

RADIATIVE RECOMBINATION IN CADMIUM SULPHIDE

by

KENNETH F. K. YUEN

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M.Sc., University of British Columbia, 1962

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August 1971

APPROVAL

Name: Kenneth F. K. Yuen  
Degree: Doctor of Philosophy  
Title of Thesis: Radiative Recombination in Cadmium Sulphide

Examining Committee:

Chairman: K. E. Rieckhoff

---

K. Colbow  
Senior Supervisor

---

R. F. Frindt  
Examining Committee

---

B. L. Jones  
Examining Committee

---

B. D. Pate  
Examining Committee

---

R. R. Haering  
Examining Committee

---

M. Gershenson  
External Examiner  
Professor  
University of Southern California  
Los Angeles, California

Date Approved: August 27, 1971

## Abstract

Luminescent centers involving Ag impurities were introduced into CdS single crystals through doping with  $\text{Cd}^{109}$  radioisotopes. Thus the Ag concentration increases with time as more  $\text{Cd}^{109}$  decays. This enables a study of photoluminescence as a function of Ag concentration in a given crystal without changing the concentrations of other impurities.

Ag impurities introduced by the radioisotope technique give rise to a new emission band at  $5600 \text{ \AA}$ , in addition to the  $6100 \text{ \AA}$  band present in Ag doped crystals using conventional techniques. The  $5600 \text{ \AA}$  emission is observed to be quenched with increasing Ag concentration at high concentrations. In addition concentration quenching by the Ag impurities occurs for the green edge, and the bound-exciton emissions,  $I_1$  (neutral acceptor) and  $I_2$  (neutral donor). The quenching effects are explained on the basis of a model assuming a donor-acceptor recombination process.

The new emission band is concluded to arise from the recombination of a bound electron with a bound hole at a distant donor-acceptor pair, with Ag as the acceptor. The acceptor role of Ag is supported by electrical conductivity measurements on  $\text{Cd}^{109}$  doped crystals. Estimates are obtained for the acceptor binding energy, the donor concentrations, and the separations of the pairs responsible for the new  $5600 \text{ \AA}$

emission and the green edge emission. The 6100 Å emission band is attributed to recombination at Ag centers closely associated with other impurity atoms. These conclusions are verified by our temperature annealing and quenching experiments.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

Luminescence of II-VI compounds, particularly that of zinc sulphide and cadmium sulphide, has been extensively studied. Investigations have been carried out on both unintentionally doped or "pure" and impurity-activated systems. A great deal of progress has been made in understanding the radiative recombination mechanisms and the nature of the centers responsible for the luminescence. Still much remains to be done before a complete understanding can be claimed; one of the reasons for this can be attributed to the difficulty of obtaining a sufficiently high degree of purity in these compounds. Usually several emission bands are observed in a material with only one kind of intentionally introduced impurity. In addition, emission bands of different origins may overlap, which often complicates the analysis and may sometimes have given rise to incorrect interpretations.

Many workers (Prener and Williams 1956; Blount, Phipps and Bube 1967; Thomas, Dingle and Cuthbert 1967; Era, Shionoya and Washizawa 1968; Gutsche and Goede 1970) have proposed association of impurities (both foreign atoms and native defects) as centers giving rise to the luminescence observed. If association of impurities is important in a

luminescence process then an impurity introduced into a crystal through the decay of radioactive host atoms is expected to give an emission different from that of the same chemical impurity which is incorporated into the crystal using conventional techniques, such as diffusion or doping during crystal growth. This thesis describes a study of luminescence in CdS single crystals into which Ag impurities are continuously introduced through the decay of radioactive  $\text{Cd}^{109}$ .

In the next two sections a brief review of the photoluminescence spectrum and the emission processes of pure and Ag doped crystals of CdS is given. Information on the luminescent properties of CdS (and other II-VI compounds) can be found in a book edited by Aven and Prener (1967), a book by Ray (1969) or in a review article by Shionoya (1970).

## 1.2 PURE SINGLE CRYSTALS OF CdS

The photoluminescence spectrum of pure single crystals of CdS generally exhibits two distinct features. At low temperature and under high excitation intensity it consists of;

a) many narrow emission lines in the spectral region of  $4860\text{\AA}$  to  $5100\text{\AA}$  and

b) broad emission bands in the green region between  $5100\text{\AA}$  and  $5600\text{\AA}$ .

a) The Sharp Emission Lines

The origin of many of the sharp emission lines is understood. These lines are attributed to the annihilation of excitons, both free excitons and excitons bound to various impurities (Thomas and Hopfield 1961, 1962; Reynolds and Litton 1963). Information on these lines can be found in a review article by Reynolds, Litton and Collins (1965).

At liquid helium temperature the main exciton emission lines are the so-called  $I_1$  and  $I_2$  lines (see figure 4.1). Thomas and Hopfield (1961) studied the Zeeman effect of these lines and made the following identification: the  $I_1$  line arises from the decay of an exciton bound to a neutral acceptor and the  $I_2$  line is due to the annihilation of an exciton bound to a neutral donor. In addition emission from the decay of an exciton bound to an ionized donor was also identified (the  $I_3$  line). On the other hand an exciton cannot be bound to an ionized acceptor, as shown by Hopfield (1964), because of the large effective hole mass to effective electron mass ratio in CdS (about 4).

The donor impurities can be many of the groups III and VII elements (Thomas, Dingle and Cuthbert 1967; Nassau, Henry and Shiever 1970) and the acceptors of the  $I_1$  line are most likely Li and Na atoms on Cd sites (Henry, Nassau

and Shiever (1970). The precise binding energy of an exciton to a donor or an acceptor impurity depends on the chemical nature of the center. However the excitons are bound only weakly to the donor and acceptor centers; hence they become dissociated at higher temperatures (40°K). At liquid nitrogen temperature only free exciton emission lines are observed.

Measurements of the excitation spectrum of the bound-exciton luminescence by Conradi and Haering (1968, 1969) and by Park and Schneider (1968) have shown that an exciton bound to a center may be produced through capture of a free exciton by the center, or directly creating an exciton at the center. The excitation spectra also show strong oscillatory behaviour with a period equal to the longitudinal optical phonon (LO) energy.

In CdS the exciton Bohr radius is about 30Å. The binding energies of excitons to ionized and neutral donors are about 4 and 7 meV respectively, and 18 meV for neutral acceptors (Thomas and Hopfield 1962). For a hydrogenic impurity in the CdS lattice whose static dielectric constant  $\kappa$  is about 10 (Berlincourt, Jaffe and Shiozawa 1963) the Bohr radii corresponding to binding energies of 4, 7 and 18 meV would be about 180, 100 and 40Å using the hydrogenic energy equation

$$a = \frac{e^2}{2\kappa E_D}$$

where  $E_b$  is the binding energy,  $a$  is the Bohr radius and  $e$  is the electronic charge. Partly because of the large spatial extent of the bound excitons, the  $I_1$  and  $I_2$  emissions can be quenched by the introduction of a third impurity (chapter 5).

#### b) The Broad Bands

The broad-band emission, known also as the green edge emission, consists of series of bands separated by regular intervals (Kroger 1940; Klick 1951; Pedrotti and Reynolds 1960). The lower intensity bands at longer wavelengths are the phonon replicas of the first band through the simultaneous emission of one or more LO phonons. In general two series of bands have been observed although as many as five series have been reported (Kingston, Greene and Croft 1968).

The zero-phonon peaks of the two series occur at about 5140 and 5180Å. In addition to being temperature dependent, the relative strength of the two series varies from crystal to crystal and with excitation intensity. The low energy series is usually dominant at 40°K while at 77° K only the high energy series is observed.

Different techniques of investigation supported the view that the low energy series arises from recombination of an electron trapped at a donor with a hole trapped at an acceptor (Pedrotti and Reynolds 1960; Colbow 1966; Henry, Faulkner and Nassau 1969). On the other hand there are two

conflicting views about the origin of the high energy series. One group (Pedrotti and Reynolds, 1960; Colbow 1966; Thomas, Dingle and Cuthbert 1967) attributed it to a free electron to bound hole recombination while some other workers (Gross, Razbirin and Permogorov 1965; Maeda, 1965; Condas and Yee 1966), supported a bound to bound transition model, the same as for the low energy series.

Pedrotti and Reynolds (1960) based their proposal on the temperature dependence of the intensities of the two series. Colbow (1966) investigated the time-resolved photoluminescence spectra as a function of temperature. From the peak shift of the bands with time and temperature he concluded that one of the series is a bound to bound while the other arises from a free to bound transition. Recently Henry et al (1969) observed, using argon-laser radiation as exciting source, discrete donor-acceptor pair lines which appeared to converge on the zero-phonon peak of the low energy series. This led them to identify the low energy series as a bound to bound recombination at distant pairs.

Gross et al (1965) also postulated that both series are donor-acceptor bound to bound recombinations of different shallow donors but the same deep acceptor. One objection to this model arises from the implication that an electron bound to the deeper of the two donor centers would thermally be ionized first, since the high energy emission predominates at



higher temperatures (Colbow, 1966). Maeda (1965) came to his conclusion of bound to bound transitions for both bands on the basis of thermal quenching of the luminescence. Condas and Yee (1966) based their proposal on a small shift of the peak of the high energy band with excitation intensity; however this is believed to be an incorrect interpretation. The correct explanation of this shift is more likely in terms of free carrier screening (Colbow and Nyberg 1967, Colbow and Dunn 1970).

Recently Gutsche and Goede (1970) questioned the above proposed models for the two series and suggested that both series of the edge emission arise from bound to bound transition between closely associated, rather than distant, donor-acceptor pairs. They based their conclusions on line widths and polarization measurements as a function of temperature. However, we question their interpretation. Our own observation on Cd<sup>109</sup> doped crystals, which is relevant to the edge emission as well, of a large peak shift of the green band due to the increasing Ag acceptor concentration in the crystal, suggests that the green emission is distant donor-acceptor pair recombination (chapter 5).

### 1.3 Ag Doped CdS Crystals

Luminescence of impurity-activated CdS crystals has not been studied as extensively as that of pure crystals. Of the many impurity-activated CdS systems probably the most studied

is the ordinary Ag doped system (CdS:Ag) that is doped during crystal growth or subsequent diffusion. The luminescence spectrum of a Ag doped crystal usually shows, even at low temperature, only a broad structureless band at about  $6100\text{\AA}$  (figure 4.1).

Schön (1942) and Klasens (1946) suggested that the recombination between free electrons and holes trapped at impurity centers is responsible for the emission in CdS:Ag. Lambe and Klick (1955) reversed the role between electrons and holes and proposed that the luminescence results from the recombination of free holes and trapped electrons. These suggestions formed the basis of two models often used in describing broad-band luminescence of II-VI compounds.

Lambe and Klick (1955) based their proposal on the simultaneous measurements of photoconductivity and photoluminescence. They introduced the model assuming free holes instead of free electrons to interpret the fact that photoconductivity has a time constant much larger than that of photoluminescence. From the observation of the effect of infrared radiation on both conductivity and luminescence they further proposed that the system has a recombination level about 0.4 eV from the bottom of the conduction band and a hole trap about 1 eV above the valence band.

Van Gool (1958) investigated Ag-activated CdS with Ga or Cl as coactivator and found that the fluorescence at low

temperature shows two bands with maxima at  $6200\text{\AA}$  and  $7300\text{\AA}$ . High Ag concentration and low coactivator concentration favours the high energy emission band; otherwise the low energy band predominates. It was also observed that annealing at low temperature ( $\approx 300^\circ\text{C}$ ) of crystals already fired at high temperature promotes the high energy emission. This led Van Gool to suggest that the short-wavelength center is probably an associate of at least two lattice defects; however he did not specify whether interstitial or substitutional Ag is involved. Gurvich et al (1965) later reported that luminescence at  $7400\text{\AA}$  could be produced by heating crystals in  $\text{CdCl}_2$  vapour and concluded that this emission originates from  $\text{Cl}_2$  molecules in the crystals.

Recently Brown et al. (1970) applied time-resolved spectroscopy to study the emission of Ag doped CdS powder and single crystals. They reported three different emissions, all in the  $6100\text{\AA}$  region. They were able to distinguish between them because of different decay times. However one of the emissions is difficult to produce and another one occurs only in samples which were doped in the presence of nitrogen, suggesting that it must be associated with nitrogen impurities. For the Ag emission they proposed, without specifying distant or associated, a donor-acceptor pair model with interstitial Ag as the donor.

Emission in the  $6100\text{\AA}$  wavelength region has also been

observed in some pure crystals (Lehmann 1966; Goede 1968; Brown, Cox, Shand and Williams 1970). This observation caused Lehmann (1966) to doubt the interpretation that the 6100Å emission originates from Ag centers. However this uncertainty has been removed (chapter 5).

To summarize: emission in Ag doped crystals has only seen limited investigation. Three different models have been suggested for the recombination process: free electron to bound hole, free hole to bound electron and pair recombination.

#### 1.4 Radioisotope Technique

Radioisotope or tracer techniques have been employed widely in diffusion studies. But the method of introducing impurity atoms into a crystal through the decay of radio-active host atoms for luminescence studies has been used only sparingly (Prener and Williams 1956; Potter, Aven and Kastner 1962; Broser and Franke 1965; Blount, Phipps and Bube 1967). All these investigations were made in ZnS.

Prener and Williams prepared ZnS powder with radio-active Zn<sup>65</sup>. They detected no change in the emission spectrum over a period during which the copper content, as a result of the decay, increased to six times the original copper content. They concluded that randomly distributed copper impurities do not give rise to emission and proposed that the copper emission originates from associated donor-acceptor pairs with copper as the acceptor. This associated pair model has often

been used in describing luminescence of II-VI compounds.

If practical, there are several advantages in using radioisotope over conventional doping techniques in studying luminescence processes in solids:

1. In a given isotope doping, provided that no radiation damage is created from the decay, any emission arising as a result of increased daughter concentration can be unambiguously attributed to the daughter impurity atoms.

2. In general a random distribution of the daughter atoms is expected using the isotope technique. Therefore if an emission arises from an impurity only if the impurity is associated with another defect, this nature of the luminescent center will be revealed.

3. A "true" relationship between luminescence efficiency and impurity concentration can be established since the concentration of the given impurity is the only parameter which varies in the crystal, other properties of the crystal being kept constant. This assumes surface changes, room temperature diffusion and radiation damage are negligible.

4. If a particular impurity, introduced through normal doping, always associates itself with other defects at high temperatures, then the way of determining its "isolated" energy state in the forbidden gap is through the isotope doping technique, or ion implantation.

5. The luminescence efficiency of a recombination process

of one chemical impurity may be dependent on the concentration of a different chemical impurity. This dependence may be observed directly and continuously as the concentration of the daughter impurity increases.

Certain requirements have to be met before the isotope technique is feasible and practical in luminescence studies:

1. The optical absorption coefficient of the compound must be large for photoluminescence studies; otherwise the activity required would be too high.

2. For a given material and a particular impurity of interest there must be a corresponding isotope available with a reasonable half life, preferably of the order of months.

3. The selected isotope should produce little or no radiation damage as this could complicate the analysis.

#### 1.5 Present Work

The main part of this thesis describes a study of the luminescence in CdS single crystals into which Ag impurities are continuously introduced through the decay of radioactive  $\text{Cd}^{109}$  whose half life is 453 days. In a given  $\text{Cd}^{109}$  doped crystal, the Ag concentration increases continuously with time as more of the  $\text{Cd}^{109}$  decays. This enables us to study photoluminescence as a function of Ag concentration in that crystal without changing the concentration of other impurities.

In particular:

- 1) The Ag impurity derived from the decay of  $\text{Cd}^{109}$  gives

rise to a new emission band, which is not present in conventionally doped Ag; the concentration dependence of this band is studied. Association of impurities to form a luminescent center have to be invoked, and a model is postulated which accounts for the difference observed between normal and isotope doped CdS:Ag.

2) The concentration quenching of the green edge emission by the derived Ag is interpreted quantitatively. The simultaneously observed shift of the green peak position provides information on the luminescence process of the green edge emission.

3) Quenching of the  $I_1$  and  $I_2$  emissions is observed and interpreted qualitatively.

## Chapter 2

### EXPERIMENTAL DETAILS

#### 2.1 Crystal Preparations

All crystals used were good quality single crystals grown by the vapour phase transport technique using argon as a carrier gas. Figure 2.1 shows the crystal-growing apparatus. The source material was Eagle-Picher<sup>a</sup> UHP grade CdS powder. The quartz tube was 1" in diameter and 30" long. The gas flow rate was regulated at 60 cm<sup>3</sup> per minute. Temperature at the source was about 900°C with a temperature gradient of about 5°C per inch along the quartz tube. Crystals obtained were in form of platelets. Length of time for growth was about 2 days.

The as-grown crystals were highly insulating, which indicates high compensation. Under high intensity UV excitation they showed intense green dege and bound-exciton I<sub>1</sub> and I<sub>2</sub> emissions at 2°K. For crystals which were annealed for 20 hours at 850°C under saturated cadmium vapour pressure the shallow donor concentration was estimated to be in the range of 1 to 5 x 10<sup>16</sup> cm<sup>-3</sup>, based on room temperature conductivity measurements and an assumed mobility of

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a. Eagle-Picher Co., Cincinnati, Ohio. The powder was from Lot 97.



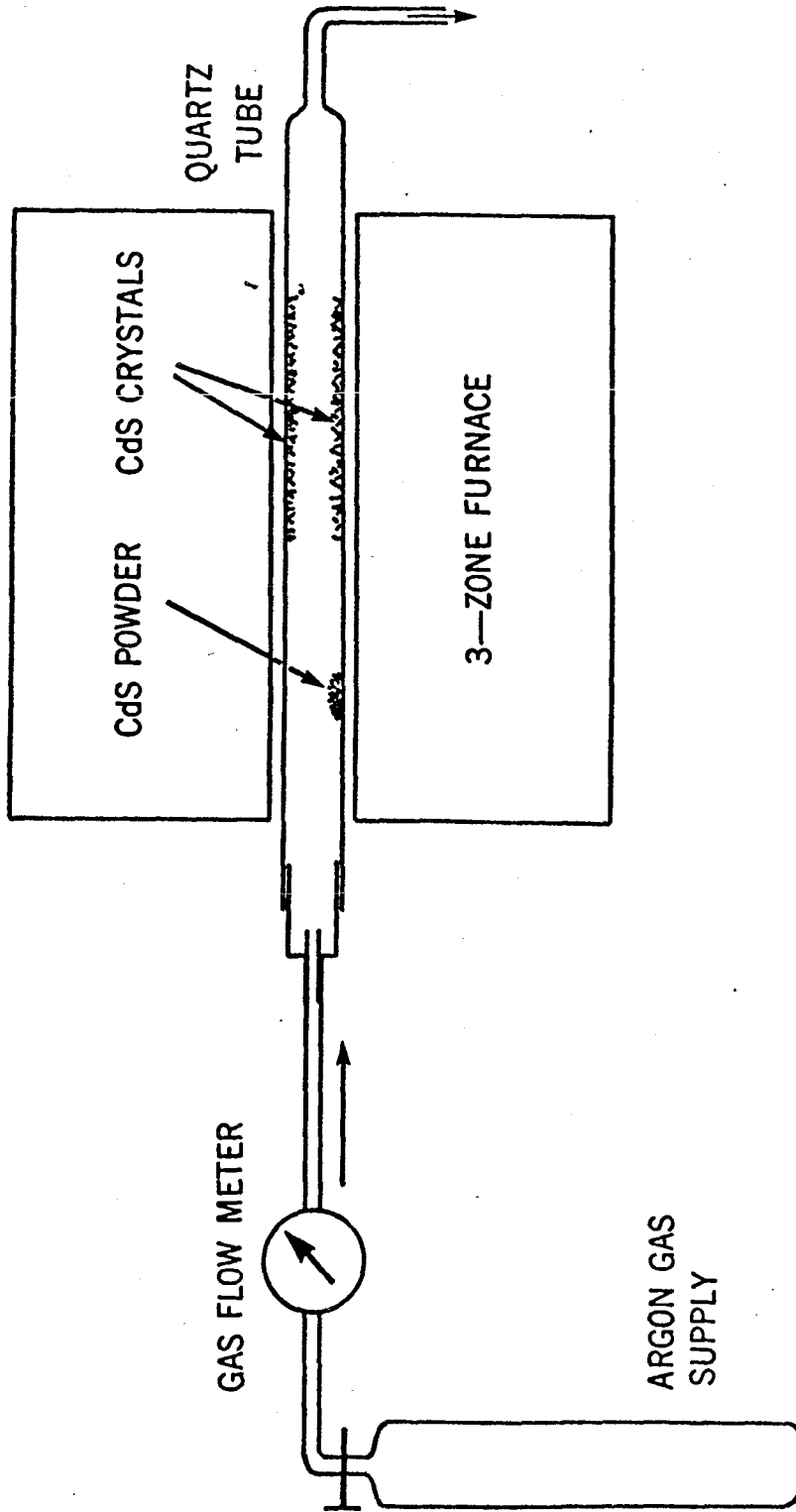


Figure 2.1 Crystal-growing apparatus.

$300\text{cm}^2 \text{ v}^{-1} \text{ sec}^{-1}$  (Spear and Mort 1963). This was based on the assumption that the annealed crystals are uncompensated and the shallow donors are completely ionized.

The radioactive  $\text{Cd}^{109}$  had to be purchased in the form of  $\text{Cd}(\text{NO}_3)_2$  solution<sup>b</sup>. The  $\text{Cd}^{109}$  was reactor-produced by neutron irradiation of  $\text{Cd}^{108}$  and the solution therefore contained a large amount of the stable  $\text{Cd}^{108}$ . From the  $\text{Cd}^{109}$  decay Ag was also present in the solution. The ratio of  $\text{Cd}^{109}$  to stable Cd was approximately 1:5,000. The Cd (both  $\text{Cd}^{109}$  and  $\text{Cd}^{108}$ ) was extracted as metal from the solution using electrolysis (see, for example, Vogel 1944). A technique described by Woodbury (1964), which involved reducing  $\text{CdO}$ , was attempted but resulted in black doped crystals. In each electrolysis about 2 mc of activity of  $\text{Cd}^{109}$  was used. The solution was made faintly alkaline with KOH and then enough KCN was added to keep the Cd in the solution i.e. containing the complex  $\text{K}_2(\text{Cd}(\text{CN})_4)$ . The final volume of the solution used for the electrolysis was about 7 ml. Usually the collecting efficiency was between 80 and 90% with about 4 mg of Cd metal deposited on the platinum electrode (cathode). The platinum electrodes employed were thin strips of about 2mm x 10mm each. Before use they were rendered grease-free

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b. Radioactive  $\text{Cd}^{109}$  were purchased from both The Atomic Energy of Canada Ltd., Ottawa, and New England Nuclear Corp., Boston.

by heating them to redness. The voltage and current used were about 5V and 6ma respectively, providing a smooth deposit of Cd on the platinum electrode.

The  $\text{Cd}^{109}$  atoms were introduced into the crystals by diffusion. A  $\text{Cd}^{109}$ -deposited platinum strip was placed in a quartz tube containing several crystals (usually between 4 and 6). Each of the crystals was a few mm long and about a mm thick. The tube was first evacuated to a pressure of about  $10^{-5}$  mm Hg and was then sealed off under vacuum with an oxygen torch, taking care not to evaporate the Cd. The sealed-off volume was less than  $1 \text{ cm}^3$ . The sealed tube was then heated in a 3-zone Linde furnace. The temperature was held constant to within  $5^\circ\text{C}$  for the desired time. The tube was then cooled to room temperature usually in about 2 hours.

After the diffusion usually two of the six  $\text{Cd}^{109}$  doped crystals were given a subsequent heat treatment in vacuum. The chosen crystals were sealed in a quartz tube of a larger volume, about  $10 \text{ cm}^3$ . As before the tube was evacuated to a pressure of  $10^{-5}$  mm Hg. After the necessary heating time the tube was then cooled rapidly to room temperature. One purpose of this treatment was to produce a different initial luminescence spectrum in some of the doped crystals. Generally crystals showed no green edge emission after the diffusion, but the edge emission could be produced in them if they were subjected to the heat treatment in vacuum, (Handelman and Thomas, 1965). The second purpose was to

increase the concentration of substitutional Ag atoms which are derived from the  $\text{Cd}^{109}$  decay in a crystal. This comes about since on heat treatment in vacuum, in contrast to the diffusion firing which was under saturated Cd vapour pressure, the concentration of interstitial Cd in the crystal is reduced. Consequently a larger fraction of substitutional  $\text{Cd}^{109}$  exists in the crystal.

Prepared from six different diffusion experiments over twenty crystals were doped with  $\text{Cd}^{109}$ . A diffusion temperature of  $600^\circ\text{C}$  and a time of 24 hours were used for most of the diffusions. The diffusion temperature and time together with subsequent treatment (if any) for the crystals considered in this thesis are given in table 4.1. The choice of temperature and time was based on the diffusion data measured by Woodbury (1964). One criterion is that the diffusion length must be much greater than the penetration depth of the exciting radiation, i.e.  $(4Dt)^{\frac{1}{2}} \gg \frac{1}{\alpha}$  where D and t are diffusion coefficient and time respectively. This condition is sufficient for optical excitation because diffusion of generated carriers is much less than  $\frac{1}{\alpha}$  (Colbow and Nyberg, 1968).

Also shown in table 4.1 are estimated initial  $\text{Cd}^{109}$  concentrations. For most of crystals considered the thickness of the crystal is much greater than the diffusion length. The absorption coefficient  $\alpha$  is about  $10^5 \text{ cm}^{-1}$  for close to band gap radiation (Gutsche and Voigt, 1967). Hence all of

the photogenerated electrons and holes are in the region very close to the surface of the excited crystal. It is therefore required to know the concentration only in this region. Knowledge of the volume concentration at the surface should be sufficient for this purpose since  $(4Dt)^{1/2} \gg \frac{1}{\alpha}$  for all crystals. In these estimates the concentration profile is assumed to be given by (Woodbury, 1964)

$$C = C_s \operatorname{erfc} \left[ \frac{x}{(4Dt)^{1/2}} \right] \quad (2-1)$$

where  $C_s$  and  $C$  are the volume concentration at the surface and at a distance  $x$  respectively. The  $D$  values used were those measured by Woodbury (1964) for undoped CdS crystals under saturated Cd pressure, conditions similar to those in our experiments.

Relative activities of the crystals were measured using a Geiger-Muller counter. Absolute activity was determined using a 3 x 3 NaI(Tl) detector with the data processed in a PDP-15 computer and a Northern 4096-channel ADC unit. In the absolute activity measurements the particles counted were the 87.7 Kev gamma. The measurements of absolute activity were undertaken by Mr. T. Bennett of the Chemistry Department. For most crystals the measured activity of each crystal was between 1 to 10 $\mu$ c.

To obtain the volume concentration of Cd<sup>109</sup> at the surface of a doped crystal equation (2-1) is integrated with respect to  $x$ . One obtains

$$\int C_A dx = C_s A \int \operatorname{erfc} \left[ \frac{x}{(4Dt)^{1/2}} \right] dx = N$$

where A is the surface area of the crystal and N is the total  $\text{Cd}^{109}$  atoms in the crystal, which is given by the measured  $\text{Cd}^{109}$  activity. For the last three crystals in table 4.1, the thickness of the crystal is less than the diffusion length. The  $\text{Cd}^{109}$  concentration is simply the number of  $\text{Cd}^{109}$  atoms divided by the crystal volume.

The procedure for diffusing Ag and Cl impurities into CdS crystals is identical to that described for diffusing  $\text{Cd}^{109}$ . Depending on the requirement the fired crystals were either annealed or cooled rapidly to room temperature.

## 2.2 Photoluminescence Measurements

For a given  $\text{Cd}^{109}$  doped crystal the photoluminescence spectrum was taken at various time intervals after the  $\text{Cd}^{109}$  doping. The first measurement was usually taken a day or two after the doping when the amount of  $\text{Cd}^{109}$  decayed into Ag is less than 1/2%. Some crystals were studied more extensively than others. Most of the studies were made at 2°K. Some measurements at 77°K were also taken.

The experimental arrangement for luminescence study is similar to that previously described (Nyberg and Colbow, 1967) and is illustrated schematically in figure 2.2. The crystals were mounted lightly with rubber cement on a brass block attached to the end of a long stainless steel rod. They were immersed in

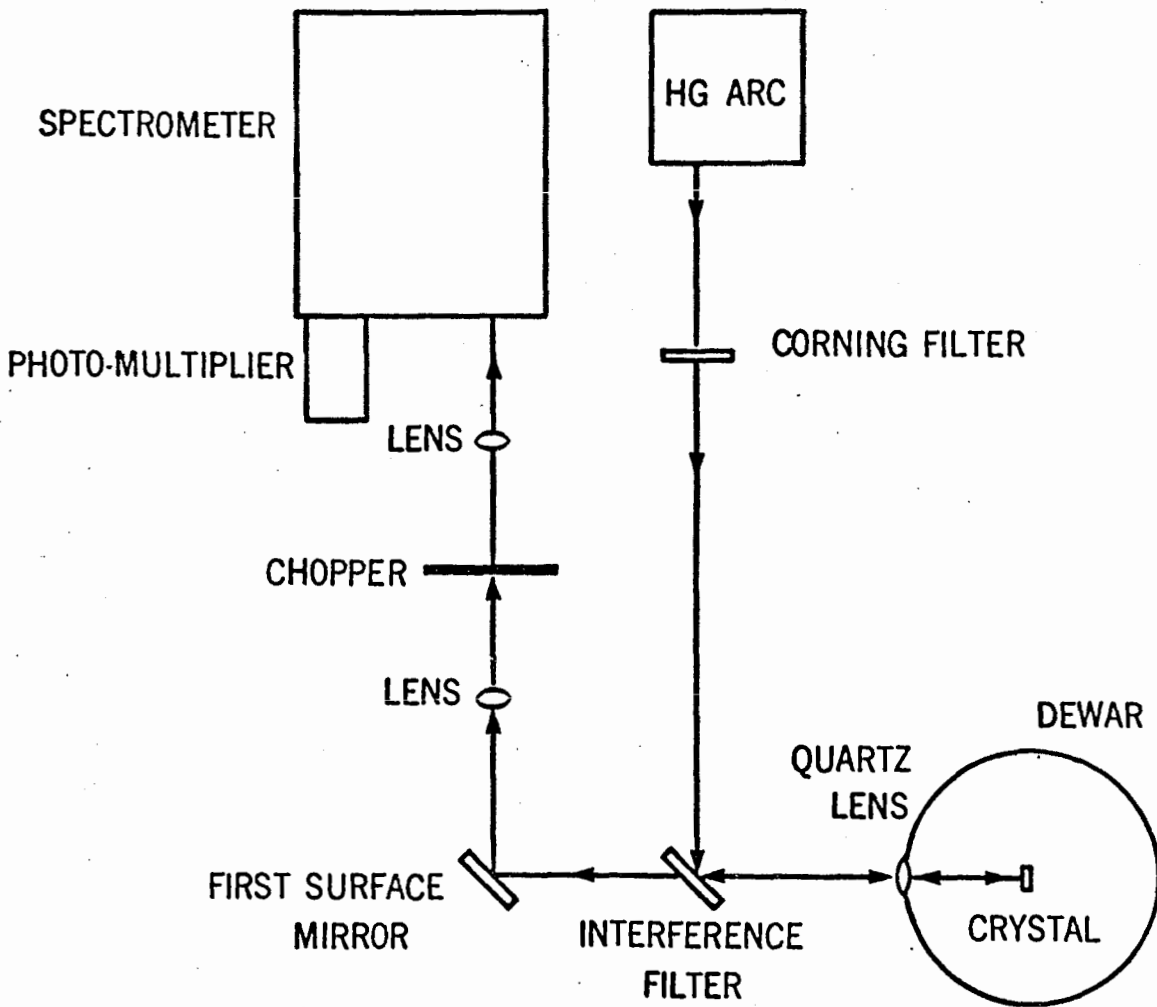


Figure 2.2 Experimental set-up for photoluminescence measurements.

liquid helium or nitrogen coolant. The excitation radiation is principally the 3650 Å band from a PEK Lab (Model 911) 100 watt high pressure mercury arc. This band is transmitted by the Corning 7-54 filter. This filter removes from the excitation source the light of the wavelengths of the luminescence under study.

Part of the optical system is common to the excitation and the detection systems. The excitation light is reflected by the interference filter (Optics Technology Inc. Series 6085, Type 450W) which reflects light of wavelengths shorter than 4200 Å incident on it at 45° angle. This reflected light is focussed onto the crystal by a f/2 quartz lens mounted on the glass dewar. The same lens collects the luminescence emitted by the crystal. The luminescence is transmitted by the interference filter, mechanically chopped, and the spectrum is analyzed in second order by a Spex Industries (Model 1700-II) Czerny-Turner spectrometer with a Bausch Lomb 1200 grooves per millimeter grating blazed at 1.3 microns. The light is detected at the exit slit with a EMI (Type 9558) photomultiplier (s-20 response), displayed by a Princeton Applied Research (Model HR-8) phase sensitive detector, and recorded on a Moseley (Model 2D-2A) X-Y recorder. A spectrometer resolution of 2.5 Å half-width was used. The wavelength calibration was done by the sharp emission lines of a low pressure mercury lamp.

It would have been desirable to have a constant excitation for all the spectral measurements of a given crystal.



Alternatively the Hg arc lamp output was monitored, using a RCA 935 (s-5) phototube in each measurement. This was sufficient for the following reason. In most of the Cd<sup>109</sup> doped crystals an emission was present in the luminescence whose intensity is independent of Ag concentration, and could thus be used as a monitor for the excitation intensity. This was true within a variation due to the inhomogeneity of luminescence over the crystal surface. Some crystals are more uniform than others, but over a probable area this variation was less than 10% for most crystals. This emission was used to normalize the excitation intensities for all the spectra of the given crystal. When a change in excitation intensity was required it was done by a Kodak Wratten neutral density filter.

For the photoluminescence of a given crystal as a function of time (i.e. of Ag concentration) the same Hg arc lamp was employed as long as it remained operational. The entire optical apparatus was disturbed as little as possible. The output of a Hg lamp generally decreases due to deterioration; usually after 50-100 hours of operation the output is about 70% of its initial value. As the decrease is most rapid at the beginning of operation a new lamp was normally operated for about two to three hours before using for measurements.

One and sometimes two ordinary Ag doped crystals, serving as control samples, were mounted with the Cd<sup>109</sup> doped crystals. Again within the variation due to surface inhomogeneity the control samples showed no changes in their emission intensities

with time. The purpose of the control samples was to provide some means of ascertaining that spectral changes observed in the Cd<sup>109</sup> doped crystals are really due to the increase of Ag from the decay and not from other effects such as variation of the excitation intensity or possibly even resulted from room temperature annealing. Ordinary Ag doped crystals were chosen as they should have properties most similar to the Cd<sup>109</sup> doped crystals.

It is well known that crystal surface conditions can influence both photoconductivity (Colbow, Jmaeff and Yuen, 1970) and photoluminescence (Nyberg and Colbow, 1967) of a CdS crystal. Oxygen adsorbed on the surface reduces the luminescence efficiency. Supposedly the oxygen is chemically adsorbed as negative ions, which are charge compensated by a depletion layer in the bulk immediately adjacent to the surface. It has been found that the adsorbed oxygen can be removed with UV illumination with the crystal in vacuum. The explanation is that photogenerated holes are attracted to the surface where they neutralize the oxygen ions, which are then free to escape.

In our spectral measurements the crystals were illuminated with UV in vacuum before they were cooled to liquid helium or nitrogen temperatures. This enables us to minimize the variation in photoluminescence efficiency due to the surface adsorbed oxygen. The measurements made when this procedure was deliberately not followed generally were less consistent; as much as

50% reduction in luminescence intensity for a given crystal has been observed.

## CHAPTER 3

### DONOR-ACCEPTOR PAIR RECOMBINATION

#### 3.1 Introduction

In the past decade paired defects of opposite charges, namely donor-acceptor pairs, have become widely recognized as essential entities in semiconductors and luminescent crystals. Reiss, Fuller and Morin (1956) and Prener and Williams (1956) concurrently noted the existence of donor-acceptor pairs in solids. The former studied the effect of pairing on electronic properties in Li doped Ge. The latter proposed that the emission in Cu-activated ZnS originates from electronic transitions in associated donor-acceptor defects.

The most direct and dramatic evidence for radiative recombination at donor-acceptor pairs was found in GaP. The emission spectrum of this compound at low temperature contained many sharp lines. Hopfield, Thomas and Gershenzon (1963) unambiguously identified the spectrum as originating from the many possible separations between donors and acceptors. They analyzed the spectra and were able to assign any particular line to a particular pair separation. Since then evidence for donor-acceptor pair recombination has been accumulating. Discrete donor-acceptor pair lines have been observed in CdS crystals (Henry, Faulkner and Naussau 1969; Reynolds and Collins 1969; Henry, Naussau and Shiever 1970) but their pair separation assignment has not been made. A review on the subject of donor-

acceptor pair recombination has been written by Williams (1968).

### 3.2 Statistical Distribution of Donor-acceptor Pairs

#### 1. Introduction

In interpreting experimental results associated with donor-acceptor pair recombination the first problem is to determine which pairs of the distribution (i.e. what are the separations of the pairs) are responsible for the observations. The second problem is to determine the electronic states of these pairs. The first problem is considered in the present section. The energy of the emission for donor-acceptor pair recombination will be discussed in the next section.

The statistical problem of the distribution function for the distance between charged defects including their coulomb interaction has been investigated mainly for liquid electrolytes. There are two essential differences in the distribution function for the liquid systems and for crystalline solids. For the liquid systems the distribution function is continuous whereas the distribution function for donors and acceptors in crystalline semiconductors is at least for small separations discrete. The other difference is in their equilibrium temperatures. In semiconductors the distribution function is not necessarily an equilibrium property at ordinary temperatures as is the case in liquids. But it can be considered as a quasi-equilibrium characteristic of the temperature during crystal preparation, assuming rapid quenching to room temperature and no appreciable movement over interimpurity distances occurs at room tempera-

ture. Since there is usually a large difference between interstitial and substitutional diffusion rate the characteristic temperature will be markedly different depending on whether both donor and acceptor occupy substitutional sites or at least one occupies interstitial lattice sites.

Bjerrum (1926) and later Fuoss (1934) were the first to consider the quantitative aspects of ion pairing. Despite some limitations the Bjerrum-Fuoss theory has been found satisfactory in the interpretation of experimental data. Reiss (1956) presented a theory of ion pairing dealing with both the equilibrium and non-equilibrium aspects of pairing. In his formulation Reiss is able to remove the use of the law of mass action which is required in the Bjerrum-Fuoss treatment of high ion concentrations in order that charge conservation is satisfied.

The results calculated by Reiss are in good agreement with those of Fuoss' theory. Nevertheless there exists one difference in the resulting expressions of the two theories that is of significance in discussing our data. This point will be discussed in details later. But first we will obtain the distribution function based on an approach taken by Fuoss (see Reiss, Fuller and Morin 1956), which is sufficient for our purpose.

## 2. Theory of Ion Pairing

Consider a solution of dielectric constant  $\kappa$  containing equal concentration  $N$  of negative and positive ions. When equilibrium is established each negative ion will have a positive ion as its nearest neighbour at a distance  $r$  away from it.

The possibility that the nearest neighbour will be another negative ion is discounted. Let  $g(r)dr$  denote the fraction of negative ions whose nearest neighbours lie in spherical shells of volume  $4\pi r^2 dr$  with the negative ions at their origin. The pair distribution function  $g(r)dr$  may be evaluated as follows.

For a given negative ion to have as its nearest neighbour a positive ion at distance  $r$ , the following must occur simultaneously:

1. There is a positive ion at distance  $r, r+dr$ .
2. There is no other ion within radius  $r$ ; otherwise the positive ion would not be the nearest neighbour.

The first probability is given by

$$4\pi r^2 c(r) dr \quad (3-1)$$

where  $c(r)$  is proportional to the concentration  $N$ . In fact  $c(r)$  should exceed  $N$  because of the attraction on positive ions due to the negative ion at the origin.

The second probability,  $Q(r)$ , can easily be shown to be

$$Q(r) = 1 - \int_a^r g(x) dx \quad (3-2)$$

where  $a$  is the distance of closest approach of two ions of opposite signs.

Hence we have the following integral equation

$$g(r) = 4\pi r^2 c(r) \left\{ 1 - \int_a^r g(x) dx \right\} \quad (3-3)$$

whose solution is

$$g(r) = 4\pi r^2 c(r) \exp\left\{ -4\pi \int_a^r x^2 c(x) dx \right\} \quad (3-4)$$

That equation (3-4) satisfies equation (3-3) may be demonstrated by substitution of the former into the latter. Note that  $c(r)$  contains the normalization constant determined by the condition

$$\int_a^\infty g(r) dr = 1 \quad (3-5)$$

#### I. Random Distribution (Unassociated)

If no attractive forces were to exist between ions then  $c(r)$  would be a constant independent of  $r$ . Furthermore if we require that

$$\int_a^{\bar{r}} 4\pi r^2 c(r) dr = 1 \quad (3-6)$$

where

$$\frac{4}{3} \pi \bar{r}^3 = \frac{1}{N}$$

then we have, setting  $a=0$ ,

$$c(r) = N \quad (3-7)$$

The requirement specified by (3-6) simply states that the average volume  $\frac{1}{N}$  should contain about one positive charge.



Therefore the distribution function of random distribution, after substituting  $c(r) = N$  into equation (3-4) and carrying out the integration is

$$g(r) = 4\pi r^2 N \exp\left(-\frac{4}{3} \pi r^3 N\right) \quad (3-8)$$

This function is plotted in figure 3.1 for  $N = 10^{16} \text{ cm}^{-3}$ . We note that the position of the maximum, the most probable distance of location of a nearest neighbour pair, occurs near  $\bar{r} = \left(\frac{3}{4\pi N}\right)^{1/3}$ , the radius of the average volume per particle.

## II. With-interaction (Associated)

To evaluate  $g(r)$  with coulombic interaction we must first compute  $c(r)$  under this condition. We assume that for small value of  $r$  the only interaction is that between the nearest neighbours themselves. Under this assumption the potential energy of interaction is simply

$$v(r) = - \frac{e^2}{kr}$$

and by Boltzmann's law,  $c(r)$  may be written as

$$c(r) = h \exp\left(\frac{e^2}{kTrk}\right) \quad (3-9)$$

Here  $T$  is the equilibrium temperature,  $k$  is Boltzmann's constant and  $e$  is the electronic charge, and if we further require that  $c(r)$  should equal  $N$  at large  $r$ ,  $h$  must be set equal to  $N$  giving

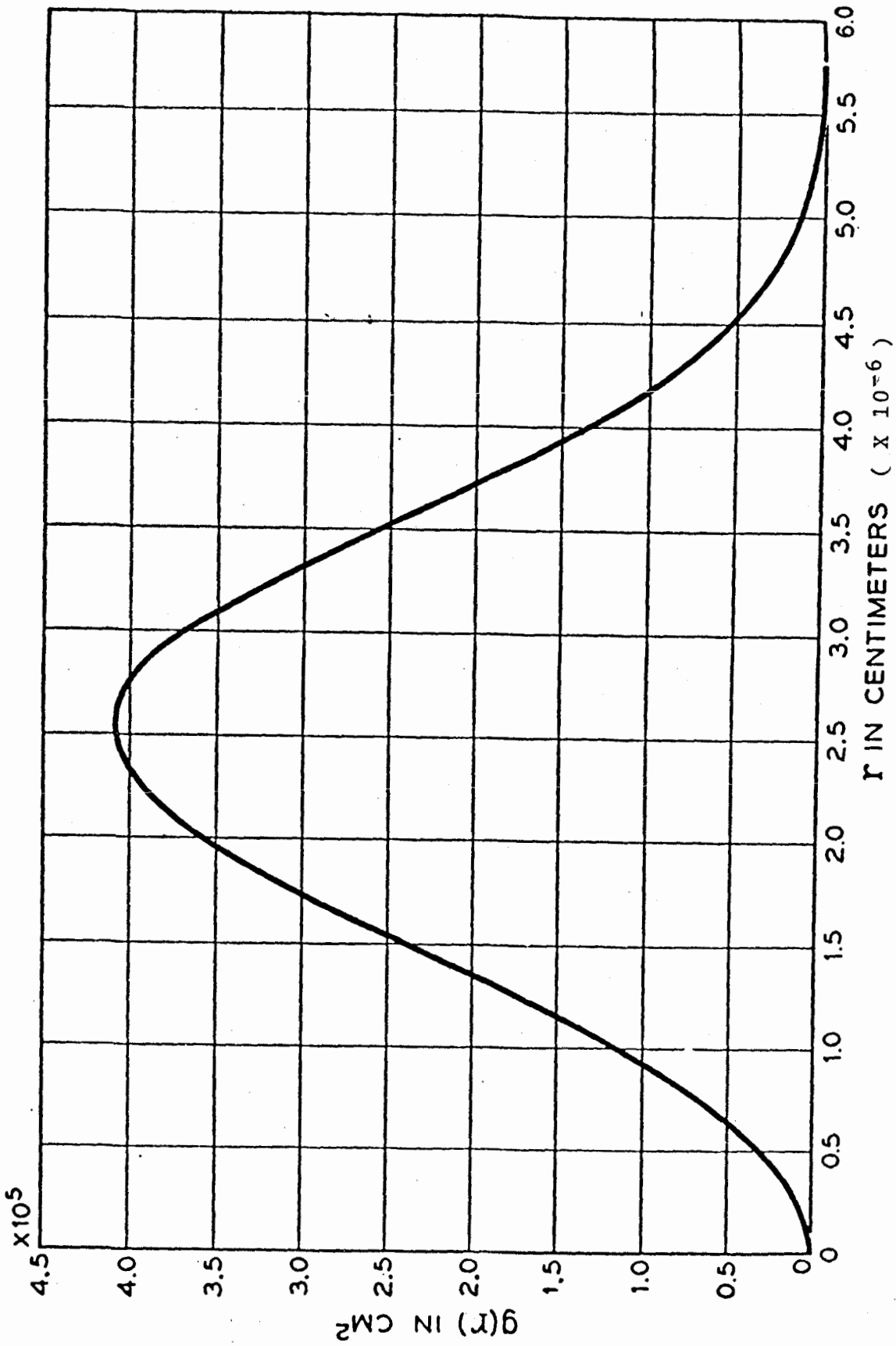


Figure 3.1 The distribution function  $g(r)$  in a random assembly of particles for a concentration  $N=10^{16}$  cm $^{-3}$  (after Reif et al 1956).

$$c(r) = N \exp\left(-\frac{e^2}{\kappa k T r}\right) \quad (3-10)$$

This also satisfies the condition that for very high temperature  $T$ ,  $c(r)$  is equal to  $N$ . Substituting  $c(r)$  from (3-10) into (3-4) we have

$$g(r) = 4\pi r^2 N \exp\left(-\frac{e^2}{\kappa k T r}\right) \exp\left\{-4\pi N \int_a^r x^2 \exp\left(-\frac{e^2}{\kappa k T x}\right) dx\right\} \quad (3-11)$$

Equation (3-11) satisfies the normalization condition:

$$\int_a^\infty g(r) dr = 1$$

This function  $g(r)$  has the form typified by figure 3.2. A large value at  $r = a$  is followed by a long minimum and this by another maximum not unlike the one in figure 3.1.

For low concentration the minimum occurs at

$$r = b = \frac{e^2}{2\kappa k T}$$

Essentially the new  $g(r)$  is the random  $g(r)$  with an exponential grafted onto it. As expected the attractive interaction greatly favours pairs of small separations.

The choice of  $h=N$  gives rise to difficulties for large  $N$  because the integral

$$\int_a^{\bar{r}} 4\pi r^2 c(r) dr = \int_a^{\bar{r}} 4\pi r^2 N \exp\left(-\frac{e^2}{\kappa k T r}\right) dr$$

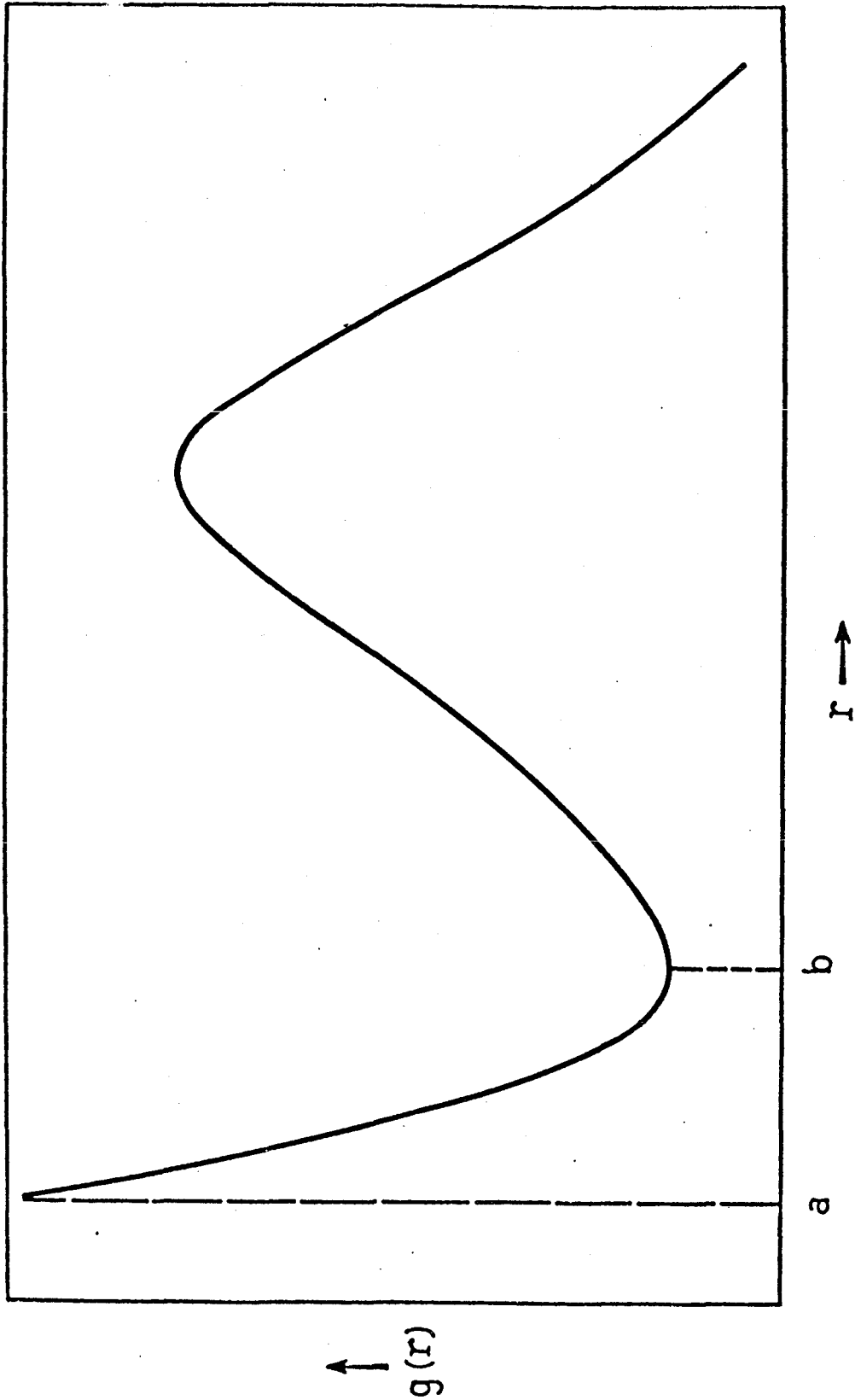


Figure 3.2 Schematic presentation of the distribution function  $g(r)$  in an assembly of interacting particles (after Reiss et al 1956).

where

$$\frac{4}{3} \pi r^3 N = 1$$

can be very much larger than unity.

Fuoss overcomes this difficulty by means of the law of mass action. He assumes paired and unpaired ions are in dynamic equilibrium and that the law of mass action could be applied. (He defines ion pairs with separation  $r < b$  as paired and others as unpaired). Letting  $P$  be the concentration of paired ions the mass action is expressed as

$$\frac{P}{(N - P)^2} = \Omega \quad (3-12)$$

where  $\Omega$  is an equilibrium constant independent of  $N$ . The value  $\Omega$  is first calculated for small  $N$  using equation (3-11) which is valid for small  $N$ . This value  $\Omega$  can then be employed for higher concentration using equation (3-12) to obtain  $P$ .

From Reiss' distribution function Prener (1956) obtained an expression for the fraction of ion pairs  $\alpha_i$  with separation  $r_i$  for impurities in solids at low concentration. He calculated  $\alpha_i$  for oppositely charged impurities occupying  $Z_n$  sites in cubic  $ZnS$  for three temperatures. The results are reproduced in table 3.1.

Thomas, Gershenzon and Trumbore (1964) performed temperature annealing experiments in an effort to detect ion pairing effects

1	$\alpha_i (T=\infty)$	$\alpha_i (1000^\circ\text{K})$	$\alpha_i (500^\circ\text{K})$
1	0.0012	0.124	0.897
2	0.0006	0.013	0.019
3	0.0024	0.025	0.018
4	0.0012	0.008	0.004
5	0.0024	0.012	0.004

Table 3.1 The first five values of  $\alpha_i$  calculated for charged impurities at zinc sites in cubic ZnS with concentration  $c \cdot 10^{-4}$  (after Prener 1956).

in their luminescent pair-line spectra in GaP. Heating crystals at different temperature did not produce any marked changes in the pair spectra. They attributed this partly to the fact that most of the paired ions are ineffective in producing recombination radiation because they are too close to bind electrons or holes separately.

### III. The Exclusion Factor Q(r)

The factor Q(r) in (3-2) is called the "exclusion factor" for it measures the chance that a positive ion is excluded from the enclosed volume  $\frac{4}{3}\pi r^3$ . Comparing equations (3-2), (3-3) and (3-4) we find that the exclusion factor is

$$Q(r) = \exp\left\{ -4\pi \int_a^r x^2 c(x) dx \right\} \quad (3-13)$$

Using the expressions (3-7) or (3-10) for c(r) we have the following for Q(r).

i) Random distribution:-

$$Q(r) = \exp\left( -\frac{4}{3} \pi r^3 N \right) \quad (3-14)$$

ii) With-interaction:-

$$Q(r) = \exp\left\{ -4\pi N \int_a^r x^2 \exp\left(\frac{e^2}{kkTx}\right) dx \right\} \quad (3-15)$$

Since

$$N < N \exp\left(\frac{e^2}{kkTx}\right),$$

$$\exp\left(-\frac{4}{3}\pi r^3 N\right) > \exp\left\{-4\pi N \int_a^r x^2 \exp\left(-\frac{e^2}{\kappa kTx}\right) dx\right\}$$

This implies that in the above treatment of ion pairing the chance of an ion being excluded from the sphere of radius  $r$  is higher in the case of no interaction.

However in Reiss' (1956) treatment of ion pairing the exclusion factor obtained for the case with-interaction is identical to that of the random case i.e.

$$Q(r) = \exp\left(-\frac{4}{3}\pi r^3 N\right)$$

for both random and with-interaction distribution.

From the preceding discussion it is seen that for the case with-interaction the chance of a positive ion being excluded from the sphere of radius  $r$  is higher in Reiss' result than in Fuoss'. Reiss' explanation for the higher  $Q(r)$  is as follows: In Fuoss' approach no account is taken of the repulsive force exerted by the positive ion in the shell  $4\pi r^2 dr$ . This force should increase the probability of not finding another positive ion inside the sphere. Furthermore the effect of the positive ion in the shell compensates that of the negative ion at the center so that to an approximation the chance of occupation of the sphere is measured by the uniform density  $N$  rather than by a concentration that contains the effect of attractive interaction only.



Reiss' result that  $Q(r)$  is identical for both random distribution and distribution with coulomb interaction will be important in analyzing our data. Furthermore, we will assume Reiss'  $Q(r)$  to be the correct one.

The preceding discussions and results on ion pairing in continuous systems are applicable to describing pairing of ionized donors and acceptors in semiconductors. Of course the essential differences between continuous and crystalline systems as discussed previously must be considered.

#### IV. Donor-acceptor Pairs

Reiss, Fuller and Morin (1956) used the distribution function to describe pairings in a semiconductor. To obtain the pair concentration  $P$  for the case where the donor concentration  $N_D$  and acceptor concentration  $N_A$  are unequal they modified the mass action equation (3-12) to

$$\frac{P}{(N_D - P)(N_A - P)} = \Omega$$

and used the same  $\Omega$  as calculated for small  $N$ . The donor-acceptor pairs which are relevant to the interpretations of our data are of order of the mean separation, which is  $(\frac{3}{4\pi N})^{1/3} \approx 290 \text{ \AA}$  for  $N=10^{16} \text{ cm}^{-3}$ . In this case the above modification is not applicable since it omits the possibility that for a given donor (or acceptor) the nearest neighbour will be another donor (or acceptor). This probability becomes appreciable for separations of order or larger than the mean spacing. Nevertheless if one of the concentrations is much larger than

the other the following discussion should be valid.

Let  $N_D$  and  $N_A$  be the donor and acceptor concentration respectively and assume  $N_D \gg N_A$ . If the donors and acceptors are randomly distributed then for a given acceptor the probability of finding a nearest neighbour donor at a distance  $r$  is

$$g(r)dr = 4\pi r^2 N_D \exp\left(-\frac{4}{3}\pi r^3 N_D\right) \quad (3-16)$$

Here the exponential gives the probability of not having a donor inside a sphere of radius  $r$ , and  $4\pi r^3 N_D dr$  is the probability of finding a donor in the spherical shell between  $r$ , and  $r + dr$ . The density  $n(r)dr$  of donor-acceptor pairs of separations  $r, r+dr$  is

$$n(r)dr = 4\pi r^2 N_A N_D \exp\left(-\frac{4}{3}\pi r^3 N_D\right) \quad (3-17)$$

where we have neglected the probability of finding another acceptor at a distance less than  $r$ . This expression for  $n(r)dr$  satisfies the normalization condition:

$$\int_a^\infty n(r)dr = N_A$$

The point to note in equation (3-17) is that the exclusion factor is determined by  $N_D$ , the higher of the two concentrations. We believe the following effects can occur if a donor or an acceptor concentration is allowed to change.

i) Self-quenching of Donor-acceptor Pair Recombination

If  $N_D$  is permitted to increase in (3-17),  $n(r)$  can start to decrease beyond a certain value of  $N_D$ . The luminescence intensity  $I(r)$  for donor-acceptor pair recombination is directly proportional to  $n(r)$  i.e.  $I(r) \propto n(r)$ . Hence if  $N_D$  (or  $N_A$ ) in a given crystal can be made to increase we may find that above a certain value of  $N_D$  (or  $N_A$ ) the intensity  $I(r)$  will decrease as  $N_D$  (or  $N_A$ ) continues to increase. This is the basis of self-quenching of donor-acceptor pair recombination. The value of  $N_D$  (or  $N_A$ ) at which quenching starts will depend on  $r$ . Higher concentration is required to quench emissions of close pairs than distant pairs.

ii) Quenching due to a Dissimilar Species

Suppose we have two species of donors and one acceptor of concentration  $N_{D1}$ ,  $N_{D2}$  and  $N_A$  respectively with  $N_{D1}$ ,  $N_{D2} \gg N_A$ . First the total number of donor-acceptor pairs  $n(r)$  ignoring the difference in donor species, is similar to (3-17),

$$n(r) = 4\pi r^2 N_A (N_{D1} + N_{D2}) \exp \left\{ -\frac{4}{3} r^3 (N_{D1} + N_{D2}) \pi \right\} \quad (3-18)$$

It is obvious from (3-18) that the number of donor-acceptor pairs of each donor species is given by

$$n_1(r) = 4\pi r^2 N_A N_{D1} \exp \left\{ -\frac{4}{3} r^3 (N_{D1} + N_{D2}) \pi \right\}$$

$$n_2(r) = 4\pi r^2 N_A N_{D2} \exp \left\{ -\frac{4}{3} r^3 (N_{D1} + N_{D2}) \pi \right\}$$

Now suppose the donor species  $N_{D2}$  is allowed to increase. This would reduce  $n_1(r)$  exponentially. Consequently the emission intensity of donor-acceptor recombination of one donor species is quenched by an increasing concentration of another donor species present in the same crystal. A similar analysis applies for the case of one donor and two acceptor species.

### 3.3 Transition Energy and Energy Peak Position of Distant Donor-Acceptor Pairs

The ground state of a donor-acceptor pair is characterized by both particles being in their respective ionized states. A donor-acceptor pair is in an excited state when an electron and a hole are captured by the ionized donor and acceptor respectively. Pair emission occurs when the bound electron recombines with the bound hole.

For large separation  $r$  the energy  $E(r)$  of emission for a bound transition between a donor-acceptor pair is given by

$$E(r) = E_g - ( E_d + E_a ) + \frac{e^2}{\kappa r} \pm nE_p \quad (3-19)$$

where  $E_g$  is the band-gap energy,  $E_d$  and  $E_a$  are the donor and acceptor binding energies respectively,  $\kappa$  is the low frequency dielectric constant of the material and  $e$  is the electronic charge. The last term represents simultaneous absorption or emission of  $n=0,1,2,\dots$  phonons of energy  $E_p$ . The rate of recombination  $W$  between the bound electron and the bound

electron and the bound hole is proportional to the square of the overlap of the donor and acceptor wave functions in the Heitler-London approximation. Where the acceptor is much deeper than the donor we have

$$W = W_0 \exp \left( - \frac{2r}{a_D} \right) \quad (3-20)$$

where  $W_0$  is a constant and  $a_D$  is the Bohr radius of the donor.

Let us assume  $N_D \gg N_A$  and suppose a fraction  $f_e(r)$  of the  $n(r)dr$  donor-acceptor pairs of separation  $r$  are in an excited state. Since the transition probability is proportional to  $\exp(-2r/a_D)$  the emission intensity  $I(r)dr$  is given by

$$I(r)dr = n(r)dr \exp \left( - \frac{2r}{a_D} \right) f_e(r) \quad (3-21)$$

Consider the zero phonon emission, the intensity per unit energy at energy  $E$ ,  $I(E)$ , is related to  $I(r)$  by

$$I(E)dE = I(r)dr$$

where  $E$  must be related to  $r$  through equation (3-19) with  $n=0$ . Now using equation (3-19) we obtain

$$dE = - \frac{e^2}{\kappa r^2} dr$$

Hence

$$I(E) = I(r) \frac{dr}{dE} \propto r^2 I(r)$$

Substituting  $I(r)$  of equation (3-21) we obtain

$$I(E) \propto r^2 n(r) \exp \left( -\frac{2r}{a_D} \right) f_e(r) \quad (3-22)$$

As we are dealing only with distant pairs we assume a random distribution for  $n(r)$ . Thus we have

$$I(E) \propto r^4 \exp \left( -\frac{4}{3} \pi r^3 N_D \right) \exp \left( -\frac{2r}{a_D} \right) f_e(r) \quad (3-23)$$

The above description of  $I(r)$  ignores all excess donors which are not nearest neighbours of acceptors. This seems justified, since the overlap integral decreases exponentially with distance from the acceptor, and thus nearest neighbour donors are expected to make a dominant contribution to the recombination rate.

The emission peak energy is obtained by maximizing  $I(E)$ , leading to the following equation

$$-\frac{2}{a_D} - 4\pi N_D r^3 + \frac{4}{r} + \frac{1}{f_e} \frac{df_e}{dr} = 0 \quad (3-24)$$

The solution  $r$  of equation (3-24) gives the pair separation which corresponds to the energy  $E$  of the maximum of  $I(E)$ .

Now  $f_e(r)$  is determined by the rate equation (Hagston 1971)

$$\frac{df_e(r)}{dt} = \{ 1 - f_e(r) \} g \sigma(r) - f_e(r)W$$

where  $\sigma(r)$  is the capture cross-section for pairs separated by  $r$  and  $g$  is the generation rate.

For continuous excitation,

$$\frac{df_e(r)}{dt} = 0$$

Hence we have

$$f_e(r) = \frac{1}{\left\{ 1 + \frac{w}{g} \sigma(r) \right\}}$$

Let us assume that in the region of interest, for separation of  $50 \text{ \AA}$  to  $400 \text{ \AA}$

$$\sigma(r) \propto r^2$$

then equation (3-24) becomes

$$f_e(r) \frac{2r}{a_D} + 4\pi N_D r^3 - 2f_g(r) = 4 \quad (3-25)$$

where  $f_g(r) = 1 - f_e(r)$  is the fraction of pairs of separation  $r$  in the ground state.

We now consider two limiting cases:

1) Saturation limit [ $f_e(r) \approx 1$ ]

For this high excitation limit equation (3-25)

becomes

$$2r/a_D + 4\pi N_D r^3 = 4$$

If  $4\pi N_D r^3 \ll 1$  then  $r = 2a_D$

2) Weak excitation limit [ $f_e(r) \approx 0$ ]

For this case  $r$  is completely determined by the concentration  $N_D$  and is

$$r = \left( \frac{3}{2} \pi N_D \right)^{1/3}$$

Suppose  $a_D = 25 \text{ \AA}$  and  $N_D = 10^{16} \text{ cm}^{-3}$

We then have

$$r = 2a_D = 50 \text{ \AA}$$

and

$$r = \left( \frac{3}{2} \pi N_D \right)^{1/3} \approx 370 \text{ \AA}$$

This shows that for continuous excitation the variation in  $r$  may be large depending on the excitation intensity and the impurity concentration. On the other hand pulse excitation results in a smaller variation in  $r$  (Hagston 1971).

In the above discussion we have assumed the capture cross-section  $\sigma(r)$  of a pair of separation  $r$  to be proportional to  $r^2$ . This seems reasonable from the following consideration. Suppose capture of the first particle by a pair in its ground state (i.e. both donor and acceptor are ionized) is the rate limiting process, say a hole by the acceptor. Because of the coulomb repulsion from the ionized donor, to a first approximation a hole will not be bound to the acceptor unless it comes to within a distance  $R$  of the acceptor where  $R$  is given by

$$\frac{e^2}{2\kappa R} = \frac{e^2}{\kappa r}$$



Hence

$$\sigma(r) \propto R^2 \propto r^2$$

For distant pairs the order of capture may be electron-hole or hole-electron. However, if  $r < a$  where  $a$  is the Bohr radius of the shallower center, say the donor, the electron-hole capture mode will not be operative. Furthermore if  $r$  is also smaller than the acceptor Bohr radius it will not be possible for the pair to capture an electron and a hole independently (Hopfield 1964).

## CHAPTER 4

### EXPERIMENTAL RESULTS

#### 4.1 Introduction

The main results of our study are contained in this chapter. Results of experiments which were performed for the purpose of providing additional information or to re-enforce our interpretations will be given in the following chapter.

The method of our study is based on measuring changes in the emission spectrum of a given  $\text{Cd}^{109}$  isotope doped crystal as a function of Ag concentration (i.e. of time). Accordingly, for a given crystal photoluminescence spectra were recorded at appropriate time intervals after the doping. Since the half-life is known the fraction of  $\text{Cd}^{109}$  decayed in a given crystal can be calculated exactly.

Let  $N_0$  be the initial  $\text{Cd}^{109}$  activity. The activity  $N$  at any time  $T$  is given by the well-known disintegration formula

$$N = N_0 e^{-\lambda t}$$

where  $\lambda$  is the disintegration constant and is related to the half-life  $T_{1/2}$  by

$$\lambda = \frac{0.693}{T_{1/2}}$$

The fraction  $f$  of the  $\text{Cd}^{109}$  decayed is given by

$$f = (1 - e^{-\lambda t})$$

Furthermore if the initial  $\text{Cd}^{109}$  concentration is known the Ag concentration derived from the decay at any time is given.

Photoluminescence of over twenty  $\text{Cd}^{109}$  doped crystals have been studied. The condition of preparation and the initial  $\text{Cd}^{109}$  concentration of the crystals discussed below are given in table 4.1. Some doped crystals have been studied more extensively than others. Results for only some of these are presented, which are considered representative of the entire study.

#### 4.2 Spectra

It is useful to discuss first the spectra of our pure and ordinary Ag doped crystals. The spectrum illustrated in figure 4.1 is typical of the pre-doped crystals used in our experiments, showing the major features at low temperature and under high intensity UV excitation. The green edge emission shows both the high and low energy series. The relative intensity of the various emissions vary slightly from crystal to crystal. The well-defined feature in the phonon replicas gives an indication of the relatively high degree of purity of the crystals.

The spectrum (figure 4.1) shows the broad structureless orange band typical of our ordinary Ag doped crystals.

Crystal	Diffusion of Cd <sup>109</sup>		Subsequent heat treatment		Initial Cd <sup>109</sup> concentration (cm <sup>-3</sup> )
	Temperature (°C)	Time (days)	Temperature (°C)	Time (hrs)	
1	600	1	600	3	1.2 x 10 <sup>17</sup>
3	600	1			1.4 x 10 <sup>17</sup>
4	600	1			1.2 x 10 <sup>17</sup>
13	600	1			6.1 x 10 <sup>16</sup>
14	600	1			7.1 x 10 <sup>16</sup>
15	600	1			
17	600	1	300	0.17	7.6 x 10 <sup>16</sup>
20	700	10			1 x 10 <sup>17</sup>
A	700	10	650	48	1.8 x 10 <sup>17</sup>
B	700	10			2.5 x 10 <sup>17</sup>

The diffusion length  $\sqrt{4Dt}$  is: 16 $\mu$  for 600° C and 24 hours  
 180 $\mu$  for 700° C and 10 days

For crystals 1 to 17 the values given are concentrations at the surface i.e. C<sub>s</sub> of equation (2-1). The last three crystals have thickness less than the diffusion length and the values given are average volume concentrations.

Table 4.1 Preparative conditions and initial Cd<sup>109</sup> concentrations.

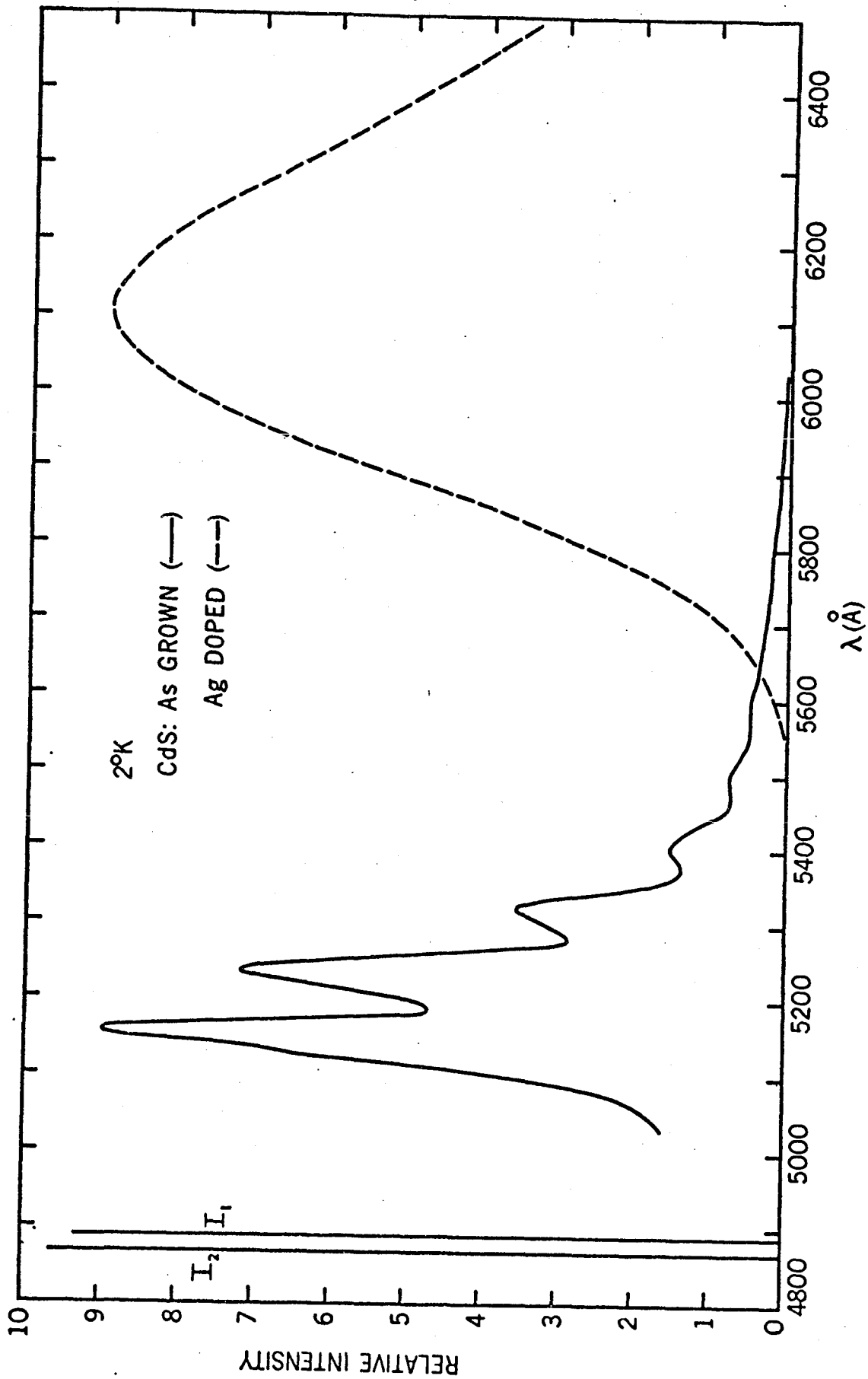


Figure 4.1 Typical CdS emission spectra at 2° K of pure and Ag doped crystals.

The peak position and the width of the band may change slightly from one crystal to another and also with temperature from 2° K to 77°K. The  $I_1$  and  $I_2$  lines and the green edge emission may or may not be present with appreciable intensity. The latter is most likely dependent on the impurity concentration of the pre-doped crystals as well as on the doping temperature and the cooling rate. It is usually possible to produce a different emission spectrum in the same Ag doped crystal through heat treatment.

The main data are contained in figure 4.2. Each of the four figures shows spectral changes in a given doped crystal as the  $Cd^{109}$  decays into Ag impurities. All the spectra are taken at a temperature of 2°K. Except for the absence of  $I_1$  and  $I_2$  lines and some loss of structure at the green spectral region similar changes are observed at 77°K. The luminescence is too weak for investigation at room temperature.

The numerical values shown on each spectrum are the fractions of  $Cd^{109}$  that had decayed in that crystal at the time the spectrum was taken. The Ag concentration derived from the decay is simply the initial concentration of  $Cd^{109}$  from table 4.1 multiplied by the fraction decayed stated on figures 4.2. The important feature

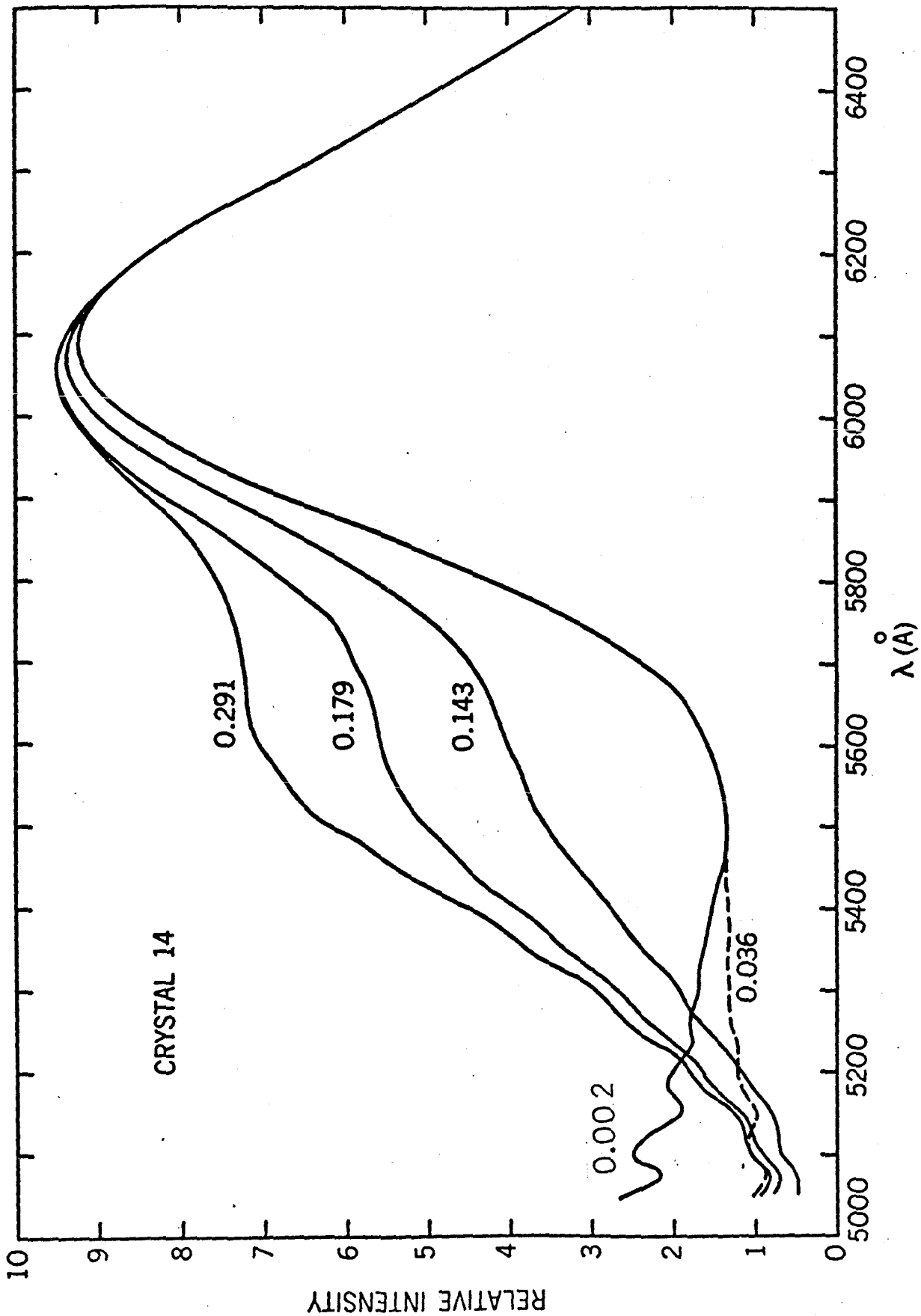


Figure 4.2A Emission spectra of crystal 14 after fractional decay of Cd<sup>109</sup>, taken at T=20 K.

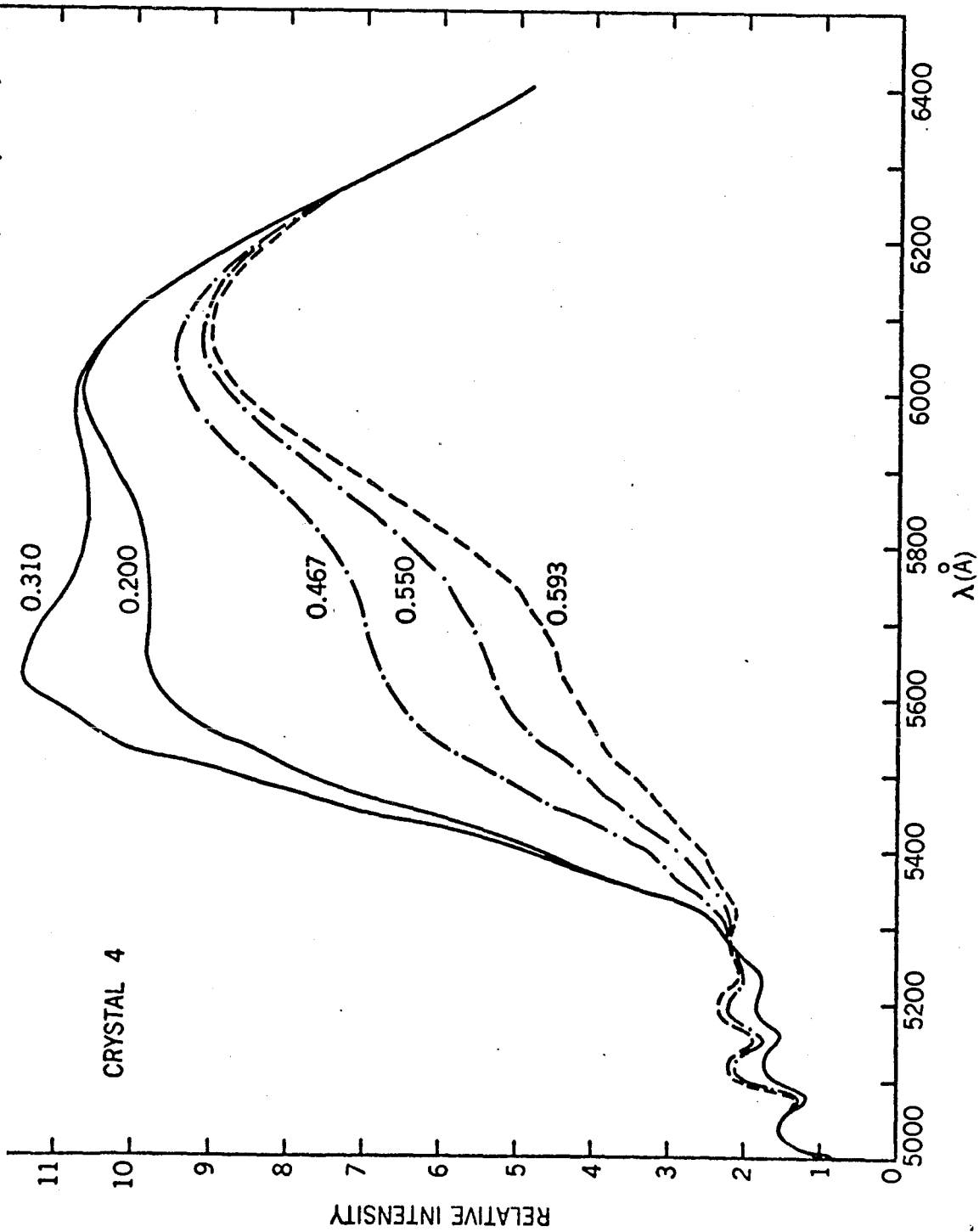


Figure 4.2B Emission spectra of crystal 4 after fractional decay of  $\text{Cd}^{109}$ , taken at  $T=2^{\circ}\text{K}$ .



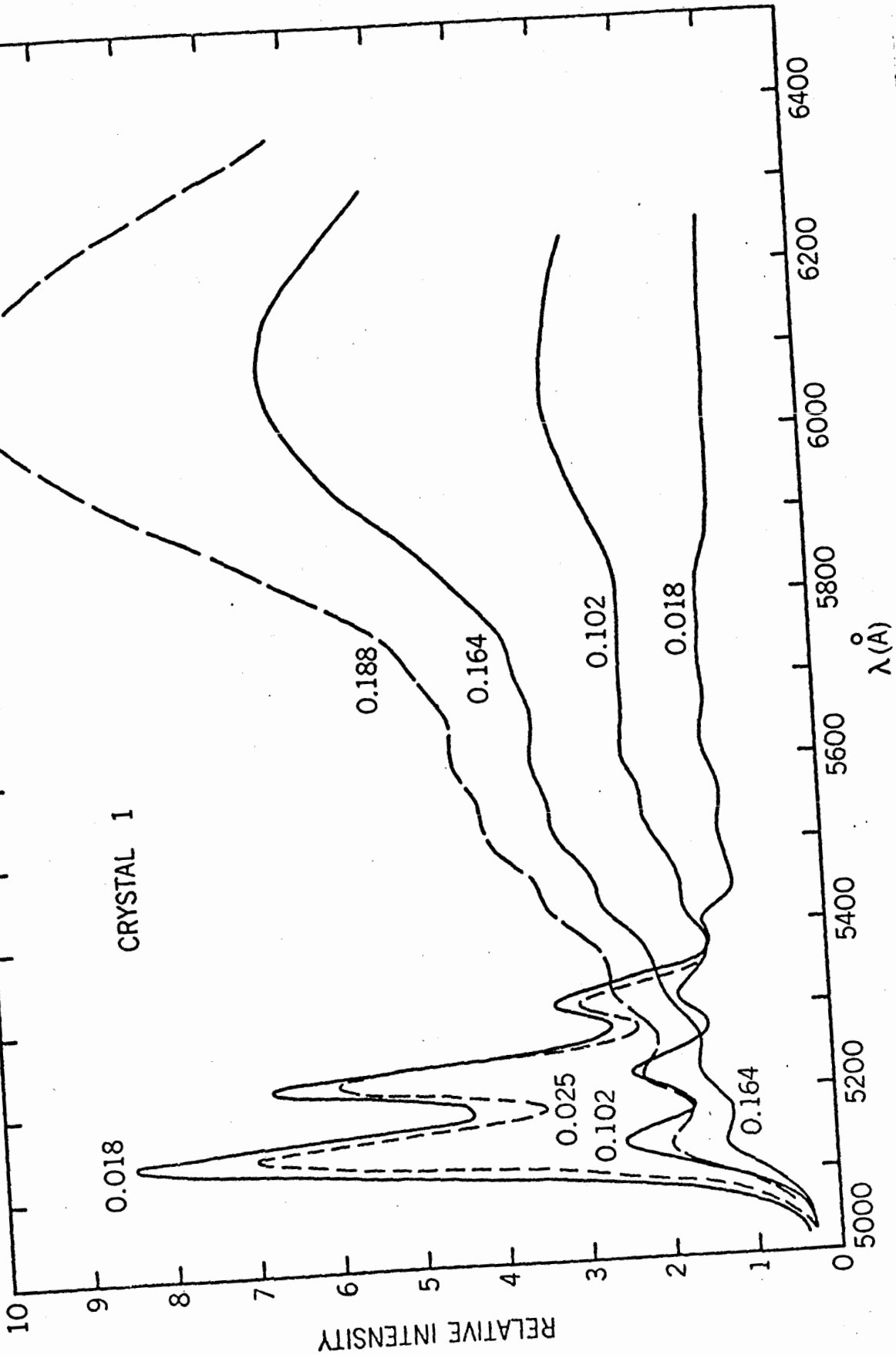


Figure 4.2C Emission spectra of crystal 1 after fractional decay of Cd<sup>109</sup>, taken at T=20 K.

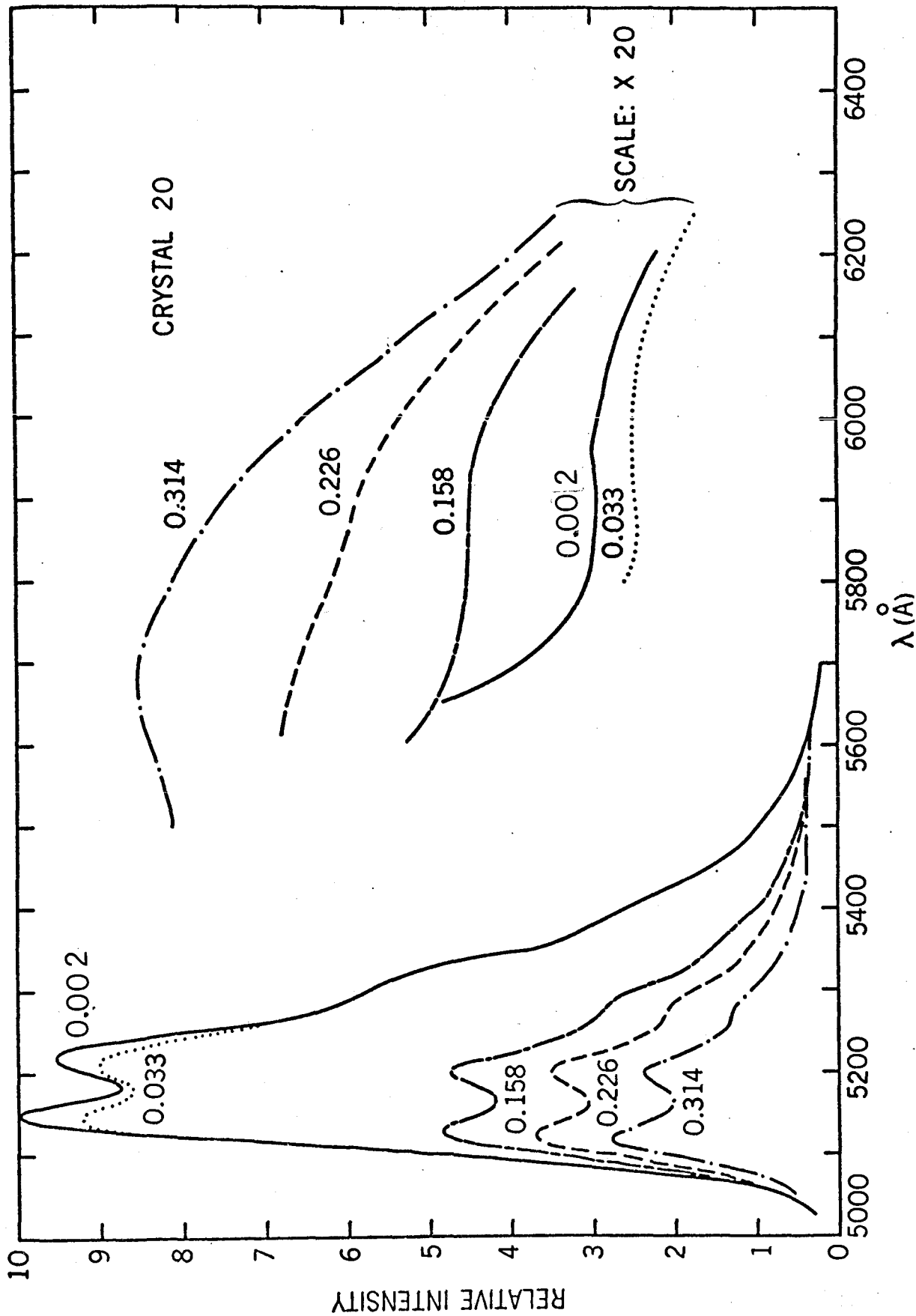


Figure 4.2D Emission spectra of crystal 20 after fractional decay of Cd<sup>109</sup>, taken at T=20 K.

common to all four crystals is that Ag impurities introduced through the decay give rise to a new emission band at  $5600 \text{ \AA}$ .

i) Crystals 4 and 14

These two crystals were prepared similarly by diffusion at  $600^\circ\text{C}$  for 24 hours with no subsequent heat treatment. Both crystals, figure 4.2A and figure 4.2B, showed strong initial emission at  $6100 \text{ \AA}$  after doping; this emission arises presumably as a result of the Ag present with the  $\text{Cd}^{109}$  dopant. Within experimental errors the luminescent efficiency of this emission in each of the crystals was constant with respect to time. Consequently for each crystal the spectra are normalized with respect to this emission.

At low concentrations the new emission increases with increasing concentration. For crystal 4 no initial measurement was taken at  $2^\circ\text{K}$  but the initial spectrum taken at  $77^\circ\text{K}$  showed only low intensity at the  $5600 \text{ \AA}$  region. For concentrations in excess of a decayed fraction 0.310 in crystal 4, the  $5600 \text{ \AA}$  emission decreases with increasing concentration. However, the high energy tail of this emission at about the  $5100 \text{ \AA}$  region, continues to increase.

The structures superimposed on the broad band are probably LO phonon replicas of an emission since they are separated by approximately 40 meV, the LO phonon energy. They may be an intrinsic part of the Ag band ( $5600 \text{ \AA}$ )

since they appear to be enhanced by the new emission. Alternatively, they may belong to the green edge emission which thus appears to retain the well-defined structure of its LO phonon replicas in spite of the large reduction in the zero-phonon band intensity with increasing Ag concentration (see particularly figure 4.2C). In any case this will not be a problem in the analysis.

ii) Crystal 1

Crystal 1, figure 4.2C, was heated to the same temperature (600°C) and for the same duration (24 hours) as the two crystals mentioned above. However this crystal was given a subsequent vacuum heat treatment at 600°C for 3 hours followed by a rapid quenching to room temperature. Visual observation before the vacuum heat treatment of the crystal showed orange luminescence at 77°K. Prepared under identical doping condition as crystal 1, in the same quartz ampoule with the Cd<sup>109</sup> dopant, two other crystals which were not given any subsequent heat treatment showed emission at 6100 Å but no green edge emission at 2°K or 77°K. Assuming crystal 1 to have similar luminescence prior to the vacuum heat treatment as that of the other two crystals, the effect of the treatment is to generate the green edge emission in crystal 1. Simultaneously the treatment reduces the original orange emission. These changes could be induced in other Cd<sup>109</sup> doped crystals as well as in ordinary Ag doped crystals. In general, however, the intensity of the green emission

generated in a doped crystal is much weaker than that of the original emission in the pre-doped crystal.

From figure 4.2C we observe that with increasing Ag concentration in crystal 1 both the 5600 Å and the 6100 Å emission increase, but the former appears to saturate. Simultaneously the green edge emission is being quenched with the peak position shifting to shorter wavelengths. The last effect is not too pronounced in this crystal and is difficult to see in the figure 4.2C. However, it is much more striking in crystal 20. In terms of absolute intensity the 6100 Å emission of crystal 1 is more than two orders of magnitude weaker than that of crystals 4 and 14.

### iii) Crystal 20

For crystal 20 the Cd<sup>109</sup> diffusion was performed for a longer duration (10 days) and at a higher temperature (700°C) than in the previously discussed crystals. No subsequent heat treatment was applied. Our purpose was to randomize the impurities, as will be discussed further in the next chapter. After the diffusion the crystal retained its bright green emission. Similar to crystal 1 the green edge emission was quenched with increasing concentration, figure 4.2D. Furthermore the increasing concentration give rise both the 5600 Å and the 6100 Å emissions; however this time the 5600 Å emission predominates, while in crystal 1 the 6100 Å band is more intense. The small initial decrease of intensity in the yellow-orange region is probably due to the quenching of the

green edge emission. In addition to having intense initial  $I_1$  and  $I_2$  lines, this crystal shows a narrow doublet at  $4878 \overset{\circ}{\text{Å}}$ , between the  $I_1$  and  $I_2$  lines (see figure 4.6A). This doublet remained constant in intensity with respect to time and was therefore used for excitation intensity normalization. The origin of the doublet is not known but it could be due to close donor-acceptor pair lines (Henry, Naussau and Shiever 1970). The position of the zero-phonon green peak is shifting continuously towards higher energies with increasing Ag concentration. The total shift between the first and the last measurement is more than  $30 \overset{\circ}{\text{Å}}$  (15 mev). The position of the peak as a function of daughter Ag concentration is plotted in figure 4.3. The solid line drawn has no theoretical significance.

#### 4.3 Concentration Dependence of Intensity

Figures 4.4, 4.5 and 4.6 show the concentration dependence of the intensity for the various emissions. The data shown includes some which has not been presented above. The fraction of the  $\text{Cd}^{109}$  decayed in a given crystal shown is also the relative derived Ag concentration. This may be converted to absolute concentration with the help of table 4.1.

In figure 4.4 the luminescence intensity as a function of Ag concentration for the emissions at  $5600 \overset{\circ}{\text{Å}}$  and at  $6100 \overset{\circ}{\text{Å}}$  has been plotted. It may be mentioned that crystal 3 which shows neither green nor  $I_1$  and  $I_2$  emissions is one of the

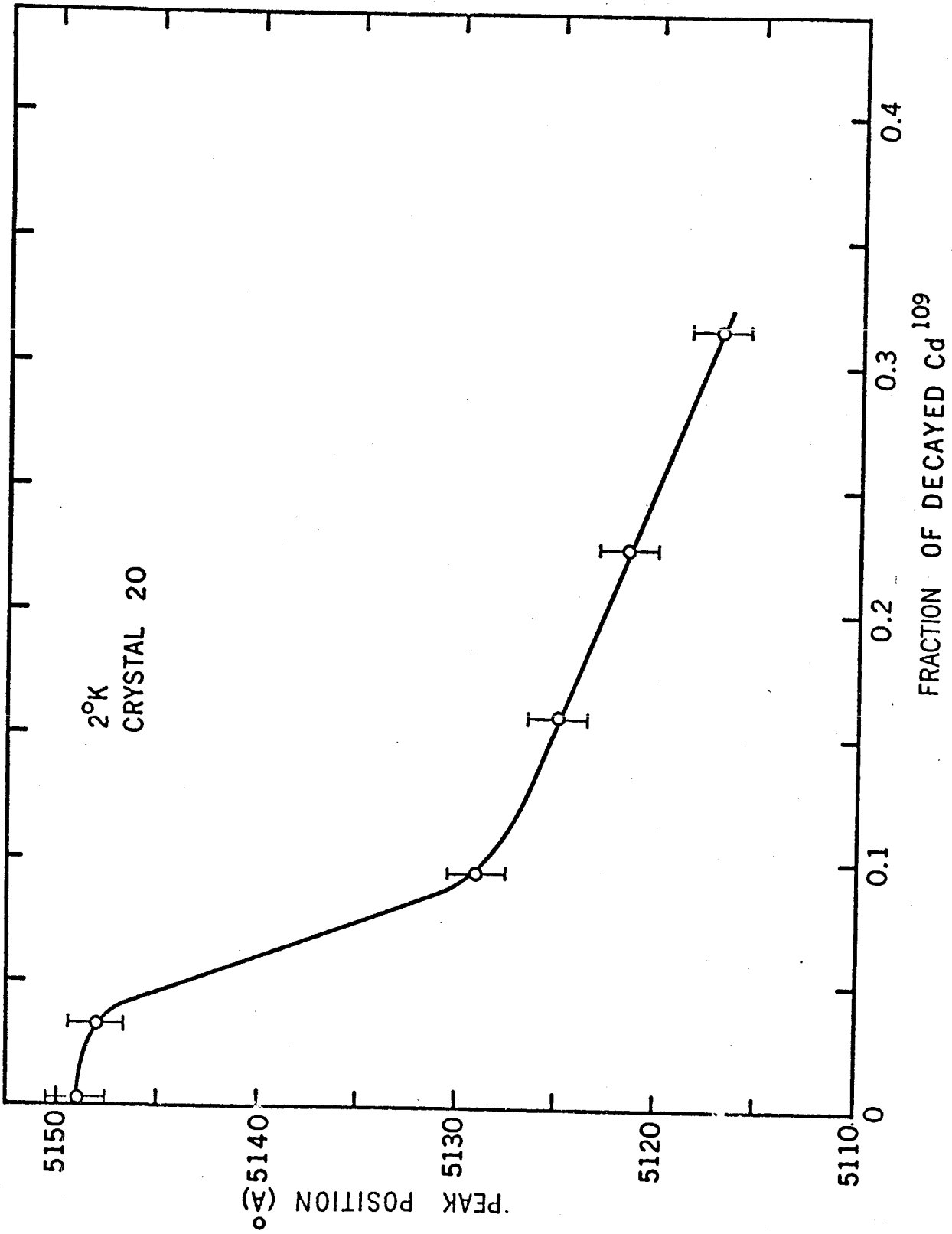


Figure 4.3 Peak position of the green edge emission band of crystal 20 as a function of decayed Cd<sup>109</sup>.

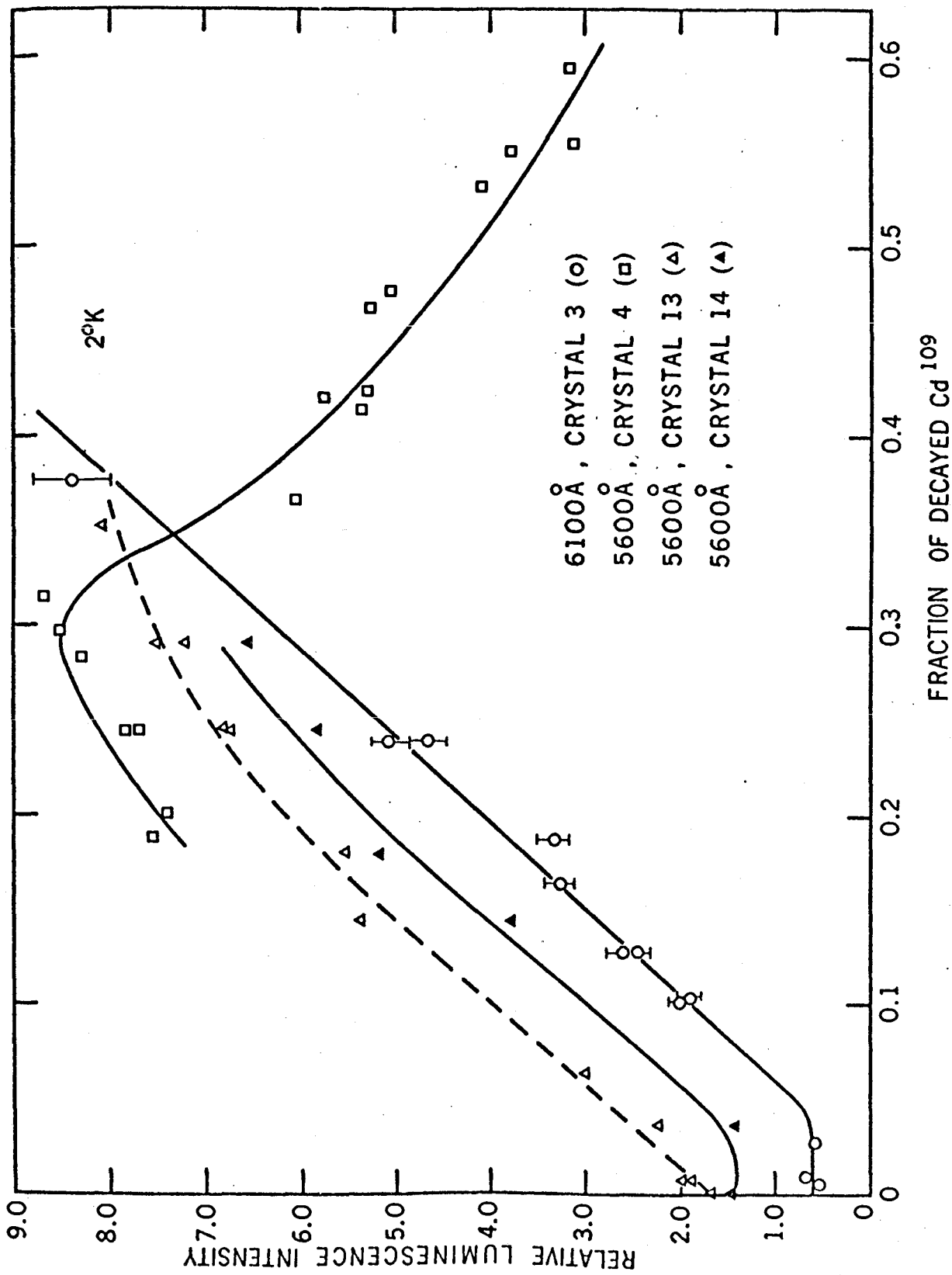


Figure 4.4 Relative intensity of the 5600 Å and 6100 Å emissions as a function of decayed Cd<sub>109</sub>.



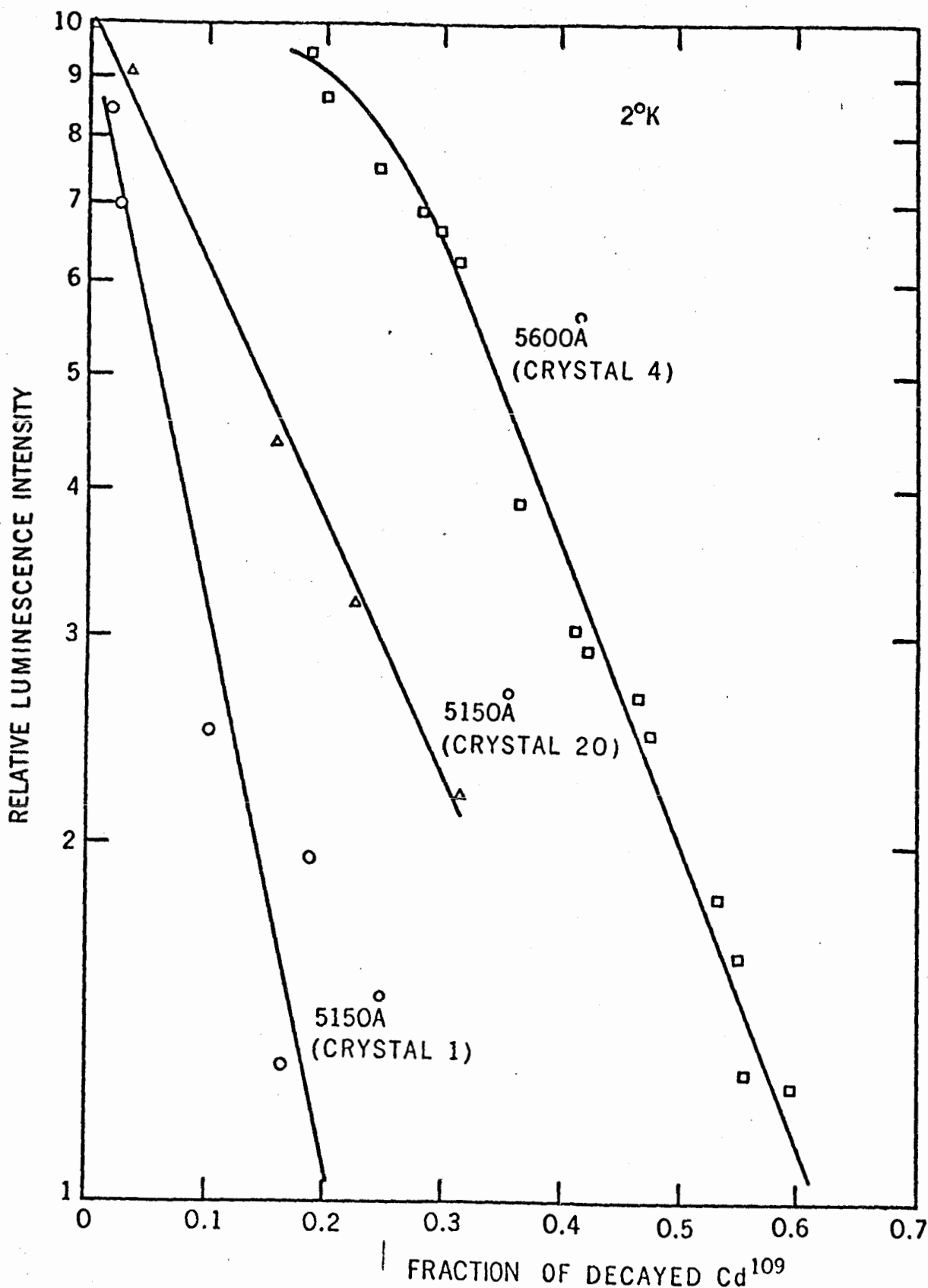


Figure 4.5 Relative intensity of the 5150 Å (green edge) and the 5600 Å emission as a function of decayed Cd<sup>109</sup> on a semi-log scale.

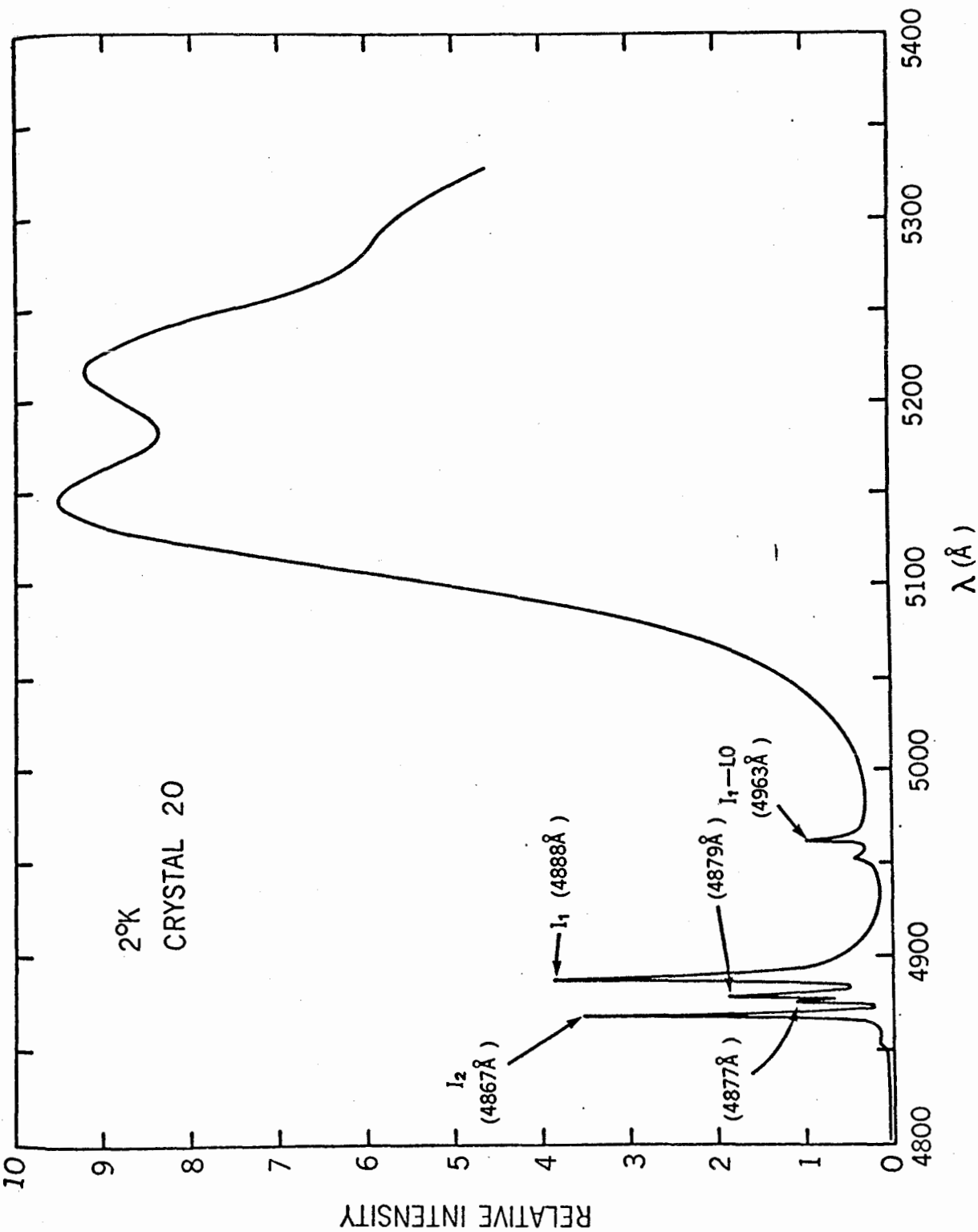


Figure 4.6A Initial spectrum of crystal 20 showing bound-exciton  $I_1$  and  $I_2$  lines and the doublet at 4878 Å.

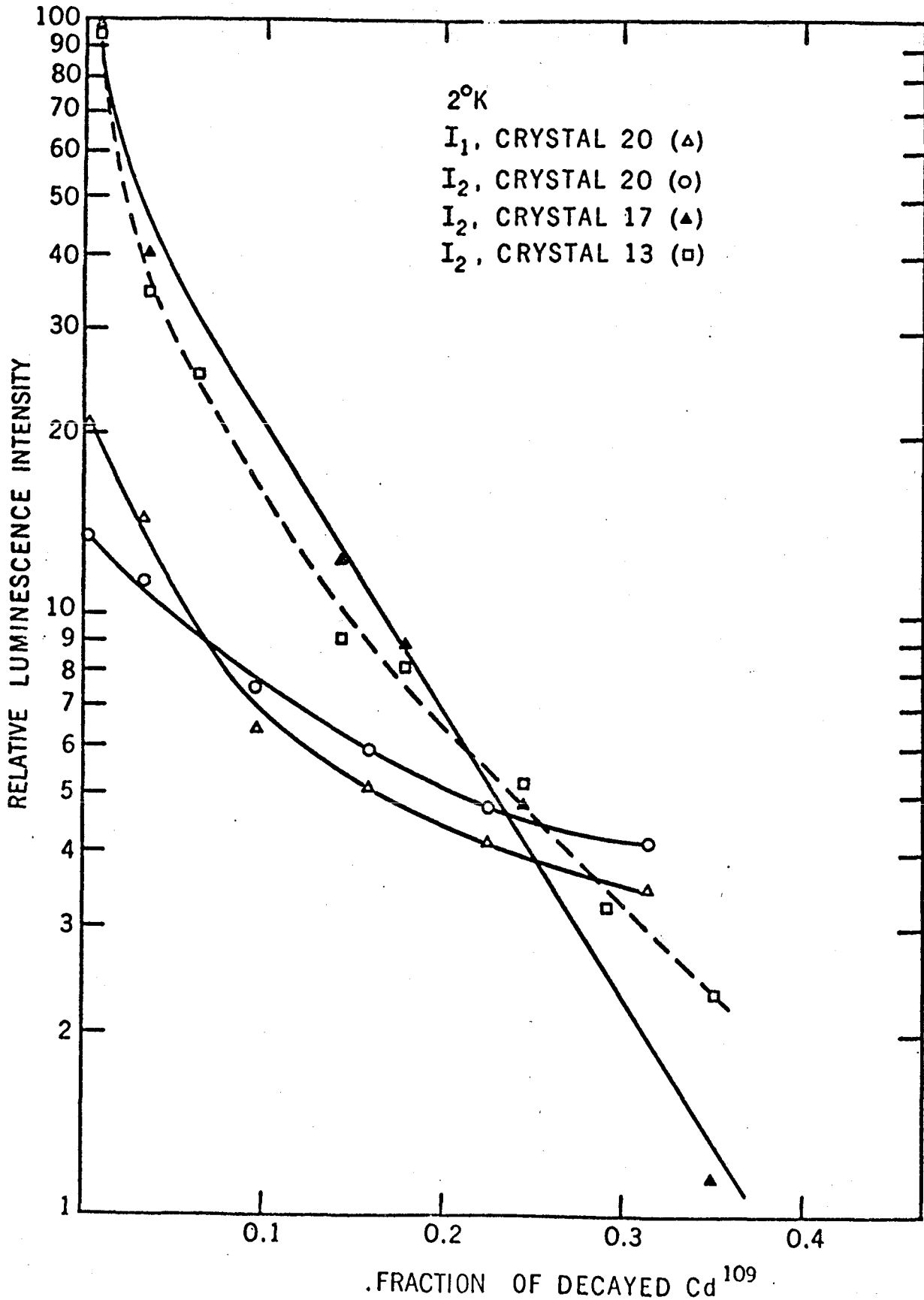


Figure 4.6B Relative intensity of I<sub>1</sub> and I<sub>2</sub> emissions as a function of decayed Cd<sup>109</sup>.

crystals doped in the same diffusion as crystal 1 but was not given any subsequent heat treatment. As the Ag concentration increases only the 6100 Å emission is observed to increase in the crystal, whereas both the 5600 Å and the 6100 Å emissions increase in crystal 1. At least up to the concentration investigated ( $5 \times 10^{16} \text{ cm}^{-3}$ ) the intensity of the 6100 Å emission is linearly dependent on the concentration. The concentration independent behaviour at low concentration results from the initial finite concentration of Ag impurities diffused into the crystal, which is estimated to be  $5 \times 10^{15} \text{ cm}^{-3}$  if we use  $1.4 \times 10^{-17} \text{ cm}^{-3}$  as the initial  $\text{Cd}^{109}$  concentration of crystal 3 (table 4.1) and take 0.04 as the fraction at which the derived Ag equals the diffused Ag. At low concentrations the emission intensity at 5600 Å depends linearly on concentration but begins to saturate for crystals 13 and 14 at a concentration of about  $1.3 \times 10^{16} \text{ cm}^{-3}$  (relative concentration of 0.2). For crystal 4 the intensity was not measured below a decay fraction of 0.19, however, from the fact that quenching occurs above a decay fraction of 0.3, one would deduce that saturation occurred earlier than for crystals 13 and 14, which is consistent with the higher estimated initial  $\text{Cd}^{109}$  concentration for crystal 4 (see table 4.1). The Ag concentrations in crystals 13 and 14 were not sufficiently high at the time of the last measurements to show a decrease

in intensity with Ag concentration. The scattering of points is believed to be due to crystal surface inhomogeneity, leading to varying amounts of internal reflections, preventing light from leaving the crystal. This gives rise to about 10% variation in luminescence intensity for different regions of the same crystal.

Figure 4.5 shows the concentration quenching of the green edge emission and the 5600 Å emission. The data for the 5600 Å emission in figure 4.4 has been normalized with respect to concentration, and replotted as  $\log$  (luminescence/concentration). The semi-log plot for the 5150 Å green edge emission is not normalized with respect to Ag concentration. The three curves indicate that the concentration quenching for the 5150 Å band and self-quenching per unit concentration for the 5600 Å emission are exponential in nature. The significance of this will be discussed in the next chapter. The poor fit of crystal 1 for large concentrations results from the uncertainty in determining how much of the emission at 5150 results from high energy tail of the new emission.

Figure 4.6A shows a spectrum of crystal 20 including the bound-exciton  $I_1$  and  $I_2$  lines. Similar to the green edge emission the bound-exciton  $I_1$  and  $I_2$  emissions were quenched with the increasing Ag concentrations, figure 4.6B. Crystal 13 and 17 showed an intense initial  $I_2$  line but no  $I_1$  emission whereas crystal 20 had both emissions. In terms of

absolute intensity  $I_2$  of crystal 17 is about ten times weaker than the  $I_1$  and  $I_2$  emission of the other two crystals. As seen from figure 4.6B the intensity of the bound-exciton  $I_2$  emission of crystals 13 and 17 decreases by about two orders of magnitude while the free exciton emission intensity of the same crystals at 77° K is reduced by less than 50% (not shown in the figure) over the concentration range of about  $7 \times 10^{14} \text{ cm}^{-3}$  to  $2 \times 10^{16} \text{ cm}^{-3}$ .

#### 4.4 Electrical Conductivity

The electrical conductivity was measured as a function of Ag concentration on three  $\text{Cd}^{109}$  doped crystals: crystals 4, A and B. Electrical connections to crystal 4 were made using In solder while silver paste (Dag dispersion) was used for the very thin ( $<50\mu$ ) crystals A and B.

The resistance of crystal 4 increased from an initial value of  $5 \times 10^9$  ohms to  $3 \times 10^{10}$  ohms when 0.21 of the  $\text{Cd}^{109}$  had decayed. The resistance of crystal A remained constant at  $1 \times 10^5$  ohms up to a decay of 0.33 of the  $\text{Cd}^{109}$ . Table 4.2 shows the resistance as a function of concentration for crystal B. In addition to the dark conductivity, the resistance was measured under room light illumination, which also served to check the continuity of the circuit. The dark resistance increases rather abruptly from  $4 \times 10^7$  ohms to greater than  $10^{12}$  ohms between 0.089 and 0.151. The resistance under illumination, on the other hand, increases more

Fraction of Cd <sup>109</sup> decayed	Resistance (ohms)	
	Dark	With Illumination
0.027	$2 \times 10^7$	$1 \times 10^7$
0.089	$4 \times 10^7$	$2 \times 10^7$
0.151	$>10^{12}$	$5 \times 10^8$
0.185	$>10^{12}$	$8 \times 10^8$
0.219	$>10^{12}$	$7 \times 10^{10}$
0.332	$>10^{12}$	$5 \times 10^{11}$

Table 4.2 Electrical resistance as a function of decayed Cd<sup>109</sup> in crystal B.

slowly over the entire concentration range. Since CdS is n-type the increasing dark resistivity with concentration means that Ag derived from the decay is an acceptor. The abrupt increase in the resistivity implies a transition from a partially to a well compensated crystal. This occurs when the Ag acceptor concentration is equal to the original uncompensated shallow donor concentration. Taking the transition to occur at a 0.1 decay fraction (table 4.2) and using an initial  $\text{Cd}^{109}$  concentration of  $2.5 \times 10^{17} \text{ cm}^{-3}$  (table 4.1) we obtain the donor concentration  $N_D = 2.5 \times 10^{16} \text{ cm}^{-3}$ , which is the same range as those in the Cd vapour annealed crystals (chapter 2). The decrease in the photoconductivity is probably due to a shortening of free carrier life time by the additional recombination centers.

#### 4.5 Summary

The Ag impurities derived from the decay give rise to a new emission band at  $5600 \overset{\circ}{\text{Å}}$  in addition to the emission of ordinary Ag doped crystals. The green edge emission and the new emission are quenched with increasing Ag concentration. Simultaneously the peak position of the green edge emission is shifted to higher energy. Also the  $I_1$  and  $I_2$  emission are quenched by the additional Ag impurities. The electrical conductivity measurements show that Ag is an acceptor. It may be noted that interstitial Ag is sometimes suggested as donors responsible for the  $6100 \overset{\circ}{\text{Å}}$  emission (Brown et al 1970).



## CHAPTER 5

### INTERPRETATIONS AND DISCUSSIONS

#### 5.1 Preliminary Considerations

$\text{Cd}^{109}$  decays into  $\text{Ag}^{109}$  via:

1. atomic core electron-capture with decay energy of 160 Kev with simultaneous emission of a neutrino and

2. a subsequent emission of a 87.7 Kev gamma ray, which is about 93% internally converted, ejecting mostly an atomic K-shell electron and the characteristic x-ray.

Consequently the maximum kinetic energy an electron in the doped crystals may acquire is 87.7 Kev. It follows from conservation of momentum that the recoil energy given to a  $\text{Cd}^{109}$  nucleus in emitting a 160 Kev neutrino, a 87.7 Kev gamma or electron is less than 0.13, 0.04 or 0.85 ev respectively. It may also be shown from conservation of energy and momentum that for a head-on elastic collision with a 87.7 Kev kinetic energy electron the energy imparted to a S or Cd atom is less than 6.6 ev or 2.0 ev respectively. Using electron bombardments, Kulp and Kelley (1960) and Kulp (1962) have measured threshold energies of 8.7 ev and 7.3 ev for the displacements of S and Cd atoms respectively in the CdS lattice. Therefore it will be assumed that a substitutional  $\text{Cd}^{109}$  atom will remain at its site after the decay and there will be no vacancies produced by the decay.

Interstitial Ag atoms have been suggested (Brown et al 1970) as centers responsible for the 6100 Å emission. However, we have found that ordinary Ag doped crystals with Ag diffusion

in vacuum or under saturated S vapour pressure showed brighter 6100 Å emission than those where the diffusion was done under saturated Cd pressure. Since the latter condition decreases the concentration of Cd vacancies, it is expected to favour interstitial Ag, while the former conditions favour substitutional Ag (Woodbury 1965). Further evidence against an interstitial Ag model for the 6100 Å emission and the new 5600 Å emission comes from the Cd<sup>109</sup> doped crystals. One would expect a very low interstitial Cd concentration in the crystals which show intense green edge and I<sub>1</sub> emissions since Li or Na atoms occupying Cd vacancies are supposed to give rise to these emissions (Henry et al 1970); a high Cd vacancy concentration implies a low Cd interstitial concentration. However, the Ag impurities derived from the decay give rise to both emissions in these crystals; in fact the 5600 Å emission is enhanced if the doped crystals had been given a vacuum heat treatment after the doping, which is expected to reduce interstitial Cd<sup>109</sup> concentration. It is therefore concluded that interstitial Ag impurities cannot be responsible for either the normal Ag emission or the new emission. This conclusion is consistent with an observation made by Woodbury (1965) in the investigation on the diffusion and solubility of Ag in CdS. He found that a concentration of  $3 \times 10^{16} \text{ cm}^{-3}$  of interstitial Ag did not change the fluorescence in the crystals.

Indication that Cl may be a prevalent impurity in CdS was given by Gurvich et al (1965) who found an increase in the Cl

content of about 0.03% in CdS specimen after being placed in an enclosed chamber with a beaker containing HCl solution. Woodbury (1967) reported that mass spectroscopic analysis of different CdS samples, most of which were UHP grade from Eagle-Picher, has indicated an Al content ranging from  $(1-10) \times 10^{15} \text{ cm}^{-3}$  and a Cl content from  $(1-5) \times 10^{16} \text{ cm}^{-3}$ . Since our CdS powder was also obtained from Eagle-Picher our crystals would be expected to have similar impurity contents. The measured shallow donor concentration ranging from  $(1-5) \times 10^{16} \text{ cm}^{-3}$  in our crystals leads us to assume that Cl forms the major donor impurities in our crystals.

Both annealed and quenched ordinary Ag doped crystals were used as control samples. Within about 10% variation due to surface inhomogeneity the luminescence spectrum of these samples remained constant with respect to time. This is supporting our assumption that effects due to room temperature diffusion are negligible.

## 5.2 Interpretations

The results will be interpreted on the assumption that substitutional Ag impurities derived from the  $\text{Cd}^{109}$  decay are acceptors. This assumption is supported by our electrical conductivity measurements on the doped crystals and is also suggested by chemical valence considerations. Furthermore we will assume that all the diffused  $\text{Cd}^{109}$  occupy substitutional lattice sites. This assumption is supported by the following:

1. A concentration of  $5 \times 10^{20} \text{ cm}^{-3}$  is estimated for the

externally diffused-in Cd atoms; this is based on a  $\text{Cd}^{109}$  concentration of  $1 \times 10^{17} \text{ cm}^{-3}$ , and a ratio of 1:5000 for  $\text{Cd}^{109}$  to stable  $\text{Cd}^{108}$  on the radioisotope solution. On the other hand one would not expect a solubility of interstitial Cd at  $600^\circ\text{C}$  to be larger than about  $10^{19} \text{ cm}^{-3}$ . Woodbury's (1965) determination of the solubility of Ag in CdS at  $600^\circ\text{C}$  in the presence of excess sulphur gave a concentration of about  $10^{19} \text{ cm}^{-3}$ , and the atomic size of Cd is larger than Ag.

2. By making the assumption that all the  $\text{Cd}^{109}$  is substitutional the analysis of the electrical conductivity data (Chapter 4) and of the concentration dependence of the intensity of the new emission (below) give the same donor concentrations as obtained from the room temperature electrical conductivity measurements on pure annealed crystals (chapter 2).

The photoluminescent efficiency in the visible spectrum of the  $\text{Cd}^{109}$  doped crystals is low compared to the as-grown crystals. This implies that recombination of free carriers is determined essentially by the non-radiative or perhaps non-visible radiative processes. The  $6100 \overset{\circ}{\text{A}}$  emission in some doped crystals remained constant independent of Ag concentration. Consequently, mechanisms other than

reduction in free carriers must be responsible if the intensity of an emission is reduced by the increasing Ag concentration.

i) 5600Å Emission

In a doped crystal let  $N_D$  be the constant donor concentration and  $N_{Ag}(t)$  be the Ag acceptor concentration which varies with time. Suppose the acceptor concentration increases from a value smaller than to a value larger than the donor concentration.

Following the model discussed in Chapter 3, the luminescence intensity of bound to bound recombination  $I(r)$  at donor-acceptor pairs of separation  $r$  is proportional to the concentration of donor-acceptor pairs  $n(r)$ . Since the exclusion factor is determined by the larger concentration of the donor or the acceptor, we find that

$$I(r) \propto n(r) \propto N_{Ag}(t) \quad \text{for } N_{Ag}(t) \ll N_D \quad (5-1)$$

$$I(r) \propto n(r) \propto N_{Ag}(t) \exp\left[-\frac{4}{3} \pi r^3 N_{Ag}(t)\right]$$

$$\text{for } N_{Ag}(t) \gg N_D \quad (5-2)$$

Therefore when the Ag concentration is much smaller than the donor concentration the luminescence intensity increases linearly with concentration. The linear dependence is shown by crystals 13 and 14 in Fig. 4.4. When  $N_{Ag}(t) \gg N_D$ , for sufficiently large  $r$  we expect  $I(r)$  to decrease with increasing Ag concentration. This self-quenching behaviour is observed in crystal 4 (figure 4.4 or figure 4.5)

At the self-quenching region a plot of

$$\ln[I(r)/N_{Ag}] \quad \text{versus} \quad N_{Ag} \quad (5-3)$$

is a straight line with negative slope  $\frac{4}{3}\pi r^3$ . Therefore the separation  $r$  of pairs responsible for  $I(r)$  can be obtained from the slope, provided  $N_{Ag}(t)$  is known. The peak emission at  $5600\text{\AA}$  of crystal 4 plotted in this manner in Fig. 4.5 has resulted in a straight line fit at high concentrations.

Using the initial  $\text{Cd}^{109}$  concentration of  $1.2 \times 10^{17} \text{cm}^{-3}$  (Table 4.1) and the slope obtained we calculated

$$r = 230 \text{\AA}$$

i.e. donor-acceptor pairs of  $230\text{\AA}$  separation are responsible for the peak emission at  $5600\text{\AA}$ . The approximate  $400 \text{\AA}$  width of the  $5600\text{\AA}$  band is believed to be mainly due to the phonon broadening rather than a variation of  $r$ . For the zero-phonon emission of donor-acceptor pairs the difference in wavelengths corresponding to separation  $r = \infty$  and  $r = 50 \text{\AA}$  is only about  $30 \text{\AA}$ .

For the linear dependent region, i.e. when  $N_{Ag}(t) < N_D$ , the semi-log plot of expression (5-3) yields a constant. Although no data were obtained in the low concentration region for crystal 4, on the basis of the emission in crystal 13 and 14 the linear dependence is assumed to hold. The transition between the linear and the self-quenching region occurs in the concentration region where  $N_{Ag}(t) \approx N_D$ . Therefore this provides a means of estimating the donor concentration. If we take the transition as being at a decayed fraction of 0.2 we obtain for crystal 4 (Fig. 4.5)

$$N_D = 2.4 \times 10^{16} \text{ cm}^{-3}$$

which lies within the range of donor concentrations estimated for our crystals (chapter 2).

For the bound to bound recombination light of the same wavelength can arise from donor-acceptor pairs of different separations. This may result through the simultaneous emission and absorption of phonons. Nevertheless we assume that the donor-acceptor pair emission at  $5600 \text{ \AA}$  originates principally from pairs of one particular separation.

It is difficult to determine accurately the Ag acceptor binding energy due to the broadness of emission band. Taking the position of the no phonon emission between distant pairs at  $5600 \text{ \AA}$ , and neglecting the coulomb energy, we obtain using equation (3-19)

$$E_A = 0.34 \text{ ev}$$

for the acceptor binding energy, where we have used a band gap energy of  $E_g = 2.583 \text{ ev}$  (Hopfield and Thomas 1961) and donor energy of  $E_D = 30 \text{ mev}$  (Colbow 1966). This value for  $E_A$  is likely an overestimate because the emission at  $5600\text{\AA}$  may involve the simultaneous emission of several longitudinal optical phonons.

ii) The Green Edge Emission

Let  $N_A$  be the concentration of the acceptor responsible for the green edge emission which is assumed to be a donor-acceptor bound to bound recombination. Let  $N_D$  and  $N_{Ag}(t)$  have the usual meaning. Suppose the concentration of the green acceptor-donor pairs of separation  $r$  is  $n_g^0(r)$  when the Ag acceptor concentration is zero. Then for a finite Ag concentration  $N_{Ag}(t)$  it follows that, since the probability of a green pair not intercepted by a Ag acceptor is  $\exp[-\frac{4}{3}\pi r^3 N_{Ag}(t)]$ ,

$$n_g(r) = n_g^0(r) \exp\left[-\frac{4}{3}\pi r^3 N_{Ag}(t)\right]$$

Hence the intensity of the green accepto-donor pairs of separation  $r$  is

$$I_g(r) = I_g^0(r) \exp\left[-\frac{4}{3}\pi r^3 N_{Ag}(t)\right]$$

Therefore a plot of



$\ln I_g(r)$  versus  $N_{Ag}(t)$

gives a negative slope  $\frac{4}{3} \pi r^3$ . The exponential property of quenching by a dissimilar species is indeed satisfied experimentally by the green edge emission at  $5150 \text{ \AA}$ , the wavelength of the initial peak position of the zero-phonon band, Fig. 4.5.

From the measured values of the slope one obtains, using the initial  $\text{Cd}^{109}$  concentration as given in Table 4.1,  $r = 280 \text{ \AA}$  for crystal 1 and  $r = 230 \text{ \AA}$  for crystal 20. Comparing these with the  $r$  obtained for the emission at  $5600 \text{ \AA}$  one notes that both emissions arise from pairs of approximately the same separations. This is what one would expect for the following reason. The fact that both the green and the Ag acceptors have much larger binding energies, and thus smaller radii than the donor implies the same recombination rate for the same pair separation, independent of the acceptor species. This means that for approximately the same concentrations, if pairs of the green acceptor species of a particular separation contribute significantly to the green edge emission so will pairs of the same separation of the Ag acceptor to the Ag emission. For crystal 4, the donor concentration is estimated to be  $2.4 \times 10^{16} \text{ cm}^{-3}$ , which gives an average separation of  $218 \text{ \AA}$ .

Based on the measurements of the peak shift of the low energy band with time after excitation and a simple hydrogenic theory, Colbow (1966) obtained  $r = 127 \text{ \AA}$  for the separation of

the donor-acceptor pairs responsible for the bound to bound emission at  $10^{-4}$  sec after excitation. An acceptor binding energy  $E_a = 170$  meV was used in this calculation of  $r$ . An acceptor binding energy  $E_a = 165$  meV would have given  $r = 240 \text{ \AA}$  for his measurements. The possibility of lowering the value of  $E_a = 170$  meV by an  $\text{TO}_2$  phonon energy of 5.5 meV has already been mentioned by Colbow (1966). This uncertainty of the acceptor binding energy results from the difficulty of assigning the zero phonon line.

As the Ag concentration increases the emission intensity given by equation (3-23) for the green edge emission would have  $[N_{\text{Ag}}(t) + N_{\text{D}}]$  in place of  $N_{\text{D}}$  in the exclusion factor. Consequently equation (3-25) becomes

$$f_e(r) \left( \frac{2r}{a_{\text{D}}} \right) + 4\pi r^3 [N_{\text{Ag}}(t) + N_{\text{D}}] = 4 + 2f_g(r)$$

One sees from the above equation that for a constant  $f_e(r)$ , as  $N_{\text{Ag}}(t)$  increases  $r$  must decrease correspondingly in order for the equation to remain satisfied. In other words the peak position of the green edge emission must move to higher energy (or shorter wavelength) continuously as the Ag concentration increases. This explains the peak position shift of the green edge band as shown in Fig 4.3.

One can also explain the peak shift as follows: A given green acceptor-donor pair is no longer a pair if a Ag acceptor is introduced into a site closer to the donor than the existing

green acceptor. The larger the separation of a green pair the the greater is the probability that the pair is eliminated and thus transformed into a Ag acceptor-donor pair. Consequently the degree of quenching of the green pair emission increases with increasing pair separation, resulting in the peak position moving towards higher energy, corresponding to smaller pair separation.

The origin of the green edge emission is still controversial (chapter 1). The above analysis on quenching and peak shift shows, in agreement with previous proposals (Pedrotti and Reynolds 1960; Colbow 1966; Henry, Faulkner and Naussau 1969), that the green emission for the low energy series arises from bound to bound recombination at distant donor-acceptor pairs and does not originate from closely associated pairs as advocated by Gutsche and Goede (1970).

### iii) Quenching of $I_1$ and $I_2$ Emission

An increasing Ag concentration in a crystal can reduce the emission intensity of the  $I_1$  and  $I_2$  lines in two ways:

1. The addition Ag impurities can break up free excitons, thereby reducing the number of excitons available for capturing, or
2. They can reduce the number of efficient acceptor or donor centers responsible for the  $I_1$  and  $I_2$  lines respectively.

On the basis that, in comparison to the bound-exciton emissions,

the free exciton emission at 77°K decreases only slightly with increasing Ag concentration it appears that the first mechanism is not responsible for the quenching of the  $I_1$  and  $I_2$  emissions.

A donor is an efficient center for the  $I_2$  emission only if the closest acceptor is far removed from it. A close nearest acceptor reduces the donor's efficiency as it increases the pair radiative recombination rate, consequently leaving the donor often in an ionized state. The close proximity of the acceptor also increases the probability of breaking up a captured exciton before it can annihilate.

The donors of the donor-acceptor pairs of large separations are more likely to have a new nearest neighbour Ag acceptor than those belonging to close pairs. Since the distant pair donors are also the most efficient ones we would expect the rate of quenching to decrease with increasing concentration. This explains qualitatively the experimental data on the  $I_2$  quenching in Fig. 4.6B.

A similar explanation applies to the quenching of the  $I_1$  emission. Being more tightly bound, a Ag acceptor in the neighbourhood of an acceptor responsible for the  $I_1$  line can ionize the  $I_1$  acceptor. However, this is probably important only for very high concentrations in view of the small acceptor Bohr radius (about 5 Å). The fact that the quenching is strongest at low Ag concentration suggests that this effect is

unimportant. Thus the most probable mechanism appears to be the breaking up of already bound excitons as has been described for the  $I_2$  quenching. As expected the concentration dependence of the  $I_1$  and  $I_2$  emission is similar, as seen in Figure 4.6B.

iv 6100 Å Emission

We propose that the 6100 Å emission originates from an associated center consisting of a Ag atom and another impurity atom, likely a donor, but not a native defect. This may at first appear unlikely in view of the fact that Ag derived from the decay also gives rise to this emission; one might expect the  $Cd^{109}$  atoms to be randomly distributed, resulting in an extremely low concentration of Ag associated centers. However the  $Cd^{109}$  atoms were diffused into the crystals. As a result a  $Cd^{109}$  atom could occupy a substitutional lattice site via one of three ways; the  $Cd^{109}$  atom

1. replaced another Cd atom occupying a substitutional site.
2. displaced a substitutional impurity atom, for example a Li atom, or
3. filled a Cd vacancy.

Had the vacancy or the displaced Li atom been associated with a second impurity, say a Cl donor, the  $Cd^{109}$  atom incorporated via one of the last two mechanism would also be associated with the Cl donor initially.

Although no experimental data are available for CdS, the

diffusion of vacancies and interstitials is expected to be sufficiently rapid above 600°C that any vacancy or interstitial associated with a  $\text{Cd}^{109}$  atom initially would have diffused away. Consequently the impurity with which a Ag atom derived from the decay is associated is unlikely to be a native defect. On the other hand diffusion of substitutional impurity atoms could be sufficiently slow that only a low degree of randomization occurs. In addition if the  $\text{Cd}^{109}$  atoms are incorporated via one or both of the last two steps and if association between Cd vacancies or Li acceptors and Cl donors is high, the concentration of Cl-associated  $\text{Cd}^{109}$  can be much larger than that which results from a random distribution. In a sense the associated Ag center model is strengthened, rather than contradicted, by the experimental observation that Ag impurities derived from the  $\text{Cd}^{109}$  decay also give rise to the 6100 Å emission. Furthermore the result should remove the uncertainty (Lehmann, 1966) concerning the interpretation that Ag centers give rise to the 6100 Å emission. The chemical nature of the associated impurity is most likely Cl, which is believed to be the major impurity in our crystals. This assumption is consistent with our observation that pure crystals heated in an atmosphere of AgCl resulted in a brighter emission than those heated in Ag alone. The actual separation of the Ag and Cl atom in the associated center is not known. However on the assumption that Ag and Cl are ionized acceptors and donors respectively one would expect the first nearest neighbour Ag-Cl pairs to have the highest con-

centration, i.e. the Ag and the Cl occupying adjacent Cd and S vacancies respectively.

For recombination at distant pairs the energy of the emitted light increases with decreasing separation, as seen from equation (3.19). Thus one might wonder why the associated pair emission at  $6100 \text{ \AA}$  occurs at a lower energy than the distant pair emission at  $5600 \text{ \AA}$ . However, on closer scrutiny one realizes the difficulties in calculating the recombination energy for close pairs. The formalism for calculating the energy has been developed by Williams (1960). However, without the knowledge of a good wavefunction no energy calculation is possible. In the limit of very small separation between the donor and the acceptor the bound to bound recombination becomes an exciton at an isoelectronic trap, a problem which so far has not been given a satisfactory theoretical solution (Faulkner and Hopfield 1967).

Our model that the  $5600 \text{ \AA}$  emission arises from a bound to bound transition at distant donor-acceptor pairs while the  $6100 \text{ \AA}$  emission originates from associated Ag centers is consistent with the following observations:

1. The Ag impurities derived from the  $\text{Cd}^{109}$  decay always give rise to the  $5600 \text{ \AA}$  emission in crystals which show the  $I_2$  or green edge emission. The existence of  $I_2$  or green edge emission means that relatively isolated donors are available for the Ag acceptors to form distant pairs. On the other hand crystal 3, which

has neither the  $I_2$  nor green edge emission, shows only an increase in the intensity of the 6100 Å emission with increasing  $Cd^{109}$  decay. Crystal 20 has undergone  $Cd^{109}$  diffusion at a higher temperature and for a longer duration than crystal 1. This should lead to a higher degree of randomization of impurities. This in turn gives rise to a relatively more intense 5600 Å emission compared to the 6100 Å emission with increasing Ag concentration in crystal 20, with the inverse behaviour for crystal 1.

2. The peak of the 5600 Å band shifts to lower energy with decreasing excitation intensity (Figure 5.1A), whereas no such shift is observed for the 6100 Å band. The former is characteristic of a bound to bound recombination (chapter 3). It may be noted that the emission intensity of the 6100 Å band depends linearly (figure 5.1B) while that of the 5600 Å band varies sub-linearly with excitation intensity.
3. The intensity of the 5600 Å emission is quenched in crystals 14 and 15 after they have been heated to a temperature of 200°C for 20 minutes (Figures 5.2A and 5.2B). For this temperature and time the diffusion length of Ag is about  $2\mu$  based on  $D = 8 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$  (Woodbury 1965), which is small compared to  $16\mu$ , the diffusion length of  $Cd^{109}$  in these crystals (Table



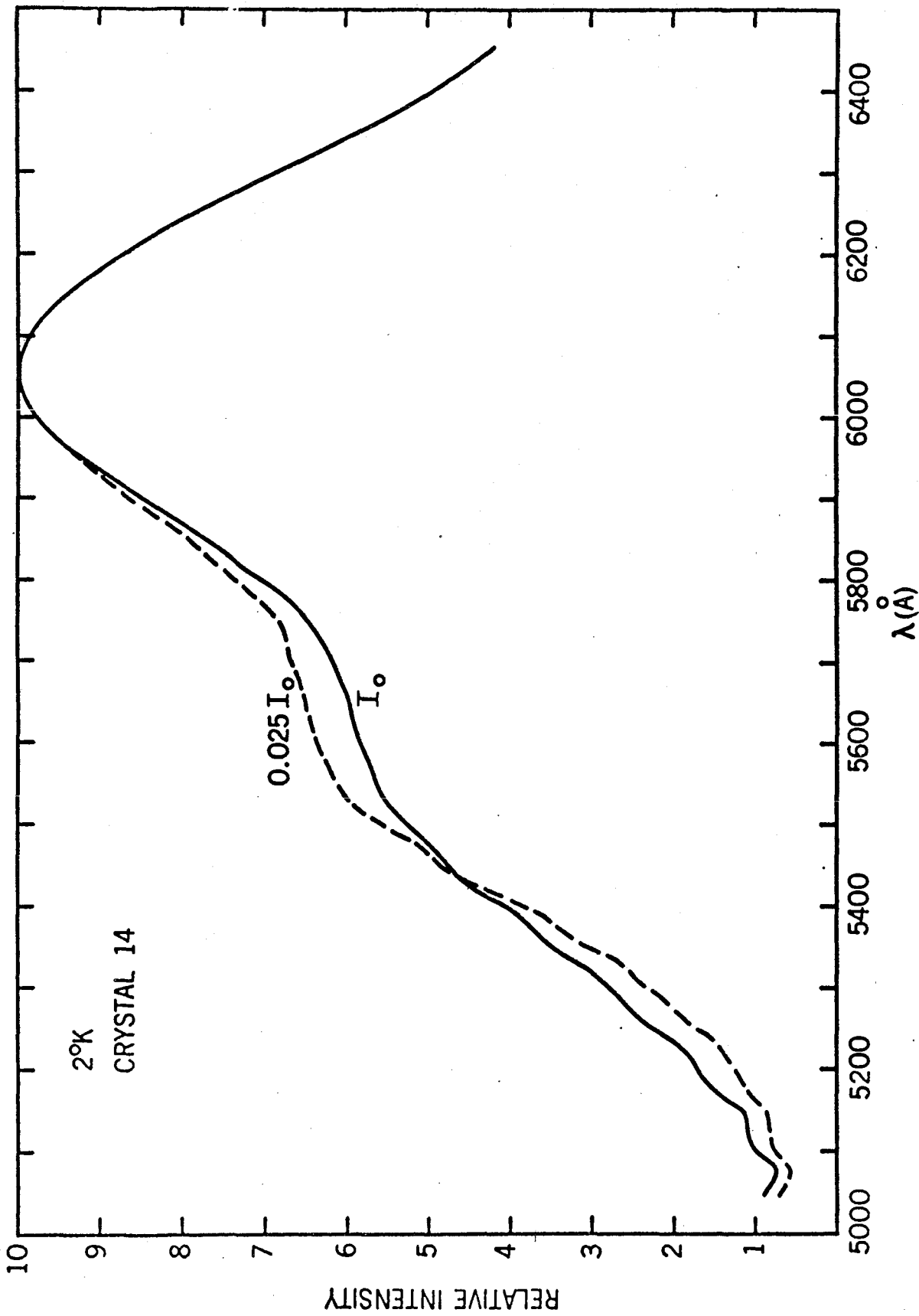


Figure 5.1A Emission spectra as a function of excitation intensity  $I_0$  and  $0.025 I_0$ .

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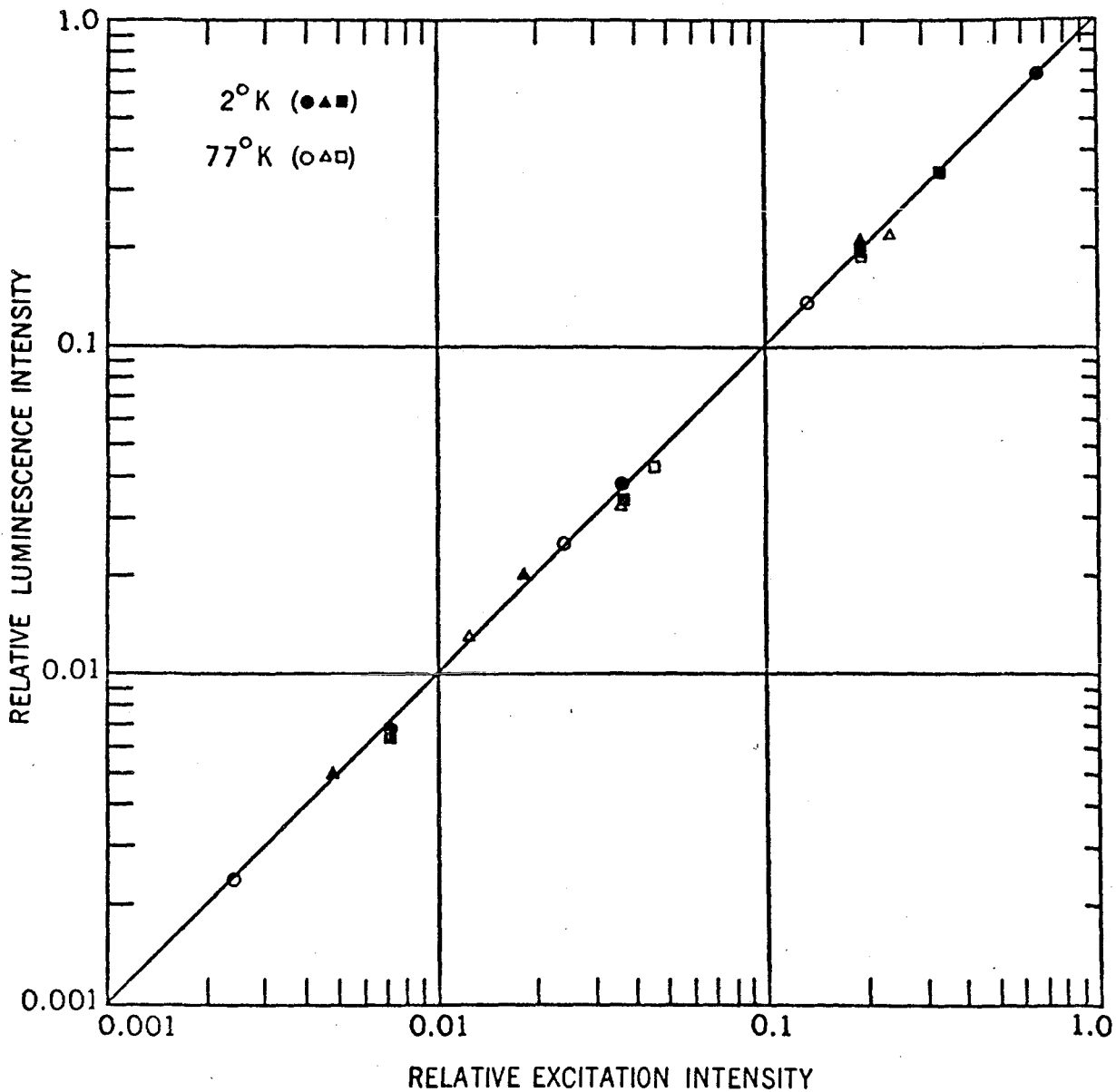


Figure 5.1B Luminescence intensity of the 6100 Å emission as a function of excitation intensity for 3 crystals.

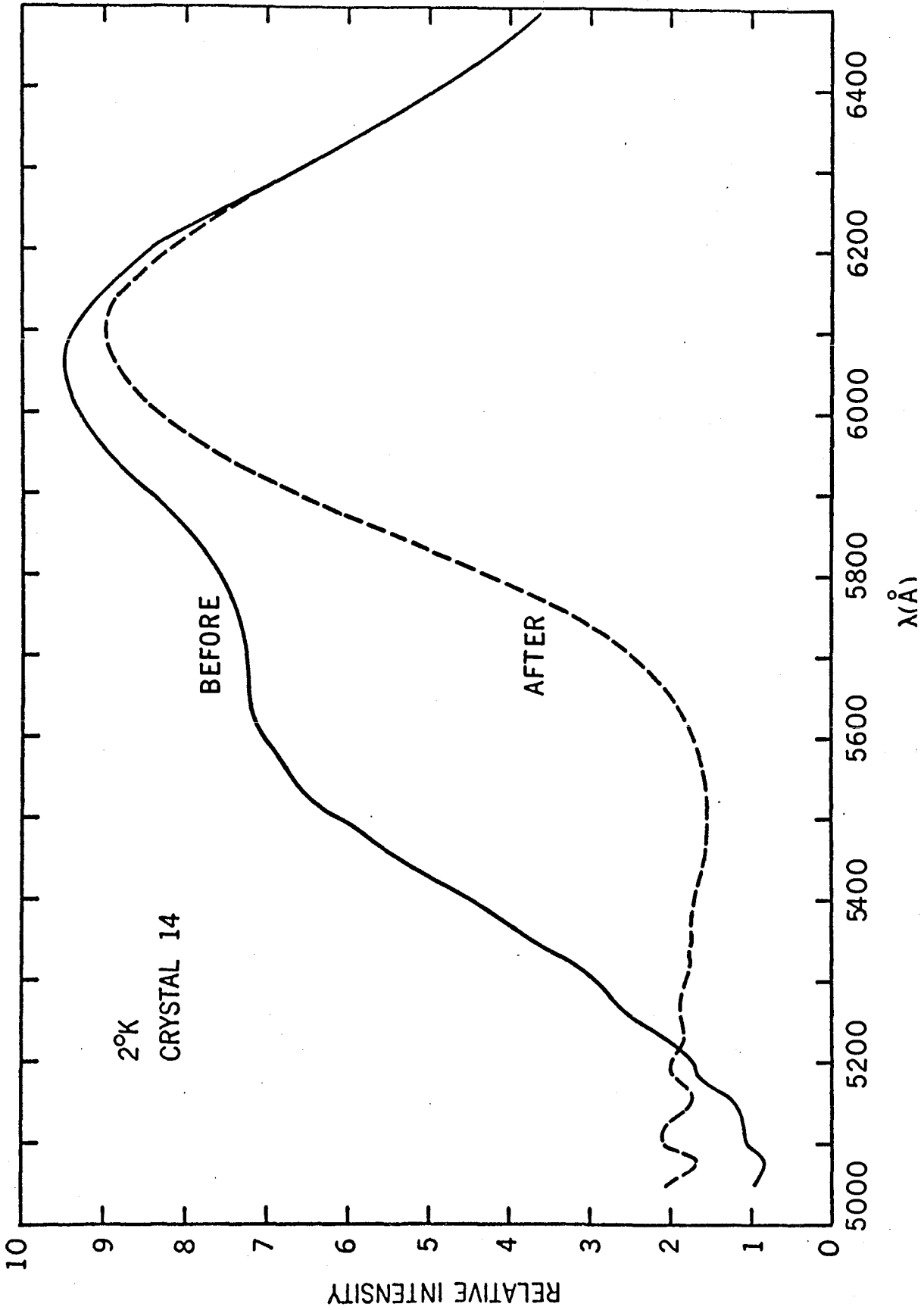


Figure 5.2A The effect of heat treatment at 200° C for 20 minutes on the spectrum of crystal 14.  
Solid line: before heat treatment.  
Dash line : after heat treatment.

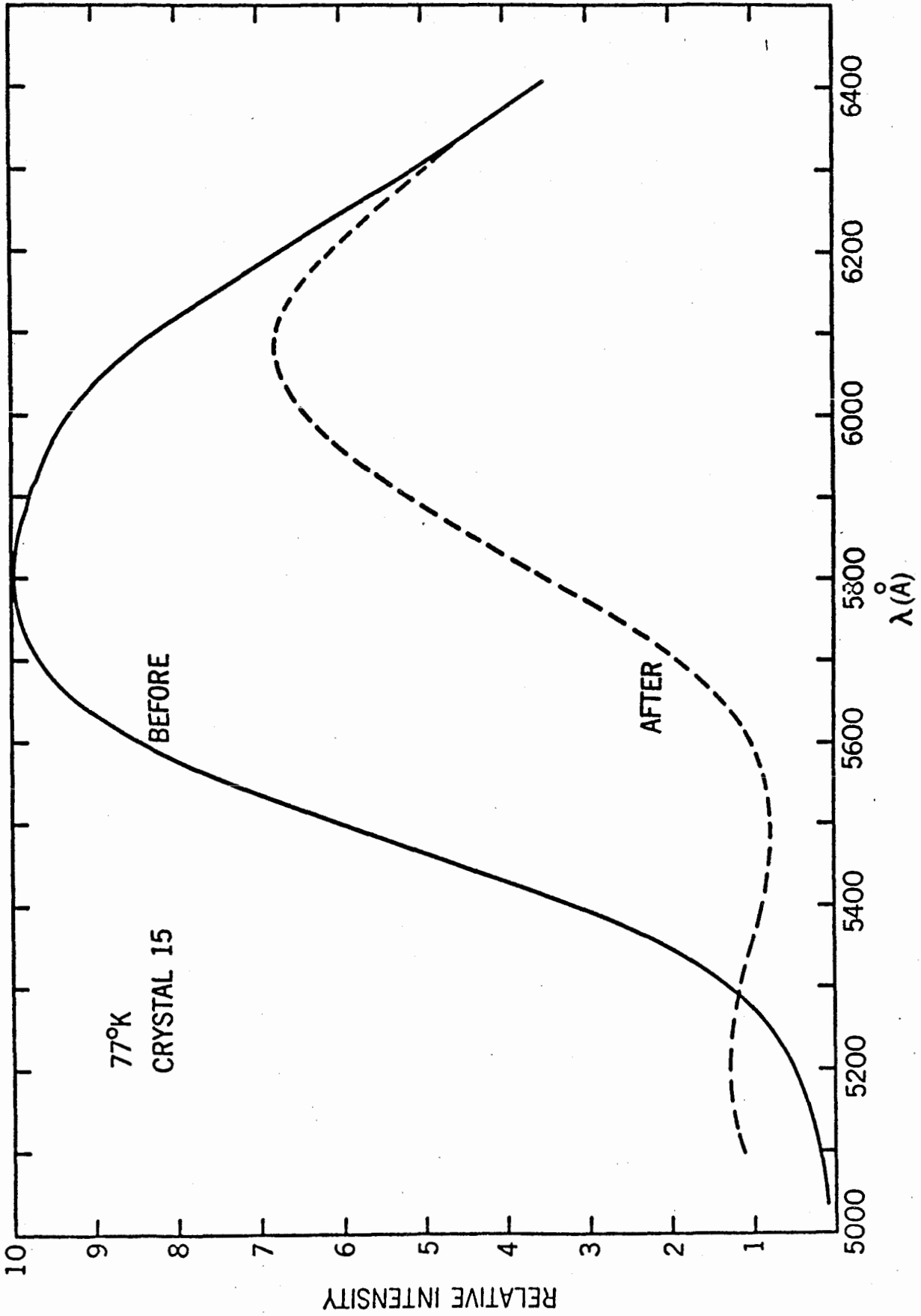


Figure 5.2B The effect of heat treatment at 200° C for 20 minutes on the spectrum of crystal 15.  
Solid line; before heat treatment.  
Dash line : after heat treatment.

4.1). The reduction in the intensity of the 5600 Å emission is attributed to the increase association of Ag acceptors and donors, thus reducing the concentration of distant pairs.

4. The 6100 Å emission is enhanced in ordinary Ag doped crystals by annealing at low temperature (van Gool 1958); conversely as we have observed it is reduced by temperature quenching. We have attempted, by temperature quenching, to produce the 5600 Å band in ordinary Ag doped crystals. Figure 5.3 shows the spectrum of a crystal which was quenched from 900°C. The measured spectrum is believed to be the sum of a 5600 Å and a 6100 Å band as represented by the dash lines.

The results of the present study should be useful to the interpretations of some other emissions arising from the deep centers Cu, Ag and Au in II-VI compounds. (For a review of deep center luminescence see Chapter 9 in Aven and Prener 1967). For example the measurements of the peak position of the Ag emission band in the  $Zn_xCd_{1-x}S$  ternary system shows that the 6100 Å band of Ag in CdS correlates with the 4000 Å band of Ag in ZnS (see Figure 9.5 in Aven and Prener for this and other correlations). Thus one can conclude that the 4000 Å emission in ZnS also arises from associated Ag centers. Also one may expect the 8200 Å Cu emission in CdS to arise from associated Cu centers.

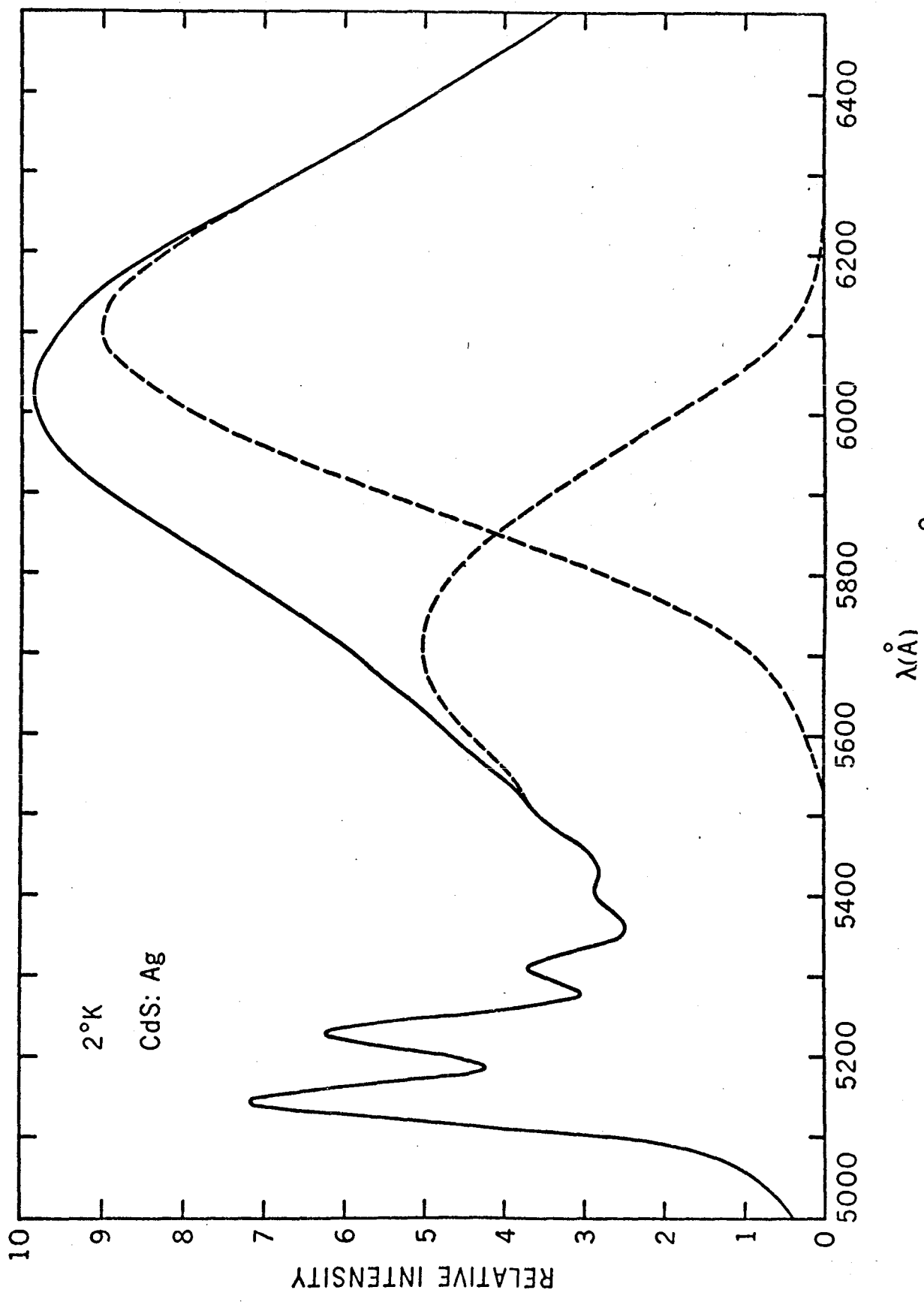


Figure 5.3 An attempt to produce the 5600 Å emission in a conventionally Ag doped crystal by quenching from 900° C. The measured spectrum (solid line) is believed to be the sum of a 5600 Å and a 6100 Å band as represented by dash lines.

## CHAPTER 6

### SUMMARY AND CONCLUSIONS

$\text{Cd}^{109}$  was diffused into CdS single crystals. For a given  $\text{Cd}^{109}$  doped crystal photoluminescence spectra were taken as a function of Ag concentration resulting from the decay of the radioactive  $\text{Cd}^{109}$ . The Ag impurities derived from the decay give rise to a new emission (5600 Å), which is not present in conventionally Ag doped crystals. The intensity of this emission increases linearly with increasing Ag concentration, but is quenched with increasing concentration above  $4 \times 10^{16} \text{ cm}^{-3}$  Ag impurities. The concentration quenching by the Ag impurities of the green edge emission, and the bound-exciton  $I_1$  (neutral acceptor) and  $I_2$  (neutral donor) is also observed. Simultaneously the peak position of the green edge emission is shifted towards higher energy with increasing Ag concentration.

The new emission is interpreted as arising from a bound electron to bound hole recombination at distant donor-acceptor pairs with the Ag impurities as the acceptors. The dependence of emission intensity on Ag concentration is predicted theoretically by the pair distribution function. The analysis of the experimental data gives  $r = 230 \text{ Å}$  for the separation of the donor-acceptor pairs responsible for the new emission at 5600 Å. The analysis also gives a donor concentration of  $2.4 \times 10^{16} \text{ cm}^{-3}$  for crystal 4. The binding energy of the Ag acceptor is estimated to be 0.34 eV, based on the peak position

of the new emission band. The measurement of electrical conductivity as a function of Ag concentration in Cd<sup>109</sup> doped crystals also shows that Ag is an acceptor. In addition it gives about the same donor concentration for crystal B as that given above, which is also in the same range as those obtained from room temperature electrical conductivity measurements on annealed pure crystals.

The quenching of the green edge emission is also interpreted quantitatively based on the pair distribution function. The separations of the pairs responsible for the green edge emission are found to be 230 Å and 280 Å for crystals 20 and 1, respectively. This is approximately the same as that of the new Ag acceptor-donor pair separation (230 Å). The peak shift provides further evidence that the low energy series of the green emission arises from bound to bound recombination at distant donor-acceptor pairs and not at closely associated pairs as has recently been advocated. The concentration dependence of the quenching of I<sub>1</sub> and I<sub>2</sub> emissions is qualitatively explained.

The emission band at 6100 Å, which is present in conventionally Ag doped crystals, is also observed to increase in intensity with increasing Ag concentration in the Cd<sup>109</sup> doped crystals. Because this emission is also seen in some pure crystals doubt has been raised about the interpretation that the emission originates from Ag centers. However our experimental observations remove this uncertainty. Furthermore it



is concluded that the Ag center responsible for this emission is associated with another impurity atom, but less likely with a native defect.

The conclusion that the new emission arises from recombination at distant Ag acceptor-donor pairs while the 6100 Å emission originates from closely associated Ag centers is consistent with the correlation between intensity of the new emission and that of the green edge or the I<sub>2</sub> emission in a Cd<sup>109</sup> doped crystal. It is also consistent with the results of the temperature annealing and quenching experiments performed.

The present study has demonstrated the usefulness of the isotope technique in the investigation of luminescence processes. It is hoped that greater use will be made of the isotope technique in this area of investigation.

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