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DIFFUSION AND LUMINESCENCE OF RARE EARTHS
IN CADMIUM SULFIDE

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

by

Dexter George Girton, B.S. in E.E., M.S.

* * * * * * *

The Ohio State University
1959

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<td>metal (cation) component of binary crystal</td>
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<td>X</td>
<td>nonmetal (anion) component of binary crystal</td>
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<td>$V_M$</td>
<td>vacant M-site</td>
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<td>$V_X$</td>
<td>vacant X-site</td>
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<td>interstitial M</td>
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INTRODUCTION

Rare earth doped II-VI compounds, such as CdS:Yb, are of considerable research interest and have several potential applications. The research interest has many facets such as luminescence, optical absorption, electron paramagnetic resonance (EPR), host crystal defect, and diffusion studies. Some potential applications include narrow band luminescent diodes, laser diodes, and phosphors for cathodoluminescent applications.

The luminescent properties of rare earth doped II-VI compounds arise from features of the rare earth elements and the II-VI compounds. The emission from the trivalent rare earth ions results from transitions occurring between certain 4f electron levels. These transitions, which are not allowed in an isolated ion, may be allowed when the ion is in the perturbing fields of a solid or liquid. In the host the 4f electrons of the rare earth are fairly well shielded by the outer valence electrons and therefore, the position of the energy levels shift only slightly and the line width of the transitions remains quite narrow. Several II-VI compounds provide the proper host to make these transitions possible as well as being transparent to the emission.
Most of the studies of emission from rare earth ions in II-VI compounds have been reported on crystals doped during growth, although Kingsley and Aven prepared ZnSe:Er by diffusion for paramagnetic resonance and fluorescence studies. Papalardo and Dietz prepared CdS:Yb by diffusion, but only made optical absorption measurements. Recently, Watts and Holton prepared CdS:Yb and CdS:Dy by diffusion for EPR studies. The present investigation is the only known study of the properties of rare earth diffusion in II-VI compounds.

To date we have diffused Pr, Nd, Ho, Er, Tm, and Yb into CdS, and Ho, Er, Tm, and Yb into ZnSe and observed the rare earth emission spectra. For a given temperature and chalcogen pressure, the emission characteristics are very reproducible from run to run and, for Yb, Nd, and Er in CdS, as good as the best crystals we had

+ References are repeated at end of dissertation.

prepared by doping during vapor phase growth. The emission of Pr, Ho, and Tm has been observed in CdS prepared by diffusion for the first time. Previous attempts to prepare these later three materials by vapor phase growth were unsuccessful.

The technique of producing rare earth doped CdS crystals by vapor phase transport is very sensitive to details of preparation compared to the diffusion technique. As an illustration of this, the luminescence of Tm in CdS prepared by diffusion is roughly as strong as for similarly prepared Yb in CdS. However, no luminescence was observed in crystals prepared with Tm by vapor phase growth methods. Furthermore, it has been observed in some vapor phase grown crystals, that the intensity of the rare earth emission was not constant over the entire volume of a single crystal. Also, it is much more difficult to control the properties of crystals doped during vapor phase growth than those doped by diffusion.

The present diffusion study has centered on CdS:Yb because Yb gave the strongest luminescence in crystals grown by the vapor phase method. Vapor phase growth was initially used before it was realized that diffusion would be effective. Less extensive investigations of other rare earths in CdS (and ZnSe) are made in this study, and they indicate a diffusion behavior similar to Yb.
In this study, the luminescent intensity of $\text{Yb}^{3+}$ in CdS as a function of depth from the surface was used to imply some properties of the diffusion. Radioactive tracer techniques are typically used to study impurity diffusion, but this method was not used because we are not presently instrumented for it. On the other hand, luminescent profiles yield useful information about the diffusion and the manner in which the ion is incorporated into the lattice.

The luminescent spectra and profiles of rare earth diffused CdS (and ZnSe) as well as the profiling technique are presented in Chapter 5. These constitute the major contribution resulting from this study. The diffusion mechanism is explained in Chapter 6 by means of a proposed atomic model. Chapter 2 gives the theoretical framework for discussing the model. The essential luminescent and diffusion related properties of the rare earths, Cd, S, and other elements are discussed in Chapters 3 and 4.

The usual approach in diffusion studies of elemental crystals has been to measure the diffusion coefficient over a range of temperatures and use this information to determine the diffusion mechanism. Although this approach has been extended to compound crystals, several complications typically arise. For compound crystals, the diffusion profiles are often more complex and an accurate determination of the diffusion coefficient
becomes difficult. Gradients in stoichiometry, which are difficult to measure, alter the solubility of the impurity as a function of depth from the crystal surface. Little is known about the surface impurity concentration during diffusion because the status of the impurity source is obscured by the occurrence of various compounds formed from the crystal constituents and the impurity element.

An attempt is made in this study to define all the parameters of our diffusion process rather than make a major study on one aspect. This approach results in some tendency for the various topics discussed to appear unrelated. The reader should bear in mind that this study is an initial investigation into a complex and not too well understood process. Suggestions for further work are included in Chapter 6.
CHAPTER 1
METHODS OF PREPARING RARE EARTH DOPED CdS

The preparation of rare earth doped CdS by diffusion is briefly discussed in this chapter (more details in Chapter 5). Vapor phase growth of rare earth doped CdS is described in detail, with attention drawn to the uncertainties and variable results of this process so that the development of the diffusion process may be properly appreciated.

1.1 Diffusion

Diffusion is a fairly simple process to carry out experimentally. The crystal to be diffused and the diffusing element or elements are sealed in a quartz tube. The diffusion ampoule is then heated for a length of time, cooled, and opened.

The diffusion of an element into the crystal is controlled by the nature of the diffusing element and the crystal chemistry. The crystal chemistry is determined by the chemical components of the crystal, crystal defects, the ambient phase, temperature, and time. These factors can be controlled during diffusion except for unknown foreign atoms and certain crystal defects which arose sometime during the history of the crystal.

If samples are taken from the same boule of "pure" CdS, then the unknown foreign atom concentrations and crystal defects are
likely to be nearly the same in each sample. This is a valid assumption for materials from selected suppliers using the best crystal growth techniques developed to date for CdS and related materials. Thus the diffusion becomes reproducible. For example, in a series of five Yb diffusions in CdS (at 960°C, 33 atm. S, 1 hr), the intensity of the rare earth emission varied at most 30 percent under identical excitation conditions. (More details of the crystal preparation and measurements are given in Chapter 5.)

Sometimes it is desirable to have samples doped uniformly (or nearly uniformly) throughout a specified portion of the crystal. In principle this is easier for crystals doped during vapor phase growth than crystals doped by diffusion. In diffusion, the concentration at a fixed depth depends on the diffusion coefficient and time. Thus, it is possible that the depth (or the sample thickness) of interest, the diffusion coefficient, and the allowable time are such that it is practical to prepare samples by diffusion for certain applications. This would be the case for Yb diffused CdS (e.g., at 960°C, 33 atm. S, 1 hr) samples intended for diode fabrication. In this case the depth of fairly uniform concentration in about 50 μ, which is more than sufficient for a diode formed by ion implantation.

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It is also practical to prepare samples of mm dimensions by longer diffusions.

1.2 Vapor Phase Growth

A description of our method of preparing crystals doped with rare earths during vapor phase growth is given below. Other methods are described in the literature. The steps in our process are named so that reference can be made to them.

Starting material:

CdS: Submicron size CdS powder, type S-20 described as luminescent grade, available from Sylvania Electric Products, Inc., Chemical and Metallurgical Division, Towanda, Pennsylvania.

Rare Earth: Commercially available rare earth nitrates (or chlorides). For example, for Yb doped crystals, ytterbium nitrate, 99.9% purity, \((\text{Yb} \cdot \text{NO}_3)_3 \cdot 6\text{H}_2\text{O}\) was used. It is available from American Potash and Chemical Corporation, Rare Earth Divisions, West Chicago, Illinois.

A. Charge Preparation

1. Mixing - Typically, 2.0 g \(\text{Yb(NO}_3)_3 \cdot 6\text{H}_2\text{O}\) was dissolved by 4.0 ml \(\text{H}_2\text{O}\) (double distilled).
This solution was mixed with 10.0 g CdS powder by mechanical stirring and then ultrasonically agitated.

2. **Drying** - The wet mix was poured onto a small petri dish, placed in a bell jar, and dried by vacuum evaporation for approximately 8 - 12 hrs. at room temperature.

3. **Heat and Chemical Treatment** - The dried mix was then ground to a very fine powder in a ceramic mortar and pestle. This ground and dried mix was spread out in a half-round quartz boat about 1" across and 6" long. The boat was placed in an enclosed quartz tube (in a furnace at room temperature) in which a mixture of He and H₂S was flowing at a pressure of 1 atm. The rate of flow of each of these gases was monitored by identical floating ball type flow meters. The rate of flow was adjusted so that the ball in the meter monitoring the H₂S was twice as high (numerically) as the ball in the He flow meter. The furnace which was set for 800°C had a warm-up rate of about 600°C/hr. After about 8 hours at 800°C the boat was pushed
out of the furnace hot-zone to the cold end of the flow tube. There the boat was allowed to cool to about 130°C and then was removed from the flow tube.

4. Vacuum - The chemically treated powder was placed in a clean 8 mm I.D. x 12 mm O.D. quartz tube. The tube was baked for about 8 hours under vacuum at temperatures ranging from 300°C to 600°C for different runs. Heating time varied from 10 minutes to 12 hours.

B. Encapsulation

The bake-out furnace was removed and the quartz tube was sealed off at about 2 x 10^{-5} torr pressure. The charge powder was shaken to one end of the capsule while the other end (usually the flat end) was cleaned of clinging powder particles by heating it with a torch.

C. Growth

The capsule was placed in a furnace which had two controllable temperature zones. Although for different runs the temperatures of the zones were varied, the seed end (crystal growth end) of the capsule was maintained at 50 to 75°C lower than the powder charge end. Seed end temperatures ranged from 1025 to 1250°C. After 3 days the capsule was
cooled slowly, roughly 700-1000°C/hr., by gradual removal from the furnace. Some capsules were removed suddenly.

D. Annealing

If a small amount or no emission resulted from the above as-grown crystals, they were annealed at 800°C in saturated S vapor (approximately 20 atm.) for one hour.

The purpose of some of the above steps and suspected uncontrollable (or difficult to control) factors will now be given.

The mixing and drying is simply a method of getting the ytterbium nitrate adsorbed onto the submicron size CdS powder particles. The heat and chemical treatment have several purposes:

a. Heating was used to drive off the water of hydration from the ytterbium nitrate. A slow warm-up was employed so that hopefully this water can escape before temperatures are reached at which oxides could form. On occasion a white powder, probably Yb₂O₃ was observed. This indicates that an uncontrollable amount of this compound could have been forming during this step. Yb₂O₃ is likely a stable compound at 800-1300°C, and once formed, the Yb would probably not be available in the vapor phase transfer process.

b. The H₂S was used for two reasons. Some of the hydrogen disassociated and provided a reducing atmosphere to
carry off oxygen. Also, the free sulfur hopefully replenished any sulfur lost from the CdS (there is some doubt as to the necessity of this replenishment). The amounts of disassociated H$_2$ and S was unknown, but in principle there would be some control of them by the flow rates and the fraction of He present.

c. In the preparation of high purity undoped CdS crystals, varied heating periods up to several days and 500-1000°C temperatures have been used.\(^8,9\) This heat treatment was used to drive off unwanted (and usually unknown) volatile impurity substances and thus helped purify the CdS powder. A similar process may be operative in the heat treatment of the rare earth impregnated charge mix, but its advantage may be counterbalanced by the formation of rare earth sulfides. On many occasions a brown-green layer, probably rare earth sulfides or oxysulfides, was found on top of the powder after removal from the flow tube. The usefulness of rare earth sulfides in this type crystal growth process is unknown.


Only limited information pertaining to any of the possible chemical reactions can be found in the literature. Reactions involving ytterbium nitrate with CdS have not been described. Some information regarding the action of H₂S on Yb₂O₃ has been published.¹⁰ At 700°C Yb₂O₃ in a H₂S atmosphere is slowly transformed to a mixture of Yb₂S₃ and Yb₂O₂S. At 900°C the transformation is rapid but Yb₂O₂S is still present. A temperature of 1250°C is required to eliminate oxygen and the product is Yb₃S₄. (It should be realized that an attempt to eliminate oxygen from the rare earth impregnated charge by heating to temperatures above 980°C at 1 atm. pressure would be unsuccessful because the CdS would sublime.)

The adsorption of H₂S, SO₂, O₂, H₂O, and S₂ onto CdS powder has recently been investigated by studying the density and conductivity changes of the powder.¹¹ In the temperature range studied (200-400°C), the CdS powder was found to have a strong affinity for O₂, SO₂, and H₂S. The affinity for these molecules was attributed to a strong surface attraction for S²⁻ and O²⁻ type particles. The adsorption of H₂S, O₂ and H₂O increased with the gas pressure but decreased with temperature. S₂ adsorption increased with both pressure and temperature.


The purpose of the vacuum bake-out was to remove excess S. When the bake-out procedure was not used, too much pressure occurred in the capsule during crystal growth. This pressure was evident when the charge end of the quartz capsule, which had softened at the growth temperature, slowly expanded to the diameter of the furnace muffle tube. Also, excess vapor pressures will inhibit the vapor transfer process. The amount of S eliminated by the bake-out procedure is a function of the temperature, pressure, and length of heating. Although the time and temperature are easy to control, the amount of excess S remaining in the charge mix was still undetermined. A trial and error type procedure led to a bake-out at 600°C for about 8 hours. Some of the volatiles given off condensed on the colder part of the quartz tube. Sometimes a white substance appeared as a thin coating in addition to the usual yellow S coating. The white substance would appear once in a while in the bake-out even though the previous preparatory steps in a series of runs were thought to be identical. This was another unknown and uncontrolled factor.

The crystal nucleation and type of growth, whether single or polycrystalline, were relatively uncontrolled. Occasionally, a single crystal would be obtained, but usually the boule would be polycrystalline with 3 to approximately 50 crystals. Often cracks would occur during cooling, and sometimes the boule would adhere to the walls of the tube so tightly that the quartz would crack also.
During a 9-month period, 36 boules were grown on a trial and error basis. Toward the end of this period a few crystals were showing a moderate amount of luminescence, but none were as good as those grown by Anderson at Stanford University. He experimented for about one year before producing some crystals with good luminescence.

Most of the crystals grown by Anderson showed luminescence only after annealing in S vapor at 800°C. No improvement was noticed when crystals grown here were annealed in S vapor. In fact, OSU as-grown crystals, which showed moderate luminescence, gave no emission after annealing in S or Cd vapor.

One attempt was made to produce a crystal by vapor phase growth using a "pure" CdS crystal in the charge end of the growth capsule and a small piece of Yb metal turning (perhaps 100 mg) in the middle of the capsule. CdS transfer was reduced, probably by the vapor pressure of the Yb, but a few small crystals showed some emission. Then a diffusion of the type previously described was tried and shortly the major effort of the present diffusion study began.

The chemistry of CdS crystals doped during growth is complicated by the presence of O and N, when Yb (NO₃)₃ ⋅ 6H₂O is used in the preparation. The presence of O in some form was indicated by the appearance of a white residue which remained
after crystal growth. This residue is believed to be $\text{Yb}_2\text{O}_3$, since Yb sulfides (see Table 10) and $\text{Yb}_2\text{O}_2\text{S}$ are colored.\textsuperscript{10}

Even though a particular experimenter is successful in producing CdS:Yb crystals by vapor phase growth in one laboratory, he may have difficulty reproducing his result in another laboratory. There are many areas for research in vapor phase grown crystals doped during growth. This is still a potentially useful technique. However, methods of process control will have to be refined to a point where (1) consistent, reproducible results are obtained and (2) some basic knowledge of reaction kinetics at each stage of the process is available.
CHAPTER 2

SOLUBILITY AND DIFFUSION OF DEFECTS IN CdS

A survey of the theory of solubility and diffusion in solids as well as published experimental data for CdS are presented in this chapter. This will be used as a framework to discuss the experimental results in Chapter 6.

2.1 Defects in Solids

Solubility and diffusion depend on the defect structure of a solid. Several authors\textsuperscript{12-21} have described various defects in

\begin{itemize}
  \item \textsuperscript{15} H. G. Van Bueren, Imperfections in Crystals, North-Holland Publishing Company, Amsterdam (1960).
  \item \textsuperscript{17} F. A. Kroger and H. J. Vink, Solid State Phys., 3, 307 (1956).
  \item \textsuperscript{19} G. Brouwer, Philips Res., 9, 366 (1954).
  \item \textsuperscript{20} R. A. Swalin, Thermodynamics of Solids, Wiley, New York (1962).
\end{itemize}
elemental and compound crystal structures. Using the notation of Van Gool, a brief description of defects in binary crystals is given here for use in later discussions.

2.1.1 Description of Defects in Binary Crystals

A metal (cation) component M and a nonmetal (anion) component X are the constituents of the binary compounds MX considered here. The vacancy of a metal atom is denoted by $V_M$, and a vacant nonmetal atom by $V_X$. Impurity atoms on lattice sites are denoted by their chemical symbols with the appropriate subscript.Interstitial atoms are written as $M_i$, $X_i$, Yb$_i$, etc. Associated centers are written by bracketing the components, for example $(V_MV_X)$, $(X_iV_M)$, etc.

Free holes and electrons are described by $h$ and $e'$, respectively. Similarly, effectively charged centers are written as $V_M^+$, $M_i^+$, $(Yb^+_MY_M)^-$, etc. Centers with two effective charges are indicated by $V_X^{++}$, $X_i^{++}$, etc.

The concentration of defects is indicated by square brackets such as, $[V_X]$, and $[Yb^+_M]$, and $[(Yb^+_iV_M)]$. Following tradition, the concentrations of free holes and electrons are indicated by $p$ and $n$, respectively. Thus $[h] = p$ and $[e'] = n$.

The symbols * and ' have been used to indicate effective charges. However, the + and - symbols are used to indicate real charge of ions, as is customary. Thus Yb$^{3+}$ indicates the triply ionized Yb atom.
A subscript g is used to indicate an atom or molecule in the gaseous state. Examples are Cd\textsubscript{g}, S\textsubscript{2g}, and Yb\textsubscript{g}.

The defect notation used in this section is that which seems to be emerging more and more in the current literature, although it is not free from ambiguities. For example, (Cu\textsubscript{Cd}V\textsubscript{Cd}) could represent several types of defect centers in which the components of the association have different charge states. (To emphasize neutrality a superscript * or x may be used in literature, e.g., V\textsuperscript{*}\textsubscript{Cd}, Cu\textsuperscript{+}, (Cu\textsubscript{Cd}V\textsubscript{Cd})\textsuperscript{x}). Several types of notation have been used by various authors to describe defects and this can lead to confusion when comparing different writings. Van Gool\textsuperscript{13} (pp. 21-24) makes a comparison of some of the different notation used in the literature and points out a few of the difficulties encountered by merely replacing one set of symbols with another. For example, certain symbols have been used with an assumed (and perhaps hidden) thermodynamic meaning which does not permit them to substitute directly for the most obvious replacement of another set.

Macroscopic crystalline defects, such as dislocations, grain boundaries, and voids, will not be considered in the discussion of the solubility of defects. Although these defects affect
diffusion in some cases\textsuperscript{22-25}, their concentrations are not within the range of control of the allowed temperature and pressure for most diffusion experiments. Precipitates of Cd or S are sometimes found in CdS, and their concentration is affected by diffusion temperatures and pressures.\textsuperscript{26} However, since they are concentrated in macroscopic regions of the crystal, they will similarly be neglected in solubility considerations.

The term "native defect" will be used in a general way to include vacancies, interstitials, holes and electrons, and their associates. The term "defect" will be used to include impurity atoms, native defects, and associates, but not macroscopic crystal-line defects such as dislocations, grain boundaries, voids and precipitates.

In general, impurity ions will be electrically compensated by some type of defect of opposite polarity. The position of the ion in the lattice together with the means of charge compensation comprise the incorporation mechanism.


\textsuperscript{26}V. S. Babinchuck and V. V. Seroyuk, Soviet Phys. Solid State, 10, 509 (1968).
2.2 Defects in CdS

At the present, only limited information is available on the type and concentration of native defects in CdS at diffusion temperatures. Boyn\textsuperscript{27} has calculated the concentration of native defects at 800°C as a function of Cd pressure but few measurements of any of the concentrations above 400°C are known. Measurements of current flow at 400-730°C have been made as a function of the ambient vapor pressure\textsuperscript{28}, but the corresponding electron concentration has not been determined.

It is not known with certainty whether S vacancies or Cd interstitials are the dominant defect responsible for the n-type conductivity of CdS. Recent literature favors Cd interstitials and vacancies as the dominant defects, and at diffusion temperatures these are thought to act as double donors and double acceptors, respectively.\textsuperscript{27}

S interstitials are likely to occur in high concentrations in CdS under the high S pressure present in our diffusion runs. However, because negative charge states of S\textsubscript{i} are improbable due to the size of the negative S ions these defects should always be neutral.\textsuperscript{27} Therefore, S vacancies and interstitials will not be considered in later discussions involving charge balance.


Experimental data on the type of site occupied by rare earths in II-VI compounds are just beginning to emerge. Optical data have indicated a multiplicity of sites\textsuperscript{2}, and recent EPR measurements have identified isolated trivalent rare earth ions substituted for metal ions in wurtzite and zinc-blende II-VI crystals.\textsuperscript{5} In particular, the sites Er\textsubscript{\textit{Cd}}\textsuperscript{3+} and Yb\textsubscript{\textit{Cd}}\textsuperscript{3+} have been identified in CdS, and two unknown types of sites for Er and Yb were also found. More measurements will have to be performed in order to clarify the unknown sites and the type defect association present.

2.3 Solubility of Defects at Diffusion Temperatures

Many defect reactions occur in a crystal under thermal equilibrium. Other reactions occur between the crystal and its ambient gas (or liquid). Albers\textsuperscript{12} has discussed the physical chemistry of defects and Van Gool\textsuperscript{13} has given a general procedure for calculating the solubility of defects. These calculations are based on the mass action law of physical chemistry, charge balance between oppositely charged defects, and an assumed incorporation mechanism. The functional relationship between the defect concentrations and the ambient pressures can thus be obtained. Attempts to experimentally verify this type calculation can be found in the
Only limited agreement has been obtained, probably because the incorporation mechanisms are more complex than was assumed.

Solubility calculations can be used in two ways. One is to assume an incorporation mechanism and calculate the pressure dependence of the defect concentrations. However, if other than a simple incorporation mechanism and charge compensation are allowed, the mathematical difficulties multiply greatly. The other way is to use the experimentally determined pressure dependence to help deduce the incorporation mechanism. These aspects are illustrated in the following calculation of defect solubility in CdS:Yb.

Consider the following ten defects for Yb doped CdS:

\[ V_{\text{Cd}}, V'_{\text{Cd}}, V''_{\text{Cd}}, \text{Cd}^+, \text{Cd}^+_1, \text{Cd}^+_i, \text{Cd}^+_i, e^+, \text{h}^+, \text{Yb}^2_{\text{Cd}}, \text{and Yb}^3_{i^+}. \]

Although other defects may be important, such as \((\text{Yb}^4_{\text{Cd}, \text{Cu}_{\text{Cd}}})^3\), these are sufficient to illustrate the value of solubility relations as well as point out the problems encountered. The following reaction equations describe the removal of a Cd atom at a Cd site to the gaseous state (and vice versa) and the ionization of a Cd vacancy:

---


Similarly, the creation of a Cd interstitial and its ionization can be described by

\[ \text{Cd}_{\text{Cd}} + \text{Cd}^* \rightarrow \text{Cd}^* + \text{Cd} \quad (2.4) \]

\[ \text{Cd}^* + e' \rightarrow \text{Cd}^* + e'. \quad (2.5) \]

The reaction between \( e' \) and \( h \) is given by

\[ 0 + e' + h, \quad (2.7) \]

The reaction between substitutional and interstitial Yb is given by

\[ \text{Yb}_{\text{Cd}}^* + \text{Yb}^* + V_{\text{Cd}'}', \quad (2.8) \]

and the relation between Cd, \( S_2 \) and solid CdS is given by

\[ \text{CdS} + \frac{1}{2} \text{S}_2 = \text{Cd} + \frac{1}{2} \text{S}_2, \quad (2.9) \]

By using the law of mass action and some minor algebraic manipulation on the above reactions one obtains the following equations:

\[ \frac{P_{\text{Cd}}^2}{P_{\text{S}_2}} = K_{\text{CdS}} \quad (2.10) \]
\[
[V_{Cd}] = K_{oCd}^{-1} = K_0^{1/2} P_s^{1/2} = K_1^{1/2} P_s^{1/2} \quad (2.11)
\]

\[
[V_{Cd}'] = K_2 [V_{Cd}] n = K_1 K_2 n P_s^{1/2} \quad (2.12)
\]

\[
[V_{Cd}''] = K_3 [V_{Cd}'] n = K_1 K_2 K_3 n^2 P_s^{1/2} \quad (2.13)
\]

\[
[\text{Cd}^+_1] = K_4 [V_{Cd}]^{-1} = K_4^{-1} P_s^{1/2} \quad (2.14)
\]

\[
[\text{Cd}^+_2] = K_5 [\text{Cd}^+_1] n^{-1} = K_1^{-1} K_4 K_5 n^{-1} P_s^{1/2} \quad (2.15)
\]

\[
[\text{Cd}^+_1]^* = K_6 [\text{Cd}^+_1] n^{-1} = K_1^{-1} K_4 K_5 K_6 n^{-2} P_s^{-1/2} \quad (2.16)
\]

\[
[\text{Yb}^+_i^*] = K_{si} [\text{Yb}^*_{Cd}] [V_{Cd}']^{-1} = K_{si} (K_1 K_2 K_3)^{-1} [\text{Yb}^*_{Cd}] n^{-2} P_s^{-1/2} \quad (2.17)
\]

\[
p = K_{eh} n^{-1}, \quad (2.18)
\]

where \( p \) with the appropriate subscript is a partial pressure, and the constants \( K \) (with the identifying subscript) are the thermodynamic equilibrium constants of the reactions.

Charge neutrality requires

\[
[\text{Yb}^*_{Cd}] + 3[\text{Yb}^+_i^*] + [\text{Cd}^+_1] + 2[\text{Cd}^+_1]^* + p = n + [V_{Cd}'] + 2[V_{Cd}'']. \quad (2.19)
\]

Thus, Eqs. (2.11) - (2.19) is a system of nine equations containing the ten defect concentration variables. The remaining equation will come from the reaction relation describing an incorporation mechanism for \( \text{Yb} \). Consider the reaction.
which describes one incorporation mechanism among many which are possible. Relation (2.20) describes an Yb atom in the gaseous state replacing a Cd atom, and removal of the Cd atom to the gaseous state (and vice versa). The mass action law for (2.20) and Eq. (2.10) give

\[ n = K \left[ \frac{[Yb^*]_C}{Cd} \right]^{-1} p_{Cd}^{-1} p_{Yb} = K_{im} \left[ \frac{[Yb^*]_C}{Cd} \right]^{-1} p_{S2}^{1/2} p_{Yb}. \]  

(2.21)

The ten Eqs., (2.11) - (2.19) and (2.21) can in principle be solved for each of the defect concentrations. For example, a fourth order polynomial in \([Yb^*]_C\) can be derived by substituting the right hand sides of Eqs. (2.12) - (2.18) into Eq. (2.19) and then eliminating \(n\) by using Eq. (2.21). The coefficients of the polynomial involve the constants \(K_1\), \(K_2\), ..., \(K_6\), \(K_{eh}\), \(K_{si}\), and \(K_{im}\), and the pressures \(p_{S2}\) and \(p_{Yb}\), and thus a solution of the polynomial would be a complicated expression containing these factors.

One of the problems with the above is obvious, i.e., it is impractical to find an analytical expression for a fourth order polynomial. Another complication, less obvious though, is that the constants \(K_{si}\) and \(K_{im}\) are unknown, and thus even if an analytical solution existed it would not give an explicit expression for \([Yb^*]_C\) as a function of \(p_{S2}\) and \(p_{Yb}\). A computer
solution of such a polynomial would be practical once numerical values are assigned to all the constants. (See Table 4 for an evaluation of $K_1, K_2, \ldots, K_6$).

It can be seen from the above that rather simple defect reactions can lead to polynomials with very complicated solutions. A simplifying assumption, due to Brouwer and utilized by others, is to divide the range of $[Yb^+_Cd]$ into regions and approximate the neutrality conditions, Eq. (2.10), in each region by neglecting all but one type defect of each polarity. Thus, for low values of $[Yb^+_Cd]$ the Yb centers could be compensated by electrons, at intermediate values of $[Yb^+_Cd]$ compensation might occur by means of $V'^*_Cd$, and for high values of $[Yb^+_Cd]$ neutrality could occur from $V'^*_Cd$. (See Van Gool, pp. 69-78, for a calculation of Ga solubility in CdS using a different set of defects. Both Yb and Ga are trivalent ions in CdS, but Ga has a 28% smaller ionic radius.)

The validity of the Brouwer approximation has yet to be proven by experiment. Only one type of Yb site is allowed in each region of the approximation, and in view of the EPR data discussion in section 2.2 this probably is not a reasonable restriction. At present there is little information available which would indicate the impurity concentration levels in which the different compensation schemes might be valid. In spite of
these difficulties it is instructive to calculate the func-
tional dependence of the Yb concentration using the Brouwer
approximation. This has been done for $Yb_{Cd}$ and $Yb_{i}^{**}$ com-
pensated separately by electrons, $V_{Cd}'$ and $V_{Cd}''$, with the
results presented in Table 1.

Measurement of the spectra responsible for exciting
rare earth emission in ZnS indicates that the rare earth ions
are associated with some type of acceptor defect. This type
association is believed to occur in CdS, and the last two
lines of Table 1 show calculations based on possible incorpo-
ration mechanisms for two types of associates.

It is highly probable that solid $Yb_{2}S_{3}$ is present
during our Yb diffusions, and the relation between $p_{Yb}$ and $p_{S_{2}}$
is given by

$$p_{Yb}^{2}p_{S_{2}}^{3/2} = K_{Yb_{2}S_{3}}\,\,\, (2.22)$$

which comes from the reaction

$$2Yb_{2}S_{3} \rightarrow 4Yb + 3S_{2}. \,\,\, (2.23)$$

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31. J. D. Kingsley, J. S. Prener, and M. Aven, Phys.
Rev. Letters, 14,136 (1965); W. W. Anderson and S. Razi,
Proceedings of the International Conference on Luminescence,
p. 1662, Publishing House of the Hungarian Academy of Sciences,
Budapest (1966).
TABLE 1. HIGH TEMPERATURE DEPENDENCE OF THE SOLUBILITY OF Yb IN CdS AS A FUNCTION OF S_2 AND Yb PRESSURE (P_{S_2}) AND P_{Yb} (Computation based on the Brouwer approximation^19)

<table>
<thead>
<tr>
<th>Neutrality Approximation</th>
<th>Incorporation mechanism reaction</th>
<th>Yb gas present</th>
<th>Yb \text{2S_{3}} (solid) present</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Yb}_{\text{Cd}}]^n) = n</td>
<td>(\text{Cd}<em>{\text{Cd}} + \text{Yb}</em>{g} + \text{Yb}<em>{\text{Cd}} + \text{e}^' + \text{Cd}</em>{g})</td>
<td>(P_{S_2}^{1/4}) (P_{Yb}^{1/2})</td>
<td>(P_{S_2}^{-1/8})</td>
</tr>
<tr>
<td>(3[\text{Yb}_{i}^{***}]= n)</td>
<td>(\text{Yb}<em>{g} + \text{Yb}</em>{i}^{***} + 3\text{e}^')</td>
<td>(P_{Yb}^{1/4})</td>
<td>(P_{S_2}^{-3/16})</td>
</tr>
<tr>
<td>([\text{Yb}<em>{\text{Cd}}]^n = [\text{V}</em>{\text{Cd}}]^n)</td>
<td>(2\text{Cd}<em>{\text{Cd}} + \text{Yb}</em>{g} + \text{Yb}<em>{\text{Cd}} + \text{V}</em>{\text{Cd}}^i + 2 \text{Cd}_{g})</td>
<td>(P_{S_2}^{1/2}) (P_{Yb}^{1/2})</td>
<td>(P_{S_2}^{1/8})</td>
</tr>
<tr>
<td>(3[\text{Yb}<em>{i}^{***}]=[\text{V}</em>{\text{Cd}}]^n)</td>
<td>(3\text{Cd}<em>{\text{Cd}} + \text{Yb}</em>{g} + \text{Yb}<em>{i}^{***} + 3\text{V}</em>{\text{Cd}}^i + 3 \text{Cd}_{g})</td>
<td>(P_{S_2}^{3/8}) (P_{Yb}^{1/4})</td>
<td>(5/16)</td>
</tr>
<tr>
<td>([\text{Yb}<em>{\text{Cd}}]^n = 2[\text{V}</em>{\text{Cd}}]^n)</td>
<td>(3\text{Cd}<em>{\text{Cd}} + 2\text{Yb}</em>{g} + 2\text{Yb}<em>{\text{Cd}}^{'} + 3\text{Cd}</em>{g})</td>
<td>(P_{S_2}^{1/2}) (P_{Yb}^{2/3})</td>
<td>constant</td>
</tr>
<tr>
<td>(3[\text{Yb}<em>{i}^{***}]= 2[\text{V}</em>{\text{Cd}}]^n)</td>
<td>(3\text{Cd}<em>{\text{Cd}} + 2\text{Yb}</em>{g} + 2\text{Yb}<em>{i}^{***} + 3\text{V}</em>{\text{Cd}}^i + 3\text{Cd}_{g})</td>
<td>(P_{S_2}^{3/10}) (P_{Yb}^{2/5})</td>
<td>constant</td>
</tr>
<tr>
<td>(3[\text{Yb}<em>{i}^{***}]= [\text{V}</em>{\text{Cd}}]^n)</td>
<td>(2\text{Cd}<em>{\text{Cd}} + \text{Yb}</em>{g} + (\text{Yb}<em>{i}^{***} \text{V}</em>{\text{Cd}}^i) + 2\text{Cd}_{g})</td>
<td>(P_{S_2}^{1/4}) (P_{Yb})</td>
<td>(P_{S_2}^{1/4})</td>
</tr>
<tr>
<td>([\text{Yb}_{i}^{***}]= n)</td>
<td>(2\text{Cd}<em>{\text{Cd}} + \text{Yb}</em>{g} + (\text{Yb}<em>{i}^{***} \text{V}</em>{\text{Cd}}^i) + \text{e}^' + 2\text{Cd}_{g})</td>
<td>(P_{S_2}^{1/2}) (P_{Yb}^{1/4})</td>
<td>(P_{S_2}^{5/16})</td>
</tr>
</tbody>
</table>
In Table 1, Eq. (2.22) relates the pressure dependence of the Yb concentration if Yb gas is present to the pressure dependence if solid Yb$_2$S$_3$ is present. The molecular composition of S vapor is complex and has not yet been settled.\textsuperscript{32} At high temperatures and low pressures (e.g., 960°C, 3 atm.) mostly S$_2$ molecules are present, but at higher pressures (or lower temperatures) some or all of S$_2$, S$_3$, ..., S$_8$ are believed to be present. Then reaction (2.9) would be replaced by

\[
\text{CdS} + \text{Cd}_g + \sum_{n=2}^{8} \left( \frac{n}{n} \frac{P_{S_{2n}}}{P_{S_2}} \text{S}_{ng} \right)
\]

and the calculation of defect concentrations becomes more complex. Some of our samples were diffused under temperatures and pressures which produce more than one type of S molecule (see Chapter 5) and this reduces the applicability of Table 1 for those cases.

At the present, quantitative measurement of rare earth impurity concentrations in CdS by spectrochemical analysis are not reliable below 0.01 atomic % ($2 \times 10^{18}$cm$^{-3}$). The limits of resolution of measuring rare earth concentrations in CdS by radioactive tracer methods have not been evaluated yet. Inferences regarding solubility for certain rare earths

can, however, be drawn from less direct measurements such as absorption and luminescence. In our measurements on diffused samples, the luminescent intensity will be used to indicate relative Yb concentration in the surface region of samples prepared under different S pressures (see Chapter 6). Luminescence, however, indicates only the optically active Yb concentration and does not distinguish one type center from another.

Eqs. (2.11) - (2.14), which are valid for any incorporation mechanism, give qualitative insight into the solubility obtainable during vapor phase growth compared to that which can be obtained by diffusion. These equations show that the concentration of Cd vacancies is proportional to \( p_{S_2}^{1/2} \).

High S pressures (e.g., 60 atm.) can be utilized in diffusion but not in vapor phase growth since sublimation is retarded by pressure. Thus, it is seen that the number of sites available for Yb ions to enter substitutionally can be made higher in diffusion than in vapor phase growth.

Eq. (2.17) also valid for any incorporation mechanism, shows that the ratio \([\text{Yb}^{i-}]/[\text{Yb}^-_{Cd}]\) is proportional to \( n^{-2} \) and \( p_{S_2}^{-1/2} \). The electron concentration \( n \) can be calculated once an incorporation mechanism is assumed, but difficulties arise which are similar to those encountered in the calculation of the Yb concentration. (The Brouwer approximation can not be used since there are two types of positively charged defects, i.e., \( \text{Yb}^-_{Cd} \) and \( \text{Yb}^{i-} \).)
The discussion on solubility in this section has not included rare earth association with deep level impurity acceptors, such as Cu, Ag, and Au. Concentrations of 0.3 ppm Cu have been found in high purity ZnS, and this was enough to affect rare earth luminescence. It is possible that our CdS samples contain significant amounts of Cu, although we have little knowledge of the quantity. (See Chapters 5 and 6.) The quartz diffusion ampoules typically contain 0.5 ppm Cu (as CuO), and this may be a source of Cu during the diffusions.

2.4 Redistribution of Charge Carriers Upon Cooling

When a crystal at diffusion temperatures (e.g., 1000°C) is rapidly cooled to room temperature, the electrons and holes will redistribute while the positions of the impurity and host atoms are assumed to remain fixed. The defects are no longer in thermal equilibrium and the calculation of electron and hole distributions is more difficult. (See Van Goool, Albers, and Kroger et. al. for a treatment of this problem.) The affect of cooling will be briefly discussed in a qualitative manner.

Our method of detecting rare earths in CdS, i.e., luminescence, might be sensitive only to rare earth ions which are associated with some type of deep level defect. It is possible that the rare earth associates at low temperatures

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(say 0-300°K) are different than at diffusion temperature. If, for example, one considers that Cd vacancies associate with rare earth ions, some of the associations may change with temperature because \([V''\text{Cd}]\), \([V'\text{Cd}]\), and \([V\text{Cd}]\) will change while \([V''\text{Cd}] + [V'\text{Cd}] + [V\text{Cd}]\) remains constant. The correlation between the high temperature solubility calculations in Table 1 and the low temperature luminescence measurements is somewhat reduced by the charge redistribution.

Rare earth ions in CdS are donors, and if similar to other donors (see Chapter 3) in CdS, the ionization energy would be approximately 0.03 eV. At 960°C \((kT = 0.106 \text{ eV})\) thermal ionization produces trivalent ions during diffusion. After cooling, certain rare earths may exist in other ionic states. For example, Eu and Sm may be in the divalent state. In our luminescence experiments, the appearance of the trivalent rare earth spectrum is sufficient evidence to show the existence of trivalent ions.

2.5 Diffusion in Solids

Diffusion in a solid is accomplished by the motion of atoms. Several mechanisms have been proposed to account for the transport of diffusing atoms\(^{14,34}\), and a brief description of these mechanisms is given here.

2.5.1 Diffusion Mechanism

a. Vacancy mechanism

Some lattice sites are unoccupied in any crystal. If an atom adjacent to a vacancy jumps into the vacant site, the atom is said to have diffused by a vacancy mechanism. This mechanism is used to explain many diffusions. The diffusion of Au in CdS has been explained in this manner by Nebauer.29

b. Interstitial mechanism

If an atom jumps from one interstitial site to the next, it is said to diffuse by an interstitial mechanism. Atoms which are small compared to crystal constituent atoms tend to diffuse by this mechanism. Many diffusions are explained on this basis.

c. Interstitialcy mechanism

If an interstitial atom exchanges position with a lattice atom, the interstitial atom is said to diffuse by the interstitialcy mechanism. Vacancies are not needed for this mechanism to operate. This mechanism has been used to explain self-diffusion of Ag in AgBr.35

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d. Other mechanisms involving interstitial atoms

Shewmon\textsuperscript{34} discusses two other mechanisms which involve interstitial atoms. One, which has no name, involves two atoms located at the same interstitial site. Diffusion occurs by the rotation of the pair of atoms to a different direction or by the displacement of one of the atoms to form a new pair at one of the nearest neighbor sites. This mechanism is feasible for self-diffusion in a Cu crystal.\textsuperscript{36}

Another mechanism is called the crowdbian. Atoms in a straight line in close-packed metals can be crowded together when an extra atom is placed in the line. This requires little additional energy and diffusion occurs by in-line motion of the crowded row.

e. Ring mechanism

If two or more atoms change lattice positions by rotation, diffusion is said to occur by a ring mechanism. This mechanism has been proposed to account for diffusion in body centered cubic metals.

f. Dissociative mechanism

If an atom energetically favors a normal lattice site but migrates via interstitial sites, diffusion is said

\footnote{36J. Gibson, A. Goland, M. Milgram, and G. Vineyard, Phys. Rev., 120, 1229 (1960).}
to occur by a dissociative mechanism. This mechanism was proposed by Frank and Turnbull\(^ {37}\) to explain Cu diffusion in Ge. Many diffusion processes including Cu and Ag in II-VI compounds have thus been explained. According to Woodbury\(^ {38}\) the fast diffusing interstitials often have an equilibrium concentration which is many orders of magnitude less than the equilibrium vacancy concentration.

An example of a different type of interstitial interaction has been proposed by Chang and Pearson\(^ {39}\) for Zn diffusion in GaP. They state that the rapidly diffusing interstitial concentration \([\text{Zn}_i]\) is determined by the substitutional concentration \([\text{Zn}_c\text{Ga}]\) through charge compensation.

In general, any type of defect can associate with others while diffusion may be faster via one (or more) of the dissociated (or partially dissociated) defects having a different diffusion mechanism.


Another example of a dissociative mechanism is ambipolar diffusion (see, Kroger, p. 796) in which the electric field produced by ionization of the diffusing impurity effects the diffusion rate of the ions. Here the electrons diffuse faster than the ions and set up an electric field which increases the ionic diffusion rate.

g. Macroscopic crystalline defect mechanisms
Dislocations can provide rapid diffusion channels from which impurities (and defects) then diffuse into the bulk crystal. Thus, a knowledge of the density and type of dislocations is needed. Grain boundaries, voids, and other such defects are usually of low concentration and therefore can sometimes be eliminated from a particular crystal or neglected in a diffusion analysis.

h. Mechanisms associated with the surface
The crystal structure near the surface is necessarily different than in the bulk crystal. Thus, diffusion mechanisms will be different. Some of these surface effects have been considered by Kroger (p. 182). One possible effect is a barrier in the surface region which affects the rate at which atoms transfer to and
from the crystal. This restriction results in a high concentration of diffusing atoms in the surface region of the crystal. A second effect concerns the evaporation of the crystal during diffusion which would occur at low vapor pressures for certain crystals. By proper choice of temperatures and pressures this can be avoided for diffusions in CdS.

The above mechanisms have been based on atomic models. A quantitative theory of diffusion based on a quantum mechanical approximation of phonon amplitudes has recently been published for elemental crystals, but a corresponding theory applicable to binary crystals has not yet been given. Recent surveys of the various treatments of diffusion and their limitations are presented in the literature.

2.6 Continuum Approach to Diffusion

The previous discussion on diffusion mechanisms was based on recognizing discreet atoms. A continuum approach has also been developed. It permits the deduction of certain properties of the diffused material through an analysis of the defect concentration

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profile. Several authors\textsuperscript{42-45} have described the continuum approach and a brief description is given here.

The most common assumption used in the continuum study of diffusion in solids is that the rate of flow of a diffusing substance at an arbitrary point is proportional to the concentration gradient at that point. Let $C(x,t)$ represent the concentration and let $J(x,t)$ be the rate of particle (or defect) flow. Then in the x direction the assumption becomes

$$J = -D \frac{\partial C}{\partial x} \quad (2.25)$$

where D is the constant of proportionality known as the diffusion coefficient. Eq. (2.25) is known as Fick's first law.


Fick's second law is obtained from the first law by applying the arguments of continuity of particle flow (i.e., no particle sources or sinks) to a differential volume of the solid. One obtains in the $x$ direction

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} (D \frac{\partial C}{\partial x}).$$  \hfill (2.26)

Crank has given solutions to Eq. (2.26) under a variety of conditions. When $D$ is not constant the concentration profiles become much more complicated. In some cases an analytical solution is possible while in other cases a computer solution may be needed.

Two cases exist, where $D$ is assumed constant, having solutions which commonly appear in literature on diffusion. One case has the boundary conditions

$$C(x,0) = 0, \quad 0 < x.$$  \hfill (2.27)

$$\int_0^\infty C(x,t) \, dx = k_s, \quad t > 0$$

where $k_s$ is the quantity of diffusant per unit area surface at $t = 0$. The solution to Fick's second law is then

$$C(x,t) = \frac{k_s}{\sqrt{\pi Dt}} \exp \left(-\frac{x^2}{4Dt}\right).$$  \hfill (2.28)

This corresponds closely to a thin layer of diffusant deposited on the surface of a solid before diffusion. The functional dependence of Equation (2.28) is called a Gaussian distribution.
The other case has

\[ C(o,t) = C_o, \quad o \leq t \]  

(2.29)

\[ C(x,o) = o, \quad o < x \]

for boundary conditions. The solution to Fick's second law gives

\[ C(x,t) = C_o \text{erfc} \frac{x}{2\sqrt{Dt}} \]  

(2.30)

where erfc \( y \) is the complementary error function. Physically, this case corresponds closely to a diffusion in a gaseous (or liquid) atmosphere in which the surface concentration \( C_o \) of the solid is maintained by the ambient atmosphere.

When actual diffusion profiles have a complex appearance, they may be approximated by various methods. Often they are divided into regions, and each region approximated by a Gaussian or complimentary error function. The region of a crystal near the surface often has properties that differ greatly from the bulk region. In many cases there is an obviously different type of diffusion near the surface. Fisher\(^{46}\) has developed a method of separating the volume diffusion from the surface diffusion. Matano\(^{47}\) has developed a procedure for deriving the diffusion coefficient from a diffusion profile when the diffusion is concentrated dependent.


In diffusion, the native defect situation and the mechanism of incorporating impurities may change as a function of distance from the surface of the crystal. In principle, each defect situation would have its own diffusion coefficient, which increases the difficulty of interpreting diffusion profiles. This situation is more noticeable in compound crystals than in elemental crystals because gradients in the stoichiometry greatly alter the defect situation.

If a particular diffusion does not follow Fick's law, the diffusion is said to be non-Fickian. This type diffusion has been found in II-VI compounds, for example, Ag in CdS\textsuperscript{48} and Au CdTe.\textsuperscript{49} Very little analysis has been done on non-Fickian diffusions.

2.7 Relation Between the Diffusion Coefficient $D$ and Atom Kinetics

The relation between the diffusion coefficient and the kinetics of diffusion has been discussed by several authors.\textsuperscript{34,45,50-52} The diffusion coefficient $D$ is always of the form

\begin{equation}
D = \text{some function of } \text{kinetics of diffusion.}
\end{equation}


\[ D = D_0 \exp \left( \frac{-\Delta E}{kT} \right) \]

where \( \Delta E \) is the energy required to move the diffusing particle, \( k \) is Boltzman's constant, \( T \) is the absolute temperature, and \( D_0 \) is a factor which depends on the crystal structure, defect concentrations, the diffusion mechanism, and other factors. The migration of atoms in crystals is an extremely complex phenomenon and a general method of calculating \( \Delta E \) and \( D_0 \) has not yet been given. Zener has given a semi-empirical approach to calculating \( \Delta E \) and \( D_0 \).

Explanations of diffusion in II-VI compounds have been based on the diffusion mechanisms outlined in sections 2.5.1, and our rare earth diffusions will similarly be explained (see Chapter 6).

2.8 Survey of Literature on Diffusion in CdS

Recent surveys of diffusion in CdS and other II-VI compounds have been given by Woodbury, Reynolds, and Yarbrough. Only two references to rare earth diffusion in CdS are known.

Table 2 summarizes the characteristics and conditions of diffusion in CdS which have been taken from literature. Every element which is known to have been diffused at the time of writing

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<table>
<thead>
<tr>
<th>TABLE 2. CHARACTERISTICS OF DIFFUSION IN CdS (Tabulated From Literature).</th>
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**Note:** Diffusion coefficients and other parameters are tabulated from literature sources. Refer to the cited references for detailed experimental conditions and results.
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<tr>
<th>Diffusion Model</th>
<th>Diffusion Coefficient ( \text{Du} / \text{cm}^2 \text{s} )</th>
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<th>Effusion Product</th>
<th>Effusion Product ( % )</th>
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**Notes:**
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**Legend:**
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TABLE 2 (Continued)

<table>
<thead>
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<th>Reference</th>
<th>Details</th>
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has been listed. Only the most complete or recent experimental data has been used.

Several facts can be observed from Table 2. Thorough studies of the diffusion processes have not been made for most of the elements listed. Also, some of the relevant variables, such as vapor pressure, have not been given in the literature of some investigations. The reason for some of the omissions is simple. Many of the diffusions were performed to obtain samples for certain measurements (e.g. absorption) and were thus not the object of diffusion studies as such. Therefore, considerable research needs to be done in order to adequately explain the diffusion mechanisms.

Although many diffusions have been made in a S atmosphere there is no data on the diffusion of S in CdS. The reason for this is not clear. The diffusion of S in ZnS has been studied by Gobrecht et. al.\(^6^5\) who found \(D = 8 \times 10^{-5} \exp \left(\frac{-2.2eV}{kT}\right)\) between 740 and 1100°C at 0.5 atm. S.

The diffusion of Cd and S vacancies in CdS has not been measured because their presence is not as easily detected as interstitials and impurities. The solubility of various types of Cd

vacancies and interstitials has been calculated by Boyn. He made absorption measurements on samples annealed in Cd and S atmospheres, and assigned absorption bands to Cd vacancies, but did not correlate the absorption coefficient with vacancy concentration.

By looking at the variety of diffusion models proposed as well as omitted ones in Table 2, it is seen that diffusion in CdS is not very well understood. This situation also exists for the other II-VI compounds.
3.1 Ionic Size, Charge, and Electronegativity

Ions which are similar in size, charge, and electronegativity tend to substitute for each other. These factors are often used as guidelines to help decide the manner in which the ion is incorporated into a lattice. For example, interstitial S in CdS is believed to be neutral because \( S^- \) and \( S^{2-} \) are considerably larger than atomic S.\(^{27} \) It is easy to visualize in diffusion that small ions (or atoms) would tend to migrate via the interstices while the larger ions (or atoms) would favor vacancies, if size alone is considered. Slater\(^{66} \) gives a good discussion of atomic and ionic radii with respect to interaction in crystals.

Table 3 lists the ionic and atomic radii and the electronegativity of elements which have been diffused in CdS. A few elements which are similar to the diffused elements have also been

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included. The values listed have been taken from literature\textsuperscript{66–68}.

Figure 1 shows graphically the percent mismatch of ionic size of the trivalent rare earth ions replacing various Group II cations. It is apparent from Figure 1 that the ionic radii of Cd\textsuperscript{2+} are closest to the radii of the trivalent rare earth ions.

3.2 CdS Properties

CdS crystallizes in the wurtzite (hexagonal) and zinc-blende (cubic) structures. Unless stated otherwise, the wurtzite structure is implied when CdS is described. In CdS each Cd atom is surrounded by a tetrahedron of S atoms (and vice versa), with the nearest neighbor distance of 2.52 Å.

CdS is typically an n-type semiconductor by virtue of Cd interstitials (or S vacancies) which act as donors.\textsuperscript{27}

\textsuperscript{67}Handbook of Chemistry and Physics, 45th edition, Chemical Rubber Co., Cleveland (1964).

Figure 1. Percent mismatch of ionic size of trivalent rare earth ions replacing selected Group II elements.
Recently, Anderson and Mitchell have produced p-type CdS by P ion implantation, and Chernow et. al. by Bi ion implantation. Although the relationship of Cd interstitials and S vacancies in the electrically active centers is important, it is not well understood. The concentration of native defect centers depend heavily on the stoichiometry.

Although phase diagrams have been determined for CdTe$^{12}$ and ZnTe$^{69}$, none has been determined for other II-VI compounds. The existence region of CdS is not known but is expected to be similar to that of CdTe and ZnTe.

Upon heating, CdS dissociates into Cd and S vapor with a fraction of less than $10^{-5}$ CdS molecules present at 741$^\circ$C. Upon heating, CdS dissociates into Cd and S vapor with a fraction of less than $10^{-5}$ CdS molecules present at 741$^\circ$C. Thus, for low S vapor pressures, Eq. (2.22) is valid and the total pressure $p_t = p_{Cd} + p_{S_2}$ has a minimum value of $p_{t_{\text{min}}} = 1.863 K_{CdS}^{1/3}$ when $p_{S_2} = \frac{1}{2} p_{Cd}$ (at 960$^\circ$C $p_{t_{\text{min}}} = 4.97 \times 10^{-6}$ atm. = 3.77 x $10^{-3}$ torr). The minimum total pressure is not necessarily the pressure associated with a stoichiometric CdS crystal. The type defect situation present in the crystal determines the stiochiometric pressure (see Van Gool$^{13}$, Chapter 4).

Table 4 lists the properties of CdS taken from the literature$^{6,27,29,67,70}$ which are related to defects and diffusion.

---


TABLE 4. PROPERTIES OF CdS

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<td>Cd atoms (per cm³)</td>
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<tr>
<td>S atoms (per cm³)</td>
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<td>Maximum melting temperature, $T_m$ (°C)</td>
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<td>Minimum pressure at $T_m$ (atm.)</td>
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<td>Band gap, $E_g$, @ 20°C (eV)</td>
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<td>@ 77°K (eV)</td>
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<tr>
<td>$E_g = 2.43 - 5.2 \times 10^{-4}$ ΔT (eV)</td>
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**TABLE 4. (Continued)**

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<td>$p_{OD}^2 p_{S2} = K_{CdS}$ (atm. $^3$)</td>
<td>$1.25 \times 10^{12} \exp \left( \frac{-6.75 \text{eV}}{kT} \right)$</td>
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<tr>
<td>$[V_{Cd}] = K_1 p_{S2}^{1/2}$</td>
<td>$\left(2.7 \times 10^{19} \exp \left( \frac{-1.12 \text{eV}}{kT} \right)\right) p_{S2}^{1/2}$</td>
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<td>($[V_{Cd}]$ in cm$^{-3}$; $p_{S2}$ in atm.)</td>
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<tr>
<td>$[V_{Cd}'] [V_{Cd}]^{-1} n^{-1} = K_2$ (cm$^3$)</td>
<td>$(2N_C)^{-1} \exp \left( \frac{1.9 \text{eV}}{kT} \right)$</td>
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<tr>
<td>$[V_{Cd}''][V_{Cd}']^{-1} n^{-1} = K_3$ (cm$^3$)</td>
<td>$(0.5N_C)^{-1} \exp \left( \frac{1.3 \text{eV}}{kT} \right)$</td>
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<tr>
<td>$[Cd_i][V_{Cd}] = K_4$ (cm$^{-6}$)</td>
<td>$4 \times 10^{44} \exp \left( \frac{-5.45 \text{eV}}{kT} \right)$</td>
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<tr>
<td>$[Cd_i'][Cd_i]^{-1} n = K_5$ (cm$^{-3}$)</td>
<td>$2N_C \exp \left( \frac{-0.05 \text{eV}}{kT} \right)$</td>
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<tr>
<td>$[Cd_i''][Cd_i']^{-1} n = K_6$ (cm$^{-3}$)</td>
<td>$0.5 N_C \exp \left( \frac{-0.20 \text{eV}}{kT} \right)$</td>
</tr>
<tr>
<td>$p_{n} = K_{eh}$ (cm$^{-6}$)</td>
<td>$N_{C} N_{V} \exp \left( \frac{-E_g}{kT} \right)$</td>
</tr>
<tr>
<td>$p_{min} = (p_{OD} + p_{S2})<em>{min} = 1.86 K</em>{CdS}^{1/3}$ (atm.)</td>
<td>$2.04 \times 10^{4} \exp \left( \frac{-2.25 \text{eV}}{kT} \right)$</td>
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</table>
The dominant electrically active defects in CdS are believed to be Cd vacancies and interstitials, although S vacancies have not been completely ruled out. S interstitials are believed to be neutral because of the large size of $S^-$ and $S^2$ ions.

3.3 Vapor Characteristics of Cd, S, and the Rare Earths

In general, diffusion depends on the vapor pressure of the ambient atmosphere. Saturated vapor pressure data of the elements have been published by Nesmeyanov, Stull and Sinke, and Honig.

The ideal gas law can be used to calculate partial pressures when only one type molecule is present. When more than one type of molecule is present, the needed thermodynamic constants have been taken from literature.

3.3.1 Cd Vapor

Cd vapor consists exclusively of single atoms. Shiozawa et. al. have compiled various data taken from


literature and arrived at equations which give the saturated Cd vapor pressure for 200-1500°C (5x10⁻⁷ - 100 atm.) with a probable accuracy of better than 3 percent. Below the melting point (321°C) they give

\[ \log_{10} P_{Cd} = -5,800/T + 5.918 \]  

and above the melting point,

\[ \log_{10} P_{Cd} = -5,740/T - 1.186 \log_{10} T + 9.107, \]  

where \( P_{Cd} \) is in atm. and \( T \) is in °K. At the melting point the vapor pressure is \( 1.43 \times 10^{-4} \) atm. At 960°C the vapor pressure is 6.12 atm.

### 3.3.2 S (and Se) Vapor

The total vapor pressure (saturated) of S has been measured even though the molecular composition of the vapor is somewhat unsettled. Shiozawa et. al. have compiled various data from literature and arrived at equations which give the total vapor pressure for 20-1040°C (1 x 10⁻⁹ - 113 atm.) with a probable accuracy of better than 7%. Below the melting point (119°C) they give

\[ \log_{10} P_{S} = -5,200/T + 8.889, \]  

and above the melting point
\[
\log_{10} p_S = -6.910/T - 19.811 \log_{10} T + 4.843 \times 10^{-3} + 62.727, \tag{3.4}
\]

where \( p_S \) is in atm. and \( T \) is in °K. At 960°C the vapor pressure is 72 atm.

Typically, equilibria in II-VI compound systems involving the pressures of the components are given in terms of the monovalent M component. When it is necessary to relate the equilibria to the X component, as in our experiments, the diatomic molecule is always used. Although \( S_2 \) dominates at high temperatures and low degrees of saturation, the other polyatomic molecules, \( S_3, S_4, \ldots, S_8 \), may be present in appreciable concentrations as saturation is approached and temperatures are lowered. At very high temperatures and very low pressures the concentration of monatomic S becomes appreciable.\(^{69}\)

Using \( S_2 \) as reference, the partial pressures of the other molecular species are related by the following:

\[
\begin{align*}
S_2 & \rightarrow 2S_1 & K_{S_1} = \frac{p_{S_1}^2}{p_S} \\
S_2 & \rightarrow S_2 & K_{S_2} = 1 \\
3S_2 & \rightarrow 2S_3 & K_{S_3} = \frac{p_S^{2/3}}{p_{S_2}} \\
2S_2 & \rightarrow S_4 & K_{S_4} = \frac{p_{S_4}^{1/2}}{p_{S_2}}
\end{align*}
\]
A polynomial in $p_{S_2}$ can be derived as follows: Let $M$ be the total mass of $S$ present in volume $V$ at temperature $T$. Consider molecules $S_1, S_2, \ldots, S_n, \ldots, S_N$ and let $M_1, M_2, \ldots, M_n, \ldots, M_N$ be the respective total mass of each type molecule. Then the total mass is the sum of the component masses, i.e.,

$$M = \sum_{n=1}^{N} M_n.$$  \hspace{1cm} (3.7)

From the ideal gas law,

$$M_n = \frac{n m_S V}{RT} p_{S_n},$$  \hspace{1cm} (3.8)

where $m_S$ is the molecular weight of $S$ (i.e., 32.064 g) and $R$ is the universal gas constant. Using the relations for $p_{S_n}$ from Eqs. (3.5) with Eq. (3.7) and (3.8), one obtains

$$\sum_{n=1}^{N} n (K_{S_n} p_{S_2})^n = M \frac{RT}{m_S V}.$$  \hspace{1cm} (3.9)

The total pressure $p_S$ is given by

$$p_S = \sum_{n=1}^{N} p_{S_n} = \sum_{n=1}^{N} (K_{S_n} p_{S_2})^{n/2}.$$  \hspace{1cm} (3.10)
Our S vapor pressure calculations were based on data
assuming $S_2$, $S_6$, and $S_8$ molecules only in which case the equilib­
rium constants are given by$^{74}$

$$
\log_{10} K_8 = - \frac{21,372}{T} + 30.11, \quad K_8 = \frac{P_2}{P_8} 
$$

$$
\log_{10} K_6 = - \frac{14,363}{T} + 18.81, \quad K_6 = \frac{P_2}{P_6} 
$$

where the pressures are expressed in atm.

Se vapor consists of a mixture of $Se_2$, $Se_6$, and
$Se_8$ molecules. The Se vapor pressure was calculated using
equilibrium constants given by$^{75}$

$$
\log_{10} K_8 = - \frac{20,520}{T} + 26.5, \quad K_8 = \frac{P_2}{P_8} 
$$

$$
\log_{10} K_6 = - \frac{13,702}{T} + 16.35, \quad K_6 = \frac{P_2}{P_6} 
$$

$$
\log_{10} K_4 = - \frac{8020}{T} + 8.43, \quad K_4 = \frac{P_2}{P_4} . 
$$

where the pressures are expressed in atm.

---

$^{74}$P. Mondain-Monval: *Nouveau Traité de Chemie Minérale

$^{75}$H. Lumbroso: *Nouveau Traité de Chemie Minérale XIII,
3.3.3 Yb Vapor

It appears from the literature that Yb vapor consists only of single atoms.\textsuperscript{71} Bohdansky and Schins\textsuperscript{76} give an expression for Yb vapor pressure (saturated),

\[
\log_{10} p_{Yb} = 4.96 - 7.350/T, \tag{3.13}
\]

where \( p_{Yb} \) is in atm. and \( T \) is in °K. Eq. (3.13) is valid in the range 912-1487°C, (5.63 \times 10^{-2}-5.83 atm.). Yb melts at 824°C and boils at 1209°C. At 960°C, \( p_{Yb} = 0.10 \) atm., and by extrapolating Eq. (3.13), \( p_{Yb} = 1.28 \times 10^{-2} \) atm. at 800°C.

3.3.4 Vapor of the Other Rare Earths

Mesmayanov\textsuperscript{71} gives some information concerning the vapor characteristics of the other rare earths. Honig\textsuperscript{73} shows vapor pressure curves of all the rare earths for pressures in the range \( 1.3 \times 10^{-14} - 1.3 \) atm. At 960°C, the vapor pressures taken from the curves are as follows (in atm.):

- \( \text{Yb} - 1.3 \times 10^{-2} \)
- \( \text{Eu} - 1.0 \times 10^{-2} \)
- \( \text{Sm} - 1.0 \times 10^{-3} \)
- \( \text{Tm} - 1.3 \times 10^{-4} \)
- \( \text{Dy} - 5 \times 10^{-7} \)
- \( \text{Ho} - 2.0 \times 10^{-7} \)

\textsuperscript{76}J. Bohdansky and H. E. J. Shins, J. Less Common Metals 13, 248 (1967).
These pressures may be in disagreement with later measurements. For instance, the formula of Bohdansky and Schins, Eq. (3.11) gives the vapor pressure of Yb at 960°C as $1.0 \times 10^{-1}$ atm. The order of magnitude of the rare earth pressures, however, could be used as a factor to help decide the status of the rare earth source during diffusion. That is, in a diffused sample the rare earth concentration and resulting luminescent intensity could be thought to be proportional to the rare earth vapor pressure during diffusion. Our data (Chapter 5) shows that this is unlikely.

3.4 Rare Earth Compounds with S, Se, and Te

The compounds formed by the rare earths with S, Se, and Te are rather complex. French and Russian workers have studied many of these compounds and found a vast range of
characteristics. There is no data available regarding the thermodynamic equilibrium constants relating the molecular constituents of the phases. The vapor characteristics of the rare earth chalcogenides have not been determined, i.e., the molecular composition and partial pressures are unknown.

Some rare earth chalcogenides have phases between which the composition can vary continuously, as shown by the following example: Domange et al. prepared Yb$_2$S$_3$ by reacting Yb$_2$O$_3$ with H$_2$S, using a two step procedure. At 1300°C the oxygen is completely eliminated, but the resulting sulfide lacks S and is close to Yb$_5$S$_7$. This sulfide was then heated at 800°C for 3-4 hours (or at 1100°C for 1 hour) during which sulfur was gained, and the result was stoichiometrically very close to Yb$_2$S$_3$. If

79 G. V. Samsonov, Hard Compounds of Rare Earth Metals With Nonmetals, Izdatel'stvo Metallurgiya, Moscow (1964) (in Russian).
the Yb$_2$S$_3$ is then heated at 1000°C in a vacuum, S is lost and the composition Yb$_3$S$_4$ is produced. Further heating at 1600°C in a vacuum gave YbS$_{1.11}$ which has massive Yb vacancies but few S vacancies. Heating at 1350°C with Al present in a vacuum did not reduce the S content. Flahaut et. al.\textsuperscript{10} state that the composition can be varied continuously, and that the particular composition obtained depends upon the temperature and pressure during preparation.

Tien et. al.\textsuperscript{82} state that Sm, Eu, and Yb which have both divalent and trivalent states, form sulfides which dissociate more readily when heated than do the sulfides formed by rare earths having only the trivalent state. He also states that YbS is the most volatile of the monosulfides. Picon et. al.\textsuperscript{78} state that the properties of Yb$_2$S$_3$ are significantly different than the other rare earth sulfides.

In our Yb diffusions with excess S (3-33 atm. at 960°C) it seems reasonable to assume from the above discussion that Yb$_2$S$_3$ would be the predominant sulfide present. Two cases can be distinguished (as in Table 1) regarding

the possible nature of the $\text{Yb}_2\text{S}_3$ vapor, one where the vapor consists of Yb atoms dissociated from S molecules and the other where the vapor consists of only $\text{Yb}_2\text{S}_3$ molecules.

The known properties of rare earth sulfides, selenides, and telurides, which relate to our type of diffusions have been taken from literature\textsuperscript{77-80} and listed in Table 5. In our experiments the color of a rare earth chalcogenide is at present about the most useful information available for type identification, and where known it has been listed with the crystal type in Table 5. Known continuous transitions between phases are indicated by arrows.

3.5 Rare Earth - Cd Compounds

When a rare earth is heated with Cd (as in some of our diffusions) the vapor characteristics are likely quite different than when excess S is present. There is no known information on the vapor characteristics for rare earth-Cd compounds, although the structure of these compounds have been studied.\textsuperscript{83} Some phases of the Yb-Zn system have recently been investigated\textsuperscript{84}, but no similar information is known for rare earth-Cd systems.


\textsuperscript{84}J. T. Mason and P. Chiotti, Trans. of AIME, 242, 1167 (1968).
<table>
<thead>
<tr>
<th>Compound</th>
<th>M</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
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<td>$M_2S_3$</td>
<td>a</td>
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<td>a</td>
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</tr>
<tr>
<td></td>
<td>orange</td>
<td>yellow-green</td>
<td>brown-grey</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
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<td>$\gamma$,2100</td>
<td>$\gamma$,2040</td>
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<td>--</td>
<td>--</td>
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<td>$\gamma$</td>
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<tr>
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<td>$\eta$</td>
<td>$\eta$</td>
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<td>$\zeta$</td>
<td>$\zeta$</td>
<td>$\zeta$</td>
<td>$\zeta$</td>
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<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
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<td>--</td>
<td>--</td>
<td>(does not exist)</td>
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<td>--</td>
</tr>
<tr>
<td>$MTe$</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>--</td>
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<td>--</td>
<td>--</td>
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<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

#### Crystal Structures

- **c**: unknown type (α form possess exact stoichiometry for Pr, Nd, Sm, and Gd).
- **β**: unknown type.
- **γ**: cubic, Th$_3$P$_4$ type.
- **δ**: monoclinic, unknown type.
- **ε**: hexagonal, Al$_2$O$_3$ type.
- **ζ**: orthorhombic, Sc$_2$S$_3$ type.
- **η**: orthorhombic, U$_2$S$_3$ type.
- **x**: compound has been produced, structure unclassified.
- **a**: cubic, NaCl type.
- **b**: Yb$_2$Se$_4$ has two structures, hexagonal and orthorhombic.
- **γγ**: Denotes known continuous transitions between phases.
3.6 Other Rare Earth Compounds

When a diffusion ampoule which contains excess S is opened after heat treatment, a mild odor of \( \text{H}_2\text{S} \) is always observed. (The source of \( \text{H} \) is unknown). No \( \text{H}_2\text{S} \) is noticed when excess Cd is present in a diffusion. It is remotely possible that rare earth-II compounds could be present during diffusion. The crystal structure of these compounds has been studied\(^{85}\), but there is little information available which would help discern their presence in our experiments.

It is possible that Cd-rare-earth-S compounds are formed during diffusion (See Chapter 5). There is no literature on these compounds known to the author.

CHAPTER 4

RARE EARTH LUMINESCENCE IN CdS

The relation between rare earth diffusion and the resulting luminescence in CdS can be better understood by a brief discussion of the mechanism of rare earth luminescence in CdS.

4.1 Shielding of 4f Electrons

The 4f electrons in the rare earths are fairly well shielded by the outer 6s (and 5p, for Gd) valence electrons. Thus, the 4f electrons do not enter into chemical bonding but 4f-4f transitions are permitted when the trivalent ion is in the perturbing field of certain hosts. The position of the energy levels shift only slightly and the width of the transitions remains quite narrow. (See Wybourne for a discussion of the spectroscopic properties of the rare earths.)

4.2 Rare Earth Ion Excitation in CdS

A rare earth ion must be in an excited state before it can emit radiation. If white light is incident upon rare earth doped CdS, two mechanisms could be considered to excite the rare

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earth ion. One is direct absorption by the ion. Another is resonance excitation in which the rare earth ion is coupled to a host lattice or impurity defect. In the latter an acceptor type defect associates with the rare earth donor, and the recombination energy absorbed by the acceptor is transferred nonradiatively to the rare earth ion. (Broser\textsuperscript{87} describes energy transfer processes in greater detail.)

Studies of the excitation spectra for rare earth doped ZnS show that the excitation energy is associated with a host lattice absorption and not direct absorption within the 4f shell.\textsuperscript{31} We believe that this process also operates in rare earth doped CdS.

The relative positions of some of the rare earth energy levels and the associated acceptor level affect the efficiency of energy transfer between the two defects. When the energy of recombination through an acceptor is near an excited rare earth energy level, line emission will be observed if an emitting 4f-4f transition occurs, and when these energy levels are sufficiently separated, no rare earth emission will occur. Kingsley et. al.\textsuperscript{31}

have been able to "tune in" various levels of a rare earth ion in 
$Zn_xCd_{1-x}S$ by varying the energy level of the associated acceptor 
(Cu or Ag). They observed broad band emission from Cu or Ag when the 
composition of $Zn_xCd_{1-x}S$ was such that the band did not over­
lap a rare earth emitting level. When the levels overlap, the band 
emission is strongly suppressed and then the intensity of the rare 
earth emission depends heavily upon the Cu concentration.

Our CdS samples, untreated or annealed in S vapor, show 
no band emission in the vicinity of the $Yb^{3+}$ emitting line ($\approx 1 \mu$). Emission peaks from Cu in CdS appear at various energies depending on 
the Cu concentration. If our rare earth diffused CdS contains 
no significant impurities other than the rare earth, then the most 
likely deep level acceptor is a Cd vacancy, which from absorption 
measurement, possesses an energy level 1.1 eV above the valence 
band.27

The particular deep level defect which is effective in 
energy transfer to rare earths depends on the relative defect con­
centrations. Curie (p. 121) states that impurity concentrations as 
low as 1 - 10 ppm cause vacancy emission to disappear.88 Kingsley 
et. al.31 found that Cu concentrations as low as 0.3 ppm are

88 D. Curie and J. S. Prenner in Physics and Chemistry of 
II-VI Compounds, p. 435, edited by M. Aven and J. S. Prenner, North­
Holland Publishing Co., Amsterdam (1967); D. Curie, Luminescence in 
present in high purity fluorescent grade ZnS and this was enough
to effect Er emission in this material. It is possible that our
CdS samples contain significant amounts of Cu (see Chapter 6 for
a discussion of Cu in our samples).

The trivalent rare earth energy levels (from Dieke and
Crosswhite\textsuperscript{89}) are shown in Figure 2, with the observed emitting
levels in CdS indicated by the arrows. Also shown are the energy
levels corresponding to the peaks of the broad emission bands
associated with known deep level acceptors.\textsuperscript{88} The variety of condi-
tions under which CdS samples have been prepared makes it diffi-
cult to ascertain from the literature what the correct positions
of the emission bands of deep level acceptors should be. For
example, Curie and Prener (p. 472)\textsuperscript{88} list Cu as having an emission
peak at 1.05 µ (≈ 1.2 eV), while the original literature from
which they took this value describes CdS doped with both Cu and
In. (See Grillot and Guintini\textsuperscript{90} for reference to CdS:Cu). Simi-
lar difficulties exist for the energy level usually attributed to
Cd vacancy emission.

\textsuperscript{89}G. H. Dieke and S. M. Crosswhite, Appl. Optics, 2, 675 (1963).

\textsuperscript{90}E. Grillot and P. Guintini, Comptes Rendus, 239, 418 (1954).
Figure 2. Energy levels of the trivalent rare earth ions. Observed emitting transitions in CdS are indicated by arrows. Also shown are the energies of emission bands of known deep level acceptors in CdS (right side).
If the rare earth excitation process described by Kingsley et. al.\textsuperscript{31} is valid for CdS, then it should be possible to excite certain rare earth levels by codoping with the appropriate deep level acceptor. Figure 2 can be used as a guide to determine the particular impurity to be used as a codopant. For example, it might be possible to excite Nd to emit in the 1.7-2.0 eV (red-orange) region by codoping with Ag.

4.3 Rare Earth Concentration and Luminescent Intensity

The previous discussions regarding deep level defect association with rare earth ions and rare earth emission were based on the assumption that pairing between rare earth ions did not occur. This assumption is valid for low rare earth concentrations.

Van Uitert and Johnson\textsuperscript{91} have studied energy transfer between rare-earth ion pairs in materials such as tungstates, vanadates, and oxides and found the luminescent intensity to be proportional to the rare earth concentration up to approximately $10^{20}$ ions cm$^{-3}$ ($\approx 0.5$ atomic %). They found that resonant transfer between remote ions by way of transitions that are matched in energy appears to be essentially dependent on concentration alone. Recent EPR studies in rare earth halides have

shown significant pairing between other rare earth ions for concentrations of 0.1 - 2 atomic percent.\(^{92}\)

In light of the studies on rare earth halides and the studies of Van Uitert and Johnson, it is concluded that concentration quenching of luminescence due to rare earth ion pairing begins to set in at rare earth concentrations of about 0.1 - 0.5 atomic percent.

4.4 Photoexcitation of Rare Earth Luminescence

When white light is incident on CdS, only those wavelengths with energy near the band edge are responsible for exciting electron-hole pairs. The optical absorption coefficient near the band edge is on the order of \(10^5\) cm\(^{-1}\), and thus excitation penetrates the surface to a depth of about 0.1 \(\mu\).\(^{70}\) The minority carrier diffusion length in CdS is on the order of 0.1 - 2 \(\mu\)\(^{87}\), which is the depth to which recombination takes place via deep level acceptors. The recombination energy can be transferred from these deep centers to rare earth ions over distances up to 100 \(\AA\).\(^{87}\) Thus, the rare earth ions are excited to a depth on the order of 0.1-2 \(\mu\).

Photoexcitation discriminates against rare earth ion excitation in voids and grain boundaries. In these situations the excitation of the rare earth ion would be different, although the rare earth concentration in these places as a result of diffusion could be much higher or lower than the bulk material.
CHAPTER 5

EXPERIMENTAL PROCEDURE AND RESULTS

5.1 Sample Characteristics and Preparation

Vapor phase grown boules of CdS were supplied by Dow Corning. This material was characterized by a free electron concentration of \( n = 3.5 \times 10^{15} \, \text{cm}^{-3} \) and Hall mobility of 350 \( \text{cm}^2/\text{volt-second} \) at room temperature. There were microscopic voids and decorated precipitates in some samples. Single crystal rectangular samples of nm dimensions were sawed from the boules. The ZnSe was polycrystalline, UHP grade from Eagle-Picher. Polycrystalline samples were sawed from the ingots. The CdS and ZnSe samples were lapped, polished on one side, etched in a solution of 0.5 M \( \text{K}_2\text{Cr}_2\text{O}_7 \) in 16 N \( \text{H}_2\text{SO}_4 \), and thoroughly washed in distilled water. A sample, excess S (or Se), and 5 mg of rare earth metal (turnings) were sealed in a 3.6 cm\(^3\) quartz ampoule at about 2 \times 10^{-5} \text{ torr} (\approx 3 \times 10^{-8} \text{ atm.}). The mass of rare earth metal used in our diffusions (5 mg) was more than sufficient to establish saturated pressures (see section 3.3.4) if sulfide formation is ruled out. The mass of S(or Se) used in each diffusion was large enough so that at most 10% could be used in the formation of sulfides.
For the CdS luminescent profile measurement, single crystals 1 x 5 x 5 mm were sawed from a boule so that the c-axis was perpendicular to the 5x5 mm faces. The boule was oriented by etching it one minute at room temperature in a solution of six parts HNO$_3$, six parts CH$_3$COOH, and one part H$_2$O, which produces sharply defined hexagonal etch pits on the Cd surface. Both 5x5 mm surfaces of the sawed samples were lapped on a cast iron plate using 600 grit (13 μ) Al$_2$O$_3$. The surface was then polished flat to = 0.2 μ over the whole surface by polishing on a tin plate using 0.3 μ Al$_2$O$_3$ abrasive. The S surface was polished because 0.5 M K$_2$Cr$_2$O$_7$ in 16 N H$_2$SO$_4$ was used as a polishing etch on this surface. The polisher and precision polishing jig are shown by Plates 1 and 2.

5.2 Purity and Preparation of Rare Earth Metals and Other Elements

Rare earth metals were purchased as 99.9% pure with respect to other rare earths. No information was available from the supplier on nonrare earth impurities. Some metals were already in the form of turnings or granules of convenient weight while others were in ingot form and turnings were produced by use of a milling machine. The turnings were not etched but were kept

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Plate 1. Semiconductor Polisher.
Plate 2. Precision polishing jig. (a) photograph showing actual size; (b) simplified diagram showing main parts of jig.
as clean as possible. (Spedding and Danne\textsuperscript{94} list several etches for rare earth metals.) The turnings of metals which oxidize rapidly, Eu, Pr, Nd, and Sm, were used immediately or stored under vacuum. The tweezers which were used to handle the turnings had to be etched when changing from one rare earth metal to another or the emission spectra would show contamination.

The S in granular form was purchased as 99.999\% pure with no information on the impurities present. The Se in shot form was 99.999\% pure with 1 ppm Cu and Ag present. Individual tweezers were used to handle the S and Se.

The Cd turnings used in some diffusions were machined from ingots having a purity of 99.999\%, with impurities unquoted. A few diffusions were performed with small quantities of Cu, Ag, or Au which had been scraped from larger pieces of these metals by means of a clean stainless steel razor blade. The purity of the Cu, Ag, and Au, was 99.9999\%, 99.9+\%, 99.999\%, respectively, with impurities unquoted. In order to prevent contamination, the tweezers used to handle these metals was etched each time before handling a different metal.

5.3 Diffusion Ampoule Preparation and Heat Treatment

Quartz tubes, 8 mm I.D. x 12 mm O.D. x 1 ft. long, were fabricated with a bulb like end. Two diffusion ampoules can be obtained from this tube. Each tube was washed inside with soap and water using a brush and then rinsed. The tube was etched in a 10 percent solution of HF for about 3 minutes, thoroughly rinsed with distilled water, and dried by vacuum. While under vacuum, the tube was flame heated to a temperature just below the softening point to drive off any volatile impurities which might have adhered to the inner wall.

A CdS (or ZnSe) sample which had just been etched and thoroughly rinsed in distilled water was placed in the above clean quartz tube and dried at room temperature by vacuum. Then the rare earth turning and S (or Se) were put in the bulb end of the tube with the sample, and the tube was evacuated to about 1-2 x 10⁻⁵ torr and sealed off. The sample was then shaken from the bulb end to the other end of the ampoule as shown in Figure 3.

The ampoule was inserted, sample end first, slowly into a furnace heated to a preset temperature. The slow warm-up time (≈ 1 min.) was used to prevent the boiling S (or Se) from throwing some of the rare earth turnings onto the sample. After heating, the ampoule was rapidly removed and air cooled by holding the bulb end with pliers. The ampoule cooled to 100°C in about 1-1.5
Figure 3. Diffusion ampoule before heating. (a) diagram showing arrangement of ampoule contents; (b) photograph showing actual size.
minutes, and the bulb end was cooled first to prevent S (or Se) from condensing on the sample. After the S (or Se) had solidified (= 5 minutes for S), the ampoule was opened by crushing the sample end in a vise.

5.4 Spectrometer, Sample Holders, and Sample Description

All emission spectra were recorded at 77°K on a Perkin-Elmer model 98-G spectrometer using a 640 line/mm grating. No correction was made for the spectrometer and detector spectral sensitivity. Excitation was by means of an XBO 1600 W xenon arc lamp filtered by a saturated CuSO₄ solution. A 7102 photomultiplier was used as the detector. The spectrometer layout is shown in Figure 4(a). The spectra were recorded from rectangular samples cemented on a glass rod and positioned in a quartz dewar as shown in Figure 4(b). A photograph of the spectrometer system is shown by Plate 3.

5.5 Diffusions Performed and Resulting Spectra

a. Diffusions with excess S or Se

Diffusions were attempted in CdS and ZnSe using Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Yb. Emission was observed from Pr, Nd, Ho, Er, Tm, and Yb in CdS and Ho, Er, Tm, and Yb in ZnSe. Figures 5-7 show the resulting spectra. The observed transitions are listed in Table 6.
Figure 4. Diagram of Spectrometer System. (a) Spectrometer layout showing optical path; (b) quartz dewar and sample.
Plate 3. Photograph of spectrometer system.
Figure 5. Photoluminescence of Pr, Nd, and Ho diffused CdS.
Figure 6. Photoluminescence of Er, Tm, and Yb diffused CdS.
Figure 7. Photoluminescence of Yb, Tm, Er, and Ho diffused ZnSe.
TABLE 6. GROUPS OF RARE EARTH LINES SEEN IN EMISSION IN CdS AND ZnSe.

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<td>1&lt;sub&gt;G&lt;/sub&gt;₄ → 3&lt;sub&gt;H&lt;/sub&gt;₄</td>
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<tr>
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<td>CdS&lt;sup&gt;(a)&lt;/sup&gt;</td>
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<td>4&lt;sub&gt;F&lt;/sub&gt;₃/₂ → 4&lt;sub&gt;I&lt;/sub&gt;₉/₂</td>
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<td>ZnSe</td>
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<td>5&lt;sub&gt;I&lt;/sub&gt;₄ → 5&lt;sub&gt;I&lt;/sub&gt;₈</td>
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<td></td>
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<td>.65 μ</td>
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</tr>
<tr>
<td>Er&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>CdS&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>.99 μ</td>
<td>4&lt;sub&gt;I&lt;/sub&gt;₁₁/₂ → 4&lt;sub&gt;I&lt;/sub&gt;₁₅/₂</td>
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<td></td>
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<td>.81 μ</td>
<td>4&lt;sub&gt;I&lt;/sub&gt;₉/₂ → 4&lt;sub&gt;I&lt;/sub&gt;₁₅/₂</td>
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<tr>
<td></td>
<td>ZnSe&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>.99 μ</td>
<td>4&lt;sub&gt;I&lt;/sub&gt;₁₁/₂ → 4&lt;sub&gt;I&lt;/sub&gt;₁₅/₂</td>
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<td>.86 μ</td>
<td>4&lt;sub&gt;S&lt;/sub&gt;₃/₂ → 4&lt;sub&gt;I&lt;/sub&gt;₁₃/₂</td>
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<td>.81 μ</td>
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<td>.66 μ</td>
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<td>.55 μ</td>
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<tr>
<td>Tm&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>CdS</td>
<td>.80 μ</td>
<td>3&lt;sub&gt;F&lt;/sub&gt;₄ → 3&lt;sub&gt;H&lt;/sub&gt;₆</td>
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<td></td>
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<td>.70 μ</td>
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<tr>
<td></td>
<td>ZnSe</td>
<td>.80 μ</td>
<td>3&lt;sub&gt;F&lt;/sub&gt;₄ → 3&lt;sub&gt;H&lt;/sub&gt;₆</td>
</tr>
<tr>
<td></td>
<td></td>
<td>.71 μ</td>
<td>3&lt;sub&gt;F&lt;/sub&gt;₃ → 3&lt;sub&gt;H&lt;/sub&gt;₆</td>
</tr>
<tr>
<td>Yb&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>CdS&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>.99 - 1.06 μ</td>
<td>2&lt;sub&gt;F&lt;/sub&gt;₅/₂ → 2&lt;sub&gt;F&lt;/sub&gt;₇/₂</td>
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<tr>
<td></td>
<td>ZnSe</td>
<td>1.04 μ</td>
<td>2&lt;sub&gt;F&lt;/sub&gt;₅/₂ → 2&lt;sub&gt;F&lt;/sub&gt;₇/₂</td>
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</table>

(a) These line groups previously reported for crystals doped during growth<sup>2</sup>.

(b) These line groups previously observed by Kingsley and Aven<sup>3</sup>. 
Although the main purpose of our diffusion experiments was not to make a quantitative study of the reproducibility of the resulting rare earth luminescence, it was noted that rare earth luminescence in CdS prepared by diffusion was "many orders of magnitude" more reproducible than luminescence from vapor phase grown rare earth doped CdS. In a series of five Yb diffusions in CdS (at 960°C, 33 atm. S, 1 hour), the intensity of the rare earth emission varied at most 30 percent under identical excitation conditions. Also, the Yb$^{3+}$ spectra was always that shown in Figure 6. Although a smaller number of repeated diffusion runs were made for some of the other rare earths in CdS and ZnSe, a similar reproducibility was noted. In order to obtain enough signal strength for certain weak rare earth spectra (e.g., Pr in CdS), a rather low spectral resolution (23 Å) was used in Figures 5 - 10 to maintain consistency. These data are not intended to show the details of the rare earth line emission but are meant to indicate certain spectral changes which occur as a result of various conditions of diffusion. This low resolution results in some tendency to emphasize the broadband background emission with respect to the narrow line emission of the rare earth.

Figure 8 shows the change in the rare earth spectrum for three different conditions of diffusion of Yb into CdS. Qualitatively, both higher temperature and higher sulfur pressure enhance
Figure 8. Variation in details of Yb$^{3+}$ emission of Yb diffused CdS for various diffusion conditions.
the appearance of the shorter wavelength emission as in Figure 8(a) and reduce the longer wavelength emission as in Figure 8(c). Emission characteristics of as-grown CdS:Yb are similar to that shown in Figure 6 and 8(a). It has also been observed that the emission of Nd, Er, and Yb in CdS becomes more complex, i.e., emission between individual peaks within the narrow band tends to occur, with increasing sulfur pressure. In all cases, a multiplicity of emissive rare earth ion sites are observed as indicated by the large number of resolvable lines (not shown in this paper). These different sites are due to rare earth ions affected by the crystalline electric field of different near neighbor crystalline defects (nearest neighbor, next nearest neighbor, two nearest neighbors, etc., Cd vacancies, S interstitials, uncontrolled foreign ion impurities or rare earth ion pairing). The type and concentration of these various defects are largely controlled by the chalcogen pressure and temperature.

Qualitatively, the height of the broad emission bands in Figures 7 and 9 (relative to the rare earth narrow band) tends to reduce at the higher diffusion temperature while the intensity of the rare earth emission increases. Similar effects were observed for the other rare earth ions. Under certain diffusion conditions, it was found that emission from Pr and Ho in CdS could be "lost" in
Figure 9. Variation in Tm$^{3+}$ and broadband emission of Tm diffused CdS for various diffusion conditions.
the broad bands. However, for a given rare earth ion - II-VI compound combination, the relative strengths of the broad band and narrow line emission remained constant under identical diffusion runs.

The effect of Cu, Ag, and Au on the Yb emission in our CdS samples was investigated by including small quantities of these metals in the diffusion ampoule. The effect on the Yb emission spectrum of adding = 5μg, = 75μg and 300μg Cu in the diffusion ampoule is shown in Figure 10(a). The emission curve for 75 μg added shows a prominent peak at 1.06 μ with other small peaks which appear at exactly the same wavelengths as for the emission of the Yb diffusions at 800°C in Figure 8(b) and (c). The major effect on the Yb emission spectrum of adding 300 μg Ag was to reduce the peak intensity by approximately 15 percent. Similarly, the main effect of adding 200 μg Au was to reduce the peak Yb emission by approximately 20 percent.

The broad band emission of our CdS samples having different treatments was measured and is shown in Figure 10(b). Samples heated for one hour at 960°C and 33 atm. S always show a band (apparently) peaking at about 0.72 μ. This band, is reduced when a sample is annealed 1 hour in 6 atm. Cd at 960°C and when a high amount (300 μg) of Cu is present with 33 atm. S, but is not significantly reduced when a rare earth and/or small amounts of Cu are present.
Figure 10. Effect of Cu on Yb$^{3+}$ and broadband emission in diffused CdS. (a) effect of Cu on Yb$^{3+}$ emission; (b) effect of Cu on broadband emission [(a) and (b) have identical intensity scales].
b. Yb Diffusions with Excess Cd

(1) An Yb diffusion in CdS at 960°C under 6 atm. Cd pressure (saturated) for one hour was carried out. The emission intensity was reduced by a factor of 300 from that for the 33 atm. S, 960°C, 1 hour diffusion of Figure 6. The broad bands appeared as in Figure 10(b), for a 6 atm. Cd anneal. The Yb emission is not evident when traced to the scale of Figure 10. The precipitates (see section 5.1) do not anneal out in a Cd atmosphere. (They do anneal out during a diffusion with excess S.)

(2) A previously Yb diffused CdS sample (at 33 atm. S, 960°C, 1 hour) was again Yb diffused at 960°C and 1 hour, except the atmosphere was 6 atm. Cd. The peak emission intensity was reduced by a factor of eight and the 1.06 μm and other peaks occurred as in Figure 10 for = 75 μg Cu added.

(3) Further diffusion of the sample in (2) for one day under the same conditions reduced the intensity an additional factor of 3.5 while the spectral shape remained nearly the same.

c. Diffusions Using Various Yb-Sulfide Source Arrangements

Several Yb diffusions were performed and the spectra observed in an attempt to determine the status of the rare earth source during diffusion. The resulting spectra will be described qualitatively since similar features are present in Figures 6 and 10.
(1) A CdS crystal was sealed under $2 \times 10^{-5}$ torr in a small quartz capsule fabricated from 4 mm I.D. x 6 mm O.D. quartz tubing with a very fragile pigtail type end, as shown in Figure 11. This small capsule was sealed with 5 mg Yb and S (for 33 atm. at 960°C) in a quartz diffusion ampoule. The ampoule was heated 10 minutes in a 960°C furnace during which the usual yellow-white flash occurred. The pigtail end of the inner capsule was then broken by jarring the whole ampoule while in the furnace. The ampoule was then heated for one hour. The spectral shape of the resulting emission was the same as for 33 atm. S pressure (Figure 6(c), but the intensity was reduced by a factor of ten.

(2) A diffusion was performed identical to the above except the ampoule was cooled to room temperature before breaking the pigtail of the inner capsule. The spectral shape and intensity of the emission was similar to the above diffused sample.

(3) A diffusion similar to (1) above was performed except the ampoule was heated one hour before breaking the inner capsule. The peak of the emission intensity was as intense as for (1) and (2) but the background emission in the vicinity of the rare earth line was increased approximately ten fold.

(4) A diffusion was performed identical to (3) except the ampoule was cooled to room temperature before breaking the inner capsule. The peak of the emission intensity was reduced from that
Figure 11. Diffusion ampoule with sample sealed in inner ampoule having fragile pigtail end. (a) diagram showing arrangement of ampoules before heating and breaking of fragile pigtail; (b) photograph showing actual size.
for (1) and (2) by an approximate factor of twenty. The background emission in the vicinity of the rare earth line was approximately five times greater than for the samples of (1) and (2).

(5) A rare earth source was prepared by heating 5 mg Yb and S (for 33 atm. at 960°C) for one hour in an ampoule with no CdS sample present. The resulting sulfides were removed and used as the rare earth source in a diffusion at one hour, 33 atm. S pressure. The resulting emission was very close to that in Figure 6.

(6) Commercially available Yb$_2$S$_3$ in powder form with a purity of 95-99% was used in place of Yb metal as a rare earth source. A diffusion with ~65 mg Yb$_2$S$_3$ and S (for 26 atm. at 960°C) for one hour was performed. The resulting emission was very close to that in Figure 6. (The Yb$_2$S$_3$ retained its original yellow color.)

(7) A diffusion was performed identical to (6) except that no excess S was used. The spectral shape of the emission was similar to the emission of Figure 8(c), except the peak intensity was reduced by an approximate factor of four.

(8) A diffusion was performed similar to (6) except 2.5 atm. Cd pressure was present. No Yb emission was observed from the sample, and the broadband emission was as for a sample annealed in Cd vapor, Figure 10(b). (After diffusion the Yb$_2$S$_3$ had an army green color appearance.)
From these eight experiments it appears that (1) a coating type rare earth source, which could occur as the S and Yb react during warm-up and coat the sample, is not the only rare earth source present during diffusion, and (2) the predominant sulfide present during diffusion is probably $\text{Yb}_2\text{S}_3$. (See Chapter 6 for further discussion.)

5.6 Ampoule Reactions; Yb Sulfide Identification

Inspection of the ampoule contents after diffusion revealed that all rare earth metals completely reacted with the S or Se, and except for Yb, retained the same shape as the original turnings.

a. The original Yb metal, slightly changed in shape, appeared black, brown, maroon, and deep blue in various areas. Surrounding the original Yb turning was a brown Yb sulfide which adhered for the most part to the quartz wall. (Small brown flakes could be seen frozen in the S). Surrounding the brown sulfide and somewhat intermingled was a yellow Yb sulfide which covered roughly three-fourths of the bulb surface area. Gold colored spots were sometimes seen in this yellow area. From Table 5, the most likely identification for these sulfides is:

- yellow - $\text{Yb}_2\text{S}_3$
- deep blue - $\text{YbS}$
- black, brown, and gold - unknown type
Figure 12(a) shows the position of these sulfides in the ampoule.

b. None of the Yb sulfides showed any Yb$^{3+}$ luminescence.

c. For Yb diffusions in CdS at 960°C and 33 atm. S, a thin yellow coating appeared on the ampoule wall in the neighborhood of the sample and extended in length approximately one-half the ampoule length, as in Figure 12(a). The position of this yellow coating was somewhat random. The CdS sample also possessed this coating in a manner which varied from sample to sample. Some samples were completely covered while others had only a few spots. (Yb diffused CdS samples were the only samples on which any spots or coating on the surface was noted after diffusion.) The yellow coating was not present on the ampoule wall when only Yb and S were reacted under the same conditions as the above diffusions.

This yellow substance is neither CdS nor a Yb sulfide as the following tests show:

(1) It does not darken when heated (CdS does)

(2) It does not sublime when heated (CdS does)

(3) It is not soluble in HPO$_3$ (Yb sulfides were found to be soluble in H$_2$SO$_4$, HNO$_3$, and HPO$_3$).

d. No Yb$^{3+}$ emission could be observed from pieces of the ampoule wall which were coated with the yellow substance described in c.
Figure 12: Color and position of reacted products in ampoule after Yb diffusion in CdS; (a) 33 atm. S at 960°C, 1 hr; (b) 6 atm. Cd at 960°C, 1 hr.
Yb diffusions in CdS under excess 6 atm. Cd at 960°C, 1 hour, produces light brown and army green color spots on the ampoule wall, as shown in Figure 12(b). These spots are most likely Yb sulfides which formed from Yb vapor and S which out diffused from the CdS as a result of the high Cd pressure. They are not present on the ampoule wall when a CdS sample is annealed in Cd vapor under the same conditions as the Yb diffusion. No identification of these sulfides has been made. Their presence, however, indicates that significant Yb vapor was present in the ampoule during diffusion.

5.7 Luminescent Profile Technique and Results

In order to observe the luminescent intensity of diffused Yb as a function of depth, the CdS crystals with dimensions 5 x 5 x 1 mm were angle lapped and polished on the tin polishing plate after diffusion. The surface opposite the sloping surface was lapped to remove the diffused layer and the edges were sawed off so that the only active surface was the sloping surface. The sample was then placed at the focus of the xenon lamp output by cementing it in a scanning jig which consisted of a 0.16 mm slit directly in front of the sample. The jig allowed the sample to move and then be accurately positioned while the spectrometer recorded the luminescent spectra. The edge of the sample through which
the photoluminescence was observed was polished. Assuming the rare earth excitation process described in Chapter 4 to be operative, the width of the scanning slit gives a depth resolution of 2.8 μ and 14 μ for samples polished at 1° and 5°, respectively. A diagram of the scanning jig and sample geometry is shown in Figure 13. Plate 4 is a photograph of the scanning jig. Figures 14 and 15 show the luminescence profiles of Yb diffused into CdS under different conditions. The area under the spectral trace of Yb emission above the lattice emission was used to assign the luminescent intensity for each value of depth. The data points follow neither a Gaussian distribution nor a complementary error function. The dashed curves in Figure 14 are complementary error function curves.
Figure 13. Sample geometry and scanning jig used for photoluminescent profile measurements; (a) sample geometry showing path of excitation light and observed luminescence. Dotted line indicates sample boundary before angle polishing. *+ indicates polished surfaces; (b) diagram of sample and light path for sample mounted in scanning jig; (c) simplified diagram of scanning jig and quartz dewar.
Plate 4. Scanning jig used for luminescent profile measurements.
Figure 14. Photoluminescent intensity profiles for Yb diffused into CdS at 960°C.
Relative Emission Intensity

LEGEND
○ 4 Days at 800°C and 12 Atm. S
△ 16 Days at 800°C and 7 Atm. S

Depth into Crystal in μ
Normalized to 4 Day Diffusion

Figure 15. Photoluminescent intensity profiles for Yb diffused into CdS at 800°C.
CHAPTER 6

DISCUSSION OF EXPERIMENTAL RESULTS AND CONCLUSIONS

The purpose of this Chapter is to discuss the results presented in Chapter 5 taking into account the factors given in Chapters 2 - 5 and propose a model to explain the mechanism of rare earth discussion in CdS. The reader should keep in mind that this study is an initial investigation into a complex process and that the topics discussed may appear upon first reading to be somewhat unrelated. The discussion is an attempt to relate the parameters of our diffusion process to the topics covered in Chapters 2 - 5, although this relationship may not be obvious in places. Suggestions for further work are given in section 6.4.

6.1 Summary of Major Experimental Results

a. Photoluminescence has been observed from six rare earths (Pr, Nd, Ho, Er, Tm, and Yb) diffused in CdS under excess S and four (Ho, Er, Tm, and Yb) diffused in ZnSe under excess Se. The diffusions are reproducible.

b. For Yb diffused in CdS at 960°C for 1 hour, the emission intensity as a function of depth increases with increasing S pressure. The luminescent profile
is neither Gaussian nor a complementary error function. If luminescent intensity is assumed proportional to the Yb concentration, then part of the profile would appear to arise from a fast component of the diffusion and the other part from a slow diffusing component. A complementary error function approximation of the slow diffusing component (Figure 14) gives a diffusion coefficient $D = 1.3 \times 10^{-9}$ cm$^2$/sec for 33 atm. S pressure and $D = 1.3 \times 10^{-10}$ cm$^2$/sec. for 3.3 atm. S pressure.

c. For Yb diffused in CdS at 960°C for 1 hour, the emission intensity near the surface increases with increasing S pressure. When the S pressure increases from 3.3 to 33 atm, the peak intensity increases from approximately 7 to 60 (Figure 14).

d. For Yb diffused in CdS at 960°C for 1 hour under 6 atm. Cd pressure, the surface intensity is reduced by a factor of 300 from that for a corresponding 33 atm. S pressure diffusion.

e. The addition of Cu in Yb diffusions in CdS at 960°C, 33 atm. S, 1 hour, does not enhance the resulting luminescence. Added Cu tends to reduce the luminescent intensity and makes a prominent line appear at
1.06 μ with lower peaks appearing at 1.02μ, 1.04μ, 1.05μ, and 1.09μ (Figure 10). Added Ag and Au have only the effect of reducing the Yb luminescent intensity by 15-20%.

f. CdS samples annealed in 33 atm. S pressure at 960°C for 1 hour show no broad band emission in the vicinity of the rare earth emitting lines (= 0.8 - 1 μ). These samples show a broad emission (apparently) peaking at 0.72 μ which is identical to that occurring in samples diffused with a rare earth under the same conditions. The height of this band reduces by a factor of about 20 when the diffusion temperature is increased from 960°C to 1050°C, while (at least for Tm) the rare earth emission intensity increases by a factor of three or four.

g. Samples prevented from exposure to the Yb source only during the diffusion warm-up still show luminescence, but the intensity is reduced by an order of magnitude. Commercially available Yb₂S₃ as well as Yb sulfides prepared under the same conditions as for a diffusion give the same result as Yb metal when used as the rare earth source in a typical diffusion.
6.2 Discussion of Experimental Results

For clarity, the discussion will be divided into sections.

6.2.1 Observation of Rare Earth Emission

The observed rare earth luminescence shows that diffusion is an effective technique which may be used to introduce several of the rare earths into CdS and ZnSe. Due to the chemical similarity of the rare earth elements, it is likely that most of the elements are incorporated to about the same level of concentration under identical diffusion conditions. The failure to observe emission from rare earths in certain materials prepared by diffusion is probably due to the ion not being located in the proper crystalline field to permit 4f-4f transitions with energies near that of an associated deep level acceptor. For example, no emission was observed from our Dy diffused CdS, but EPR data\textsuperscript{5} show that Dy can be introduced as a trivalent ion into CdS by diffusion. The failure to observe luminescence from trivalent Eu is due to Eu being incorporated in the divalent state.\textsuperscript{95} Emission from trivalent Gd cannot be observed since its first excited state ($\approx 4$ eV) is higher than the band gap energy of any of the II-VI compounds (see Figure 2).

\textsuperscript{95}Philip E. Wigen, private communication.
6.2.2 Luminescent Profiles

The luminescent profiles of Figure 14 show that luminescent intensity increases significantly with increasing S pressure. This indicates that raising the S pressure increases either the rare earth concentration or the concentration of deep level acceptor associates or both. If the rare earth concentration is assumed proportional to luminescent intensity, then the diffusion coefficient would appear to increase an order of magnitude for the same increase in S pressure. This situation is indicative of a diffusion mechanism based on the concentration of Cd vacancies, since \( [V_{\text{Cd}}] \) is proportional to \( P_{S_2}^{1/2} \) and Yb can substitute for Cd. (From Table 4, \( [V_{\text{Cd}}] = 4.13 \times 10^{15} \) cm\(^{-3}\) at 960°C for 33 atm. S.) The situation may not be simple though, because some of these vacancies would be filled by rare earth ions while others likely act as acceptor associates for the ions.

Figure 14 shows that the profiles for 33 atm. S pressure follow a \( d/\sqrt{E} \) dependence fairly well. The profiles differ in intensity by a factor of approximately 3 in the 0-60 \( \mu \) range, but this is considered less significant than the \( d/\sqrt{E} \) dependence obtained in the 75-100 \( \mu \) range where the intensity varies over an order of magnitude. The \( d/\sqrt{E} \) dependence is taken as an indication that Fick's laws (of section 2.6) are obeyed for the given diffusion conditions.
The complex appearance of the profiles (i.e. neither Gaussian nor a complementary error function) may arise from the diffusion coefficient being concentration dependent. If rare earth concentration is assumed proportional to luminescent intensity, then the higher concentration parts of the profiles would appear to arise from a fast component of the diffusion while the lower portions would be due to a slow diffusion component. It could appear that the diffusion coefficient increases with concentration, which would rule out a simple vacancy mechanism of diffusion. But this is not necessarily the case. The diffusion process is complicated by the fact that there are several defects diffusing simultaneously. In a S atmosphere diffusion, Cd interstitials are diffusing out of the crystal while Cd vacancies, rare earth ions and S atoms are diffusing in. The rare earth ions are assumed to energetically prefer Cd vacancies. As the vacancies are filled the ions would tend to migrate via an interstitial mechanism, except for the occurrence of new vacancies by diffusion. Whether a vacancy or interstitial mechanism dominates for the higher rare earth concentration depends upon the relative rate of rare earth diffusion via Cd vacancies compared to that for Cd vacancies diffusion.

The luminescent profiles show a fall-off of intensity close to the crystal surface and this deserves some discussion.
Several possible reasons for this are: the incorporation mechanisms near the surface are different, high rare earth surface concentration causes quenching, out diffusion of rare earth due to nonzero cooling time (1-1.5 minutes) after diffusion, and imperfect polishing of the crystal edge through which the luminescent radiation was observed. Of these suggested reasons, the first is the most probable. Concentration quenching of luminescence is ruled out because it would prevent the occurrence of a positive slope in any portion of the luminescent profile, provided the concentration profile is assumed to have a negative slope everywhere. Also, it can be seen from Figure 14 that samples diffused at 33 atm. S show up to an order of magnitude higher luminescence than the sample diffused at 3.3 atm. S, while the profile of the latter shows a pronounced reduction in luminescent intensity near the surface.

The possibility that the reduced surface intensity results from the 1-1.5 minutes cooling from 960° to 100°C is rejected because it is unlikely that Yb would out-diffuse from depths of 7-25 µ in that short a time. During the cooling period it would require a diffusion coefficient two to three orders of magnitude higher than the value at 960°C to produce such a rapid diffusion. Also, each luminescent profile should have shown about the same drop-off if out-diffusion operates because each sample was cooled at approximately the same rate.
There is a possibility that the sample edge through which the luminescent radiation was observed may have been rounded on the portion nearest the original 5 x 5 mm surface. This would produce a cylindrical lens effect which reduces the observed intensity since the spectrometer has a small angle of acceptance (≈ 16°). It is the author's opinion that the rounding of the sample edge was insufficient to produce the observed intensity reduction.

It is unlikely that any part of the Yb concentration profile would have a positive slope. Therefore, for the luminescent profiles it is concluded that in the region of positive slope the luminescent intensity is not proportional to the Yb concentration. The highest point on each luminescent profile is probably the best indication of the Yb surface concentration. Assuming this peak to be proportional to the rare earth solubility, the profile data of Figure 14 would indicate that the solubility of Yb increases about an order of magnitude for an increase in S pressure from 3.3 atm. to 33 atm. during diffusion at 960°C for 1 hour. This rate of increase would fit the calculation where charge neutrality occurs as Yb Cd and V Cd form an associate, assuming Yb gas present during the diffusion (Table 1, seventh case). The data do not fit the cases of Table 1 where Yb Cd and Yb i are compensated by electrons, with Yb2S3 present during diffusion, where the Yb concentration decreases with increasing S pressure. The elimination of other cases from Table 1 is not as clear.
6.2.3 Emission of CdS:Yb+Cu and CdS:Cu

The data presented in Figure 10(a) show that samples in which the Cu content was increased during diffusion give significantly less Yb emission than samples diffused without added Cu. A prominent emission line at 1.06 μ begins to appear as the Cu content is increased. CdS samples which have been Cu diffused (with no Yb) to the same concentration at which the 1.06 μ line begins to appear for Yb and Cu diffused samples show little broadband emission due to Cu, as shown in Figure 10(b). Increasing the amount of diffused Cu shows a strong broadband apparently peaking at 1.0 μ which is close to the Yb line (0.99 μ). (The photodetector, having an S-1 surface, is rapidly decreasing in sensitivity with wavelength near 1 μ, and the peak of the Cu emission may actually be farther in the infrared.)

These observations are quite different from those of Kingsley et al. who found that Cu (and Ag) enhanced the emission of rare earths in Zn_xCd_{1-x}S. They observed a broadband emission due to Cu which was strongly suppressed when a rare earth emitting level was near the Cu band, and then the emission intensity depended strongly on the Cu concentration. It appears that Cu is not the dominant acceptor which transfers energy to rare earth ions in our CdS samples diffused at 960°C.
Figures 8(b) and (c) show the emission spectra of Yb in CdS diffused at 800°C, which appears similar to the emission of samples diffused with added Cu. Samples which have been Yb diffused at 960°C in a S atmosphere and then Yb diffused in a Cd atmosphere give similar emission spectra. These experiments indicate that the residual Cu concentration in our samples can be important for certain conditions of diffusion.

6.2.4 Broadband Emission

Our untreated CdS samples show weak broadband emission (apparently) peaking at 0.72 μ (1.7 eV). (It is estimated that the spectral response of monochromater and photomultiplier could have shifted the peak of this band to shorter wavelengths at most 0.04 μ). This peak is increased about four fold for a heat treatment at 960°C, 33 atm. S, and 1 hour and reduced by a factor of six for treatment at 960°C, 6 atm. Cd, and 1 hour. For either treatment the broadband is unaffected by the presence of a rare earth. The identification of this band is not easy. Curie and Prener have noted an anomalous band with peaks ranging from 0.80 μ to 0.89 μ depending on the treatment. They have suggested that this band may be due to a Cd vacancy, but they also point out the difficulties of such an interpretation.

It is the author's opinion that our band which (apparently) peaks at 0.72 μ might not be due to a Cd vacancy. Three reasons
are given: i) Boyn\textsuperscript{27} has attributed a 1.1 eV absorption for CdS annealed in S vapor to a singly ionized Cd vacancy. It is unlikely that the recombination energy would be 0.7 eV higher, although it is difficult in general to correlate absorption energies with those for emission.  

ii) When the S pressure is reduced from 33 atm. to 18 atm. at 960°C, Figure 9, the 0.72 $\mu$ band is increased by a factor of about 15. If the emission were from Cd vacancies, the intensity would reduce.  

iii) The presence of a rare earth, which tends to occupy Cd vacancies, would reduce the 0.72 $\mu$ band if it arose from Cd vacancies. The origin of this band remains unsettled.

6.2.5 Status of Rare Earth Source During Diffusion

It is conceivable that rare earth sulfides which form during the diffusion warm-up period coat the sample and then diffusion of the rare earth proceeds from this coating which acts as the source. The fact that samples prevented from exposure only during the diffusion warm-up still show luminescence rules out the possibility that a coating of rare earth sulfides is the only source present during diffusion. The fact that the rare earth emission intensity was reduced by a factor of ten indicates that a coating of some type may occur during warm-up. However, any observable coating was noted only in the case of Yb diffusion in CdS samples.
The predominant Yb sulfide present during an Yb diffusion in CdS is most likely Yb$_2$S$_3$. In an excess S atmosphere, it is reasonable to believe that the type sulfide present would contain the highest S content possible, which is Yb$_2$S$_3$. Also, commercially available Yb$_2$S$_3$ (yellow), which did not change color when used as the rare earth source in a diffusion with excess S, gave the same result as when Yb metal was used. The commercial Yb$_2$S$_3$ turned an army green color when heated in a Cd atmosphere, and no Yb emissions resulted from this type diffusion.

It is possible that the Yb$_2$S$_3$ dissociates into Yb atoms and S molecules. If this were true, it would produce more of an even coating of Yb S$_2$ on the ampoule walls when cooled. The pattern of sulfides shown in Figure 12 always appeared, however.

6.3 Proposed Diffusion Model

The following model is proposed to explain the diffusion of rare earths in CdS: Rare earth ions diffuse via a dissociative vacancy interstitial mechanism. The ions form associates with Cd vacancies as a means of charge compensation. The concentration of rare earth ions on Cd sites is much higher than the concentration of interstitial ions. Excitation of the rare earth ions is accomplished by resonant transfer of recombination energy from the Cd vacancy associates.
6.4 Suggestions for Further Work

The following proposed experiments are listed according to the most important expected result.

6.4.1 Rare Earth Concentration Profile

Rare earth concentration profiles can be obtained by standard radioactive tracer techniques. These profiles should be compared with photoluminescent profiles. Samples should be diffused under a variety of atmospheres (including Cd atmospheres) and temperatures. It would be desirable to choose a range of pressures and temperatures in which the molecular composition of S is simple. Caution must be used when interpreting any profile because an accurate interpretation is limited by the lack of knowledge of the status of the rare earth source during diffusion (see section 6.4.4).

6.4.2 Rare Earth Solubility

Spectrochemical analysis of rare earth diffused samples can give the total rare earth concentration with an accuracy of an order of magnitude (or better). Radioactive tracer techniques may be helpful, also. The samples should be fairly uniformly diffused. Samples should be diffused under a variety of atmospheres and temperatures.
6.4.3 Rare Earth Site Location

EPR studies of rare earth diffused CdS (and other II-VI compounds as well) can clarify the types of rare earth sites as well as the valency of the ions. Samples should be diffused in a Cd atmosphere as well as a S atmosphere to determine whether significant site changes occur (see section 2.3 and Eq. (2.17)). EPR measurements will yield limited information on the concentrations of various types of sites, however.

6.4.4 Status of Rare Earth Source During Diffusion

The status of the rare earth source during diffusion needs to be more thoroughly determined before concentration profiles, luminescent profiles, and solubility measurements can be more accurately interpreted. It is necessary to determine (1) if the rare earth source varies significantly with time and (2) molecular composition of the rare earth source. It might be possible to determine the first by monitoring the optical absorption of the gaseous atmosphere present during diffusion. The second can be determined by mass spectrographic methods similar to those used to determine the vapor composition of heated CdS. A simple experiment, which would yield less direct information, can be performed in which the quantity of rare earth metal (or sulfide) is varied in a series of diffusions.
6.4.5 Effect of Codopants on Rare Earth Solubility and Luminescence

The effects of codopants, such as Cu, Ag, and Au, can be investigated by including them in the diffusion ampoule and making measurements such as solubility, concentration and luminescent profiles, and EPR. The rare earth ion excitation scheme observed by Kingsley et al. can thus be examined (see section 4.2).

The residual concentration of elements in a series of CdS samples should be measured. In particular, the concentration of elements such as Cu, Ag, and Au can be determined by spectrochemical analysis.

6.4.6 Sequential Diffusion and/or Annealing

A variety of sequential diffusions can be performed which are simple to carry out and may yield rather useful information. For example, a CdS sample which has been rare earth diffused in a low pressure Cd or S atmosphere can then be annealed in S vapor at 800°C to determine if the S anneal improves the rare earth luminescence. This would be an attempt to simulate by diffusion a rare earth doped vapor phase grown crystal which might show emission only after annealing in S vapor.

The variety and design of such sequential diffusions is limited only by the ingenuity of the investigator.
6.4.7 Diffusion and Luminescence of Non-Rare Earth Elements

The diffusion and luminescence of many non-rare earth elements should be carried out using carefully controlled diffusion techniques. For example, the luminescence of Cu in CdS is somewhat obscured in the literature (see section 4.2). Now that sample preparation can be controlled, these experiments should be easy to perform.

6.4.8 Rare Earth Diffusion in Other II-VI Compounds

The technique of diffusion in CdS (and ZnSe) can be extended in an obvious way to the other II-VI compounds. The experiments proposed in sections 6.4.1 - 6.4.7 apply also. As these and other experiments are completed a somewhat unified picture of rare earth diffusion and luminescence in the II-VI compounds should emerge.

6.5 Conclusions

Diffusion has been shown to be an effective technique which can be used to introduce rare earths into CdS (and ZnSe). The preparation of rare earth doped CdS has been shown to be much simpler by diffusion than by previously used vapor phase growth methods, and the resulting photoluminescence is much more reproducible. The photoluminescence of diffused CdS (and ZnSe) can be accurately controlled by the temperature, S (or Se) pressure, and time of diffusion.
A technique has been developed for rare earth diffused CdS samples which gives photoluminescent intensity as a function of distance from the crystal surface. The shape of the resulting photoluminescent profiles has a complex appearance, being neither Gaussian nor complementary error function.

The diffusion technique has been used to simultaneously co-dope CdS with elements such as Cu. The addition of Cu in Yb diffused CdS has been shown to produce significant changes in the emission spectra.
LIST OF REFERENCES


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(95) Wigen, Philip, E., private communication.