EDGE EMISSION IN CdS CRYSTALS

A Thesis submitted to the
University of Leicester

by

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for the degree of

Doctor of Philosophy

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Acknowledgements

The author wishes to thank Professor E.A. Stewardson for the opportunity to undertake research in his Department. He is much indebted to Dr. W.E. Spear for initially suggesting the problem and for his continued interest and helpful discussions throughout the work.

The supply of crystals by Dr. Fochs, A.E.I., Rugby, Dr. Wright, Birmingham University, and Mr. McGill, E.M.I., Hayes, is greatly appreciated. Thanks are due to Miss C. Stratford for her assistance with the computing and for writing the programme.

The author would like to express his gratitude to both his wife and Mrs. A. Cheesewright for their help in the preparation of this Thesis.

Abstract

The aim of this work was to investigate the luminescent mechanism in pure CdS single crystals and to attempt to obtain unambiguous evidence in favour of one of the two models proposed in the literature (the Schön-Klasens or the Lanbe-Klick model). Experiments have been carried out on undoped specimens obtained from three different sources and an attempt has been made to correlate transport, electrical, optical and luminescent properties measured on the same specimens.

The results of electron transport measurements, based on drift mobility techniques, on a number of specimens indicated that the drifting electrons interact predominately with either a shallow centre lying at about 0.03ev or with a deeper level at 0.16ev below the conduction band. Moderate heat treatment (360°C) led to a progressive reduction in the density of the 0.16ev centres and also quenched the emission.

The other properties studied were (a) the free electron density as a function of temperature and excitation intensity, (b) the temperature and excitation intensity dependence of the luminescence (c) its spectral distribution, and (d) the optical quenching spectrum.

From the results of these experiments it is concluded that:

(i) the 0.16ev centres are not directly connected with the luminescent transition and a model based on the Lanbe-Klick transition appears unlikely, and (ii) a class II centre ($S_p > S_n$) lies between 0.13 and 0.15ev above the valence band, which accounts for the

supralinearity observed in the electron density as a function of excitation intensity, and also explains the temperature dependence of n .

The results of the electrical measurements have been fitted to a three centre model of a photoconductor. The free carrier densities and occupation of the centres have been calculated by computer as a function of temperature and excitation intensity for various sets of parameters characterising the centres. On the basis of this model the dependence of luminescence on the temperature and excitation intensity has been predicted. A comparison between the computed and experimental curves indicates that only a model in which the radiative recombination is associated with a trapped hole (in a class II centre) and a free electron (Schön-Klasens model) can predict the experimental results correctly.

It appears likely that the luminescent centre is a class II centre. The reduction in the density of 0.16eV centres below the conduction band and the loss of emission appear to be two effects which are not directly associated. It is tentatively suggested that the centre seen in transport measurements is a cadmium interstitial and that the loss of edge emission by heat treatment in a vacuum is probably due to the creation of cadmium vacancies at the surface. A reduction in the density of luminescent sites is not essential to explain the effect which is observed.

Chapter 1

INTRODUCTION

During the last few decades II-VI compounds have commanded a great deal of attention from the point of view of both fundamental and applied studies. These compounds exhibit luminescence when suitably excited, and the sulphides and selenides of zinc and cadmium and their solid solutions have found important applications in cathode ray tubes and electroluminescence. With the development of improved crystal growing techniques good single crystals of some of the II-VI compounds have become available and this has stimulated more systematic studies of the optical and electrical properties of these compounds.

Particular interest has been shown in the properties of CdS. Unlike ZnS, CdS crystallises in a stable manner only in the hexagonal wurtzite lattice. Comparatively perfect thin platelet single crystals, up to about 200μ in thickness, can be grown from the vapour phase; thicker specimens may be cut at any specified orientation from larger boule crystals which have recently been grown. When prepared with high purity starting materials, CdS crystals have a resistivity of about 10^{12} ohm cm and possess a comparatively low photoconductivity. By the introduction of donor impurities, such as chlorine or indium, the resistivity can be reduced several orders of magnitude and the material then has many of the characteristics of an extrinsic semiconductor.

The remarkably high photosensitivity which is observed in many

specimens is due to the presence of compensated acceptors in the crystals. These acceptors which are negatively charged have a much larger cross section for the capture of a free hole than they subsequently have for the capture of a free electron. In this way the recombination lifetime for free electrons, which predominately determines the photoconductive gain, is greatly increased. The photoconductive properties of CdS are now being applied in a considerable number of devices such as photocells, light meters and gamma-ray counters.

The phenomenon of luminescence can be observed in pure CdS crystals if they are cooled to 77°K and irradiated with U.V. from a mercury lamp. Three bands of emission, red, green and blue, may be observed. The green and blue bands lie just on the long wavelength side of the fundamental absorption edge and have been termed edge emission. The reference to "pure crystals" in this thesis implies that such crystals do not contain any deliberately added impurities and were not treated in any way after growth. It is of importance to emphasize this point because, for most applications, luminescent materials normally contain large densities of impurity atoms (activators and co-activators).

The observation of luminescence bands in pure crystals has led to much speculation as to their origin but despite the considerable amount of work done on them the mechanism of the luminescent process is still a controversial matter. The diversity of opinion seems to arise because authors have frequently based their conclusions on

one "crucial" type of experiment.

In the work described in this thesis, concerned primarily with the green edge emission in CdS, an essentially different approach has been adopted. An attempt has been made to correlate systematically the results of electrical, optical and luminescent experiments for each of the specimens. The result of electrical measurements were then fitted to the general model of a photoconductor discussed in Chapter 6. From this model it has been possible to predict the luminescent properties on the basis of the two previously proposed transitions discussed in Chapter 2. A comparison between the predicted and the observed properties is given in Chapter 7 and makes it possible to reach a fairly conclusive decision in favour of one of the proposed mechanisms. Undoped crystals for use in these experiments were obtained from three different sources (A.E.I. Harlow; E.M.I. Hayes; Dr. Wright, Birmingham University). This ensured that the results obtained were not representative of specific crystal properties determined primarily by the growing technique, or of impurities in a particular batch of starting materials.

Chapter 2

REVIEW AND DISCUSSION OF THE LITERATURE ON EDGE EMISSION

Green and blue luminescence in CdS crystals, cooled to 77°K, may be excited by U.V. radiation or by electron bombardment. The emission from an excited crystal lies, at 77°K, on the long wavelength side of the fundamental absorption edge of CdS. From the spectral distribution shown in fig. 2.1 one can see that it consists of two parts: some emission in the blue and a series of equidistant peaks, separated by 0.04ev, in the green. As the crystal is cooled down to liquid helium temperatures, fine structure in the emission becomes visible (fig.2.2.).

2.1. Proposed models for edge emission

(a) Blue emission

Edge emission was first observed by Kröger (1940). He found that the intensity of the blue emission was dependent on the crystal size and attributed the phenomenon to a surface effect. In reflectance measurements on CdS, Thomas and Hopfield (1959), located three absorption lines at 4873A.U., 4844A.U., and 4740A.U., (see fig. 2.1), which they identified with exciton absorption, and calculated the exciton binding energy to be 0.028ev. It is generally accepted now that the blue peaks at 4850A.U. and 4870A.U. occur through the radiative decay of excitons in agreement with the findings of Diemer and Van Hooven der Van Oordt (1958).

(b) Green emission

Kröger considered that both the green and blue emission arose from the same mechanism, namely exciton decay. Kröger and Meyer (1954) suggested that the regular spacing of 0.04ev of the peaks in the spectral distribution above 5100Å.U., shown in fig.2.1., was due to the interaction with longitudinal optical phonons. Although no measurements of the vibrational frequencies were available at the time, it has since been shown (Collins, 1959; see also Halsted et al, 1961) that the longitudinal phonon frequency is 305 cm^{-1} corresponding to an energy of 0.038ev, in good agreement with the estimates of Kröger and Meyer.

Kröger argued that in an exciton model the luminescence occurs in the pure lattice and vibrational interactions would be characteristic of the pure lattice. If an impurity centre was involved in the mechanism responsible for emission, the energetic separation of the peaks should be characteristic of the centre and not of the lattice as is found in practice. It was, however, pointed out by Lambe Klick and Dexter (1956) that as the emission is almost equal to the band gap, the carriers making the luminescent transition would be only slightly bound in their excited state. Coupled with the fact that CdS has a fairly large dielectric constant ~ 10 , the structure observed in the emission could well be characteristic of the normal vibrational modes of the lattice. A model for edge emission based on recombination through an imperfection centre is therefore not impossible, particularly as Hopfield (1959)

has shown theoretically that a shallow trap could account for the large coupling with the lattice which is observed.

Success in explaining a variety of experimental results with an imperfection model has led to the current opinion that emission is due to the radiative recombination between a trapped and a free carrier. None of the experiments performed so far has been able to provide unambiguous evidence as to which carrier is trapped, the electron or the hole. The two common models which have been proposed are illustrated in fig.2.1-1.

According to model A, proposed by Schön (1942) and Klasens (1940), the process of luminescence occurs in the following way. When an incident photon is absorbed, with energy within the fundamental absorption edge, a free electron and a hole are created. The hole is captured by the centre which thus loses its electron. Since the energy level of the ground state of the centre is assumed close to the valence band of the crystal, little energy is released when the hole is captured. This energy is expended in the form of infra-red emission or thermal energy given up to the lattice. The centre, having trapped a hole, is now in a position to participate in the process of luminescence. Luminescence occurs when a free electron is captured by the centre.

Lambe and Klick (1955) have proposed the diametrically opposite mechanism (model B). In this model, the ground state of the centre consists of an electron bound in an energy level close to the conduction band. As before, the process of luminescence may occur

when an incident photon creates an electron and a hole in the crystal. However, if the centre is filled initially, the first step, i.e. the capture of a hole by the centre, is the luminescent process. Subsequent capture of an electron by the empty centre serves only to prepare the centre again for later participation in further luminescent cycles.

The energetic distance of the centre from the band edge was evaluated by Collins (1959) in the following manner. The separation between the blue peak at 4870 Å. and the first peak ⁱⁿ ~~at~~ the green (fig. 2.1.), assumed to occur without phonon interaction, is about 0.13 eV. This is the activation energy of the centre responsible for green edge emission to within an exciton binding energy. Collins therefore placed the centre 0.15 eV from one of the band edges. In a study of the temperature dependence of edge emission intensity above 77°K, Seiwert placed the centre at about 0.11 eV. The validity of this assignment will be discussed later in Chapter 7.

2.2. Experimental studies of the luminescent mechanism

Although some experiments have been done on silver doped specimens these are not considered relevant in this review as the thesis is essentially concerned with emission from pure samples.

Lambe (1955) did a number of experiments on the rise and decay of luminescent emission and photoconductivity in pure crystals both at 4° and 77°K. The intensity of the green emission was seen to increase rapidly whilst the build up in the photoconductivity was

a relatively slow process. Considering first the possibility of an exciton model, the density of excitons formed should be proportional to the product of the electron and hole densities. If holes reach an equilibrium quickly, at the onset of the excitation, then the luminescent intensity and photoconductivity should increase in step. On the other hand, if the density of holes increased slowly then the photoconductivity might be expected to increase more rapidly than luminescence. The observation of the opposite effect, namely the rapid establishment of the luminescence with a slow rise in the photoconductivity, threw doubt on the validity of an exciton model and suggested the adoption of a model involving radiative recombination through an ~~impurity~~^{imperfection} centre. The rise and decay rates of luminescence and the photocurrent were compared at 4°K. Two light pulses of 1 millisecond duration and separated by 1 millisecond were used to irradiate the specimens. At the onset of irradiation, luminescence grew instantaneously whilst the photocurrent increased at a much slower rate. At the end of the pulse the luminescence decayed rapidly with a slower decay rate of the photocurrent. At 77°K, the emission was slow to rise on the first pulse although a rapid response was found during the second pulse. Lambe explained this in terms of model B, and attributed the behaviour at 77°K to a filling of luminescent centres with the initial pulse enabling emission to occur immediately free holes were produced by the second pulse of radiation. The immediate rise in luminescence with excitation at 4°K occurred since electrons were

already "frozen" into the centres.

Lambe, Klick and Dexter (1956) extended these ideas and studied infra-red stimulated emission and decay of photocurrent. Crystals were cooled to 4°K for the experiments and then excited with radiation of 1μ wavelength. A burst of green emission and a decay of the photocurrent were observed. The decay of the emission was slower than that of the photocurrent. They considered the three possible recombination mechanisms shown in fig.2.2-1: free electron-free hole, free electron-trapped hole, and trapped electron-free hole, in relation to the expected decay rate of luminescence. The luminescent intensity would be proportional to (np) , (np_t) , (n_tp) in the three cases respectively. Here, n and p are the free electron and hole densities whilst the subscript 't' refers to trapped carriers. The rapid rise of the luminescence with the absorption of radiation in the quenching band indicates that the equilibrium concentration of holes is quickly reached. The hole concentration would not be expected to increase with time so that luminescence should decrease as rapidly or more so than the photocurrent if the transition involved free electrons. As this behaviour is not observed Lambe, Klick and Dexter consider that the process must involve trapped electrons and free holes, i.e. the luminescent mechanism is given by model B.

Broser et al (1961) found that green emission at 4°K decayed in step with the photocurrent and considered this as evidence in favour of model A. Collins (1959) showed, however, that a comparison

between the decay times of photoconductivity and luminescence is not sufficient to allow one to differentiate between the two models. His reasoning, considering the recombination between free electrons and trapped holes, is as follows. The conductivity (σ) can be written as:

$$\sigma = n e \mu_L \quad \dots\dots(2.1)$$

where 'e' is the electronic charge and μ_L is the lattice mobility. The conductivity is therefore a measure of the free electron density. The intensity (I_L) of the luminescence emitted by the recombination would be

$$I_L = \beta n p_t \quad \dots\dots(2.2)$$

where β is the recombination constant.

Considering the kinetic processes involved the rate equations can be written;

$$\frac{d}{dt} (\log p_t) = -\beta n + \beta_1 p \left(\frac{N_1}{p_t} - 1 \right) \quad \dots\dots(2.3)$$

$$\frac{d}{dt} (\log n) = -\beta p_t - \beta_2 p \quad \dots\dots(2.4)$$

where N_1 is the concentration of hole traps and β_1, β_2 are recombination constants.

Combining equations (2.2), (2.3) and (2.4)

$$\frac{d}{dt} (\log I_L) = \frac{d}{dt} (\log n) - \beta n + \beta_1 p \left(\frac{N_1}{p_t} - 1 \right) \quad \dots\dots(2.5)$$

Equation 2.5 demonstrates that the decay times of photocurrent and luminescence are related in a manner dependent on concentrations and recombination cross sections, and experiments based solely on the comparison between these decay times are not conclusive.

In his own work Collins excited emission with pulses of 1 Mev electrons lasting for 2×10^{-8} secs. He observed both blue and green emission and measured their decay times and the bombardment conductivity. The blue emission rapidly decayed following in fact the shape of the excitation pulse. As blue emission has been assigned to exciton decay, Collins concluded that the exciton and free hole lifetimes are less than 10^{-8} secs. Spear and Mort (1963) showed by their drift nobility measurements that the hole lifetime was of the order of 10^{-7} secs, in agreement with the estimate of Nickisch (1961) from P.E.M. measurements. The decay of the green emission was found to take 20-30 μ secs., many times longer than the free hole lifetime. From this evidence, Collins concluded that the free carrier was in fact the electron, and that the luminescent mechanism was described by model A. Some doubt can arise even with this argument, since the decay of the ^{luminescence}~~photocurrent~~ could be prolonged by the release of electrons from traps filled during the irradiation and not considered in the model.

2.3. Temperature dependence of the spectral distribution

The variation of the spectral distribution of edge emission with temperature, below 77°K, has been studied by Reynolds (1960) who

observed, in agreement with Thomas and Hopfield (1959), a shift of the green emission towards longer wavelengths on cooling from 77°K to 4°K . Pedrotti and Reynolds (1960) extended the investigations in order to explain this shift which occurred in the opposite direction to the band gap. They found that at 4°K a second series of peaks ((b) in fig.2.2) appeared towards longer wavelengths, separated from the other series (a) by 0.025ev. At 77°K series (b) was relatively weak, but on cooling, the peaks broadened and intensified whilst the intensity of the primary series (a), which predominated at 77°K , decreased. The broadening of the peaks and changes in intensity cause an overlapping of the two series and lead to an apparent gradual shift of the emission. These experimental facts are explained by a theory proposed by Thomas and Hopfield (1959). At 4°K electrons from the conduction band can become bound to a trapped hole and recombination then occurs between a trapped hole and an electron bound at a shallow level. This is a possibility which was not considered by Lambe et al in their experiments at 4°K and throws doubt on the conclusions they draw from their results.

Although most workers have investigated the green emission in the temperature range from 4°K to 110°K a green emission at room temperature has been reported by Sihnoven, Boyd and Woekle (1959) and Vuylsteke and Sihnoven (1959), centred at 5240 A.U. Kulp, Detweiler and Anders (1963) studied the wavelength dependence of the emission with temperature from 4°K to 350°K . They excited blue emission with a mercury lamp and green emission with 250 kev electrons. Their

results, reproduced in fig.2.3-1 indicate an association between the green emission at 5280 A.U. at room temperature and the emission at 5002 A.U. at low temperatures. At low temperatures the wavelength of the green emission is relatively constant with temperature.

2.4. Effect of heating and electron bombardment on edge emission

Further endeavours to understand the mechanism of luminescence have resulted in a study of the effect of heating and of electron bombardment on CdS crystals. Such experiments enable tentative suggestions to be made about the nature of the defect which is responsible for edge emission, and a brief review of the literature will therefore be useful in later discussion.

Lambe (1955) heated crystals to 800°C in a sulphur atmosphere and observed a quenching of the emission. This was later verified by Collins (1959). Removal of the surface layers by etching resulted in the reappearance of the green emission showing that the bulk of the material had been unaffected by the treatment. Heating crystals in a vacuum can also produce quenching of edge emission (Kulp and Kelly 1960); weak luminescence was destroyed after heating for two hours at 450°C although strong luminescent ~~crystals were~~^{was} more difficult to quench. Wendel (1953) observed that slow cooling from 600°C produced a quenching effect whilst a rapid water quench would restore the emission. Lambe, however, claimed that annealing in a vacuum or cadmium atmosphere had no effect on the emission.

Böer, Gutjahr and Hornung (1960) observed the changes in

conductivity with heat treatment up to 350°C in different atmospheres. In an inert atmosphere, the conductivity increased whilst subsequent heating in a sulphur atmosphere resulted in the reduction of the conductivity below its original value. Reheating in a vacuum produced a rise in the conductivity, attributed to the evaporation of excess sulphur incorporated during the previous treatment. Böer, Hornung and Zimmermann (1960) showed, by chemical analysis of deposits on the container walls, that during heat treatment at 380°C in a vacuum only cadmium was evaporated from the specimens. Contrary to the conclusions of Muschler (1953) no evidence for the presence of sulphur in the deposits was obtained. This is in agreement with the findings of Woods (1957). Most CdS crystals contain some free cadmium at internal cracks or defects and heating at 350°C produces an increase in the conductivity which is accompanied by a decrease in the amount of free cadmium present. According to Woods the free cadmium is incorporated into the lattice as an interstitial.

Shirafuji and Inuishi (1961) heat treated their specimens at 850°C for one hour in atmospheres of sulphur or cadmium. From thermally stimulated current measurements they express the opinion that cadmium or sulphur vacancies are introduced by heat treatment in sulphur or cadmium atmospheres respectively.

Bombarding specimens with 200Kev electrons results in the production of edge emission in samples previously quenched (Collins 1959). Kulp and Kelly (1960) bombarded cooled non-luminescent crystals with electrons to find the threshold for the production of edge emission.

This occurred at an electron energy of 115Kev, which is the threshold for the production of a sulphur vacancy-interstitial pair. They were also able to introduce edge emission by bombarding with 2.5Kev electrons, having previously evaporated a layer of sulphur over the crystal surface. They attributed the production of the emission to the formation of sulphur interstitials. Continual bombardment resulted in a quenching of the sample and sulphur deposits at the bottom of the crystal. Niekisch (1961), on bombarding with 300Kev electrons, observed an increase in the density of electron traps with an activation energy of 0.12ev. This centre, whose activation energy lies close to that of the centre responsible for edge emission, has been attributed to sulphur vacancies.

Recently Halsted and Segall (1963) have suggested that the presence of a native double acceptor (A_2) can explain the luminescence at low temperatures in II-VI compounds. Such a centre has been identified by Hall measurements (Lorenz and Woodbury 1963) in CdTe and CdS. Crystals were previously heated in an atmosphere of cadmium at 900°C and subsequently quenched. The centre is thought to have a doubly ionised level ($A_2^{=}$) which in CdS lies 0.09ev below the conduction band. It is suggested that the emission occurs from the recombination of an exciton bound to the singly ionised level (A_2^-) or alternatively by the recombination of a hole bound to ($A_2^{=}$). Although at low temperatures the capture of an electron at an (A_2^-) site is prevented by coulomb repulsion, an exciton, because of its neutrality, may easily reach the site. It is suggested that a luminescent centre associated

with the valence band in this manner would explain why the energy of the emission remains sensibly constant with temperature compared to the band gap variation in the low temperature region.

Chapter 3

APPARATUS AND EXPERIMENTAL METHODS

In this chapter, the experimental methods and apparatus used in the investigations will be described. Most experiments involved accurate measurements of temperature and some difficulty was experienced with chromel-alumel and copper-constantan thermocouples at the lower temperatures. In the range below about 100°K the e.m.f. of the thermocouples, measured with a precision potentiometer, appeared to deviate from those given in tables (e.g. Handbook of Chemistry and Physics), presumably due to impurities in the wires. For this reason the thermocouples used in the following experiments were calibrated at the temperatures of boiling nitrogen, boiling oxygen, and dry ice.

3.1. Electron transport measurements

In these experiments the variation of the drift mobility with temperature was studied. The method, which was essentially the same as that used by Spear and Mort (1963), employs a fast electron pulse to generate free carriers. A block diagram of the electron bombardment gear is shown in fig.3.1-1. Pulses of 30Kev electrons were focussed magnetically on to the specimen S. These pulses, between 10 nsec and 100 nsec long, were obtained by modulating the control grid G which was biased negative with respect to the filament F. This was done by switching a charged delay line DL with a mercury wetted relay. The relay was run through a high voltage coupling condenser from a generator at earth potential at a repetition frequency of 50

or 100 c/s. Suitable adjustment of the phase of the electron pulse could be made by means of a phase shift network. The duration of the pulses was determined by the length of the delay line, and their magnitude by the potentiometer P.

The incident electron pulse penetrated a few microns into the top of the specimen and produced electron-hole pairs in this region. About 2 nsec before the arrival of the excitation pulse, a pulsed electric field was applied across the specimen for a few milliseconds and, depending on its polarity, either electrons or holes could be drawn into the crystal volume. The charge displacement at the bottom electrode B, caused by the drifting carriers, was integrated at the input to a cathode follower C.F. and the output signal displayed on wide band electronic equipment. The sensitivity of the display system was such that the transit of about 10^6 carriers produced a signal of 0.5nV at the oscilloscope and the overall band width was of the order of 80Mc/s.

For the observation of well defined transit times it is important to prevent an appreciable build up of an internal space charge which frequently results from deep trapping. Space charge may be prevented by using a low level of excitation of $10^4 - 10^5$ carriers per pulse. In addition, polarisation of the specimens by carriers injected from the electrodes was kept to a minimum by pulsing the applied field at 50c/s. Paralysis of the amplifiers by large field transients was prevented by shunting the input of the cathode follower with two semiconducting diodes. These effectively shorted the input

for any signals greater than about 100 mV. It was ensured that the amplitude of the transit signals was much smaller than this, and lying well within the linear portion of the diode characteristics. From the oscilloscope trace a direct measure of the transit time t_t was obtained.

Specimen Mounting

For these transport measurements the crystals were fitted with evaporated gold and indium electrodes on top and bottom respectively. The thickness of the specimens could be measured to within $\pm 1\mu$ by means of an optical lever arrangement (Spear, Adams and Henderson, 1965). Specimens were mounted on a thin mica base M, as shown in fig. 3.1-2, and electrical contact to the bottom electrode was made by attaching a thin wire W with silver paste. An artificial blocking electrode was produced by evaporating gold on to a thin pyrex film of about 0.5μ thickness. This was held by a spring loaded ring R in contact with the top gold electrode, which was left electrically floating. This arrangement eliminated carrier injection through the top electrode during the transit. An indium electrode and pulsed field were found essential when using a blocking electrode, because during the transit a positive space charge is accumulated beneath the blocking contact. It appears that during the off period of the applied field the indium electrode allows electrons to be injected into the crystal volume by the space charge field in the crystal. This seems to lead to an effective neutralisation of the positive space charge.

The specimen holder used is shown schematically in fig. 3.1-3a.

The copper rod, which could either be heated electrically or suitably cooled, enabled the specimen temperature to be set at the required value. The nica base M was fixed tightly by four screws to the top of the copper rod (fig. 3.1-3b), with a drop of silicon oil between the nica and the rod to improve the thermal contact. The cathode follower was housed in the screened box S.B. as close as possible to the bottom electrode to avoid stray capacities. For measurements, the complete holder was fitted on to the bottom of the electron bombardment gear and an 'O' ring used to provide a vacuum seal.

3.2. Heat Treatment

Specimens were heated in a vacuum or an atmosphere of nitrogen. The simple annealing furnace is shown in fig. 3.2-1. Any electrodes on the specimens were removed by the abrasive action of a small brush lubricated with xylene before the crystals were placed in the boat B at the centre of the pyrex tube. This tube, surrounded by a muffle furnace, could either be evacuated or filled with gaseous nitrogen. After treatment at 360°C the samples were pulled gradually towards the end of the furnace and allowed to cool before exposure to the atmosphere.

3.3. Edge emission intensity measurements

The experimental arrangement is illustrated in fig. 3.3-1. To excite edge emission, U.V. radiation from a Hg-lamp was focussed by a quartz lens on to the specimen. The U.V. was isolated by means of a Kodak Wratten 18B filter and a solution of copper sulphate was used

to eliminate any infra red radiation passed by the filter. Crystals, attached to a copper plate, were cooled in the specimen holder shown in fig. 3.3-2. The copper plate could be firmly screwed to the holder at H. Liquid nitrogen in the reservoir R maintained the specimen temperature at 77°K for over an hour. A copper rod could be screwed into the plug P to cut off the flow of nitrogen through the tubes T. The holder H warmed slowly (at about 1°K per minute) and enabled luminescence intensity to be studied as a function of temperature. The glass metal seals L were used for simultaneous conductivity measurements.

The spectral distribution of the edge emission was analysed with a monochromator of the Littrow type (Optica C F 4) which employed a plane grating ruled at 600 lines/mm. as the dispersing element. Its resolution was about 15 A.U./mm slit width. Monochromatic radiation was collected by a photomultiplier (E.M.I. 9592B) and the output signal fed to a Varian recorder. For intensity measurements as a function of temperature the monochromator was set at 5250 A.U. with a resolution of 150 A.U. Absolute intensity values of the incident U.V. and of the edge emission were obtained with the aid of a Hilger-Schwarz thermopile.

3.4. Photoconductivity measurements

For the measurements of the conductivity, indium electrodes were evaporated on to the top surface of the crystal in a "Gap-cell" geometry. The electrodes were 2 to 3 mm. long and separated by about 1mm. Crystals were mounted on thin mica on a copper plate and

electrical contact to the electrodes made with thin copper wire attached with a suspension of colloidal graphite in alcohol. Good thermal contact was ensured by a drop of silicon oil between the mica and copper plate. The ohmic nature of the electrodes was tested and all measurements were made under ohmic conditions.

The temperature dependence of the conductivity was initially measured in the apparatus described in section 3.3. Since these measurements were not carried out under thermal equilibrium conditions, the possibility of a small lag between the thermocouple and the specimen existed.

The temperature controlled specimen holder shown in fig.3.4-1a represented a considerable improvement in this respect. The specimen, mounted on the copper plate, was firmly attached to the centre rod R. The rod was isolated from the outer casing, C, by a "Mycalox" ring M. The enclosure was evacuated using indium wire as a vacuum seal. A 5ohm heater, H, insulated with asbestos paper tape, was wound on the copper rod and electrical access to the heater, electrode contacts and the thermocouple, was made available through glass-metal seals G. The outer connections on the glass metal seals were coated in black wax to increase the electrical insulation and avoid large leakage currents due to frosting. The window, W, for irradiation with U.V. or I.R. was made of calcium fluoride and the top, T, from perspex.

The specimen temperature was measured with a chromel P-alumel thermocouple and a calibrated potentiometer. The null reading was registered by a scalar galvanometer and the light spot from the

scalamp focussed on to a phototransistor coupled to the energizing coil of a relay. The simple circuit is given in fig. 3.4-1b. The centre rod was cooled with a flask of liquid nitrogen kept at a fairly constant level. When the potentiometer became unbalanced (specimen cooled) the light spot moved away from the phototransistor and the relay actuated the heater. The temperature stability obtained in this way was $\pm 2^{\circ}\text{K.}$ with a minimum temperature of 85°K.

The intensity of the incident U.V. was varied by means of Kodak Wratten neutral density filters. These were calibrated with the U.V. source, used to excite the emission, and the thermopile. With high resistance specimens, $R > 10^9$ ohms, an Ecko vibrating reed electrometer was used to measure the current, whilst for currents $> 3 \times 10^{-9}$ amp a moving coil galvanometer was employed.

3.5. Infra-red quenching experiments

In these experiments the specimens were irradiated with U.V. through the top port, P, and a small surface mirror was used to reflect the U.V. on to the crystal. The infra red radiation was obtained from a Nernst filament and was focussed by a surface concave mirror through the calcium fluoride window on to the specimen. Three filters, Si, Ge, and InSb, enabled the spectral regions $1-12\mu$, $2-12\mu$, $7-12\mu$, respectively to be investigated. In some of the experiments a small infra-red spectrometer (Grubb Parsons) was used for better resolution in the $1-3\mu$ range.

Chapter 4

EXPERIMENTAL RESULTS

The properties which were investigated can be placed under four sub-headings: Transport, Electrical, Optical and Luminescent properties. The experimental measurements which are reported were made in order to establish a general pattern of behaviour in crystals obtained from different sources. The results described in this chapter are fairly typical examples of the general behaviour of the crystals. A more complete summary of the results is given in Tables 1 and 2*.

The crystals were all grown from the vapour phase and measured about 1cm^2 in area and between $10-400\mu$ in thickness. In the majority of specimens the c-axis was in the plane of the crystal surface, although one of the crystals, B3, had been grown with the c-axis lying perpendicular to the plane of the crystal surface.

4.1. Electron transport measurements

The investigation upon which this thesis is based was originally suggested by the results of the transport measurements. These were planned as an extension of the work done by Spear and Mort (1963) on the electron and hole transport in CdS, which led to the typical temperature dependence of the electron drift mobility μ_e shown by curves A and A¹ in fig. 4.1-1. At the higher temperatures μ_e coincides closely with the lattice mobility curve μ_L and leads to an average value of $265\text{cm}^2\text{sec}^{-1}\text{V}^{-1}$ at room temperature. With decreasing T, μ_e

* Bound at the end of the figures.

passes through a maximum and then decreases.

In the continuation of this work it was found that a number of platelet crystals led consistently to the temperature dependence illustrated in curve B. This behaviour has also been observed in specimens cut from larger boule crystals. The room temperature value of μ_e in these specimens (referred to as type B crystals in the following) was only about 1/10 of that of the more common type A crystals mentioned above. With decreasing T, μ_e decreased rapidly.

Experimentally, the measurements on these specimens proved difficult at the lower temperatures. Below about 250°K the end of transit signals became curved and t_t was no longer well defined. This effect was probably due to the loss of the drifting carriers due to deep trapping.

The effect of heat treatment on type B crystals has been investigated and fig. 4.1-2 shows some of the results. Curve 1 refers to an untreated crystal; the points on curve 2 and 3 were obtained after heating in a vacuum to 360°C for five minutes and two hours respectively. A further example, referring to another type B crystal, is given by curve 4 which after heating showed an even larger increase in electron drift nobility.

Subsidiary experiments showed that in the temperature range investigated and with the excitation used during transport measurements, the steady state electron Fermi level always remained well below the 0.16ev centres. The heat treatment weakened considerably the intensity of the emission from the crystals in all cases (Chapter 2),

with complete quenching after heating for about two hours. Curves 3 and 4 in fig. 4.2-2 refer to crystals no longer showing any visible emission.

4.2. Dependence of photoconductivity on temperature and excitation intensity

The ohmic nature of the indium electrodes evaporated on to the specimens was tested by plotting the current-voltage characteristic of each gap-cell, both with and without excitation. Typical curves obtained are shown in fig. 4.2-1. All conductivity measurements were taken in the linear region of the characteristics.

In fig. 4.2-2 the electron density n for a number of specimens under U.V. excitation is shown as a function of temperature in the low temperature regions. For the calculation of n it was assumed that the region of current flow extended from the surface to within an ambipolar diffusion length $\sim 10^{-4}$ cm (Spear and Mort 1963). Any contribution to the photocurrent from mobile holes was considered negligible.

In many luminescent specimens, e.g. W.F.1, a pronounced decrease of n was observed with rise in temperature. In a more resistive specimen, fig. 4.2-2c, a shoulder is noticeable at 105°K where the electron density is $8.5 \times 10^{10} \text{ cm}^{-3}$. This corresponds to the condition when the electron Fermi level lies about 0.14 eV below the conduction band and might be due to the emptying of a trapping level. A similar feature which was observed in n vs. excitation curves will be mentioned later. In luminescent crystals which possessed an

electron density of the order of 10^{14} cm^{-3} , e.g. crystal 424B, n at first increased with increasing temperature. A similar behaviour was shown by the non-luminescent specimen L2.

Fig. 4.2-3 gives the position of the electron Fermi level ($\mathcal{J}_e$) below the conduction band as a function of temperature. It shows that with increasing temperature the electron Fermi level moves away from the conduction band. This was a common feature observed in all crystals investigated including specimens 424B and L2. The plot also shows (specimen W.H.1.) that after heat treatment $\mathcal{J}_e$ moves closer to the conduction band at a given temperature.

The position of the Fermi level for electrons in several crystals at 80°K and 110°K are listed in Table 2.

The dependence of the electron density upon the excitation density (F) was investigated over as wide a range of intensities as possible. Fig. 4.2-4 shows some typical examples of $\log n$ vs. $\log F/F_{\text{max}}$ curves at various temperatures for specimens, both before and after heat treatment which quenched the luminescence. At low excitation the electron density varies approximately as $F^{0.5}$; visible luminescence begins in the supralinear range where $n \propto F^{>1}$. This applies for both WH1 (at 78°K) and WH2 (at 90°K). After quenching of the emission by heat treatment the electron density rises by almost two orders of magnitude and supralinearity, in the previously luminescent range, has disappeared. The electron density is now almost proportional to $F^{0.5}$. Non-luminescent specimens (as grown), e.g. L2., also show a sublinear dependence on F throughout the excitation range. A

"shoulder" is evident (WH.2.) both before and after heat treatment when the Fermi level is situated about 0.14ev below the conduction band, [c.f. fig. 4.2-2(c)].

Crystal B.3. showed no supralinearity with the excitation used although it luminesced brilliantly. The quantum efficiency for luminescence was almost 100 per cent in this specimen, compared to the majority where the efficiency was much lower ~ 5 per cent or less. The crystal in this case had been grown with the c-axis perpendicular to the surface of the specimen. At 80°K the electron density was of the order of 10^{14} cm^{-3} .

4.3. Dependence of luminescent intensity on temperature and excitation intensity

Fig. 4.3-1 shows the luminescent intensity (I_L) as a function of $(1/T)$. It demonstrates, quite markedly, the rapid decrease of the luminescent intensity with temperature, a characteristic property of all the crystals investigated. For $T > T'$, where T' is defined by the intersection of the tangents from the high and low temperature ranges, I_L is proportional to $\exp(-\epsilon_L/kT)$; ϵ_L is found to lie between 0.11 and 0.16ev. Values of ϵ_L and T' for individual specimens are given in Table 2.

The luminescent intensity was measured with excitation intensities ranging from 4×10^{12} to 4×10^{14} photons $\text{sec}^{-1} \text{ cm}^{-2}$. Assuming that excitation occurs to an average depth of about one micron, the maximum excitation density F_{max} was of the order of 4×10^{18} photons

$\text{sec}^{-1}\text{cm}^{-3}$. Fig. 4.3-2 shows that for all specimens, I_L vs. F curves are supralinear at high excitation although some break to almost linear dependence at low F . In the case of L3A, a highly resistive specimen, a squared dependence is evident throughout the range.

4.4. Spectral distribution of Luminescence

The spectral distribution of the emission was investigated for crystals at 78°K ; only green luminescence was visible or detectable. This emission, fig. 4.4-1, consisted of a prominent peak situated at 5140 A.U. (2.41ev.) and further equally spaced peaks towards longer wavelengths. The separation of these peaks due to phonon interactions (see Chapter 2) was $\sim 0.04\text{ev.}$, in agreement with the observations of Kröger and Meyer (1954). Curve (b) shows the effect of heat treatment. The intensity of the emission was reduced whilst the spectral distribution remained unaltered.

4.5. Infra-red quenching experiments

Attempts to quench the photoconductivity of samples by exciting holes from levels close to the valence band led to negative results. Under U.V. excitation at 80°K no conclusive quenching was observed either with the spectrometer or by focussing filtered radiation from a Nernst filament on to the specimen.

Quenching of the photoconductivity with radiation $\sim 1\mu$ was observed in several crystals at room temperature and 80°K . It was found that at both temperatures the electron density increased after

heat treatment. A comparison was made between the change in electron density Δn when the crystal was irradiated with infra-red, before and after heat treatment had quenched the emission. In all cases Δn was found to have increased after heat treatment. In L3A for instance it changed from 2×10^{10} to $3 \times 10^{13} \text{ cm}^{-3}$, whilst in specimen WQ2 a smaller change from 1.5×10^{13} to $4 \times 10^{13} \text{ cm}^{-3}$ was observed. In non-luminescent samples, as opposed to heat treated specimens, Δn was much higher, of the order of 10^{14} - 10^{15} cm^{-3} .

Chapter 5

DISCUSSION OF EXPERIMENTAL RESULTS

The electron drift mobility measurements will be discussed first. The results of the measurements on type A specimens were interpreted in terms of a transition from a lattice to a trap controlled drift mobility according to the expression

$$\mu_e = \mu_L \left[1 + (N_1/N_C) \exp \epsilon_1/kT \right]^{-1} \dots\dots (5.1)$$

N_1 and ϵ_1 denote the density and energetic depth below the conduction band of the centre which interacts with the drifting electrons. From the fit of equation 5.1 to the experimental data (solid lines in fig. 4.1-1) the given values of N_1 and ϵ_1 were obtained. It has been shown that at infinite dilution ϵ_1 tends to a value of 0.049ev.

On the basis of equation 1 the observed behaviour of type B specimens suggests that generated electrons interact predominantly with a level of deeper centres in these crystals. It can be shown that in the presence of two types of centre an additional term $(N_2/N_C) \exp \epsilon_2/kT$ has to be added to the denominator of equation 1. For type B crystals the centre densities are such that $(N_2/N_C) \exp \epsilon_2/kT \gg 1 + (N_1/N_C) \exp \epsilon_1/kT$; the opposite condition would apply in type A specimens in which the shallower centres have a predominating effect on the transport. From the results for type B crystals values of ϵ_2 between 0.15 and 0.16 ev and densities of the order of 10^{16} cm^{-3} were obtained. Equation 5.1 has been fitted to the experimental points in fig. 4.1-2 and the

solid lines represent the calculated curves. It is found that heating results in a progressive reduction in the density of 0.16ev centres from 4×10^{16} to $2.6 \times 10^{15} \text{ cm}^{-3}$, whilst curve 4 represents a decrease in N_2 to $3.4 \times 10^{14} \text{ cm}^{-3}$ after heating. μ_e at room temperature now closely approaches the lattice mobility and the effect of shallower centres ($E_1 = 0.03\text{ev}$, $N_1 \sim 10^{17} \text{ cm}^{-3}$) becomes noticeable.

It is unlikely that this observed decrease in the trap density can be explained by the introduction of shallower donors by the heat treatment. Although shallow donors would ionise and fill the deeper centres with electrons, reducing their role in transport measurements, this would require the electron Fermi level to lie near to the centres i.e. about 0.16ev from the conduction band. Experimental measurements have shown, however, that in fact the Fermi level, under excitation, lies much deeper in the forbidden band (about 0.26ev below the conduction band). It is far more likely that the progressive reduction in centre density is due to annealing during the heat treatment.

The activation energy of these centres is almost identical to the activation energy of the luminescent centres (0.15ev) as evaluated by Collins (1960). The simultaneous reduction in luminescent intensity and the density of centres might suggest a correlation between the two. As the centres revealed by drift mobility measurements are without doubt associated with the conduction band, the observations reported could be taken as evidence for a Lambe-Klick model (model B) of

luminescence. There are essentially two general criticisms that may be made of such a correlation. Firstly, transport measurements were made in a temperature range from 400°K to 250°K whilst the luminescence only occurs at low temperatures. Extrapolation of results from one temperature range to another may lead to difficulties since the centres could exhibit different behaviour in the two temperature ranges. Secondly, drift mobility is concerned essentially with the bulk; carriers travel through the specimen and any traps investigated would be characteristic of the bulk of the material. Luminescence, on the other hand, because of the small absorption depth of the U.V., occurs in the surface regions. Luminescence and drift mobility therefore are associated with essentially different regions of the crystal.

The above criticisms do not apply to the photoconductivity measurements described in Chapter 4, as they refer to the electron density in the surface regions and were made in the luminescent temperature range. It is therefore reasonable to attempt a correlation between n and the luminescence. As shown clearly by fig. 4.2-3 the electron Fermi level in the low temperature range always lies closer to the conduction band than the 0.16ev centres, even for the most resistive crystal. If it can be assumed that the occupation of these centres is controlled predominantly by the thermal release of electrons into the conduction band (see section 6.3), it follows that throughout the luminescent temperature range the 0.16ev centres will remain almost completely filled with electrons. The

observed exponential decrease of I_L with temperature (fig. 4.3-1) can only be explained if the Fermi level actually passes through the level with increasing temperature. For this to occur in the temperature range from 80° to 110°K the centres would have to lie much closer to the conduction band and the emission should then occur at shorter wavelengths than those at which it is observed.

These considerations throw considerable doubt on a correlation between a 0.15 or 0.16 eV level below the conduction band and the luminescent centre, and with it ^{on} the validity of the Lambe-Klick model. In addition quite a number of type A specimens luminesced, some strongly, although the density of 0.16 eV centres in these crystals is comparatively small, less than 10^{14}cm^{-3} . This further suggests that the centres are not associated even indirectly with the luminescent centres since, if they were, the intensity of the emission from type B crystals should be greater than from type A specimens. It might be suggested that although the electron traps are fully occupied, the observed temperature dependence of I_L could be connected with changes in the free hole density. On the basis of the calculations in Chapter 6 this possibility seems unlikely.

The supralinearity in n vs. F curves observed in most of the specimens (fig. 4. 2-4), suggests that a sensitizing centre lies close to the valence band. The thermal release of holes from such a centre with rise in temperature would also explain the generally observed decrease in n .

An explanation of the supralinearity was put forward by Rose

(1955, 1957) who assumed that two classes of recombination centres exist in the forbidden band, differing by the values of their capture cross sections S_n , S_p , for electrons and holes respectively. Class I centres have equal cross sections for the capture of either carrier, $(S_n \sim S_p)$, whilst class II centres have a much larger cross section for hole capture, $(S_p \gg S_n)$. Rose assumed an energy distribution of the class II centres to explain supralinearity in the photocurrents (fig. 5.1a). With increasing excitation (fig. 5.1b) the hole Fermi level moves through the distribution of class II centres towards the valence band and more holes are trapped at these centres; the electron density then becomes supralinear with F .

Bube (1957) and Klasens (1958) both demonstrated that the assumption of an energy distribution of class II centres is unnecessary with a model involving two types of recombination centres. Supralinearity in n arises when with increasing excitation the hole Fermi level and consequently the demarcation line (Chapter 6) move towards the valence band and approach closely a level of class II centres. The class II centres begin to fill without contributing substantially to the recombination with free electrons, the electron lifetime begins to increase and n becomes proportional to $F^{>1}$.

If at a fixed value of F in the supralinear range the temperature is increased, the rate of thermal release of holes from these centres rises. This will destroy the sensitisation by providing increased recombination through class I centres (thermal quenching). The electron lifetime decreases leading to the

observed decrease in n with rising temperature.

Although the above discussion of the photoconductive and luminescent measurements has thrown considerable doubt on the Lambek-Klick model of the green luminescence in CdS it cannot be regarded as proof that the Schön-Klasens model is the correct one. It is clear that experimental data alone cannot lead to an unambiguous decision as to the correct mechanism, and an attempt has therefore been made in the following chapters to fit the experimental data to as general a model of a photoconductor as possible. As the above qualitative discussion indicates, the model should include a class II centre which in principle would account for the observed supralinearity of n vs. F curves and the observed temperature dependence of n .

Chapter 6

ANALYSIS OF A GENERAL MODEL FOR A PHOTOCONDUCTOR

Before considering the general model for a photoconductor it appears essential to discuss the distinction between trapping and recombination centres. Under excitation the densities of free electrons and holes in a non-degenerate photoconductor are described by the electron and hole quasi-Fermi levels, $\mathcal{F}_e$ and $\mathcal{F}_h$, in the following manner:

$$n = N_c \exp^{-(\epsilon_c - \mathcal{F}_e)/kT}$$
$$p = N_v \exp^{-(\mathcal{F}_h - \epsilon_v)/kT}$$

where N_c and N_v are the effective densities of states at the conduction and valence band edges, ϵ_c and ϵ_v . With increasing excitation n increases and the Fermi levels move closer to their respective bands.

A trapping centre is one from which the carrier will be thermally released before it can capture and recombine with a carrier of the opposite sign. A recombination centre, on the other hand, is one in which a carrier will recombine with a carrier of the opposite sign before being thermally released. The demarcation line, for electrons, between traps and recombination centres is defined as the energy level at which an electron would have equal probability of thermal release or of recombining with a hole. States lying

above the demarcation line would take on a predominantly trap-like character, since the rate of thermal exchange with the conduction band increases exponentially as the centres lie further from the demarcation line. Rose calculates that the rate increases 100-fold, at room temperature, 0.1ev from the demarcation line. Likewise states lying below this line act predominantly as recombination centres.

It may be shown that the demarcation line is related to the position of the corresponding Fermi level (fig. 6.1) in the following manner:

$$E_d = J + kT \log \left(\frac{n_r}{p_r} \right)$$

where E_d is the energetic distance of the line from the band edge. n_r is the number of filled and p_r the number of empty centres.

The separation between the Fermi level and the demarcation level is normally fairly small. It will be appreciated that as the Fermi levels move towards their respective bands with increasing excitation, or decreasing temperature, their respective demarcation lines move with them. The density of centres which lie between the demarcation lines and therefore act as recombination centres increases. Whether or not a centre acts as an effective trap or as a recombination site will depend therefore largely on the level of excitation and the temperature.

6.1. The General Model.

The model of a photoconductor to be discussed here assumes the existence of three centres in the forbidden band. The model and the transitions involved are shown in fig. 6.1-1(a), (b).

Centre 1 is a hole trap lying E_1 ev above the valence band, possessing cross sections S_{n1} , S_{p1} , for electron and hole capture respectively. These centres are essentially of class II type so that $S_{n1} \ll S_{p1}$. Centres 2, on the other hand, are typical class I recombination centres with S_{n2} and S_{p2} of the same order of magnitude, lying sufficiently deep in the forbidden band that thermal release of trapped carriers may be neglected. Centres 3 are electron traps, empty in the absence of excitation.

A quantum efficiency of unity is assumed in the creation of electron-hole pairs by optical excitation across the band gap; this enables the density of electron-hole pairs created per second F to be equated directly to the excitation density.

The recombination constants (β_{ni} ; β_{pi}) denote the product of the capture cross section (S_{ni} ; S_{pi}) and the thermal velocity for electrons and holes respectively. Centre densities are denoted by N_i and the density of filled states, i, by n_i . P_1 represents the probability per unit time of thermal release of a hole in level 1 into the valence band. Similarly, P_3 , represents the probability of thermal release of an electron from levels 3 into the conduction band.

$$\text{i.e. } P_1 = N_v \beta_{p_1} \exp(-\epsilon_1/kT)$$

$$\text{and } P_3 = N_c \beta_{p_3} \exp(-\epsilon_3/kT)$$

For charge neutrality:

$$n + n_3 = p + (N_1 - n_1) + (N_2 - n_2) \quad \dots\dots (6.1-1)$$

The rates of change of the parameters n , p , n_i , are equal to zero in the steady state and may be expressed in the following manner:

$$\frac{dn}{dt} = F - n \sum_{i=1}^3 \beta_{n_i} (N_i - n_i) + n_3 P_3 = 0 \quad \dots\dots (6.1-2)$$

$$\frac{dp}{dt} = F - p \sum_{i=1}^3 \beta_{p_i} n_i + (N_1 - n_1) P_1 = 0 \quad \dots\dots (6.1-3)$$

$$\frac{dn_1}{dt} = (N_1 - n_1) P_1 - \beta_{p_1} n_1 p + \beta_{n_1} n (N_1 - n_1) = 0 \quad \dots\dots (6.1-4)$$

$$\frac{dn_2}{dt} = \beta_{n_2} n (N_2 - n_2) - \beta_{p_2} n_2 p = 0 \quad \dots\dots (6.1-5)$$

$$\frac{dn_3}{dt} = \beta_{n_3} n (N_3 - n_3) - \beta_{p_3} n_3 p - n_3 P_3 = 0 \quad \dots\dots (6.1-6)$$

From equations (6.1-4), (6.1-5), (6.1-6), the electron occupation

of the centres in the steady state are:

$$n_1 = N_1 \left\{ 1 + \beta_{p1} P / (\beta_{n1} n + P_1) \right\}^{-1} \dots (6.1-7)$$

$$n_2 = N_2 \left\{ 1 + \beta_{p2} P / \beta_{n2} n \right\}^{-1} \dots (6.1-8)$$

$$n_3 = N_3 \left\{ 1 + (\beta_{p3} P + P_3) / \beta_{n3} n \right\}^{-1} \dots (6.1-9)$$

By substitution of equations (6.1-7) - (6.1-9) into the condition for charge neutrality the following relation between p and n is obtained.

$$p = n - N_1 - N_2 + N_1 \left\{ 1 + \frac{\beta_{p1} P}{\beta_{n1} n + P_1} \right\}^{-1} + N_2 \left\{ 1 + \frac{\beta_{p2} P}{\beta_{n2} n} \right\}^{-1} + N_3 \left\{ 1 + \frac{(\beta_{p3} P + P_3)}{\beta_{n3} n} \right\}^{-1} \dots (6.1-10)$$

Finally the excitation density F can be obtained in terms of n and p by substituting equations (6.1-7) - (6.1-9) into (6.1-3):

$$F = p \left[\beta_{p1} N_1 \left(1 + \frac{\beta_{p1} P + P_1}{\beta_{n1} n} \right)^{-1} + \beta_{p2} N_2 \left(1 + \frac{\beta_{p2} P}{\beta_{n2} n} \right)^{-1} + \beta_{p3} N_3 \left(1 + \frac{\beta_{p3} P + P_3}{\beta_{n3} n} \right)^{-1} \right] \dots (6.1-11)$$

It might be expected from equation (6.1-11) that to a first approximation F will vary linearly with p . This has in fact been borne out in the computations described later. The variation of the electron density with excitation will therefore depend on the manner in which n varies with p . The conditions which should exist before

supralinearity becomes observable may be determined by the following argument.

Consider initially the case of low excitation. The quasi-Fermi level and demarcation line for electrons lie below centres 3 and those for holes lie above centres 1. In this situation the following inequalities are true:

$$\beta_{n3}n \ll P_3, \quad \beta_{p3}p \ll P_3, \quad \beta_{n1}n \ll P_1, \quad \beta_{p1}p \ll P_1$$

It can be shown from equation (6.1-10), after expansion by the binomial theorem and approximating by means of the above inequalities, that:

$$p = \frac{n P_1 (N_3 \beta_{n3} n / P_3)}{n(P_1 + N_1 \beta_{p1}) + \beta_{p2} N_2 P_1 / \beta_{n2}} \quad (6.1-12)$$

if $n < N_3$. Depending on the relative magnitudes of the terms in the denominator the free hole density will vary either linearly with or as the square of the electron density. No supralinearity would be observed in the n vs. F dependence.

With increasing excitation the Fermi level for electrons, and at slightly higher excitation the electron demarcation line, will pass through and lie above centres 3. Now $\beta_{n3}n \gg P_3$ and $\beta_{p3}p \gg P_3$ and the variation of p with n is given by:

$$p = n N_3 P_1 \left\{ n N_1 \beta_{p1} + \left(N_2 \frac{\beta_{p2}}{\beta_{n2}} + N_3 \frac{\beta_{p3}}{\beta_{n3}} \right) P_1 \right\}^{-1} \quad (6.1-13)$$

The variation of n with F will be linear if

$$\left(N_2 \frac{\beta_{p2}}{\beta_{n2}} + N_3 \frac{\beta_{p3}}{\beta_{n3}} \right) P_1 > n N_1 \beta_{p1}$$

whilst if this inequality is not satisfied and

$$\left(N_2 \frac{\beta_{p2}}{\beta_{n2}} + N_3 \frac{\beta_{p3}}{\beta_{n3}} \right) P_1 < n N_1 \beta_{p1} \quad \dots (6.1-14)$$

supralinearity ^{can be shown to} ~~will~~ occur. The onset of supralinearity should therefore be expected to occur when the two sides of the inequality (6.1-14) become approximately equal. Physically this means that the density of empty 1 centres becomes ^{approximately} equal to the sum of the densities of unoccupied recombination centres.

With even higher excitation densities the hole Fermi level and demarcation line approach centres 1. When these two lie below centres 1 it follows from equation (6.1-10) that:

$$p = \frac{n(n + N_3)}{n + N_1 \frac{\beta_{p1}}{\beta_{n1}} + N_2 \frac{\beta_{p2}}{\beta_{n2}} + N_3 \frac{\beta_{p3}}{\beta_{n3}}} \quad \dots (6.1-15)$$

i.e. supralinearity ceases when the hole demarcation level lies in the Class II centres.

The predictions of the three centre model were investigated for different set values of the parameters β_{pi} , β_{ni} , N_i and P_i . Our Elliot 803 computer was programmed to solve equation (6.1-10) for p by an iterative method with $n = 10^6, 10^7, \dots, 10^{15}$. The corresponding values of n and p were then fed into equations

(6.1-7) - (6.1-9) and (6.1-11) to obtain the corresponding values of n_1, n_2, n_3 and F .

6.2. Considerations governing the choice of parameters

(a) Centre 1 must essentially be of class II type. From the results of WH1 (fig. 4.2-3) supralinearity should begin at an excitation density of about $1/100 F_{\max}$ (i.e. $4 \times 10^{16} \text{ cm}^{-3} \text{ sec}^{-1}$). For this to occur the hole Fermi level must at low excitation intensity lie above the centres. The occupation of the centres will then be controlled by the thermal release of holes into the valence band, ($\beta_{p1} p < p_1$).

Optical quenching experiments (e.g. Taft and Hebb, 1952; Tutihasi, 1956; Bube, 1955) show that a typical class II centre exists, in CdS crystals, about 1ev above the valence band. The thermal release of holes from one of these centres, however, at 77°K is vanishingly small. In order that the Fermi level may lie above the class II centres, they must lie much closer to the valence band. The approximate condition for the onset of supralinearity is obtained by equating the two sides of the inequality (6.1-14)*. With a reasonable choice of densities, $\approx 10^{15} \text{ cm}^{-3}$, and $T = 77^\circ\text{K}$, E_1 should lie between 0.135ev and 0.15ev. This estimate shows that as far as the energy of the emission peak is concerned, centres 1 might well be associated with the luminescent transition.

(b) A reasonable value of $10^{-8} \text{ cm}^{-3} \text{ sec}^{-1}$ has been assumed in the calculations for the recombination constant β_{p1} , which implies that

* With the assumption that $\beta_{n2} = \beta_{n1} = \beta_{n3} = \beta_{p3} = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}$ [see (b) and (c) below] expression (6.1-14) may be written as: $p_1 = \beta_{p1} n' (\frac{N_1}{N_2 + N_3})$, where n' is the electron density near the onset of supralinearity. In Specimen WH1, fig 4.2-4, the possible range of n' is from 2×10^9 to $5 \times 10^9 \text{ cm}^{-3}$. Provided $N_1 \approx N_2 \approx N_3$ then E_1 should lie between 0.135ev and 0.15ev.

S_{p_1} is of the order of $2 \times 10^{-15} \text{ cm}^2$. The capture cross section of centres 1 for electrons (S_{n_1}) must be much smaller and, following Bube, it has been put at 10^{-19} cm^2 .

(c) Centre 2 which is a typical recombination centre has a kinetically controlled occupation. β_{n_2} , and β_{p_2} were assumed to be of the order of $10^{-8} \text{ cm}^3 \text{ sec}^{-1}$.

(d) The predominant electron trap (centre 3) can either have an activation energy (E_3) of about 0.15ev (Type B crystals) or lie between 0.025 and 0.043ev from the bottom of the conduction band (Type A crystals fig. 4.1-1). It has been assumed that centre 3 has the properties of a normal electron trap and that

$$\beta_{p_3} = \beta_{n_3} = 10^{-8} \text{ cm}^3 \text{ sec}^{-1}.$$

(e) In calculating N_c the generally accepted value of $n_e^* = 0.2n_e$ has been used, where n_e^* represents the effective mass of an electron. For N_v , the assumption that the hole effective mass (n_h^*) is equal to the hole mass (n_h) was made.

6.3. General results of the computations

We shall now consider some of the general results obtained from the computations based on the model. The parameters chosen in individual computations are indicated in Table 3. The cases considered fall into two main groups. ^{The first is} a series of calculations involving two centres, one lying at 0.145 or 0.135ev from the valence band and the other about 0.15ev below the conduction band. In the second series of calculations the centre lying close to the conduction

band was placed at an energetic distance of 0.03 - 0.04 eV from the band. It will be appreciated that the computations considered are by no means exhaustive. They serve, however, to illustrate the dependence of the model's main features on various parameters and provide a quantitative basis upon which to evaluate the experimental results.

Typical results of the first series of computations are given in fig. 6.3-1 (at 77°K) and in fig. 6.3-2 (at 110°K). These figures are a logarithmic plot of the densities of n , p , n_1 , n_2 , n_3 and p_1 , against the excitation density F .

The more general results which have been obtained from the calculations are as follows:

(a) The occurrence of supralinearity depends critically on the choice of N_3 in relation to N_1 and N_2 . In computation A (fig. 6.3-1), for an excitation density of $10^{16} - 10^{18}$ photons $\text{cm}^{-3}\text{sec}^{-1}$, $n \propto F^{1.5}$. At the onset of supralinearity $\beta_p, p \sim 10$, so that the condition $\beta_p, p \ll \rho_1$ is satisfied. If $N_1 < 0.5(N_2 + N_3)$, as in B and H, according to equation (6.1-14) the onset of supralinearity will be shifted to a higher electron density n' . The corresponding value of p' also increases and in cases B and H, where supralinearity is not present it can be seen that the additional condition, $\beta_p, p' \ll \rho_1$, is no longer satisfied. With an increase in both N_1 and N_3 the supralinearity is again observed (computations C and D). Now, however, the electron density is proportional to $F^{1.7}$. Evidently by proper choice of N_3 the observed range of gradients listed in Table 2 can be

accounted for.

(b) As expected an increase in N_3 decreases n over practically the whole range of F .

(c) In all calculations p varies linearly over the range of F from 10^{10} to 10^{21} photons $\text{cm}^{-3}\text{sec}^{-1}$ and is practically temperature independent between 80° and 110°K .

(d) Centre 3 is practically filled throughout the luminescent range and remains so over the critical temperature range from 80° to 110°K . The kinetic recombination process (transition $\beta p_3 p$ in the model) is therefore not effective in reducing the electron population in centres 3 and the assumption (Chapter 5) that these centres are in thermal equilibrium with the conduction band is valid. The temperature dependence of edge emission therefore cannot be explained either by a decrease in the electron population of centres 3 or by a rapid decrease in the free hole density. These results are further confirmation that the luminescence is not associated with centres 3.

(e) Alteration in the value of ϵ_1 from 0.135ev (computation C) to 0.145ev (computation D) increases the value of p_1 ; the other characteristics remaining sensibly constant.

(f) An increase in N_2 (computation I) reduces both p_1 and p by about the same factor. The effect on n and n_3 is negligible.

Computations F, M, N, and O refer to the case with $\epsilon_3 = 0.03\text{ev}$. A typical set of results (F) at $T = 77^\circ\text{K}$ is shown in fig. 6.3-3. In the range of F for which luminescence was visible in specimens, 10^{16} - 10^{18} photons $\text{cm}^{-3}\text{sec}^{-1}$, n varies approximately as $F^{0.5}$, and

reaches a value of about 10^{14} cm^{-3} at $F = 10^{18} \text{ photons cm}^{-2} \text{ sec}^{-1}$.

It is interesting to compare this result with the experimental variation of n with F on a heat treated specimen (fig. 4.2-4). It will be seen that the computation reproduces fairly well the measured characteristic.

Computation A (fig. 6.3-1) enables a physical interpretation of the variation of n with F to be made. At low excitation the density of empty recombination centres remains constant. Centres 1 remain sensibly filled with electrons, whilst increasing excitation intensity produces a rearrangement of the electrons situated in centres 2 and centres 3. With further increasing excitation intensity,

$$p = (N_1 - n_1) + (N_2 - n_2).$$

and the onset of supralinearity is observed. With increasing excitation the density of holes in centres 1 increases, and the electrons which previously occupied these centres are transferred into the empty recombination centres (empty centres 2 and 3 lying below the electron demarcation level). Because of the small cross section of centres 1 for electrons, holes in centre 1 do not add considerably to the recombination. The decrease in the density of empty recombination centres having a large cross section for electron capture increases the electron lifetime, resulting in a variation of n with F of a greater power than unity. In general, supralinearity will arise when the density of electrons transferred from centres 1 is greater than the free electron density and comparable with the density of empty centres 2 and 3.

Chapter 7

COMPARISON BETWEEN THE COMPUTED AND EXPERIMENTAL RESULTS

The computations described in the previous chapter enable the dependence of I_L on the temperature and excitation density to be predicted. For model A (Schön-Klasens):

$$I_L = \beta n_1 n p_1 \quad \dots (7.1)$$

whilst for model B (Lanbe-Klick)

$$I_L = \beta p_3 p n_3 \quad \dots (7.2)$$

The temperature dependence predicted from a number of computations are shown in fig. 7-1. It is fairly obvious that Model A predicts qualitatively, and up to a point quantitatively, the experimental temperature dependence shown in fig. 4.3-1. The gradient, ϵ_L , of the linear part of the curve A is found to be 0.22ev, considerably outside the observed range. On the other hand, calculations based on model B lead to an almost temperature independent value of I_L . Similar results have been obtained from all computations. The gradient ϵ_L , for model A, in computations B, C, and D is about 0.16ev, whilst model B still predicts an intensity independent of temperature. A shallower gradient of 0.11ev is obtained from computations F, M, and N, Again not inconsistent with experimental results (Table 2).

The dependence of I_L on the excitation density, as predicted by both models is shown in fig. 7-2 for a number of computed cases.

Computations A, C, and D, which led to supralinearity in n , show an F^2 dependence near $F_{\max}$. With decreasing excitation the gradient decreases to about 1.6. Calculation B, which did not lead to supralinearity, showed a $F^{1.4}$ dependence, whilst computations M, N, and O predict a linear variation between I_L and F . Experimentally, the dependence of I_L on F shows a wide variation ranging from F^1 to F^2 which is not contrary to the predictions of model A. Model B, however, predicts a linear dependence between I_L and F in every case.

We have shown that model B is not able to predict the rapid decrease in the intensity of edge emission with rise in temperature which is a characteristic property observed in all specimens. Model A, on the other hand, predicts qualitatively the experimental temperature dependence.

The gradient, ϵ_L , is found to be extremely sensitive to the density of the centres and upon the activation energy ϵ_3 . An increase in N_3 from 10^{15} cm^{-3} (computation A) to 10^{16} cm^{-3} (computations B, C, and D) changes ϵ_L from 0.22ev to 0.16ev. A change in ϵ_1 from 0.135ev to 0.03ev results in a change of ϵ_L from 0.16ev to 0.14ev (computations B and M), whilst increasing N_3 by a factor of ten to 10^{17} reduces ϵ_L still further to 0.11ev (computation F). Variations in N_1 (computations M, N, and B, C) have little effect on ϵ_L . This shows that the value of ϵ_L , although close to the activation energy of the luminescent centre, depends on the density and activation energy of the electron trapping level below the conduction band (centres 3). These results throw considerable doubt

on the interpretation of the temperature dependence of I_L made by Seiwert (1960). He suggested that the exponential decrease of I_L with temperature is caused by the thermal release of carriers from the luminescent site, but incorrectly associated E_L with the activation energy of the centres.

In Table 4, theoretical and experimental values of a number of parameters are compared in an attempt to explain both the electrical and the luminescent properties quantitatively in terms of the three centre model.

Crystal L3A was a highly resistive specimen with an electron density of the order of 10^{11} cm^{-3} at 80°K . The experimental values have been compared ^{with} ~~to~~ the theoretical values obtained for computation W, since these provide fair agreement with the electron densities at 80° and 110°K and with the variation of n with F . Some discrepancy appears between the values of E_L although the variation of I_L with F provides good agreement between theoretical and experimental values. In an attempt to improve the fit with n and E_L , N_3 was increased from 10^{15} to $5 \times 10^{15} \text{ cm}^{-3}$ in computation Z. The decrease in n is far in excess of that required although there is an improvement in the predicted value of E_L from 0.19 to 0.13 eV.

Crystal B3 had an electron density almost three orders of magnitude greater than L3A and a high quantum efficiency for luminescence. Transport measurements indicated that the electron drift mobility at room temperature was greater than $200 \text{ cm}^2 \text{ sec}^{-1} \text{ V}^{-1}$.

This implies that it is essentially of type A (fig. 4.1-1) with a density of 0.16ev centres less than 5×10^{14} and suggests that a comparison with a computation where the electron trapping level was placed at 0.03ev is more applicable in this case. The experimental results are compared in this instant with computation F, again with reasonable success. Computation F, unlike M, does not predict the decrease in n with rising temperature which was observed in practice although there is excellent agreement in the luminescent parameters.

Finally, the computed variation of the electron Fermi level with temperature, indicated by dotted lines in fig. 4. 2-3, shows the same trend as found in experiment.

It has been shown, in principle, that the luminescent properties of the specimens can be explained both qualitatively and quantitatively on the basis of a three centre model. The disagreement between the experimental and computed values of I_L is possibly due to the particular choice of β_n , which was made in the calculations. Because of the number of parameters involved, however, there seems little point in endeavouring to improve the agreement in Table 4. Crystal B3 emphasizes again that the luminescent properties can be explained even when the density of centres 0.15 or 0.16ev below the conduction band is small (less than 5×10^{14}).

Chapter 8

THE ROLE OF SOME DEFECT CENTRES IN CdS CRYSTALS

The existence of a luminescent centre lying 0.15ev above the valence band affords an adequate explanation of the supralinearity in the electron density, its temperature dependence and the rapid decrease in the luminescent intensity with temperature. The presence of a level lying close to the valence band was reported by Auth (1961) from results of P.E.M. measurements on single crystals of CdS. He determined the energy distribution of shallow hole traps and found it to extend over the range from 0.10ev to 0.15ev.

As edge emission is observed in pure crystals it is most likely that the centre responsible is a native defect of the lattice. The assignment of the centre to a particular defect, however, is a difficult task because of the considerable number of possible defects which can occur. Besides the simpler types, such as interstitial or vacancy sites, defects are known to coalesce to form centres of a complex nature. We shall confine our discussion here to the simpler defects and consider how well they alone can provide a qualitative explanation of the behaviour of luminescence and the deep electron traps observed in transport measurements.

In electron transport measurements, a centre 0.16ev below the conduction band was observed. Niekisch (1961) has reported a centre lying at an activation energy of 0.12ev below the conduction band, sensitive to 300kev electron bombardment, which he assigned to

a singly ionised sulphur vacancy. Assuming his assignment to be correct and the discrepancy in energy to be due to experimental error, the apparent correlation between the centre density and the intensity of the emission could be understood. Auth suggested that a sulphur vacancy in association with neighbouring sulphur ions would create a centre above the valence band. The two electrons associated with the sulphur vacancy are more loosely bound than electrons on the sulphur ions and consequently they will possess a more diffuse wavefunction. This would cause neighbouring lattice sites to become more negative and the energy of these sites would be raised with respect to the valence band. The sulphur vacancy would then have a dual role. At room temperature one of its electrons becomes thermally released into the conduction band and the site acts as an electron trap. At low temperatures the site would trap its full complement of electrons, the associated centre would be formed and luminescence observed. This would then explain the simultaneous decrease in the density of sulphur vacancies and the intensity of the edge emission by heat treatment in a vacuum and sulphur or cadmium atmospheres.

Such a model, however, would require a one to one relationship between sulphur vacancies and the luminescent sites. The presence of 0.15eV centres in sufficiently large densities should give rise to specimens with low drift mobility. Specimen B3, however, had a high mobility, greater than $200\text{cm}^2\text{sec}^{-1}\text{V}^{-1}$ at room temperature, and also luminesced brilliantly, as did many type A crystals (Chapter 5).

The variation of μ_e with temperature in type A specimens indicates that the density of deeper electron traps present is much less than 10^{14} cm^{-3} . With a one to one correlation between deep electron traps and the luminescent centres one would expect a far lower efficiency for luminescence in these crystals than is found in practice.

It is questionable, however, whether the assignment of the 0.12ev traps to sulphur vacancies is valid. 300kev electron bombardment of specimens resulted in an increase in the density of these centres and ~~to~~ⁱⁿ the production of green edge emission. Kulp (1962), however, demonstrated that incident electrons only require an energy of about 275kev in order to remove a cadmium ion from its lattice site. The traps observed by Niekisch might therefore be cadmium interstitials. A cadmium interstitial would tend to become ionised and could therefore act as an electron trap. As pointed out in Chapter 2, heat treatment in a vacuum at 350°C led to the evaporation of cadmium from the specimens (Böer et al, 1960; Woods, 1957) so that after heat treatment a decrease in the density of cadmium interstitials would be expected. The energetic position of such a site has not definitely been placed in the forbidden band and thus remains a likely explanation.

Kulp and Kelly (1960) performed a fairly convincing experiment to show that edge emission was associated with the sulphur constituent. Mention of their work was made in Chapter 2. They

favoured sulphur interstitials as the likely site for luminescence on the basis of an experiment in which they produced edge emission by stimulated diffusion of sulphur into the crystal under bombardment with low energy electrons.

If the edge emission were attributed to sulphur interstitials, and the centre seen in transport measurements to sulphur vacancies, this could in principle explain the apparent correlation between the two types of centres. If a direct annihilation of an interstitial and a vacancy were postulated, this would require the unlikely situation that both occurred in approximately equal densities in all the crystals. The loss of emission by the evaporation of sulphur interstitials from the specimens seems also unlikely since there appeared to be no evidence of the presence of free sulphur after heating at 350°C (Böer et al). There are, however, two main objections to attributing the centre responsible for edge emission to sulphur interstitials. Firstly, because of their larger ionic radius sulphur interstitials are less likely to occur in crystals than cadmium interstitials and secondly, sulphur interstitials might be expected to have a tendency to become ionised, and therefore would possess a larger cross section for electron than hole capture. The comparisons made in Chapter 7, indicate that the luminescent centre should be a typical class II centre, i.e. $S_p > S_n$; it is therefore unlikely that sulphur interstitials are directly associated with the emission.

Sulphur vacancies if they lie, as suggested by Collins, above

the valence band would explain the effect produced by heating in different atmospheres. Such a model, however, would contradict the interpretation of the electron bombardment experiments performed by Kulp and Kelly.

It is possible, however, that the loss of edge emission by heat treatment is not due to the physical reduction in the density of luminescent centres. The introduction of another centre close to the middle of the forbidden band could substantially reduce the population of holes in centres 1 and thereby reduce the intensity of the emission. The optical quenching experiments, mentioned in section 6.2, indicate that there exists a typical class II centre about 1ev above the valence band. Excitation of these centres by radiation increases the free hole lifetime and results in a decrease in the photoconductivity. It is thought that the centres affected by the quenching radiation are cadmium vacancies (Bube et al, 1962).

The result of quenching experiments reported in section 4.5. shows that the quenching is increased by the heat treatment, most probably because of the creation of cadmium vacancies during heating. Cadmium interstitials in the bulk of the material would be able, during heat treatment, to move towards the surface by jumping to neighbouring interstitial sites in the crystal lattice. The net effect would be a general reduction in the density of such sites throughout the sample. Cadmium ions, on the other hand, would not be able to move into neighbouring lattice sites, since these would

on the whole be occupied. Cadmium vacancies must be created at the surface and migrate into the volume of the specimen. Since luminescence occurs in the surface layers the production of cadmium vacancies in the surface region would be very effective in quenching the emission. Experimentally, it has been shown that a cleaved surface of a heated sample still luminesces, indicating that a surface effect is responsible for the quenching of the emission. The decrease in cadmium interstitials would explain the observations in transport measurements (a bulk effect) whilst the introduction of cadmium vacancies shifts the hole Fermi level towards the centre of the forbidden band. A higher excitation would therefore be required to increase the hole occupancy of the luminescent centres sufficiently to produce observable emission. This reasoning for the loss of emission would also explain the effect of heating samples in sulphur or cadmium vapours. Treatment in sulphur vapour would tend to remove cadmium, increase the density of cadmium vacancies and hence decrease the intensity of the edge emission. Treatment in a cadmium vapour, on the other hand, would not necessarily greatly affect the luminescent transition.

To summarise the following tentative explanation of the experiments is offered. The centre near the valence band responsible for edge emission is a defect associated with the sulphur component although the exact nature of the site is not known. The centres at 0.16eV observed in transport measurements are probably cadmium

interstitials. Heat treatment in a vacuum removes these centres from the crystal volume and cadmium vacancies are created in the surface regions. The increased density of cadmium vacancies reduces the hole population in the centres responsible for edge emission and consequently produces the loss of luminescence.

Recently, Halsted and Segall (1963) have endeavoured to explain edge emission in terms of a doubly ionised acceptor centre lying close to the conduction band. In our model we have assumed that the centres lying close to the conduction band are normal electron traps, so that some comment on their model would not be out of place.

The above authors based their model on the observation by Lorenz and Woodbury (1963) of a doubly ionised acceptor centre lying 0.09ev (at 250°K) from the conduction band. This centre was produced by heating crystals to 900°C in a cadmium atmosphere and subsequently quenching them. No evidence for such a centre was found in as-grown crystals and it would therefore seem unlikely that such a centre would, in general, exist in luminescent specimens. In view of this it is difficult to accept an explanation based on this centre as a generally valid model for luminescence in II-VI compounds.

One of the main points which Halsted and Segall put forward in favour of this model is that the wavelength at which emission occurs does not change with temperature as rapidly as the band gap, implying that a transition between a high lying acceptor level and the valence band would therefore be more consistent with observations. This point is not entirely convincing, because the almost constant wavelength of the emission in the temperature range from 4°K to 100°K is

understandable in the light of the experiments performed by Reynolds and Pedrotti (Chapter 2). At 4°K electrons might become bound to the luminescent centre in a hydrogen-like energy level. With increasing temperature the electron becomes free and emission occurs from transitions between the conduction band and the luminescent centres. The emission tends to move to higher energy with increasing temperature whilst the energy of the band gap decreases. The net effect is that the emission will not vary as rapidly as the band gap. As the change in the band gap (ΔE_g) is less than 0.05ev (Radelt 1961) in this range, the existence of a bound state for electrons 0.02ev below the conduction band would explain why $\frac{\Delta E_L}{\Delta E_g} < 0.3$ where ΔE_L is the change in the energy of the emission.

A doubly ionised acceptor level is therefore not essential to explain this effect. Although the exact nature of the luminescent centre is not apparent from the experiments performed to date, its behaviour can be readily explained in terms of a normal trapping level lying in the vicinity of the valence band.

Chapter 9

CONCLUSIONS

The comparison between the experimental and theoretical results based on a three centre model, shows fairly convincingly that green edge emission in CdS crystals is explained qualitatively by the presence of a centre which lies about 0.15ev above the valence band; the radiative recombination between free electrons and trapped holes can lead to the rapid temperature dependence of the luminescent intensity which is observed. The calculations based on the Lambek-Klick transition for luminescence (model B) do not predict correctly the observed temperature dependence or the variation of I_L with excitation.

The three centre model shows reasonable quantitative agreement with the electrical and luminescent properties investigated experimentally. The existence of a shallow ^{class II} centre lying above the valence band provides an explanation of supralinearity in the electron density and the rapid decrease in the electron density with rise in temperature observed in some specimens.

The spread in the observed values of ϵ_L and the apparent discrepancy between the values reported here and those of Seiwert is explained by the model. The computations show that the slope ϵ_L is critically dependent on the density of centres in a particular crystal. As the density of imperfections will differ from one specimen to another a spread in ϵ_L is not unexpected.

The similarity between the activation energy of the luminescent site (0.15ev) and the centres observed in transport measurements (0.16ev) appears purely fortuitous. The simultaneous reduction in the centres present and the loss of edge emission are two effects which do not appear to be directly connected.

It is suggested that the electron trapping centre which plays an important role in transport measurements is a cadmium interstitial. The apparent correlation by heat treatment mentioned above appears to stem from the fact that cadmium is evaporated from the crystal. This has the dual effect of reducing the density of cadmium interstitials throughout the crystal and of increasing cadmium vacancies in the surface regions. The cadmium vacancies which act as deep class II centres trap holes previously occupying the luminescent centres. The quenching of the emission occurs because of the insufficient density of holes in those centres. Heat treatment in vacuum and in a sulphur or cadmium atmosphere can be explained in this way and the density of the luminescent centres need not necessarily alter.

It appears that heat treatment in different atmospheres tells one very little about the centre responsible for edge emission. The work of Kulp and Kelly, Niekisch, and Collins indicated that the centre is probably due to the sulphur constituent of the crystals, although the exact nature of the site which is formed is still uncertain.

The attempts to provide experimental proof of the existence of

shallow hole trapping centres by the quenching of the photoconductivity were not conclusive (section 4.5). As the presence of such centres has been observed by Auth, it can only be assumed that the failure of specimens to respond to infra-red stimulation was due to insufficient intensity in the 7-11 μ wavelength region.

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Fig 2.1 Spectral distribution of Edge emission.
(after Collins 1959).

Fig 2.2 Shows the 'doublet' structure in Edge emission which occurs on cooling below 77°K.

(after Pedrotti & Reynolds, 1960).

Model A

Model B

Fig 2.1-1 The two proposed models for edge emission.

Fig 2.2-1 Three recombination mechanisms considered by Lambe, Klick and Dexter.

Fig 2.3-1 Temperature dependence of emission from CdS
(after Kulp, Detweiler and Anders 1963).

Fig 3.1-1 Block diagram of the electron bombardment gear.

Fig 3.1-2 Specimen mounting arrangement.

Circuit for the cathode follower housed in the screened box (S.B).

Fig 3.1-3 Specimen holder for transport measurements.

Fig 3.2-1 Diagram of the annealing furnace used in the experiments.

Fig 3.3-1 Diagram of the experimental arrangement.

Fig 3.3-2 Specimen Holder.

(a) Temperature controlled specimen holder.

(b) Circuit for temperature control.

Fig 3.4-1.

Fig 4. 1-1. Temperature dependence of the electron drift mobility in Type A and Type B crystals.

Solid lines calculated from equation 5.1 using the following parameters:

Curve A $\epsilon_1 = 0.043 \text{ eV}$, $N_1 = 3.5 \times 10^{15} \text{ cm}^{-3}$.

Curve A' $\epsilon_1 = 0.03 \text{ eV}$, $N_1 \approx 10^{17} \text{ cm}^{-3}$, $N_2 < 10^{14} \text{ cm}^{-3}$.

Curve B $\epsilon_2 = 0.16 \text{ eV}$, $N_2 = 5 \times 10^{16} \text{ cm}^{-3}$.

Fig 4.1-2 Effect of heat treatment on Type B crystals.

Solid curves are calculated:

Curve 1, untreated crystal $\epsilon_2=0.16\text{ev}$, $N_2 \approx 4 \times 10^{16}$
 $N_1 \leq 4 \times 10^{17}\text{cm}^{-3}$

Curve 2, short heat treatment, luminescence
 weakened, $N_2 = 8.7 \times 10^{15}\text{cm}^{-3}$

Curve 3, further heating, luminescence quenched,
 $N_2 = 2.6 \times 10^{15}\text{cm}^{-3}$, $\epsilon_2=0.03\text{ev}$, $N_1 = 1.5 \times 10^{17}\text{cm}^{-3}$

Curve 4, different crystal, emission quenched,
 $N_2 = 3.4 \times 10^{14}\text{cm}^{-3}$, $N_1 \approx 8 \times 10^{16}\text{cm}^{-3}$.

Fig 4.2-1 Typical i-V characteristics illustrating the ohmic nature of the gap-cells.

Fig 4.2-2 Shows the temperature dependence of the free electron density for a number of specimens.

Fig 4.2-3 Diagram indicating the temperature dependence of the electron Fermi level exhibited by the specimens.

Fig 4.2-4 Variation of n with excitation.

$$F_{max} \sim 4 \times 10^{18} \text{ photons cm}^{-3} \text{ sec}^{-1}$$

* indicates the onset of visible emission.

Fig 4.3-1 Examples of the temperature dependence of I_L .

Fig 4.3-2 Shows the dependence of I_L on the excitation density for a number of crystals.

Fig 4.4-1 Spectral distribution of edge emission
(a) before, and (b) after heating.

(a) Low excitation.

(b) At higher excitation.

Fig 5.1 Illustrates the model for supralinearity proposed by Rose.

Fig 6.1 Indicates the relative positions of the Fermi and demarcation levels under excitation.
 n_r is density of recombination centres for holes.
 p_r is density of recombination centres for electrons.

- (a) Shows the relative positions of the three centres considered in the model of a photoconductor.

- (b) The transitions involved.

Fig 6.1-1.

Fig 6.3-1 Computation A at 77°K.

Free carrier densities and occupation of centres plotted against the excitation density.

Fig 6.3-2 Computation A at 110°K.

Free carrier densities and occupation of centres plotted against the excitation density.

Fig 6.3-3 Computation F at 77°K.

Free carrier densities and occupation of centres plotted against the excitation density.

Fig 7.1 Predicted temperature dependence of I_L .

Computation coding shown in brackets.

Fig 7.2 Predicted dependence of I_L on the excitation density.

Computation coding shown in brackets.

<u>PROPERTY INVESTIGATED</u>	<u>GENERAL RESULT</u>
<p><u>1. TRANSPORT</u></p> <p>Electron drift mobility between 400°K and 250°K.</p>	<p>Shows the existence of two main groups of centres:</p> <p>(a) 0.03-0.048ev, density 10^{15}-10^{18} cm⁻³</p> <p>(b) 0.16ev below the conduction band with density of about 10^{16} cm⁻³</p>
<p><u>2. ELECTRICAL</u></p> <p>(a) free electron density n vs. excitation density F at T ~ 80°K. Excitation at 3650 A.U. F from 10^{15} to $F_{max} \leq 4 \times 10^{18}$ photons cm⁻³sec⁻¹.</p> <p>(b) n vs. T at F_{max}. T between 77°K and 130°K.</p>	<p><u>Luminescent specimens</u></p> <p>$n \propto F^{0.5}$ at lower F.</p> <p>$n \propto F^{1.1}$ to $F^{1.5}$ for $F \sim 10^{16}$ cm⁻³sec⁻¹</p> <p>Supralinearity observed in the luminescent range.</p> <p>n increased by heat treatment and F dependence altered.</p> <p><u>Non-Luminescent specimens</u></p> <p>$n \propto F^{0.5}$</p> <p>n decreases with increasing T for most luminescent specimens. In non-luminescent crystals n increases.</p>

TABLE 1.

contd. overleaf.

<u>PROPERTY INVESTIGATED</u>	<u>GENERAL RESULT</u>
<p><u>3. LUMINESCENT</u></p> <p>(a) Temperature dependence of luminescent intensity I_L from 77° to 120°K.</p> <p>(b) I_L vs. F at $T \sim 80^\circ\text{K}$ from $0.01 F_{\text{max}}$ to F_{max}.</p>	<p>Rapid decrease of I_L above $T \sim 95^\circ\text{K}$ $I_L \propto \exp(-E_L/kT)$ with E_L between 0.11 and 0.16ev.</p> <p>$I_L \propto F^2$ throughout range of F or $I_L \propto F^2$ at high F changing to near linear dependence at low F. or linear dependence.</p>
<p><u>4. OPTICAL</u></p> <p>(a) Spectral dependence of green luminescence at 80°K.</p> <p>(b) Infra-red quenching at 80°K. at room temperature</p>	<p>In agreement with published results.</p> <p>First peak at about 5140 A.U. and further equally spaced peaks resulting from simultaneous phonon emission.</p> <p>Heat treatment in vacuum reduces intensity.</p> <p>In 7-11μ region no response. 1-2μ quenching of photoconductivity. 1-2μ quenching of photoconductivity Quench increased by heat treatment. Non-luminescent samples tend to show larger quench than luminescent crystals.</p>

TABLE 1 (cont).

CRYSTAL	SLOPE $I_L \propto T$ ϵ_L ex.	T_{at} T_{max}	I_L F	n vs. T			n vs. F GRADIENT *		AFTER HEAT TREATMENT n at $F = F_L$	ROOM TEMP. MEASUREMENTS
				n_{80} cm^{-3}	n_{110} cm^{-3}	J_{80} ev *	J_{110} ev *	$F < F_L$ $F > F_L$		
EM1424C	0.14	95°K	F^{21}	2.15×10^{14}	2.45×10^{14}	0.05	0.07	-	-	-
W.D.	0.16	84°K	$F^{21} (high)$ $F^{21} (low)$	1.1×10^{13}	1.5×10^{12}	0.07	0.12	-	-	-
W.F.I.	0.15	84°K	-	1.6×10^{13}	1.5×10^{12}	0.06	0.12	0.6	1.37	-
EM1424B	0.11	83°K	-	2.7×10^{14}	4.2×10^{14}	0.05	0.07	-	-	-
WH1	-	-	-	4.8×10^{12}	2.9×10^{13}	0.07	0.09	0.78	1.25	$J = 0.27$ (u.v) after heating
WH2	-	-	-	5.6×10^{11}	-	0.09	-	0.54	1.25	$J = 0.26$ (u.v) after heating
L3A	0.15	81°K	F^2	1.1×10^{11}	8.5×10^{10}	0.10	0.146	-	1.12	-
EM120	-	-	-	5.8×10^{13}	-	0.056	-	-	1.08	$J = 0.46$ under u.v. excitation
B3.	0.112	95°K	F^{11}	9×10^{13}	7.7×10^{12}	0.055	0.10	0.6	0.6	$J = 0.29$ under u.v. excitation
L.2.	-	-	-	1.2×10^{14}	3.4×10^{14}	0.053	0.067	0.7	-	-

TABLE 2. Summary of the results.

* F_L denotes the excitation density at the onset of visible emission.
 J_{80} denotes position of the electron Fermi level below the conduction band at 80°K.

COMPUTATION CODE.	N_1 cm^{-3}	N_2 cm^{-3}	N_3 cm^{-3}	E_1 eV	E_3 eV	$\frac{1}{2} \times 10^3$ ($^{\circ}\text{K}$)	GENERAL REMARKS.	$I_L \propto F$ PREDICTED ON MODEL A.	$I_L \propto 1/T$	n at 77K cm^{-3} at $F=10^{19}$ $\text{ph. cm}^{-2}\text{sec}^{-1}$	I_L max.
A	10^{15}	10^{15}	10^{15}	0.135	0.145	7, 9, 11, 13	Supralinearity F 10^{16} – 10^{18} range. $n \propto F^{1/2}$ for $F > 10^{18}$. $T > 90^{\circ}\text{K}$, Supralinearity lost.	1.6–2	0.22 eV	10^{12}cm^{-3}	10^{15}
B	10^{15}	10^{15}	10^{16}	"	"	7, 9, 11, 13	No supralinearity, $p > n$ for $F > 10^{14}$. p linear with F .	1.5	0.16	10^{10}	10^{14}
C	10^{16}	10^{15}	10^{16}	"	"	7, 9, 11, 13	Supralinearity. $p_i >$ than in A. Effect of increased temp., more excitation necessary to fill Ni centers	2.0	0.16	3×10^{10}	$10^{15.5}$
D	10^{16}	10^{15}	10^{16}	0.145	0.145	7, 9, 11, 13	Supralinearity (1.6) $10^{17} < F < 10^{19}$. increase in value of p_i compared to (C) at given F .	2.0	0.17	10^{11}	10^{16}
E	10^{15}	10^{15}	10^{16}	"	"	7	as B. p_i increased.	1.3	—	10^{10}	10^{15}
E'	10^{17}	10^{15}	10^{16}	"	"	7	at $F \sim 10^{16}$ n increases sharply by three orders of magnitude.	$\frac{F^2}{F^{1.3}}$		10^{14}	10^{18}
H	10^{15}	10^{15}	5×10^{15}	0.135	0.145	7, 9, 11, 13	Linear.		0.18	3×10^{10}	$10^{13.5}$
I	10^{15}	10^{16}	10^{15}	"	"	7, 9, 11, 13	$n \propto F^{1.5}$ $10^{16} < F < 10^{18}$ p_i and p reduced cf. A.	1.9	0.25	3×10^{11}	$10^{15.5}$
I'	10^{15}	10^{16}	2×10^{15}	"	"	7, 9, 11, 13	$n \propto F'$, n slightly reduced cf I at higher excitation.		0.22	10^{11}	10^{14}
W	5×10^{14}	10^{15}	10^{15}	"	"		$n \propto F^{1.1}$	1.9	0.19	1.4×10^{11}	10^{14}
Z	5×10^{14}	10^{15}	5×10^{15}	"	"		$n \propto F'$	1.7	0.13	2×10^{10}	10^{13}

F	10^{16}	10^{15}	10^{17}	0.145	0.03	7, 9, 11, 13	$n \propto F^{1/2}$	1.0	0.11 eV	10^{14}	10^{18}
G	10^{16}	10^{15}	10^{16}	"	0.04	7, 9, 11, 13	n increased slightly otherwise same as F.		0.14 eV	2.5×10^{14}	10^{18}
M	10^{15}	10^{15}	10^{16}	"	0.03	7, 9, 11	$n \propto F^{1/2}$, p still linear	1.0	0.14	2×10^{14}	10^{18}
N	10^{16}	10^{15}	10^{16}	"	"	7, 9, 11	$n \propto F'$, breaks to $1/2$ power for $F > 10^{18}$. p slightly decreased towards high F .	1.0	0.14	4.5×10^{14}	10^{18}
O	10^{17}	10^{15}	10^{16}	"	"	7, 9, 11		1.0	—	5×10^{14}	10^{18}

TABLE 3.

General results of individual computations.

SOURCE	CRYSTAL	ELECTRICAL MEASUREMENTS			ϵ_L e.v.	DEPENDENCE OF I_L ON EXCITATION.	I_L at F $\sim 10^{18}$. photons $\text{cm}^{-2} \text{sec}^{-1}$
		$n_{80} \text{ cm}^{-3}$	$n_{110} \text{ cm}^{-3}$	slope n.v.F			
Experiment	L3A	1.1×10^{11}	8.5×10^{10}	1.1	0.15	F^2	5×10^{15}
Computation W	"	1.7×10^{11}	1.6×10^{10}	1.1	0.19	$F^{1.9}$	10^{14}
Computation Z	"	2×10^{10}	1.7×10^{10}	1.0	0.13	$F^{1.7}$	10^{13}
Experiment	B.3.	9×10^{13}	7.7×10^{12}	0.5	0.11	$F^{1.1}$	10^{18}
Computation F	"	1×10^{14}	1×10^{14}	0.5	0.11	$F^{1.0}$	10^{18}
Computation M	"	1.5×10^{14}	4×10^{13}	0.5	0.14	$F^{1.0}$	10^{17}

TABLE 4. Comparison between experimental and computed values.