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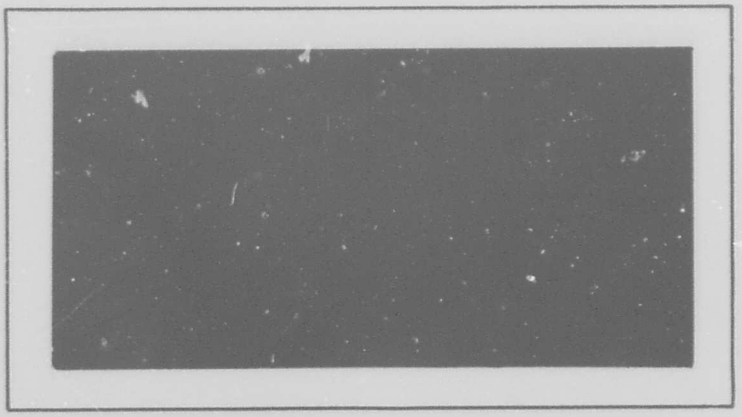

SCHOOL OF ENGINEERING

WRIGHT–PATTERSON AIR FORCE BASE, OHIO

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THE POTENTIAL USE OF ZINC SULFIDE
IN AN IMAGING INFRARED DETECTOR

THESIS

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ABSTRACT

The emission response of ultraviolet-excited ZnS to stimulating infrared radiation of 1.5 to 5.5 micron wavelengths was studied at 77 degrees Kelvin. An image of an infrared source converted to visible light by a ZnS phosphor plate was photographed. The emission spectrum of ZnS under infrared stimulation at 2.46 microns was also examined. An energy band model for ZnS based on the infrared response curve and the emission spectrum is proposed. The feasibility of using ZnS in an imaging infrared detector is further enhanced by this study.

THE POTENTIAL USE OF ZINC SULFIDE IN AN IMAGING INFRARED DETECTOR

THESIS

Presented to the Faculty of the School of Engineering of

the Air Force Institute of Technology

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by

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PREFACE

The purpose of this research was to gain information about the possible use of zinc sulfide in an imaging infrared detector. As such the research was more practical than theoretical. However, an energy band scheme was inferred from the data provided by the experiments which were performed. The model I arrived at is by no means the only one possible to describe infrared-stimulated emission in ZnS, but it does account for all of the phenomena observed. This thesis extended the work done previously in this same area by Dickman (Ref 4).

Many people gave up their valuable time to aid me in this research. Particular thanks are due my sponsor at the Solid State Laboratory, Aerospace Research Laboratories, Mr. Donald C. Reynolds. He spent much time directing my project and giving me practical help in the laboratory. I would also like to give special thanks to Dr. Philip Fraley. He, too, spent many hours helping me with equipment and listening to my problems. My advisor at the Institute, Dr. Robert Hengehold, also helped to make this thesis possible with his advice. Many other people at the Aerospace Research Laboratories aided me during my stay there, and I would like to take this opportunity to thank them all and let them know how very much I appreciated their help. It was sorely needed.

Michael J. Neary

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I. Introduction

This research was conducted as part of a continuing study of the feasibility of using ZnS phosphors as the sensing element in an imaging infrared detector. This study is being conducted at the Solid State Laboratory, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio. The final goal of this study is an imaging infrared detector capable of operating in the infrared atmospheric windows 2.0 to 2.5 microns, 3.4 to 4.0 microns, and/or 5 to 6 microns.

Background

Luminescent emission from II-VI crystals has been known and studied for some time (Ref 12:458-670 and Ref 14). This paper is the result of a direct continuation of studies on infrared stimulation of visible emission in group II-VI compounds begun by Park and Litton (Ref 9) and Dickman (Ref 4). Dickman analysed the performance of ZnS crystals with different types and concentrations of impurities. The ZnS crystals studied in the following experiments were those that Dickman found to be the most responsive to infrared stimulation (Ref 4: 39). These are melt-grown ZnS crystals, grown at ARL, intended to be as pure as possible.

Dickman's work was done with single crystals, but the experiments comprising the present research were done with many small bulk crystals. This change was made for two reasons. First, to measure any emission under low-energy infrared stimulation it was found that a large emitting surface area was needed. Second, an imaging detector constructed from ZnS phosphors would probably utilize small grains of crushed single crystals, so that single-crystal data was no longer

particularly valuable.

Goals

The goals of this research were primarily three: to extend infrared response measurements to stimulating wavelengths greater than 2.5 microns; to form an image of an infrared source converted to a visible image by a ZnS phosphor; and to further examine the energy band model for infrared-stimulated emission in ZnS. In order to fully examine the energy band model, the emission spectrum of ZnS under infrared stimulation must be known. The degree of success in achieving these goals would largely determine if research on such a detector should continue.

Organization of the Report

The report of this research is organized into three main sections. Chapter II covers some of the available models for luminescence in crystals, with special emphasis on the model of Prener and Williams (Ref 11 and Ref 10). In Chapter III the equipment and procedures used in the experiments outlined above are detailed. The results of these experiments are discussed in Chapter IV. Finally, the conclusions and recommendations for further study are presented.

II. Infrared-stimulated Emission in ZnS

Before specific models for infrared-stimulated emission are presented, some general background in the theory of luminescence will be outlined.

Background

All of the models for infrared stimulation of visible emission depend upon the crystals being excited prior to stimulation. By excitation is meant that electrons in the valence band are given enough energy to "cross" the band gap and enter the conduction band. This is, of course, just the energy required to remove an electron from a zinc-sulfur bond and free it in the lattice. The band gap in cubic ZnS at 4.2 °K is 3.84 ev (Ref 13:52). The 2536 Å line of mercury provides photons of 4.89 ev. Thus photons of ultraviolet radiation from a mercury vapor lamp are sufficient to excite the crystals.

The emission of light occurs when the electrons fall from this excited state back to the valence band, or to recombination centers in the band gap near the valence band. The lifetime of the electron in the conduction band is of the order of 10^{-8} seconds in phosphorescent sulfides of the doped ZnS type (Ref 3:2). If the electrons were to recombine immediately with the holes they vacated in the valence band, then, no luminescence would be visible after the exciting ultraviolet was removed.

However, once the electrons have been excited, they can drop spontaneously to metastable levels just below the conduction band. These levels are known as electron traps, and the energy from the ground state of the trap to the bottom of the conduction band is known

as the trap depth. The lifetime of the electron in this trapped state is a function of temperature. At room temperature thermally-agitated non-radiative transitions from the trap level are more probable than radiative transitions; thus, all experiments on infrared-stimulated emission were carried out at 77 °K, where the lifetime of the electron in the trap level is longer and the probability of radiative transitions is higher than the probability of non-radiative transitions (Ref 3:4).

Since recombination is generally not observed directly from the stable trap, the electron must be excited out of the trap to a higher energy level where radiative transitions have a much higher probability. This re-excitation from the electron trap to a higher energy level has been termed infrared stimulation. Infrared photons provide sufficient energy in this case because the energy needed to excite the electron to an excited state of the trap or back to the conduction band is much less than the energy needed to excite the electron across the band gap. If the electrons are excited back to the conduction band, they can recombine with a hole directly or be re-trapped.

At present there are three models for luminescence which may be applied to this problem: the Schon-Klasens model (Ref 7); the Lambe-Klick model (Ref 8); and the Prener-Williams model (Ref 11 and Ref 10). These are general models, and the energy band scheme derived for a particular crystal may not fit any one model entirely, but it must account for all of the observed phenomena.

The Schon-Klasens Model

One of the first models proposed for infrared-stimulated emission

was developed in the late 1940's by Schon, Klasens, and others (Ref 7). This model, like the others to be presented, postulates the existence of localized energy levels within the forbidden band gap (Fig. 1).

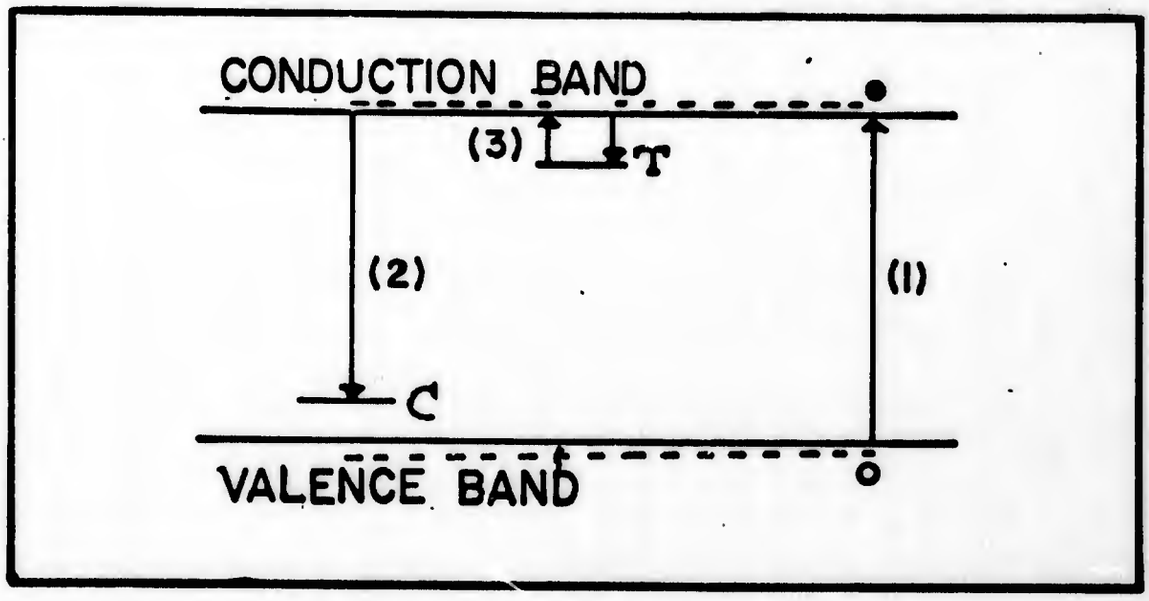

Figure 1

Schon-Klasens model for luminescence showing: (1) excitation; (2) luminescent transition; (3) trapping and re-excitation (After Ref 7:76).

The level of the luminescent center, C, may be either the direct result of an activator impurity at a lattice site, or it may be due to the presence of an interstitial activator disturbing an adjacent sulfur ion. The latter is believed more common. Klasens also stated that most of the trapping levels, T, in zinc sulfide phosphors do not belong to impurity elements but to disturbed lattice elements (Ref 7:73).

In this model the electron is excited from the valence band to the conduction band where it is free to move (1). The electron can either recombine spontaneously with a hole trapped at level C (2), or be trapped at a level T, re-excited to the conduction band (3), and then recombine (2). Recombination is accompanied by the emission of a photon. The energy of the photon, in this model, depends upon

the energy difference between the conduction band and the luminescent center C. If this model describes infrared-stimulated emission for a particular crystal, an increase in the photoconductivity of the crystal should be observed under infrared stimulation.

The Lambe-Klick Model

The model for stimulated emission proposed by Lambe and Klick (Ref 8) differs considerably from the earlier Schon-Klasens model. The Schon-Klasens model relies on electron capture in the luminescent center to provide the visible emission. Since the energy difference between the luminescent center and the valence band is small, the trapping of the hole in the center involves low energy infrared emission or phonon creation. In the Lambe-Klick model the hole-electron roles are reversed. The electron is excited into the conduction band (1)(Fig. 2), where it is free to migrate. The hole in the valence

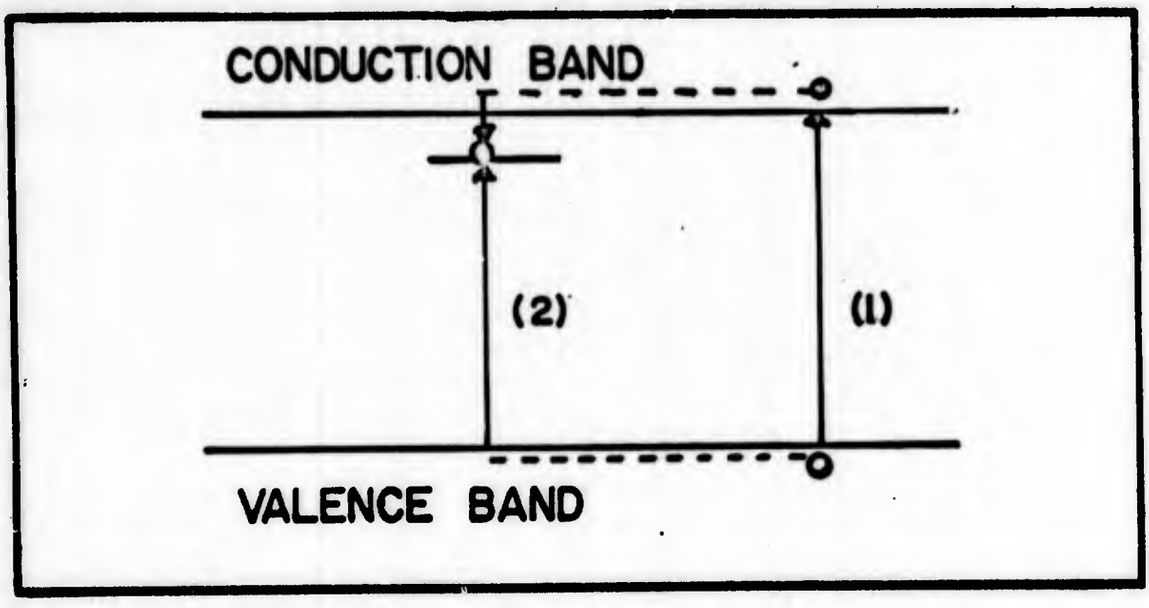

Figure 2

Lambe-Klick model for luminescence showing: (1) excitation; (2) capture of a hole by a center near the conduction band (From Ref 8:910).

band migrates until it is captured by a center near the conduction band. Hole capture gives rise to the luminescence in this model (2). An electron is then captured by the center, with infrared emission or phonon creation, and the center returns to its initial condition. The Lambe-Klick model accounts for some properties (such as photoconductivity) of the sulfide phosphors more easily than the Schon-Klasens model because electrons are free in the conduction band for a longer time before they recombine.

The Prener-Williams Model

The Prener-Williams model is the most complicated, but most complete of the three models. The luminescent emission is caused by associated donor-acceptor luminescent centers (Ref 11). In zinc sulfide the zinc and sulfur atoms form four complete tetrahedral bonds. Zinc sulfide is a covalent crystal, but there is a concentration of charge from the hybrid sp^3 bonds near the S^{++} ions. Therefore, the $Zn^{=}$ and S^{++} ions are a more convenient basis for the description of crystal binding than the covalent model (Fig. 3a). If an element of group IB (Cu, Ag, Au) were to be substituted at a lattice site for a zinc ion, one of the bonds formed with the four nearest sulfur ions would be missing an electron. This incomplete bond gives rise to a localized energy level, E_b, above the valence band (Ref 10:344) (Fig. 3b). The energy E_b is the energy required to remove an electron from a complete zinc-sulfur bond and place it in the incomplete bond. A similar scheme arises when an element of group VA (P, As) replaces a sulfur ion at a lattice site. Any impurity atom which causes localized energy levels above the valence band is called an activator. The

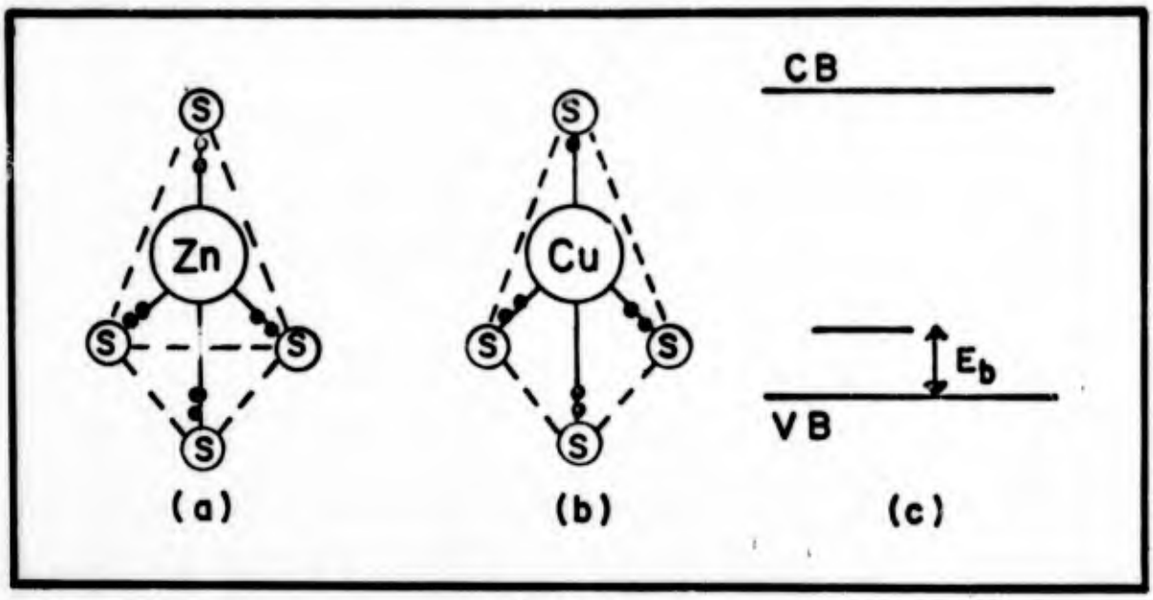

Figure 3

Acceptor Centers (Activators) (Ref 10:344)
(a) Normal zinc-sulfur bonds; (b) Bonds formed by a Cu impurity at a zinc lattice site; (c) Localized energy level E_b.

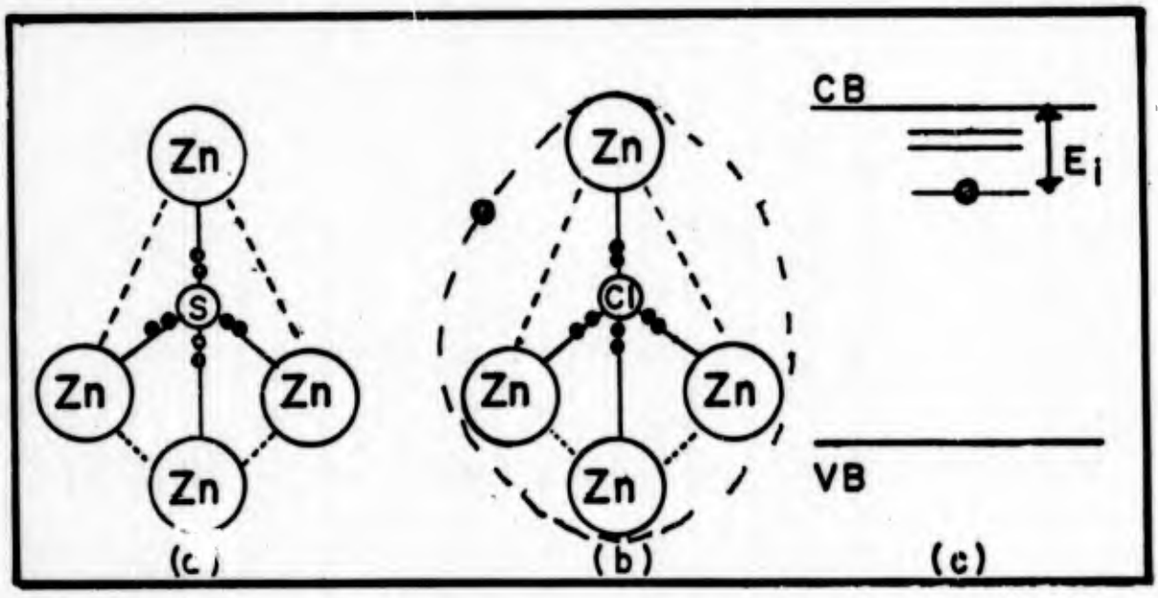

Figure 4

Donor Centers (Co-activators) (Ref 10:345)
(a) Normal sulfur-zinc bonds; (b) Bonds formed by a Cl impurity at a sulfur lattice site; (c) Localized donor level E_i.

localized energy levels above the valence band act as hole traps.

Now consider an impurity from group VIIA, such as Cl, at a sulfur lattice site. This situation would result in four complete tetrahedral bonds being formed with neighboring zinc atoms with an excess electron bound in the coulomb field of the local excess positive charge (Ref 10: 345) (Fig. 4). This results in a series of hydrogen-like localized energy levels near the conduction band. The energy E_i is the energy required to ionize the trapped electron into the conduction band, and is of the order of the ionization energy of a hydrogen atom in a medium whose dielectric constant is that of zinc sulfide (Ref 10:345). A similar energy scheme applies if group IIIA elements are substituted as impurities at zinc sites. Any impurity ion which causes localized energy levels in the band gap near the conduction band is called a co-activator.

The activator and co-activator are both necessary to explain luminescence in this model. Because of the excess negative and positive charges, respectively, there is an electrostatic attraction between the activator and co-activator at the time the crystal is formed. Thus the distribution of the activators and co-activators, with respect to each other, is not completely random. If the activator and co-activator become nearest neighbors, the localized energy levels due to the separated co-activator-activator system vanish because of the overlap of the orbit of the electron trapped by the co-activator and the field of the activator. The perturbation of the periodic crystal potential, which is that of a charge for the separated system, is now that of a dipole (Ref 10:345). It is concluded by Prener and Williams that second and third nearest neighbor systems are responsible for most lumin-

escence.

Transitions from the ground state of the co-activator near the conduction band to the activator levels near the valence band are not observed because the wavefunctions are localized and do not overlap. However, the wavefunctions of the excited, hydrogen-like states of the co-activator overlap the wavefunction of the activator, and transition, with accompanying luminescence, is facilitated from these excited states (Ref 10:346). The complete energy scheme of the Prener-Williams model is summarized in Figure 5.

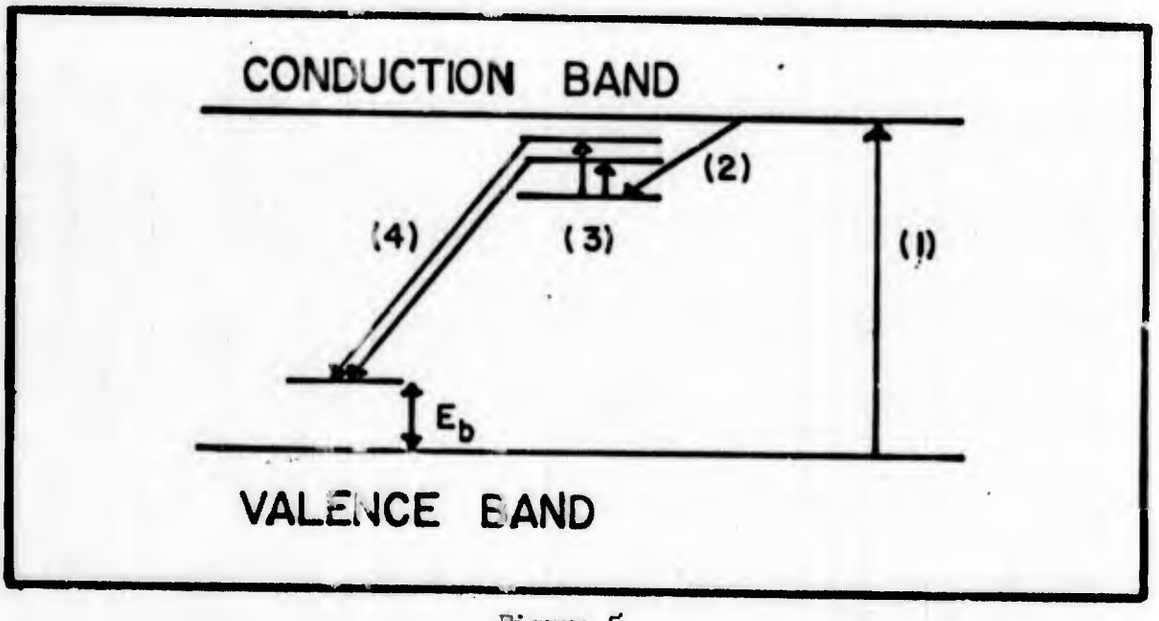

Figure 5

Prener-Williams Model for Luminescence (After Ref 10:345)
(1) Excitation; (2) Trapping; (3) Re-excitation or stimulation; (4) Luminescent emission.

Each of the three models for luminescence presented above are useful in explaining particular results. The Prener-Williams model is very general and flexible, and is particularly useful in describing infrared-stimulated emission. Thus the results of this study will be presented primarily in terms of the Prener-Williams model.

III. Experimental Equipment and Procedures

Three main experiments comprised this study. The first experiment was the measurement of integrated emission intensity, as measured by a 1P21 photomultiplier tube, as a function of stimulating infrared wavelength. The plot of emission intensity vs. infrared wavelength of the stimulating radiation is known as the "infrared response curve". The second experiment was the formation of a visible image of an infrared source in a plate of crushed ZnS phosphor. The third experiment was an attempt to photograph the emission spectrum of ZnS under infrared stimulation. The infrared response curve and the imaging experiment were most basic in determining the feasibility and range of application of an infrared detector built with ZnS. The emission spectrum is necessary for examining the energy band model for infrared-stimulated emission. The equipment and procedures used in these experiments will be detailed in this chapter.

Experiment #1: Infrared Response Curve

Several different elements formed the system used to obtain the infrared response curve. The crystals of ZnS must be mounted so that the stimulating radiation can reach the crystals, and the emitted light can be measured. The crystals have to be cooled since infrared-stimulated emission is a low temperature phenomenon. An infrared source, capable of producing various wavelengths over the range 1.5 to 5.5 microns, must be used to stimulate the light emitted from the crystals. The emitted light intensity must be measured. The equipment comprising these various systems will be presented separately, followed by a description of the procedure used to determine the points on the infrared

response curve.

Crystal Mounting and Cooling. It was found that a large crystal surface area was necessary to measure any emission under low-energy infrared stimulation. To obtain a large surface area, several small bulk crystals of ZnS grown in the same batch were used instead of a single crystal. Fouteen crystals with a total mass of 8.8 grams were used for the infrared response curve measurements. A mass spectrometer analysis of a crystal from this batch is contained in the table below. The analysis was performed at the Bell and Howell Research Laboratories, Pasadena, California.

Impurity Concentrations in the ZnS Sample
(In parts per million atomic)

Element(a)	Detection Limit(b)	Concentration
F	0.03	85
C	0.03	59
H	0.1	42
K	0.01	22
Na	0.00"	3.3-14
Cl	0.2	6.8
Si	0.03	6.7
N	0.03	4.2
Se	0.1	2.8
Ca	0.03	2.5
Al	0.03	1.6
V	0.03	1.5
Fe	0.07	1.1

(a) Analyses for tantalum and gold are not given since tantalum slits were used in the mass spectrometer and the sample was sparked against a high purity gold probe. Other impurities not listed had concentrations below 1 ppma except oxygen, analysis for which is interfered with by background lines of zinc sulfide.

(b) Determined for 1×10^{-7} coulomb exposure.

The crystals were placed on top of a brass block located in the bottom of a cylindrical quartz dewar (2.0 cm inside diameter x 30 cm long). The crystals were cooled by immersion in liquid nitrogen. It

was found that the signal-to-noise ratio was improved several orders of magnitude by bubbling gaseous helium under 5 psi pressure through a small diameter tube which opened approximately one-half inch above the crystals (Fig. 6). It is believed that the helium bubbling sufficiently

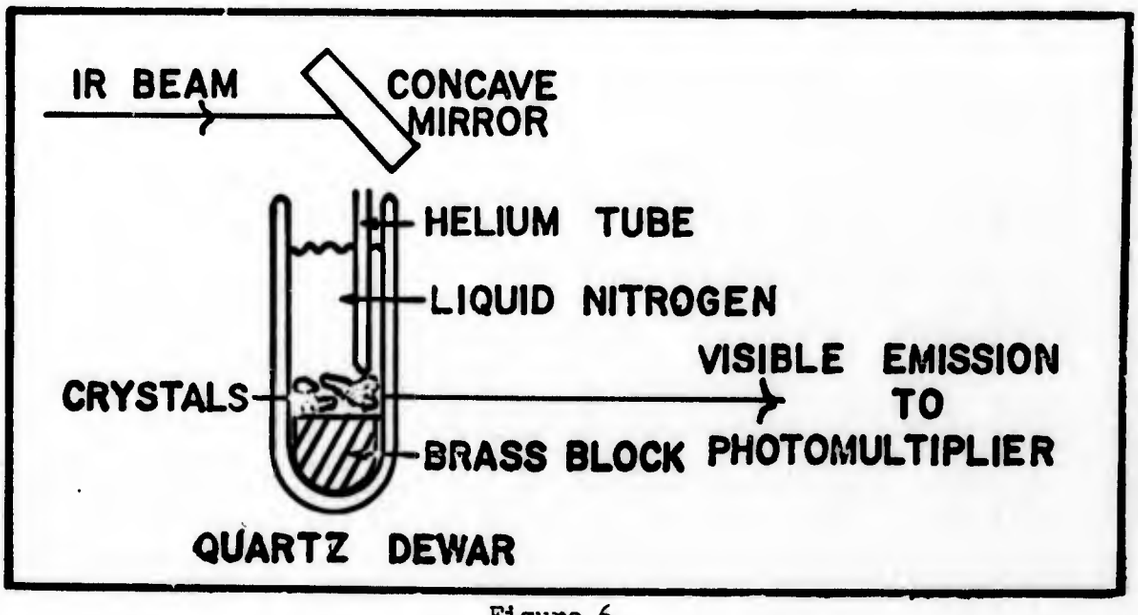

Figure 6
Dewar Arrangement for Infrared Response Measurements

lowered the temperature, by increasing evaporation in the bottom of the dewar, to cause the cessation of bubbling in the liquid nitrogen after the helium was shut off. The brass block held this temperature long enough to permit noise free measurements for about 45 seconds. Warm air was forced around the outside of the dewar to keep frost from diminishing the intensity of the emitted visible light.

Ultraviolet Excitation. The crystals were excited by ultraviolet radiation from a high pressure mercury vapor lamp powered by a General Electric autotransformer. The exciting ultraviolet light was focused on the crystals through the walls of the dewar by a 75mm quartz lens.

Stimulation Optics and Detection. The infrared source used in this experiment was a silicon carbide globar heated by a current of 4.5 amperes. The globar was mounted at the entrance slit of a Perkin-Elmer Model 12C infrared spectrometer equipped with a CaF_2 prism. This prism transmitted infrared radiation up to eight micron wavelengths. Also incorpoated into the spectrometer was a KBr high speed thermocouple. The radiation from the globar was chopped at 13 Hz so that the signal from the thermocouple could be amplified by a Perkin-Elmer Model 107 phase-sensitive amplifier. The signal from the amplifier was recorded on a Brown potentiometer recorder. The thermocouple output, though not calibrated to measure energy directly, provided a direct indication that the infrared energy was kept constant. By varying the width of the spectrometer slits manually, the energy reaching the crystals was maintained at this constant level as shown by the pen deflection of the Brown potentiometer. Thus the response curve could be plotted as a function of stimulating wavelength only. A schematic diagram of the infrared response curve equipment is shown in Figure 7.

The beam from the exit slit of the spectrometer was focused by a 1:1 front-surface mirror down the top of the quartz dewar to the crystals (Fig. 6). The use of this system meant that there was no need to correct for the infrared absorption of window materials. Atmospheric absorption of the infrared was corrected for by using the thermocouple to insure a constant infrared energy, since the optical paths to the thermocouple and to the crystals were approximately equal.

Emission Optics and Detection. The infrared-stimulated visible

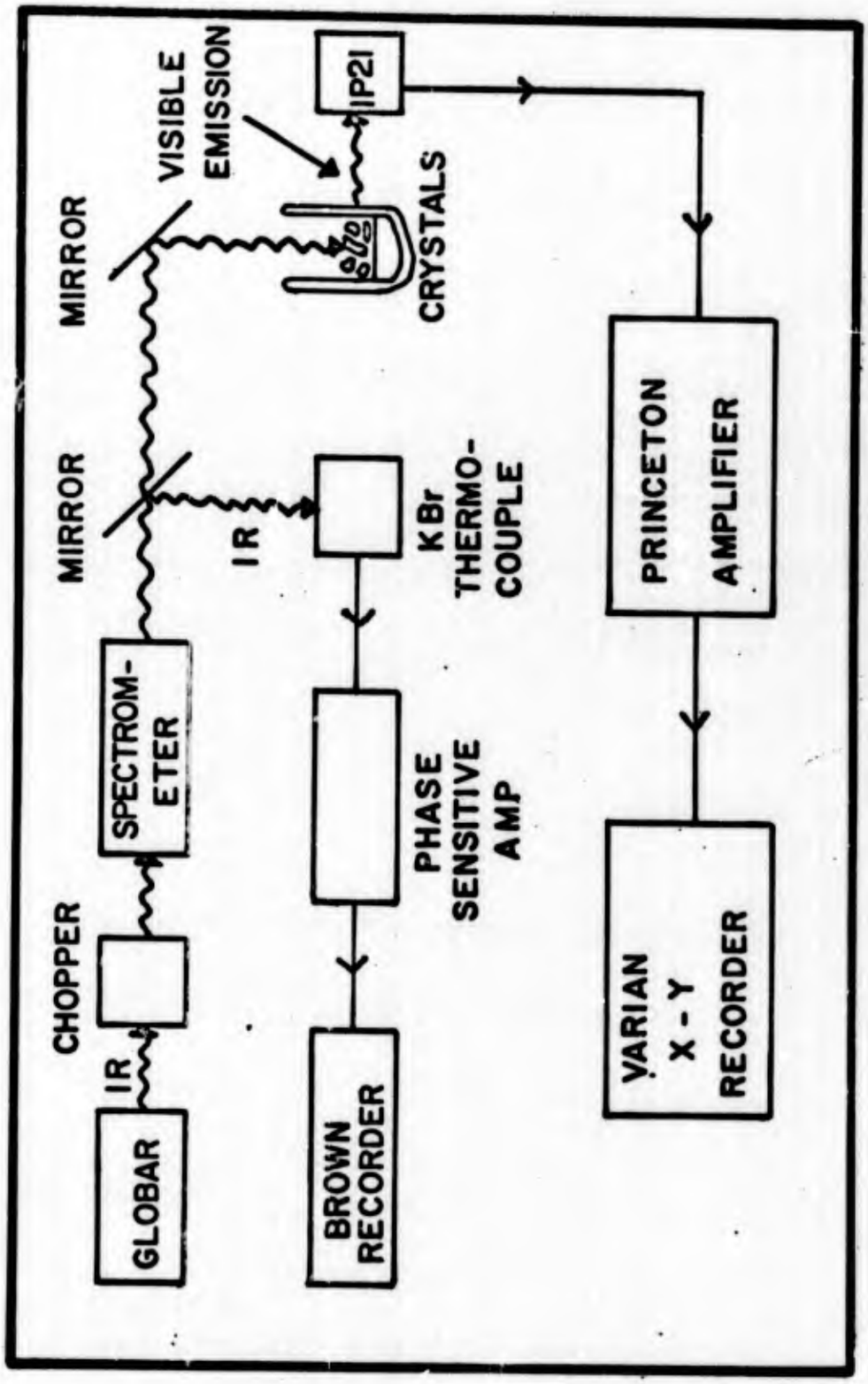

Figure 7

Schematic of Infrared Response Equipment

emission was detected by a 1P21 photomultiplier tube with an S-4 response. The voltage between the anode and the cathode of the tube was maintained at 1000 volts by a Keithley Model 242 regulated high voltage supply. The visible emission from the crystals was focused on the photomultiplier by a 55mm quartz lens.

The infrared beam was chopped at 16 Hz during the measurement of the stimulated emission by a Princeton Applied Research chopper. The chopper provided the reference input to a Princeton lock-in amplifier. The output of the amplifier was then recorded on a Varian Associates X-Y recorder. Any luminous emission not stimulated by the chopped infrared beam was therefore not recorded. This system allowed a constant signal to be recorded before the signal-to-noise ratio was ruined by bubbles in the dewar.

Procedure for Determining Infrared Response Curve

The infrared response curve was taken point-by-point. This was done so that the infrared energy could be adjusted to a constant value at each infrared wavelength where a measurement was made. Ideally, the wavelength drive and the slit drive of the spectrometer should have been coupled to provide a continuous curve at constant energy. Such equipment was unavailable for this experiment.

To obtain each point on the infrared response curve the crystals, immersed in liquid nitrogen, were excited for three minutes with ultraviolet radiation from a high pressure mercury vapor lamp. The crystals were kept in the dark after excitation for 100 seconds to allow some of the spontaneous luminescence to decay. The crystals were then exposed to the infrared beam and the intensity of the resultant visible

emission was recorded. The points on the response curve were taken approximately every 0.05 microns from 1.5 to 3.3 microns. The response from 3.3 to 5.5 microns was measured by opening the slits of the spectrometer as much as possible (2mm) and varying the wavelength continuously over this range by hand.

Helium gas was bubbled through a small tube in the dewar for about two and one-half minutes before the crystals were exposed to the infrared. The gas was turned off just prior to exposing the crystals. This procedure provided about 45 seconds of relatively constant, noise-free signal from the photomultiplier.

Experiment #2: Imaging Experiment

This experiment was performed in order to determine whether an infrared image could indeed be converted to a visible image by using ZnS phosphors.

Equipment and Procedure. A phosphor plate was constructed using a circular aluminum sheet 3 inches in diameter as a substrate. A layer of finely crushed ZnS crystals was fixed to the aluminum plate with Duco cement. The finished phosphor plate was placed in a shallow circular dish insulated with plastic foam so that the plate could be cooled with liquid nitrogen.

The infrared source that was imaged in the plate was the tip of a Weller S-400 soldering gun. The image of the tip was focused on the phosphor plate with a 75mm quartz lens. A #2540 Corning filter was placed between the tip and the plate so that no visible light from the soldering tip could reach the plate.

The visible image of the soldering tip formed in the plate was

then viewed through a light intensifier with a gain of about 40,000. An attempt was then made to photograph the image of the tip formed in the plate from the viewing aperture of the light intensifier.

The crystal phosphor plate was cooled by immersion in liquid nitrogen. The phosphor was excited for about one minute using a low pressure mercury vapor lamp as the ultraviolet source. After the background luminescence had decayed, the infrared image was permitted to strike the plate. The image was then focused in the light intensifier and photographed.

Experiment #3: Emission Spectrum Under Infrared Stimulation

Equipment. The crystals used for measuring the emission spectrum of ZnS under infrared stimulation were from the same batch as those used in the two experiments described above. Again, many small bulk crystals were used to increase the surface area studied (fifteen crystals with a total mass of 7.5 grams). The crystals were mounted and cooled as described above (Fig. 6), except that no helium gas was used for this experiment. Excitation of the crystals was accomplished with a high pressure mercury vapor lamp.

The infrared source used in this experiment was a Bausch and Lomb high intensity grating monochromator with a tungsten light source. The exit slit was fixed at 3mm. A #2540 Corning filter was placed between the tungsten light source and the grating monochromator to eliminate higher order visible light in the infrared beam. The exit slit was placed about two inches from the side of the dewar and the beam was brought through the side of the dewar directly. There was no need to consider infrared windows since the monochromator employs quartz lenses.

The emission spectrum was photographed with Kodak Type 103F film. The film was mounted in a spectrometer with a Bausch and Lomb grating as the dispersing element. The spectrum from 3600 Å to 5600 Å could be photographed on one sheet of film.

Procedure. The crystals, immersed in liquid nitrogen, were excited for three minutes with a high pressure mercury vapor lamp. The film was exposed to the crystal emission after the ultraviolet lamp was removed and the infrared beam allowed to stimulate the crystals. The infrared-stimulated emission decayed appreciably within three minutes, but the emission persisted for over one-half hour. After a thirty minute exposure the crystals were re-excited with ultraviolet and the film was exposed again while the infrared radiation was on the crystals. The crystals were excited with ultraviolet twice, so that the film was exposed to the infrared-stimulated emission from the ZnS for a total of about sixty minutes. The film was calibrated by use of a low pressure mercury vapor lamp.

The results of the three experiments described above are presented in Chapter IV.

IV. Results and Discussion

The results of the three experiments comprising this research are described in this chapter. At the end of the chapter, another experiment which was attempted, with some suggestions on its possible completion, is discussed.

Infrared Response Curve

One of the main purposes of this study was to determine the infrared response of ZnS to stimulating wavelengths greater than 2.5 microns. This experiment has shown that ZnS, containing certain impurities (see the table on p. 12), has little or no response to wavelengths greater than 3.3 microns. If there were any response, it was below the limits of detection of the equipment used in this experiment. Thus any device operating at 77 °K could not be used to detect infrared radiation at wavelengths greater than 3.3 microns using these crystals as the sensing element. Perhaps more sensitive detection equipment for the visible emission would allow the range of these crystals to be extended further into the infrared.

The response curve (Fig. 8) is very useful in determining the energy band structure for infrared-stimulated emission. Stimulated emission occurs when electrons are excited out of a trapped state to a higher energy level where they can recombine with a hole in an acceptor center near the valence band, in accordance with the Prener-Williams model. Thus emission is enhanced when the stimulating radiation provides photons of the proper energy to excite the electrons to an emitting level.

If a hydrogen-like model for the trapping center (donor levels)

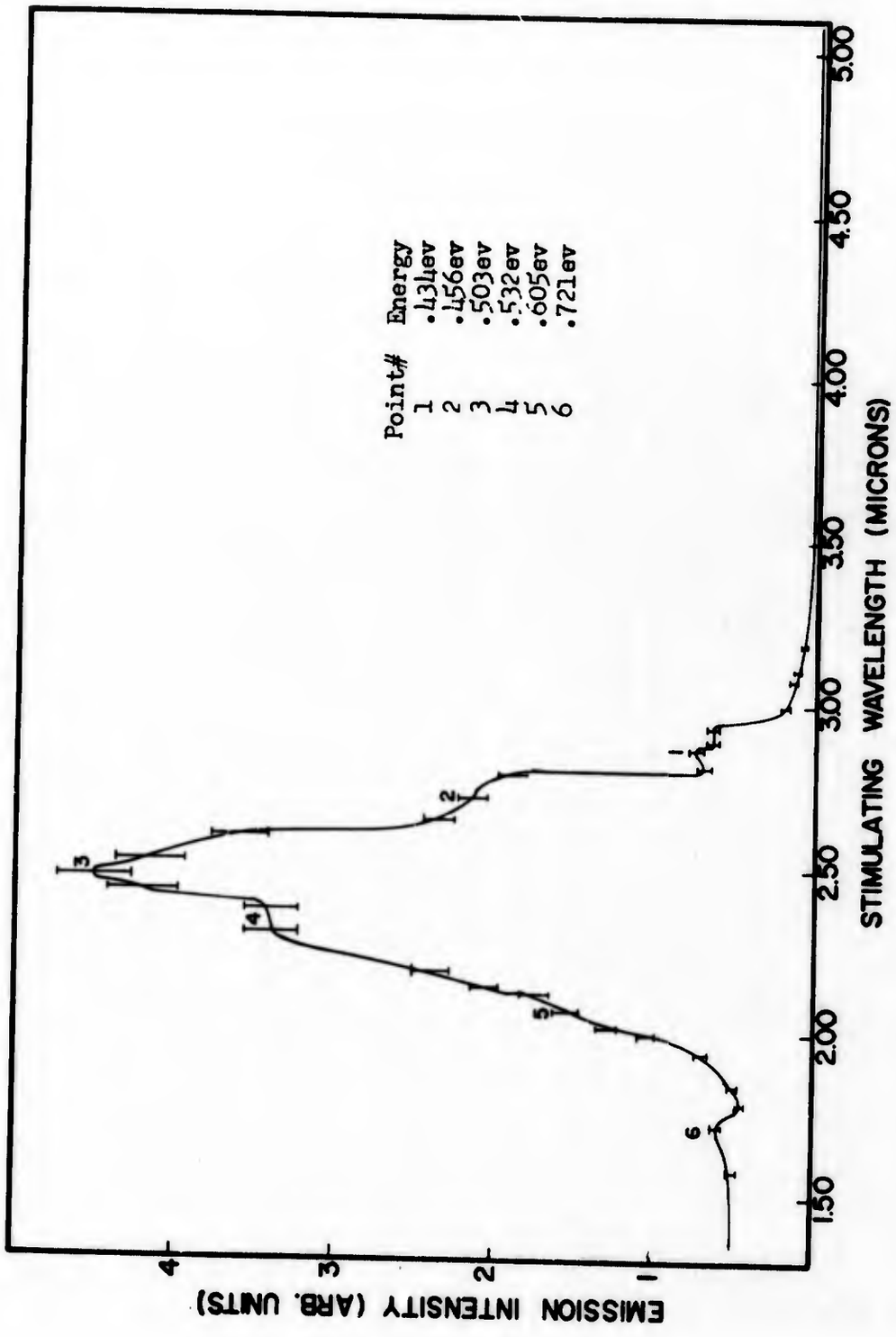

Figure 8

Infrared Response Curve

(Ref 10:345) is assumed, one can compute the energy differences between the levels of the center using the relation $E_n=E(1-(1/n^2))$, where E_n is the energy of the n^{th} level and E is the ionization energy of the trap (trap depth). One has only to assume that one of the energies E_n is known experimentally to be able to compute all of the others. There are six peaks or points of inflection on the infrared response curve (Fig. 8). It is assumed that these points indicate energies at which electrons are excited from the ground state of a stable trap to higher excited states of the trap. Recombination can occur due to the overlap of the wavefunctions of the electrons in these excited states of traps with the wavefunctions of holes in acceptor levels.

The main peak of the infrared response curve was located at 2.46 microns or energy .503ev. This peak is labeled #3 in Fig. 8. The error in locating a point on the curve is no greater than $\pm$0.03 microns, equivalent to an energy error no greater than $\pm$0.017ev near a wavelength of 1.5 microns. This peak is caused by photons of energy .503ev exciting electrons from the ground state, E_1 of a trap to the first excited state of the trap, E_2. The hydrogen model predicts that the second excited state of the trap, E_3, will occur at .597ev above the ground state, or .093ev above E_2. There is an inflection point on the curve (labeled #5 in Fig. 8) at .605ev which is within the limits of error. There is also a certain error in assuming a hydrogen-like model for the energy levels of the excited states of the trap. States of this trapping center higher than E_3 could not be resolved. The energy required to ionize an electron from this trap and free it into the conduction band is E=.672ev (trap depth).

The energy differences of all six numbered points in Figure 8

were investigated in a similar manner. It was concluded that there were four trapping centers in the ZnS sample examined. The first excited state of a different trap was indicated by point #2 with E_2=.456ev. The next excited state of this trap E_3, as predicted by the hydrogen model, should occur at E_3=.540ev. There is a minor hump in the response curve at point #4 with energy .532ev, which is again within the limits of resolution. The depth of this trap is .608ev. States of this trap higher than E_3 could not be resolved.

If point #1 is assumed to indicate the first excited state of a third trap with E_2=.434ev, the next excited state predicted by the hydrogen model should occur at E_3=.515ev. This state is within .011ev of the main peak at point #3 (energy .503ev) and could not be resolved. The depth of this trap is .578ev. Point #6 is assumed to indicate the first excited state of a fourth trapping center with E_2=.721ev. Higher excited states of this trap were not investigated. The depth of this trap is .961ev. The results of this analysis of the trapping centers found in this ZnS sample are summarized in Figure 9.

The dominance of the peak at 2.46 microns (energy .503ev) indicates either that these traps have a much higher population of trapped electrons at the time of infrared stimulation or that luminescent transitions from the first excited state of this trap are much more probable than from the other trapping centers. The most likely explanation is that the ZnS crystals used to obtain the infrared response curve contained many more of these traps than any of the other traps. Dickman also saw this trapping center (Ref 4:36), even though the crystals he used to obtain the infrared response curve were doped in a different manner than those used to obtain the curve of Figure 8. There are two

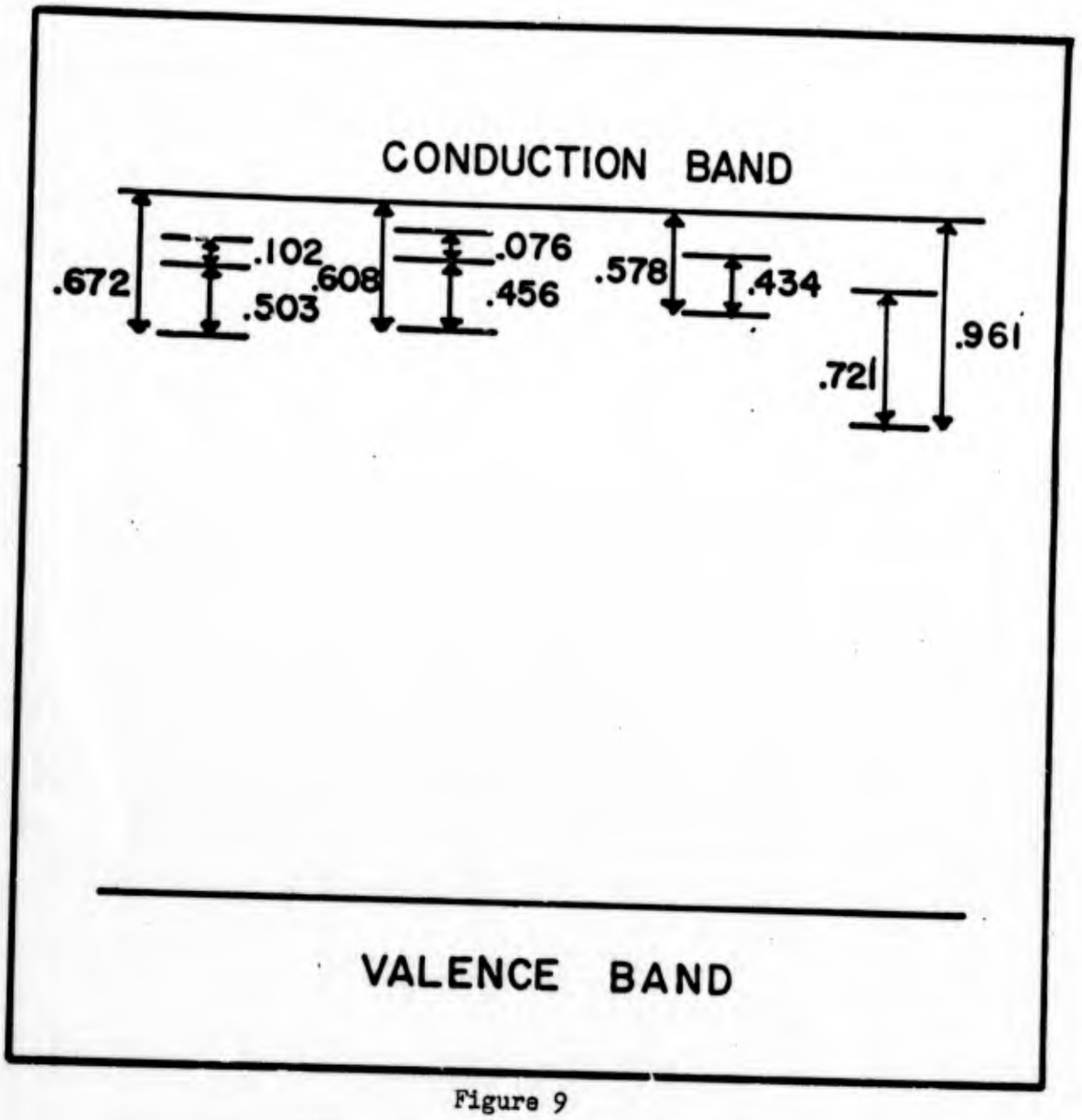

Figure 9

Proposed Trapping Systems in ZnS Sample
(Numbers indicate energy in ev)

possible reasons that both curves peak at 2.46 microns. Neither the crystal used by Dickman nor the crystals used in this experiment was investigated for oxygen impurities when analyzed by a mass spectrometer at the Bell and Howell Research Laboratories. Thus, this trap could be caused by oxygen impurities in both samples. The other possibility is that the trap is caused by a defect in the host ZnS lattice as proposed

by Bube (Ref 2:717-718). There is not enough evidence from this research to uniquely determine the cause of any particular trap.

Another very useful piece of information found in this experiment is the fact that the traps stimulated by the infrared radiation emptied fast enough to respond to a 16 Hz chopper. A practical imaging detector would either have to be chopped or scanned. It is now known that the infrared beam can be chopped or scanned at least at 16 Hz successfully. It was indicated that the chopping frequency could be increased to 400 Hz with no appreciable loss of emission intensity, but higher chopping frequencies than 16 Hz were not examined in detail.

Imaging Experiment Results

It was found that a phosphor plate constructed of crushed ZnS crystals could be used successfully to convert an infrared image to a visible image. A photograph taken of the image of a soldering gun tip in a ZnS phosphor plate is shown in Figure 10. The bright line in the photograph is the image of the tip. The photograph was taken from the viewing aperture of a light intesifier. The light intensifier was necessary because the image was too dim to photograph by its own light except by a long time-exposure. The division between the two arms of the soldering tip was clearly visible to the eye in the light intensifier, but the photograph is slightly over-exposed in the area of the tip itself. The dark, pointed protrusion over-laying the dish in the top of the photo-

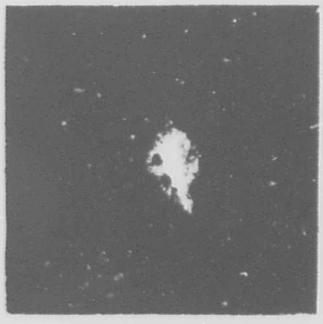

Figure 10
Photograph of Infrared Image Converted to a Visible Image by a ZnS Phosphor Plate

graph is the corner of a lens-holder. The dark blotches near the edge of the dish are places where the phosphor broke loose from the plate when the plate was cooled in liquid nitrogen.

Emission Spectrum Under Infrared Stimulation

The emission spectrum of the excited ZnS sample under infrared stimulation at 2.46 microns was photographed on Kodak Type 103F film. A positive print of the spectrum is shown in Figure 11. The emission

Figure 11
Emission Spectrum Under Infrared Stimulation
(Numbers above arrows are wavelengths of emission lines in Å)

lines in the spectrum, indicated by arrows in Fig. 11, could be located to within ±0.1 Å in relation to the mercury calibration spectrum. Line separations were measured with a Gaertner Scientific Corp. plate reader. Other films of the emission spectrum, although of lower quality, showed that the calibration spectrum in the film in Fig. 11 did not obscure any emission lines. The film shown provided the best definition of the emission lines.

As indicated in Fig. 11, there are five lines in the emission spectrum. These lines are located at 3806.7 Å, 4090.6 Å, 5188.6 Å, 5499.4 Å, and 5519.5 Å. The lines are caused by emitted photons of energies: 3.2569ev, 3.0309ev, 2.3895ev, 2.2544ev, and 2.2462ev, respectively. The energies above are uncertain by ±0.0001ev. The emission

lines were located in relation to prominent mercury calibration lines in each region of the spectrum. The American Institute of Physics Handbook (Ref 1) was used to obtain the numerical values of the calibration lines.

The analysis of the causes of the observed emission lines leads directly to a proposed energy band model for infrared-stimulated emission in the ZnS sample.

Energy Band Model for Infrared-stimulated Emission

An energy band model, based on the Prener-Williams model, can be postulated using the data of the infrared response curve and the emission spectrum. The model proposed here is not definitive and is based only upon the information acquired from one batch of ZnS crystals in the experiments described above.

Electrons were excited to the first excited state of a trap of depth .672ev by infrared radiation of 2.46 microns while the emission spectrum was being photographed. The band pass of the Bausch and Lomb infrared monochromator with a 3mm exit slit was wide enough to also excite electrons into the first excited states of the traps of depth .608ev and .578ev shown in Fig. 9. The first excited states of these traps lie, respectively, .152ev and .144ev below the conduction band. If electrons in these excited states were to recombine with holes in acceptor centers near the valence band at the same energy level, the resulting emission lines should have an equivalent energy separation of 0.008ev. This is just the energy separation of the emission lines at 5499.4 Å and 5519.5 Å. The acceptor level energy is 1.44ev above the valence band. A schematic of the proposed energy band model is shown in Fig. 12.

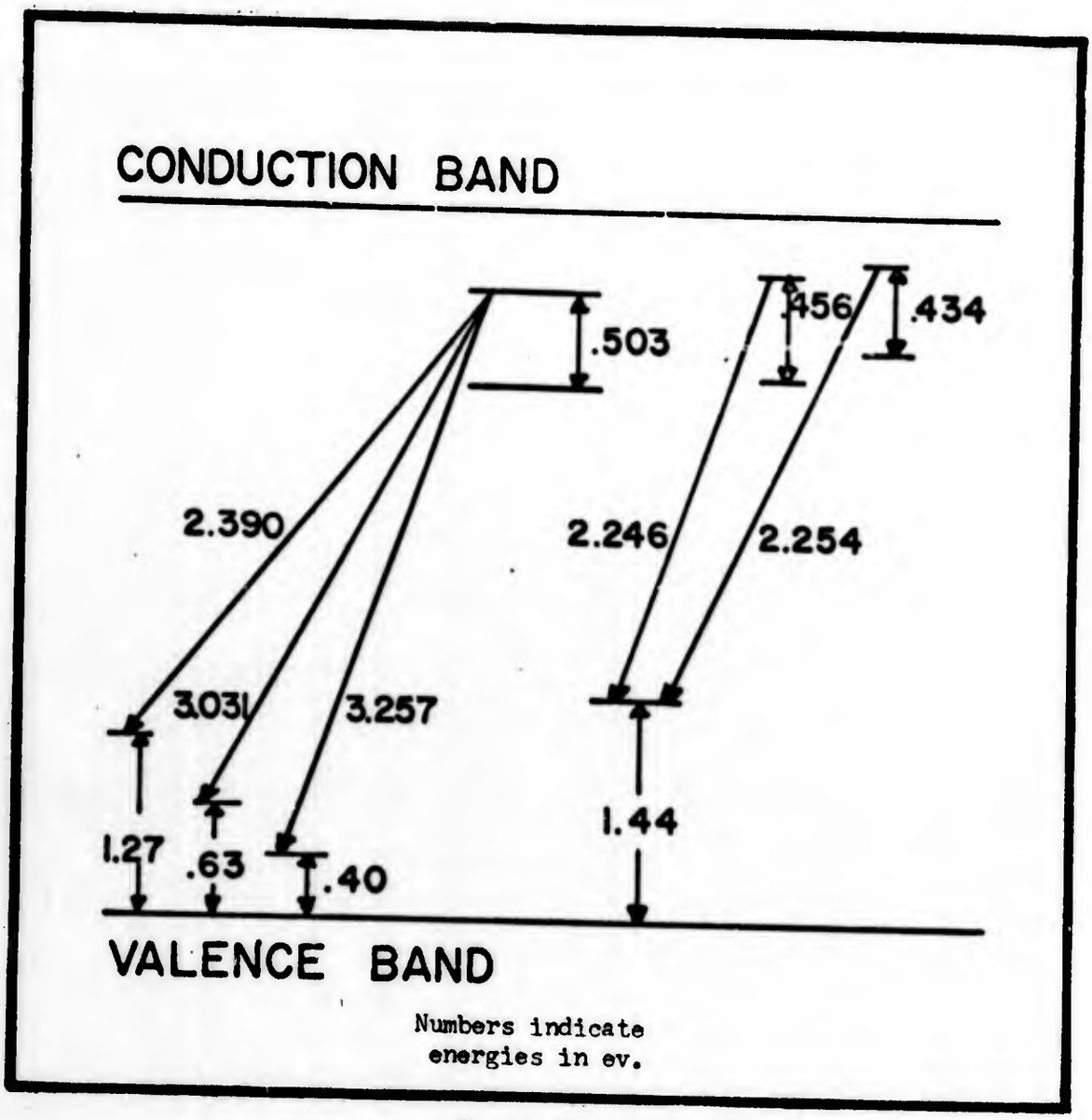

Figure 12
Proposed Energy Band Model for Infrared-stimulated Emission in ZnS

The energy separations of all the emission lines were carefully examined. The energy band model shown in Fig. 12 is the result of that analysis. The three lines at 3806.7 Å, 4090.6 Å, and 5188.6 Å seem to be caused by electrons from the first excited state of the trap of depth .672ev recombining with holes in three different localized energy levels near the valence band. These levels are .40ev, .63ev and 1.27ev above the valence band, with a possible error of ±0.02ev. The longitudinal optical phonon energy in ZnS is .042ev (Ref 13:50), so that

phonon interactions are not responsible for the observed line separations. Other attempts to explain the emission spectrum, such as excitation of the other trap found from the infrared response curve, excitation of higher excited states of the traps, etc., were made. But with only the data of the infrared response curve and the emission spectrum to work with, it was found that the radiative transitions indicated in Fig. 12 are the most probable in this sample. Still, the model appears very complex.

Simultaneous Chopping Experiment

An attempt was made to take the infrared response curve measurements while chopping both the exciting ultraviolet light and the stimulating infrared radiation. One two-blade Princeton chopper was used to interrupt each beam alternately, so that only one beam was permitted on the crystals at any time. This experiment was attempted on a ZnS single crystal mounted on the cold finger of a liquid nitrogen dewar. By chopping both beams it was thought that the ultraviolet light would replenish the traps emptied by the infrared. The stimulated emission was to be detected with a 1P21 photomultiplier tube. By selecting the phase setting on a Princeton lock-in amplifier connected to the chopper and the photomultiplier, it was hoped that the signal from the photomultiplier could be recorded only during that part of the chopping cycle that the infrared was on the crystal. Thus, the stimulated emission could be measured at a relatively constant value, before the emission intensity could decay.

However, the radiation from either a high pressure mercury vapor lamp or a xenon arc lamp used to excite the crystal was so intense that the photomultiplier was saturated during that part of the cycle that

the ultraviolet was on the crystal. The chopping frequency was 16 Hz, and the photomultiplier did not recover fast enough to measure the stimulated emission while the infrared beam was on the crystal. This problem might be solved a number of ways. A photomultiplier with a different response could be used so that it would not be so sensitive to radiation near the ultraviolet wavelengths needed for excitation of the crystal. Filters might be used, both in front of the photomultiplier and in the ultraviolet beam, so that excitation could be accomplished without saturating the photomultiplier. The filter in the ultraviolet beam should transmit wavelengths short enough to excite electrons across the band gap and cut out wavelengths long enough to activate the photomultiplier. The filter in front of the photomultiplier should transmit only visible light with wavelength longer than the cut-off wavelength of the filter in the ultraviolet beam. Such filters were not available for this experiment. If no combination of filters as described above could be found, it may be possible to keep the photomultiplier in the dark for that part of a cycle that the ultraviolet is on the crystal. This could be done with a second chopper synchronized with the first to keep the photomultiplier dark during the ultraviolet "on" part of a cycle.

The success of chopping the ultraviolet and the infrared beams alternately could provide much information valuable to the production of an imaging infrared detector. Knowledge of the excitation time required to maintain an equilibrium electron population in the traps could be obtained by varying the chopping frequency. The filling of the traps by the ultraviolet light and the emptying of the traps by the infrared may be accomplished at different rates. Equilibrium

between the two processes might be attained by chopping the beams at two different frequencies. The beam to which the crystal reacted more rapidly would be allowed on the crystal for a fraction of one cycle. The beam to which the crystal reacted more slowly would be allowed on the crystal for the remainder of the cycle. Such knowledge would certainly aid in the final production of an imaging infrared phosphor. Unfortunately, the problems involved in this experiment were not resolved successfully during the course of this research.

V. Conclusion and Recommendations

Two of the objectives of this research were completely realized. The infrared response curve beyond 2.5 microns to 5.5 microns was examined. It was also demonstrated successfully that ZnS phosphors can be used to convert an infrared image to a visible image. The emission spectrum of ZnS under infrared stimulation was examined, but rather than clarifying the energy band model of ZnS, it seems to have made the model more complex. This does not mean that the model presented in this paper is wrong, but that it needs further investigation.

If ZnS phosphors are to be used as infrared detectors at wavelengths longer than 3.3 microns, co-activators will have to be found to produce the shallower traps needed for longer wavelength stimulation. The identification of these co-activators and the determination of the proper concentration of co-activator, if such co-activators exist, are areas requiring much more systematic study.

The photograph shown in Fig. 10 was made using a crude ZnS phosphor plate. Further study should determine the optimum size of the ZnS crystals used to convert infrared to visible light images. Another possibly useful technique is the fixing of a thin layer of ZnS crystals onto a clear substrate. It may be possible to put an infrared image on one side of such a plate and obtain the visible image directly on the other side. The imaging properties of a thin film of ZnS should also be examined to determine if a thin film is a better imaging element than a layer of small crystals (Ref 5).

The energy band model for infrared-stimulated emission proposed in this paper was based only on the data gathered during this study.

The dependence of the emission spectrum on the wavelength of the stimulating infrared radiation should be studied to further clarify the energy band model for infrared-stimulated emission.

This research has indicated that zinc sulfide can be used as the sensing element in an imaging infrared detector. But much more research must be done to identify the optimum phosphor to be used in a device operating in a particular atmospheric window.

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The emission response of ultraviolet-excited ZnS to stimulating infrared radiation of 1.5 to 5.5 micron wavelengths was studied at 77 degrees Kelvin. An image of an infrared source converted to visible light by a ZnS phosphor plate was photographed. The emission spectrum of ZnS under infrared stimulation at 2.46 microns was also examined. An energy band model for ZnS based on the infrared response curve and the emission spectrum is proposed. The feasibility of using ZnS in an imaging infrared detector is further enhanced by this study.

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