temperatures, however, the pressure dependence becomes progressively weaker. It is also found that specimens with a comparatively high room temperature hole mobility (at atmospheric pressure) show a weaker pressure effect, i.e. their doubling pressure is higher. This conclusion is borne out by the results presented on Table 5.10, giving the values of $p_2$ and $\mu_{ho}$ for eight specimen. The plot of $p_2$ vs $\mu_{ho}$
as shown in Fig. 5.9, proves that there is a definite correlation between the quantities.

As with electrons, the orientation dependence of the effect is probably small, as seen from Table 5.10 for the results on Si37 (001) platelet\(\ ]\) compared with those of Si12 (111) platelet\(\ J\), which shows the same room temperature hole mobility \(\mu_{ho}\).

5.2 Vitreous Selenium

5.2.1 Drift Mobility of Electrons and Holes and Efficiency of Carrier Generation Under Pressure

The drift mobility of electrons and holes in vitreous Se was measured at temperatures ranging from -50\(^\circ\)C to +50\(^\circ\)C. In this interval no dependence on the pressure could be detected within the experimental uncertainty of \(\pm 3\%\), up to a maximum pressure of 5 kbar. Fig. 5.11 shows the dependence of both mobilities on the reciprocal temperature as measured at 0.8 and 4.2 kbar. The absolute values of the mobilities as well as the activation energies agree with the results of Grunwald and Blakney.
(1968) on specimen prepared by the same method used here (see section 4.1). The mobilities are somewhat higher than those reported by Spear (1957) and by Hartke (1962) which were obtained from samples evaporated on to cooler substrates.

No dependence of electron or hole lifetimes on pressure was observable.

It was of interest to investigate the pressure dependence of the carrier generation efficiency. Current transits for electrons and holes were integrated (see Fig. 4.8), and the pulse height was measured at a constant field as a function of pressure. As can be seen from graph 5.12, no significant pressure variation can be deduced from the results.

5.22 Steady State Current Measurements Under Pressure

The dc current was measured both in the dark and at several illumination levels. As can be seen from Fig. 5.13 the photocurrent vs voltage curve, at atmospheric pressure, was not ohmic, but followed

\[ j \propto E^b \]

with \( b \) between 1.2 and 1.8.
The pressure dependence measured at a field of 8 kV/cm is shown in Fig. 5.14. In all the specimen investigated, the dark-current \( i_d \) and photo-current at two illumination levels \( i_{ph} \) and \( i_{ph}' \) followed the pressure exponentially according to

\[
j = j_0 \exp \left( \frac{-p}{2.6 \text{ kbar}} \right)
\]

The current showed some relaxation: after the application of the field it decayed to a steady state value with a half time of 20 seconds. This time, however, was not affected by the pressure.

5.3 Preliminary Measurements on Trigonal Selenium

It seemed of considerable interest for the interpretation of the above vitreous Se results to compare the pressure dependence of the mobility in the disordered structure of the vitreous form with that of a similar, but ordered, structure, namely trigonal Se.

The drift mobility of holes moving in the c-direction (i.e. along the Se chains) of the platelet crystals was measured by observing the acoustoelectric interaction in this strongly piezoelectric material. The onset of the interaction causes a marked discontinuity in the gradient of the current-voltage curve occurring
at a critical potential $V'$, such that $\mu_n V'/d$ is equal to the velocity of sound along the $c$-direction.

Measurements of this type had been carried out on trigonal Se by Mort (1967), giving a value of 26 cm$^2$/Vs for the room temperature hole mobility in the $c$-direction.

Millisecond field pulses were applied to the etched specimen through nickel contacts, at intervals of about 15 seconds. The resulting pulse current was measured at room temperature, in the dark, observing the voltage drop across a 50 Ω termination. The current showed a decay to a quasi-steady-state value with a decay time of about 0.5 msec. This relaxation effect was particularly pronounced at higher fields, but was also observable at voltages far below the onset of electroacoustic interaction.

Fig. 5.15 shows current-voltage characteristics of specimen at three pressures. As can be seen from the graph, the current increases with pressure and the kink in the curve becomes less pronounced as the pressure is increased. At considerably higher pressures the discontinuity becomes unobservable, furthermore the specimen is likely to suffer from thermal breakdown due to the heavy currents flowing. Fig. 5.16 gives the histogram of 21 determinations of the discontinuity voltage for one specimen at atmospheric pressure. The mean voltage of $V' = (465 \pm 75)$ V for that distribution gives a somewhat high value for the hole mobility, namely
\[ \mu_h = (44 \pm 7) \text{ cm}^2/\text{Vs}, \] using the thickness 1.17 mm and taking the sound velocity of \( v_0(\text{Hg}) = 1.76 \times 10^5 \text{ cm/sec} \) [Mort (1967)].

Fig. 5.17 gives a plot of \( V^l \) versus the pressure for the above specimen. The results show that the pressure changes lie hardly outside the limits of accuracy of the experiment and are unlikely to exceed 20\% at the highest pressure used.
CHAPTER 6

Distance Dependence of an Intermolecular Overlap Integral

In this chapter an attempt will be made to calculate the dependence of one of the intermolecular overlaps in the unit cell of orthorhombic sulphur on small variations of the lattice spacing. The purpose of this computation was to find out whether the compression of the lattice brought about in the experiment changes the overlap sufficiently to account for the order of magnitude of the observed pressure effect on the drift mobility. It was thus considered legitimate to pick one of the eleven van der Waals contacts as being representative of the set and to calculate the corresponding overlap, using simple Slater-type atomic wavefunctions.

The method relied heavily on the previous work of Gibbons (1965, 1969), reviewed in Chapter 3.2.

Adopting Mulliken's (1949) notation, we write for an overlap between two atomic wavefunctions, say 2s and 2p, centered on atoms A and B, at distance R,

\( (2s_A, 2p_{\pi B}, R) \) or \( (2s_A, 2p_{\sigma B}, R) \)

The symbols \( \pi \) and \( \sigma \) refer to the direction of the symmetry axis of the \( p_B \) orbital; "\( \sigma \)" means that the positive lobe of the \( p_B \) wave-
function is pointing towards atom A, "n" denotes a direction perpendicular to the axis A-B. Because of the vectorial properties of the wavefunctions, a p-orbital pointing in some arbitrary direction can be resolved into components along (σ) and perpendicular (π) to the axis A-B. Thus it is always possible to break down overlaps (s,p), (p,p) ... into components involving only the standard types (s,pc), (pc,po), (pc,pc), etc. It is worth noting that (s,pc),(pc,pc) are zero for symmetry reasons, and that (s,-p) = (-s,p) = -(s,p).

The overlap chosen was that corresponding to the two 3.63 Å van der Waals contacts of every molecule in the c-direction. Fig. 6.1a gives the projection of the two puckered S₈ rings into the bc-plane; the deviation from the regular octagon shape is caused by the perspective. The meridional planes of the two rings form an angle of 78° with each other. The atom pair A, B, however, makes only an angle of 2γ = 30° with its counterpart D, C, on the adjacent ring and so we have an almost planar problem as is borne out by Fig. 6.1b.

The "bonding" wavefunction of a hybrid atomic orbital on atom A can be written, according to equ.(3.10b) as

\[ \phi_A = s_A + \epsilon p_A \]  

(6.1)

where \( s_A \) and \( p_A \) are the appropriate atomic orbital functions centered on atom A, with the positive lobe of the p-orbital pointing
towards B, and $\varepsilon = 1.83$. The functions so obtained are neither orthogonalized nor normalized. As Mulliken et al. (1949) point out, the process of orthogonalization has little effect on the computed values of the overlap integrals and will be neglected here. Normalization is not required, as only changes in the overlaps are being investigated.

Following earlier work of Gibbons (1963) (see Chapter 3.2), we calculate the intermolecular overlap of the $\sigma^\pi$ antibonding states on the atom pairs A, B and C, D. In the LCAO approximation the wavefunction $\psi$ corresponding to the molecular $\sigma^\pi$ state is made up from two $3\text{sp}^3$ hybrid orbitals centered on atoms A, B or C, D in the antibonding way.

$$\psi = \phi_A - \phi_B$$

and

$$\psi' = \phi_C - \phi_D$$

The overlap integral $S$ is then

$$S = \int \psi \psi' d\tau$$

(Note that here $\psi^\pi = \psi$)

Using (6.2) the integrand can be split up into products of atomic hybrid orbitals

$$\psi \psi' = (\phi_A - \phi_B)(\phi_C - \phi_D)$$

$$\psi \psi' = \phi_A \phi_C + \phi_B \phi_D - \phi_B \phi_C - \phi_A \phi_D$$
and further, using (6.1)
\[
\begin{align*}
\varphi_A \varphi_C &= s_A s_C + \epsilon^2 p_A p_C + \epsilon(s_A p_C + s_C p_A) \\
\varphi_B \varphi_D &= s_B s_D + \epsilon^2 p_B p_D + \epsilon(s_B p_D + s_D p_B) \\
\varphi_B \varphi_C &= s_B s_C + \epsilon^2 p_B p_C + \epsilon(s_B p_C + s_B p_C) \\
\varphi_A \varphi_D &= s_A s_D + \epsilon^2 p_A p_D + \epsilon(s_A p_D + s_A p_D)
\end{align*}
\] (6.4)

As can be seen from Fig. 6.1b one has for symmetry reasons
\[
\begin{align*}
s_A s_C &= s_C s_A = s_B s_D = s_D s_B \\
p_A p_C &= p_B p_D, \quad p_B p_C = p_A p_D \\
s_A s_C &= s_B s_D, \quad s_B s_C = s_A s_D
\end{align*}
\] (6.5)

This simplifies the expression for \( S \). Using Mulliken's notation we have
\[
S = 2(s_A, s_C, \tilde{A} \tilde{C}) + 2\epsilon^2(p_A, p_C, \tilde{A} \tilde{C}) + 4\epsilon(s_A, p_C, \tilde{A} \tilde{C}) +
-2(s_A, s_D, \tilde{A} \tilde{D}) - 2\epsilon^2(p_A, p_D, \tilde{A} \tilde{D}) + 4\epsilon(s_A, p_D, \tilde{A} \tilde{D})
\] (6.6)

Resolution of the overlaps containing p-functions into \( \pi \) and \( \sigma \) components according to the angular relation, shown in Fig. 6.1b, now gives \( S \) as the sum of eight standard overlaps \( S_i \), listed in Table 6.2 with their respective geometry factors \( g_i \) and the summation factors \( f_i \) of equ. (6.6). Starting from Slater-type atomic wavefunctions Mulliken et al. (1949) gave a table of simple formulae for the standard overlaps, involving the product of a polynomial \( P_i \) and an exponential factor, expressed in terms of the dimensionless

The parameter

\[ P_i = \mu \frac{R_i}{a_o} \]  

(6.7)

where \( R_i \) is the distance between the two atoms, \( \mu = 1.817 \) for sulphur and \( a_o = 0.529 \, \text{Å} \).

The \( S_i \) then take the form

\[ S_i = P_i \sigma_i f_i \exp (-p_i) \]  

(6.8)

The \( S_i \) were computed working to five significant figures, for six values of the distance \( AC \), starting from \( AC = 3.67 \, \text{Å} \), then going down in steps of 1%: 3.67/1.01, etc., as listed at the top of Table 6.3, together with the corresponding p-values defined in equ. (6.7). The diagonal distances \( AB \) were calculated assuming a constant bond distance \( AB = CD \). The table also gives the values for the \( S_i \) which were multiplied by \( \exp(12.6) \) in order to make the numbers more readily comparable.

Although the absolute magnitude of the overlap \( S \) (\( \approx 10^{-2} \)) is certainly very small, the relative change in \( S \) as expressed by the quantity \( y = S/S_0 \) (0%) shows a strong effect: for 5% reduction in distance the overlap increases by 53%.

The dependence of \( y \) on the distance, normalized to its value at atmospheric pressure,

\[ x = \frac{AC}{3.67} \]

was tested for power and exponential law. If a power law
\[ y \propto X^a \]

holds then \( \Delta \ln y = a \Delta \ln X \) and the ratio \( a \) of the logarithms should be constant. For an exponential dependence,

\[ y \propto 10^{bX}, \]

the quantity

\[ b = \frac{\Delta \ln y}{\Delta X} \]

should be constant.

As shown in Table 6.4 the "constants" \( a \) and \( b \) decrease from -10 to -8.7 and from -3.9 to -4.4, respectively, upon reduction of the distance \( X \) by 5%. Calculation of the deviations about the mean values comes out marginally in favour of an exponential dependence.

In conclusion one can say that the dependence of the calculated overlap on small variations of the distance is very strong. It can be approximated by

\[ S \propto 10^{-4X} = \exp(-9.25X) \]

A further result is that the overlap is the more sensitive to compression the further the centers are spaced apart.
CHAPTER 7

Discussion of the Pressure Dependence

In the first two sections of this chapter the results on the transport properties of sulphur under hydrostatic pressure will be interpreted in terms of the theories reviewed in Chapter 3 and the orbital calculation of the preceding section.

The second half of this chapter will deal with the results on selenium; in section 7.3 the transport properties will be discussed and in the last section an explanation of the steady state current measurements will be attempted.

7.1 Electron drift mobility in sulphur

In this section we will first try to estimate the dependence of the intermolecular distance on the pressure. We then apply the results of the overlap calculation of the preceding chapter and arrive at an estimate for the pressure dependence of the mobility.
As shown by Table 2.1 the compressibility of sulphur is strongly anisotropic, the dilatation in the c-direction is only half of that in the a-b plane. This can be understood from the structure of the unit cell shown in Fig. 7.1: looking at the model along the $[\bar{1}10]$ and the $[\bar{1}10]$ directions one finds that the structure is composed of layers of sulphur rings that are lined up along the above directions, comparable to the stacking order of plates in a dishwasher with four racks on top of each other. The lining-up directions of adjacent racks make an angle of $78^\circ$ and this is the same angle formed by the meriodional planes of the two molecules considered in Chapter 6. In Fig. 7.1 the centers of the sulphur rings forming a line have been connected by tape so as to help the reader.

Since the bonds linking the atoms on one ring are much stronger than the van der Waals forces between adjacent rings, it is reasonable to assume that the rings are comparatively incompressible. We can then proceed to calculate the fraction of the linear dimension of the crystal (in a particular direction) that is taken up by incompressible matter and thus arrive at an estimate for the decrease in the intermolecular distance if the whole lattice is compressed by a certain amount. Taking the diameter and the thickness of a sulphur ring as measured between the nuclei as $4.5 \, \AA$ and $1.6 \, \AA$ respectively, and the unit cell dimensions as $(a + b)/2 = 16.6 \, \AA$ and $c = 24.5 \, \AA$, we
can compute the filled fraction of space in the $\{1\overline{1}0\}$ direction as follows: in the bottom quarter of the unit cell (or the ground-floor rack of the dishwasher) we have $4 \times 1.6 \AA$ rigid matter and $2 \times 4.5 \AA$ in the layer above. This result is repeated for the remaining two quarters of the unit cell, so that on the average a fraction $(6.4 + 9.0)/16.6 = 0.465$ is incompressible in the $\{1\overline{1}0\}$ direction and we take it as representative for the $a$-$b$ plane. In the $c$-direction we have $(4 \times 4.5)/24.5 = 0.735$.

Assuming an isotropic compressibility for the remaining fraction of space we would immediately expect a much smaller over-all compressibility in the $c$-direction because there is less compressible matter. In fact, one can predict that the ratio of the compressibilities in the $a$-$b$ and the $c$-direction should be equal to the ratio of the remaining spaces

$$\frac{\kappa_a + \kappa_b}{2\kappa_c} = \frac{(1-0.465)}{(1-0.735)} = 2.05 \quad (7.1)$$

This value agrees to within 15% with the experimentally determined anisotropy listed in Table 2.1. This confirmation allows us to describe the effect of a hydrostatically applied pressure by an isotropic reduction of the average intermolecular spacing $a$ as follows:
The results are plotted in Fig. 7.2.

We have now all the data necessary for a calculation of the distance dependence of a non-adiabatic hopping mobility as reviewed in Chapter 3.1. As shown by the temperature dependence of the electron drift mobility under pressure the activation energy and hence the polaron binding energy $E_b$ remain unchanged. This would make the term $a^2J^2$ in (3.8) solely responsible for the observed pressure effect. If we assume that the electron can transfer along the ring in search of an easy jump to the next molecule we will then have

$$\mu \propto \sum_{i} (a_i J_i(a_i))^2 \quad (7.3)$$

where the intermolecular distances start from $3.33 \text{ Å}$, the shortest van der Waals contact. As shown by the example calculated in the preceding chapter, the $J_i$ will be rapidly decreasing functions of "a" and this will limit the sum to a few terms corresponding to short jumps along strong overlaps. It would thus appear that the particular overlap investigated in Chapter 6 with $a = 3.67 \text{ Å}$ can very well be taken as a typical sample.

Let us now compare the experimental mobility changes with those expected from the calculation. For a pressure of 2.2 kbar
(doubling pressure) we get from Table 7.2 a dilation
\( \Delta a/a = -1.9\% \) and taking the overlap to depend on the distance as

\[ S \propto a^{-10}, \quad \text{(see page 62)}, \]

we obtain \( \Delta J/J = 20\% \) and finally

\[ \frac{\Delta \mu}{\mu} = 36\%; \]

experimentally one finds that the mobility has increased by 100\% at that pressure. Considering the approximate nature of the models applied to the calculation of both the hopping probability and the \( J \)-dependence, an order of magnitude agreement is already reassuring. Weaknesses in the theory may be seen in the fact that equ. (3.8) was derived for a one-dimensional model crystal, while sulphur is a complicated anisotropic material. Secondly, the muffin-tin approximation used in equ. (3.11), p.25, for the conversion of the overlaps \( S \) into resonance integrals \( J \) may be too crude.
7.2 Hole Drift Mobility in Sulphur

In this section we will first show that the hole mobility temperature dependence at all pressures can be phenomenologically described by a trap controlled mobility, as already mentioned in Chapter 3. In this model, the pressure dependence can only be accounted for, if it is assumed that the density of the centers depends on the pressure. The implications of this conclusion will be discussed.

Equ. (3.1) for a trap controlled drift mobility can be rearranged to read

\[ \frac{\mu_L}{\mu_D} = 1 + \frac{N_L}{N_h} \exp \left( \frac{\epsilon}{kT} \right) \]

with \( \mu_L = bT^a \), and the effective density of states \( N_h \). From an analysis of the hole mobility temperature dependence for a particularly trap-free crystal measured by Gill et al. (1967) one finds \( a = 2.3 \). Neglecting the temperature dependence of \( N_h \), a plot of

\[ \frac{\tau^{-2.3}}{\mu_D} \text{ vs } \exp \left( -0.2 \text{ eV}/kT \right) \]

should give a straight line with a slope of \( N_L/bN_h \) and an intercept of \( 1/b \). Fig. 7.3 shows such a plot containing data taken from
Adams and Spear (1964), Gill et al. (1967) and the figures 5, 8a and 8b. The symbols used on the graph are identical with those in the original figures. The intercept for the two curves taken from Gill et al. is about twice that of the other work; for the sake of comparison, however, it was decided to shift the corresponding data points downwards by $1.35 \times 10^7$ units in order to make the intercepts coincide.

As can be seen from the graph, the temperature dependence of the hole mobilities with and without pressure fits equ. (3.1) quite well. From the graph one can find the trap density $N_t$ and this quantity is plotted in Fig. 7.4. Again the same symbols are used.

The influence of pressure on the drift mobility can only be accounted for in this model if we assume the trap density $N_t$ to be decreasing with pressure. From the few data points available the nature of the functional dependence cannot be decided with any certainty. Nevertheless, Fig. 7.4 shows that an exponentially decreasing $N_t$ fits the results reasonably well. However, more data on a wider range of trap densities are needed to firmly establish this result. In a tentative explanation we can try to account for the effect by assuming the trapping centers to arise from thermally generated point defect such as Frenkel or Schottky
defects. Both processes are thermally activated

\[ N_t \propto \exp \left( -\Delta g / \gamma kT \right) \]

where \( \Delta g \) is the Gibbs free energy per center and the constant \( \gamma \) (1 or 2) depends on the particular type of defect. In sulphur we have a weakly bound molecular crystal, which is at room temperature not very far from the melting point (119°C). Its low melting enthalpy and the noticeable vapour pressure suggest that a certain amount of thermally generated disorder is likely to occur. This disorder will tend to decrease the density of the crystal and pressure will tend to counteract the increase in the volume. From the principle of least action we can therefore expect the pressure to reduce the number of traps \( N_t \). In fact, Nachtrieb and Lawson (1955) actually determined the pressure derivative of the Gibbs free energy

\[ \left( \partial \Delta g / \partial p \right)_T = \Delta v. \]

Here \( \Delta v \) is the so-called activation volume associated with the production of a point defect. It usually amounts to a fraction of 0.5 to 1.0 of the molecular volume. Taking the value \( \Delta v = 10^{-27} \text{ m}^3 \) for sulphur, one obtains for a pressure of 5 kbar a change in the activation energy of 3.5 eV and this would be more than enough to account for the dependence depicted in Fig. 7.4. Unfortunately,
however, this model also should lead to a change in the slope of the temperature dependence of the mobility, and this has not been observed in the experiment.

Recently Ghosh and Spear (1968) measured the drift mobility of electrons and holes in liquid sulphur. Their results present strong evidence for a thermally activated hopping motion of holes in that phase and this is supported by the work of Gibbons (1969) on the electronic structure of sulphur. In the liquid, the hole is localized long enough on a sulphur ring for a rearrangement of the orbitals to take place with the result that the overlap is reduced and then becomes comparable to that for electrons. As a consequence the holes will propagate in the liquid by a hopping motion in a way very similar to the electrons. It seems likely that such an orbital rearrangement may also occur in the solid if lattice defects locally reduce the normal overlap, thus forming a trapping center. The escape probability $P$ from that center is then given by equ. (3.6) as for non-adiabatic hopping. Because of the $J^2$ pre-exponential factor a strong pressure dependence, much the same as for the electron mobility, can be expected. As the temperature is raised, the influence of traps on the mobility is reduced and we get a smaller pressure dependence. Both conclusions are in agreement with the experiment, but appear to
contradict the basic assumptions on which the model for a trap
controlled mobility is based. For the derivation of equ. (3.1)
one assumes the density of the holes in the band, \( h \), and in the
trapping centers, \( H \), to be in thermal equilibrium with one another
according to the Fermi-distribution

\[
H = \frac{N_t}{1 + \exp \left( \frac{|E_\hbar - \varepsilon|}{kT} \right)}; \quad h = N_h \exp \left( -\frac{\varepsilon}{kT} \right) \tag{7.4}
\]

Here \(|E_\hbar - \varepsilon|\) is the energy difference between the Fermi level
and the trapping centers and \( N_h \) is the effective density of states
of the hole band. It is of interest to note that it is of no
importance whether the Fermi level is a quasi Fermi level or not.

The density of holes in the band will be given by the equili-
brum between the rates of hole trapping, \( \beta h (N_t - H) \) and release, \( HP \),

\[
\frac{dh}{dt} = -\beta h (N_t - H) + HP \tag{7.5}
\]

where \( P \) denotes an escape probability of the form given in equ. (3.6).

In the experiment we observe a constant hole current during
the time of the transit indicating a constant hole density \( h \). By
putting \( \frac{dh}{dt} = 0 \) we get

\[
H = \frac{N_t}{1 + \frac{P}{\beta h}} \tag{7.6}
\]

and by comparison with (7.4)

\[
\frac{P}{\beta} = N_h \exp (-\varepsilon/kT). \tag{7.7}
\]
From this equation we see that the assumption of \( P \) to be dependent on the overlap can only be reconciled with thermal equilibrium conditions of this model if the capture probability \( \beta \) and hence the lifetime with respect to shallow traps also depends on the overlap in the same way. This is why the effective mobility \( \mu_D \)

\[
\mu_D = \frac{h}{h + H} \quad \mu_L = \mu_L(1 + H/h)^{-1}
\]

is insensitive to the form and magnitude of the probabilities \( P \) and \( \beta \) as long as the thermal equilibrium is known to be established.

It would thus appear that the assumption of a pressure dependent escape probability cannot explain the experiments when assuming a single trap model in thermal equilibrium conditions.
Both explanations put forward so far are of a rather tentative nature and they are only partly verified by the experiment. It would therefore be of interest to get more experimental evidence, particularly on crystals with smaller $N_t$. At the same time further work is needed towards the derivation of an alternative expression describing both the temperature and the pressure dependence of the hole mobility in sulphur.

7.3 Transport Properties of Vitreous Selenium

The absence of any measurable pressure effect on the transport properties of vitreous and trigonal Se suggest that the conduction
mechanism is fundamentally different from that in a molecular solid such as orthorhombic sulphur and more akin to conventional band conduction. In fact, both trigonal and vitreous Se are composed of the typical spiral Se-chains. In vitreous Se they are of random length and orientation, but x-ray evidence shows that the short range order is very similar to that of the trigonal form. As already discussed in Chapter 3.3 the lattice mobilities for vitreous and trigonal Se are probably of the same order of magnitude ($\sim 10 \text{cm}^2/\text{Vs}$). In this picture the charge carriers would preferentially propagate along the chains and occasionally get trapped on a defect center where they stay until they are thermally activated by a phonon. This visualization of the carrier motion is supported by the strong anisotropy found for mobility and conductivity in trigonal Se.

The lattice mobility of both vitreous and trigonal Se will depend on the pressure through changes in lattice spacing $a$, the bandwidth $2J$ and the phonon spectrum, as characterized by the Debye temperature $\theta$, in the following way

$$\mu_L \propto a^2 J^b \theta^c.$$  

The exponents $b (1 \leq b \leq 2)$ and $c (-2 \leq c \leq 0)$ are constants of the particular theoretical model chosen. For Se at 5 kbar we have from Table 2.1 a change in $a^2$ of $-4\%$, and from Table 2.3 we find that the
Debye temperature is likely to increase by +3%, the total change introduced by both quantities being less than -10%. In contrast to the treatment of S in the preceding chapter, the bandwidth 2J will in this case depend on the intramolecular overlap integral rather than the intermolecular integral. The bond length along the chains is probably little affected by pressure (as was also assumed in Chapter 6) and hence a much smaller resultant increase in J can be expected. We arrive thus at the conclusion that the lattice mobility in vitreous and trigonal Se should be very little pressure dependent, probably decreasing with pressure by a few per cent for the first 5 kbar. This result will also hold for the trap controlled range; if the localizing centers arise out of the disordered structure, we would expect no strong pressure dependence of their number and activation energy.

As was mentioned earlier on, the structures of monoclinic Se and of orthorhombic sulphur are very similar and a comparison of their transport mechanism under pressure would be particularly interesting. Unfortunately, however, no such measurements have been carried out so far; but it appears possible to estimate the dependence of the resonance integral on the pressure from the results of the preceding chapter. The average atomic distances as derived from the densities of S and Se are nearly the same and so
are the compressibilities. The expressions for the overlap integrals $S$ of equ. (6.8) for the two materials read as follows

$S_{\text{Se}} \propto P_{\text{Se}}(p_{\text{Se}}) \exp(-p_{\text{Se}})$ for Se

and

$S_{\text{S}} \propto P_{\text{S}}(p_{\text{S}}) \exp(-p_{\text{S}})$ for S.

Here the $p$ are the distance parameters as defined in equ. (6.7), and the $P_x$ are polynomials of order 6 for $\sigma$-type overlaps and 5 for $\pi$-type overlaps.

The order of the selenium polynomials $P_{\text{Se}}$ is one higher than those for $S$ because we are now dealing with $4s$ and $4p$ orbitals. As was shown in Chapter 6 (p.62), the distance dependence of the overlaps could be expressed by

$S \propto a^{-\gamma}$

where $a$ is the intermolecular spacing and the exponent $\gamma$ is decreasing from 10 to 8.7 for 5% reduction in distance. In Se the Slater $\mu$ value of equ. (6.7) is 1.55 for $s$ and $p$ orbitals and hence the resultant $p$ value will be 17% smaller than that of sulphur for the same intermolecular spacing.

It follows that we have to expect the overlaps in Se to be roughly by a factor $(1.17)^{10} \approx 5$ larger than for S.

For the distance dependence we extrapolate the dependence of $\gamma$,
as quoted above, for 5% to 17% reduction. We obtain
\[ Y = 10 \times 0.87^{17/5} = 6.2. \]
Allowing for the higher order of the Se 4s, p polynomials we find \( Y_{Se} = 5.2. \) This would give an increase in the overlap of 26% for 5% compression; the corresponding value for sulphur was 50%. On the basis of this rough estimate one would expect the electron mobility in monoclinic selenium to be considerably higher than in sulphur, but showing only half the pressure increase. In fact, the electron mobility at atmospheric pressure is of the order of \( 2 \text{cm}^2/\text{Vs} \) as mentioned already in Chapter 3.3.

7.4 Steady State Current Measurements on Vitreous Selenium

Finally let us consider the implication of the drift mobility results in vitreous selenium on the pressure dependence of the steady state currents. As the experiment showed, neither the mobilities nor the photogenerative efficiency depend measurably on the pressure, but at the same time the d.c. current exhibits a strong effect. A similar result was found to apply for trigonal Se by Krishunas and Daukantite (1966). From this we conclude that the carrier density in both cases must have been increased by the pressure. As borne
out by Fig. 5.14, the pressure dependence in vitreous Se is the same both in the dark and under strongly absorbed illumination, which will only affect a narrow region below the top contact. This suggests that we are not dealing with a bulk-controlled process, but rather with a contact phenomenon.

It is suggested that the application of pressure modifies surface conditions in such a way as to enhance the injecting properties of the contact. A possible reason for this could be a decrease in the activation energy for the charge carrier injection under compression. This model has been applied successfully to the pressure dependence of the conductivity in organic molecular solids by Rice and Jortner (1965), a more detailed description of this explanation is found in section 2.4.

In summary we can say that the study of the drift mobility in low mobility solids over a modest range of pressures provides us with information on the overlap between states participating in the conduction process. As the two center resonance integral $J$ is of central importance in the theoretical treatment the experimental approach used here should be of value in identifying the type of transport mechanism involved and should extend the experimental background for a meaningful test of the existing theories.
7.5. Suggestions for Future Work

In view of the experimental results presented in this investigation, it would appear of interest to apply high pressure techniques to a wider range of low mobility solids, both crystalline and amorphous. In particular, monoclinic Se and the molecular organic crystals such as Pyrene, Naphthalene and Copper Phthalocyanine are likely candidates for a strong pressure dependence of the conduction process.

Results of such work and their comparison to the steady state conductivity under pressure would further clarify the influence pressure has on the injection properties of the contacts and should thus provide a more meaningful basis for the interpretation of d.c. conductivity under pressure.

As shown in section 7.2 the pressure effect on the hole conduction in the transition region from the lattice mobility to a trap controlled mobility might help to decide on the nature of the localizing centers involved and a more detailed investigation is necessary before final conclusions can be drawn.
References

Emin and Halsz (1969), to be published.
Gibbons, D. J. (1969), to be published.
Landwehr, G. (1956), Z. Natf. 11a, 257.
(1959), ibid. 14a, 520.
Rosen, J. (1951) RCA Rev 12, 362.
Smith, A. C. (1958), Thesis, published in Report HP2, Gordon McKay Laboratory, Division of Engineering and Applied Physics, Harvard University, USA.
(S1969b), Applied Optics Suppl. (USA) 2, 8.


Compressibility of orthorhombic sulphur

Linear dilatation: Pressure, $10^3$ kg/cm$^2$

<table>
<thead>
<tr>
<th>Direction</th>
<th>4</th>
<th>8</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100] $30^\circ$C</td>
<td>0.0180</td>
<td>0.0304</td>
<td>0.0412</td>
</tr>
<tr>
<td>[100] $75^\circ$C</td>
<td>0.0190</td>
<td>0.0323</td>
<td>0.0427</td>
</tr>
<tr>
<td>[010] $30^\circ$C</td>
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<td>0.0277</td>
<td>0.0370</td>
</tr>
<tr>
<td>[010] $75^\circ$C</td>
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<td>0.0334</td>
<td>0.0433</td>
</tr>
<tr>
<td>[001] $30^\circ$C</td>
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<td>[001] $75^\circ$C</td>
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Volume dilatation:

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<td></td>
<td>0.0466</td>
<td>0.0784</td>
</tr>
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</table>

Compressibility of vitreous Se
C.E.Weir, J.Res.Nat.B.Stand. 52 (1954) 247

Pressure, $10^3$ atm

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
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<tr>
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<td>0.049</td>
<td>0.066</td>
<td>0.080</td>
<td>0.092</td>
</tr>
</tbody>
</table>

Table 2.1 Compressibilities of orthorhombic sulphur and vitreous selenium
Fig. 2.2 Melting curves of hexagonal Se (a) and orthorhombic S under pressure.

(a) B.C. Deaton and F.A. Blum, Phys. Rev. 137 (1965) A 1131
(b) K.B. Ward, B.C. Deaton, Phys. Rev. 153 (1967) 947
<table>
<thead>
<tr>
<th>Quantity</th>
<th>0 kbar</th>
<th>10 kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $\rho$, $g/cm^3$</td>
<td>rh.S</td>
<td>2.085</td>
</tr>
<tr>
<td></td>
<td>vi.Se</td>
<td>4.82</td>
</tr>
<tr>
<td>Density $\rho$, $g/cm^3$ (vi. Se)</td>
<td></td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>5.26</td>
<td></td>
</tr>
<tr>
<td>Melting temp., °C</td>
<td>mo.S</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>tr.Se</td>
<td>217</td>
</tr>
<tr>
<td>Melting temp., °C (rh)</td>
<td></td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td></td>
</tr>
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<td>Absorption edge, eV</td>
<td>rh.S</td>
<td>2.90</td>
</tr>
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<td></td>
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<td></td>
</tr>
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<td>Absorption edge, eV (Se)</td>
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</tr>
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<td></td>
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<td></td>
</tr>
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<td>Velocity of sound, m/s</td>
<td>γSe</td>
<td>3350</td>
</tr>
<tr>
<td></td>
<td>3550</td>
<td></td>
</tr>
<tr>
<td>Velocity of sound, m/s (γ = 0.65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Permittivity, $\varepsilon$</td>
<td>rh.S</td>
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</tr>
<tr>
<td></td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Permittivity, $\varepsilon$ (from CM rel.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>vi.Se</td>
<td>6.24</td>
</tr>
<tr>
<td></td>
<td>7.56</td>
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</tr>
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<td>Debye temperature, °K</td>
<td>rh.S</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>209</td>
<td></td>
</tr>
<tr>
<td>Debye temperature, °K (γ = 1.4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Compressibility, $10^6$ bar$^{-1}$</td>
<td>rh.S</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Compressibility, $10^6$ bar$^{-1}$ (vi. Se)</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3  Pressure dependence of some properties of orthorhombic sulphur and vitreous selenium
Fig. 2.4 COMPARISON OF RENORMALIZED DRIFT MOBILITY AND CONDUCTIVITY MOBILITY AS FUNCTIONS OF PRESSURE FOR ELECTRONS

Taken from A.C.Smith, Techn. Rep. No. HP-2, Gordon McKay Lab., Harvard University, Mass., USA (1958)
Figure 2.5 Pressure dependence of electron and hole drift mobility in anthracene. The electron mobility in the direction perpendicular to the ab-plane is constant and was omitted from the graph. Taken from: R.G. Kepler, Organic Crystals Conference, J.J. Brophy and J.W. Buttery, ed., MacMillan (1961)
Table 2.6 Electrical Resistance of Organic Compounds under High Pressure.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pressure</th>
<th>Qcm</th>
<th>Activation Energy, eV</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>kbar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>0</td>
<td>$1.3\times10^{14}$</td>
<td>0.82</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>$10^7$</td>
<td>--</td>
<td>b</td>
</tr>
<tr>
<td>Violanthrone</td>
<td>0</td>
<td>$2.3\times10^{10}$</td>
<td>0.39</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>8.4</td>
<td>$1.2\times10^7$</td>
<td>0.34</td>
<td>a</td>
</tr>
<tr>
<td>Violanthrone A</td>
<td>0</td>
<td>$2.3\times10^{10}$</td>
<td>0.39</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>$3.7\times10^3$</td>
<td>0.10</td>
<td>c</td>
</tr>
<tr>
<td>Quaterrylene</td>
<td>0</td>
<td>$10^8$</td>
<td>0.30</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>$7\times10^3$</td>
<td>0.08</td>
<td>c</td>
</tr>
<tr>
<td>Coronene</td>
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<td>0.85</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>$&gt;10^6$</td>
<td>--</td>
<td>c</td>
</tr>
<tr>
<td>DPPH</td>
<td>0</td>
<td>$10^{13}$</td>
<td>0.85</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>127</td>
<td>$1.1\times10^4$</td>
<td>0.11</td>
<td>c</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0</td>
<td>$10^{14}$</td>
<td>0.75</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>$2.3\times10^3$</td>
<td>0.07</td>
<td>c</td>
</tr>
</tbody>
</table>
| Tetrathiotetra-
| 1        | $4\times10^4$ | 0.2-0.25 | c |
| 161                | $1.6\times10^2$ | 0.17 | c       |

References

Figure 3.1 Hole drift mobility in orthorhombic sulphur versus reciprocal temperature. Taken from A.R. Adams and W.E. Spear, J. Phys. Chem. Sol. 25, (1964) 1113.
Figure 3.2 Energy level diagram for the sulphur $S_8$ ring and the solid according to Gibbons (1969).
Figure 4.1 First high pressure apparatus.
H hydraulic press, PL plunger, C cylinder, SP sealing piston, SC sample cell, TH thermocouple, P piston, M manganin cell, SPE specimen, W window, WP window piston, F flange.
Figure 4.2  Block diagram of the second high pressure apparatus. $H_1$, $H_2$ hydraulic handpumps, $E$ graduated expansion cylinder, $V$ shut-off valve, $MC$ manganin cell, $SB$ specimen bomb, $J$ circulation jacket, $SP$ pressurized spark gap.
Figure 4.3 Manganin cell.
MANGANIN GAUGE

Figure 4.4 Manganin gauge circuit.
Figure 4.5 Specimen chamber assembly. J jacket, SP specimen capsule, W sapphire window, P piston, TH thermocouple, C Harwood 5 M high pressure fittings, SB specimen bomb, F flange.
Figure 4.6 Nanosecond light source.
I insulation, P PTFE insulation, R 500 MO Resistor,
V valve, O neoprene O-ring, A Allen screw, Re reflector,
G spark gap, C condenser lens, F focusing lens,
M mounting rod.
Figure 4.7 Specimen capsule.
I iron wire, P Acetal Rod back electrode, SP specimen, Q quartz front electrode, W worm screw, N Nesa coating, S sapphire window, Sr spring, A gold wire, B back plate.
Fig. 4.8 Circuits and idealized pulse shapes in drift mobility experiments

a Charge integration, $RC \gg t_t$

b Current pulse, risetime $\ll t_t$

c Differentiated current pulse, $CR_2 \ll t_t$
Figure 5.1  Distribution of electron drift mobilities, (a), and hole drift mobilities, (b), in orthorhombic sulphur specimen.
Fig. 5.2 Aging effects on the drift mobility in S
(a) Histogram showing the variation of the ratio $\mu_h/\mu_e$ with time. The quantity $(t_2-t_1)$ is 480 days.
(b) Histogram showing the variation of the electron mobility with time. Again $(t_2-t_1)$ is 480 days.
Table 5.3 Evaluation of the doubling pressure for the electron drift mobility from the results of 19 pressure runs.

<table>
<thead>
<tr>
<th>Crystal Temp. No.</th>
<th>Doubl. press. kbar</th>
<th>Weight wi</th>
<th>Product ( P_w ) kbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>2.10</td>
<td>3.0</td>
<td>6.30</td>
</tr>
<tr>
<td>19</td>
<td>2.07</td>
<td>3.5</td>
<td>7.35</td>
</tr>
<tr>
<td>19</td>
<td>2.00</td>
<td>3.5</td>
<td>7.00</td>
</tr>
<tr>
<td>20</td>
<td>2.25</td>
<td>1.0</td>
<td>2.25</td>
</tr>
<tr>
<td>106</td>
<td>1.60</td>
<td>1.0</td>
<td>1.60</td>
</tr>
<tr>
<td>106</td>
<td>2.00</td>
<td>2.0</td>
<td>4.00</td>
</tr>
<tr>
<td>114</td>
<td>2.20</td>
<td>12.0</td>
<td>26.4</td>
</tr>
<tr>
<td>105</td>
<td>2.00</td>
<td>3.0</td>
<td>6.00</td>
</tr>
<tr>
<td>114</td>
<td>2.34</td>
<td>6.0</td>
<td>14.00</td>
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<tr>
<td>113</td>
<td>2.08</td>
<td>2.0</td>
<td>4.16</td>
</tr>
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<td>112</td>
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<td>2.5</td>
<td>5.60</td>
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<td>2.68</td>
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<td>2.28</td>
<td>3.0</td>
<td>6.80</td>
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<td>2.52</td>
<td>2.5</td>
<td>6.30</td>
</tr>
<tr>
<td>128</td>
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</tr>
<tr>
<td>137[001]</td>
<td>2.34</td>
<td>3.5</td>
<td>8.20</td>
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</table>

Weighted mean: \( \Sigma w_i = 65.0 \times 142.76 \) kbar

The standard deviation for a single measurement in the above ensemble is (with an average weight of 3.4)

\[
\sigma = \sqrt{\frac{\Sigma w_i (P_i - 22 kbar)^2}{3 \times (19 - 1)}} = \sqrt{\frac{2.25}{61.2}} \approx 0.2 kbar
\]
Table 5.4 Drift mobilities of three sulphur crystals at various stages of preparation

(a) Nesa electrodes

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Thickness, μm</th>
<th>Electron mobility, cm²/Vs</th>
<th>Hole mob., cm²/Vs</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 25</td>
<td>410</td>
<td>4.6x10⁻⁴</td>
<td>1.45</td>
</tr>
<tr>
<td>S 90a</td>
<td>315</td>
<td>4.4x10⁻⁴</td>
<td>1.0</td>
</tr>
<tr>
<td>S 90b</td>
<td>230</td>
<td>4.4x10⁻⁴</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Thickness reduced by etching and grinding to 252 and 120 μm.

Electron mobility, cm²/Vs | 4.1x10⁻⁴ | 4.1x10⁻⁴ | 4.2x10⁻⁴ |
Hole mobility, cm²/Vs     | 2.0       | 1.85      | 1.8      |

(b) Semitransparent Au electrodes

Conducting gold electrodes were evaporated on to the three specimen and the mobilities were measured again.

Electron mobility, cm²/Vs | 4.9x10⁻⁴ | 4.0x10⁻⁴ | 4.2x10⁻⁴ |
Hole mobility, cm²/Vs     | 2.35      | 1.3       | 1.5      |
Figure 5.5 Dependence of the electron drift mobility on the pressure in orthorhombic sulphur in the direction perpendicular to the (111) face of the specimen.
Figure 5.6 Temperature dependence of the electron drift mobility in orthorhombic sulphur at two values of the pressure. Direction perpendicular to (111).
Orthorh. Sulphur
S124 d=355 μm
(111) face

Figure 5.7 Pressure dependence of the hole drift mobility in orthorhombic sulphur at three temperatures. Direction perpendicular to the (111) face of the specimen.
Figure 5.8a Temperature dependence of the hole drift mobility in orthorhombic sulphur at two values of the pressure for specimen S124.
Figure 5.8b Temperature dependence of the hole drift mobility in orthorhombic sulphur at two values of the pressure for specimen S 112.
Table 5.10  Doubling pressures for the hole mobility in sulphur. Direction perpendicular to (111) face.

<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Temper. °C</th>
<th>Doubling press., kbar</th>
<th>$\mu_n(21^\circ C)$</th>
<th>$\mu_e \times 10^4$</th>
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<tbody>
<tr>
<td>S</td>
<td>19</td>
<td>2.6± 0.1</td>
<td>0.33</td>
<td>1.45</td>
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<td>105</td>
<td>20</td>
<td>2.5± 0.3</td>
<td>0.33</td>
<td>1.45</td>
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<tr>
<td>106</td>
<td>22</td>
<td>2.45± 0.6</td>
<td>0.6</td>
<td>3.7</td>
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<td>112</td>
<td>-23</td>
<td>2.4±0.15</td>
<td>0.8</td>
<td>4.3</td>
</tr>
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<td>113</td>
<td>21</td>
<td>3.7± 0.5</td>
<td>2.2</td>
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<td>2.2</td>
<td>3.8</td>
</tr>
<tr>
<td>123</td>
<td>22</td>
<td>5.0± 0.8</td>
<td>2.2</td>
<td>3.8</td>
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<tr>
<td>124</td>
<td>-44</td>
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<td>3.9± 0.6</td>
<td>1.1</td>
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<td>87</td>
<td>5.4± 0.2</td>
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<tr>
<td>128</td>
<td>84</td>
<td>5.0± 0.8</td>
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</tr>
<tr>
<td>137 (001)</td>
<td>23</td>
<td>2.3± 0.1</td>
<td>0.8</td>
<td>5.1</td>
</tr>
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</table>

Figure 5.9  Doubling pressures vs room temperature hole mobility.
Figure 5.11 Temperature dependence of the electron and hole drift mobility in vitreous selenium at two values of the pressure.
Figure 5.12 Pressure dependence of the generation efficiency of the charge carriers in vitreous selenium
Figure 5.13 Photo-current density versus field for vitreous selenium at atmospheric pressure. The symbols $i_{ph}$ and $i'_{ph}$ stand for the photo-current at two different illumination levels.
Figure 5.14  Pressure dependence of the steady state dark and photo current in vitreous selenium. The applied field was 8 kV/cm.
Fig. 5.15  Pulsed current–voltage characteristics of a trigonal Se crystal in c-direction under hydrostatic pressure. The onset of electro-acoustic interaction produces a kink in the curves at some voltage $V'$. 
Fig. 5.16 Histogram of the interaction voltage $V'$ at atmospheric pressure and 21°C.

Fig. 5.17 Acoustoelectric interaction voltage $V'$ versus pressure at 21°C. The direction of carrier flow is the c-axis.
Fig. 6.1  (a) Relative position of the two $S_8$ molecules considered for the calculation of the intermolecular overlap.  
(b) Distances and angles for the overlap of atoms $A, B$ with $C, D$. 

$CA = 3.63 \, \text{Å}, \quad AB = 2.048 \, \text{Å}, \quad \gamma = 15^\circ$
<table>
<thead>
<tr>
<th>$S_i$</th>
<th>Polyn. Geometry factor</th>
<th>Exponent factor, $f_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$(3s,3s,AC)$</td>
<td>$(53)$ +1</td>
</tr>
<tr>
<td>2</td>
<td>$(3s,3p\sigma,AC)$</td>
<td>$(59)/9$ $\sin\gamma$</td>
</tr>
<tr>
<td>3</td>
<td>$(3p\sigma,3p\sigma,AC)$</td>
<td>$(56)$ $\sin^2\alpha\sin^2\gamma$</td>
</tr>
<tr>
<td>4</td>
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<td>$(62)(\cos^2\gamma-\cos^2\alpha\sin^2\gamma)$</td>
</tr>
<tr>
<td>5</td>
<td>$(3s,3s,AD)$</td>
<td>$(53)$ +1</td>
</tr>
<tr>
<td>6</td>
<td>$(3s,3p\sigma,AD)$</td>
<td>$(59)/9$ $\sin\beta\cos\gamma$</td>
</tr>
<tr>
<td>7</td>
<td>$(3p\sigma,3p\sigma,AD)$</td>
<td>$(56)$ $\sin^2\beta\cos^2\gamma$</td>
</tr>
<tr>
<td>8</td>
<td>$(3p\pi,3p\pi,AD)$</td>
<td>$(62)$ $-(\cos^2\beta\cos^2\gamma+\sin^2\gamma)$</td>
</tr>
</tbody>
</table>

$\gamma = 15^\circ$, $\varepsilon = 1.83$, $\overline{AC} = 3.67$ Å, $\overline{AD} = 4.13$ Å.

The angles $\alpha$ and $\beta$ depend on the $\overline{AC}$, for the value chosen above they are $\alpha = 8.32^\circ$ and $\beta = 28.5^\circ$. The notation for the $S_i$ and the equation numbers referred to under $P_i$ are taken from Mulliken et al, Jnl, Chem. Phys. 17 (1949) 1248.

Table 6.2 Components of the intermolecular overlap integral of two antibonding $\sigma^*$ molecular wavefunctions constructed from hybridized atomic functions $\Psi = s + \varepsilon p$. 

| ΔC | 3.6684 | 3.6320 | 3.5964 | 3.5615 | 3.5273 | 3.4937 |

\[ S_{\text{exp}(1.6)} \] Intermolecular distance reduced by:

<table>
<thead>
<tr>
<th>i</th>
<th>0%</th>
<th>-1%</th>
<th>-2%</th>
<th>-3%</th>
<th>-4%</th>
<th>-5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9957.2</td>
<td>10711.7</td>
<td>11499.1</td>
<td>12324.6</td>
<td>13190.3</td>
<td>14086.3</td>
</tr>
<tr>
<td>2</td>
<td>1987.5</td>
<td>2168.2</td>
<td>2347.4</td>
<td>2530.7</td>
<td>2725.8</td>
<td>2937.3</td>
</tr>
<tr>
<td>3</td>
<td>98.7</td>
<td>109.2</td>
<td>118.8</td>
<td>129.1</td>
<td>140.0</td>
<td>152.0</td>
</tr>
<tr>
<td>4</td>
<td>8287.4</td>
<td>9012.9</td>
<td>9781.0</td>
<td>10593.1</td>
<td>11457.0</td>
<td>12363.5</td>
</tr>
<tr>
<td>5</td>
<td>-3774.0</td>
<td>-4038.2</td>
<td>-4323.9</td>
<td>-4618.0</td>
<td>-4922.9</td>
<td>-5240.4</td>
</tr>
<tr>
<td>6</td>
<td>-9608.2</td>
<td>-10344.3</td>
<td>-11141.6</td>
<td>-11948.5</td>
<td>-12836.2</td>
<td>-13743.3</td>
</tr>
<tr>
<td>7</td>
<td>-6093.2</td>
<td>-6599.9</td>
<td>-7151.7</td>
<td>-7727.3</td>
<td>-8334.4</td>
<td>-8971.5</td>
</tr>
<tr>
<td>8</td>
<td>2499.4</td>
<td>2685.8</td>
<td>2888.5</td>
<td>3097.9</td>
<td>3315.4</td>
<td>3542.9</td>
</tr>
</tbody>
</table>

| So | 3354.8 | 3705.4 | 4017.6 | 4381.6 | 4735.0 | 5126.8 |

| y | 1.00 | 1.10 | 1.20 | 1.31 | 1.41 | 1.53 |
|---|
| lgy | 0.0000 | 0.04313 | 0.0780 | 0.1158 | 0.1496 | 0.1841 |

Table 6.3 Interatomic distances and the corresponding normalized overlaps \( S_{\text{exp}(12.6)} \) as a function of the percentage distance variation. Also given is the normalized total overlap \( S_0 \), the ratio \( S/S_0(0\%) = y \), and \( \text{lg} y \).
Table 6.4 Dependence of the overlap $S$ on small distance variations. Tests show that the results can be described equally well by an exponential or a power law.
Figure 7.1 Unit cell of orthorhombic sulphur.

The rings of every rack are lined up in the [110] and the [110] direction as indicated by the tape. Also shown is an example of the overlap geometry used in Chapter 7.

\[
\begin{align*}
a &= 10.47 \text{ Å}, & b &= 12.87 \text{ Å} \\
c &= 24.49 \text{ Å}
\end{align*}
\]
Figure 7.2 Percentage change of the intermolecular distance in orthorhombic S as a function of the pressure.
Figure 7.3 Plot of $\mu' T^{-2.3}$ vs $\exp(-0.2eV/kT)$ for the hole drift mobility in sulphur. The data were taken from Figs. 8a+b, A.R. Adams and W.E. Spear, J. Phys. Chem. Solids 25(1964)1113, points marked "AS", and W.D. Gill, G.B. Street and R.E. Macdonald, ibid. 28(1967)1517, points marked "GSM".
Figure 7.4 Density of hole trapping centers as evaluated from Figure 7.3 versus pressure. The vertical scale is logarithmic. The lines drawn correspond approximately to 

\[ N_t \propto \exp(-p/5\text{kbar}) \]