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EDGE EMISSION IN ZnSe SINGLE-CRYSTALS AT LOW TEMPERATURES

THESIS

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Preface

This thesis concerns the study of fluorescence in zinc selenide single-crystals at low temperatures and culminates in a proposal of an energy model which accounts for the observed edge emission. I have attempted to present enough theory to explain the origin of edge emission and sufficient description of experimental apparatus to familiarize the reader with equipment used.

A discussion of experimental procedures and a tabulation of results precedes the analysis of data. Since, to my knowledge, there is no published information concerning the study of zinc selenide edge emission, a rather detailed analysis of results is presented to aid the reader in understanding the reasoning followed to arrive at the proposed energy model.

I should like to express my sincere appreciation to Professor L. S. Pedrotti, Dr. D. C. Reynolds, and Mr. C. W. Litton, all of whom made the writing of this thesis possible.

Oliver W. Larson

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Abstract

Fluorescence occurring near the fundamental absorption edge of ultraviolet-light irradiated zinc selenide single-crystals was examined between 4.2°K and 77°K. The zinc selenide fundamental absorption edge, as determined by reflection techniques, was observed to decrease from 2.83 eV at 4.2°K to 2.82 eV at 77°K. Spectrographic analysis of edge emission at these temperatures indicated that the fluorescence near the edge could be explained on the basis of energy levels within the band, which were attributed to impurities, and on the basis of phonon interactions.

Based on the results of this study, an energy model for zinc selenide fluorescence has been proposed. The energy model contains the observed separation of the valence-to-conduction-band gap at 4.2°K and 77°K and two impurity levels located within the gap. The fluorescence observed has been attributed to transitions between the impurity levels, between the conduction band and an impurity level, and between the valence band and an impurity level. No band-to-band transitions were observed. This model accounts for the transitions at 4.2°K and 77°K and the change in these transitions as the temperature changes from 4.2°K to 77°K.

EDGE EMISSION IN ZnSe SINGLE-CRYSTALS AT LOW TEMPERATURES

I. Introduction

Purpose and Scope

Zinc selenide single-crystals at low temperatures were excited to fluorescence by irradiation with ultraviolet light. The purpose of this thesis was to study the ZnSe fluorescence near the fundamental absorption edge. The fundamental absorption edge is defined as that minimum incident-energy which a crystal can absorb. Edge emission refers to fluorescent energies of slightly lower magnitude than that of the fundamental absorption edge.

Zinc selenide edge emission was measured at 4.2°K and 77°K; emission at intermediate temperatures was examined qualitatively to determine the manner in which the energies changed. As a result of this study, an energy model for zinc selenide edge emission has been proposed.

Approach to the Problem

Objectives in this study of fluorescence were to obtain the value of the fundamental absorption edge and to determine the nature and magnitude of edge emission. Spectrographic analysis was used for all wavelength determinations, and these values were converted to equivalent energies.

Analysis of 4.2°K and 77°K reflection spectra provided values of the fundamental absorption edge at these temperatures. Zinc selenide edge emission energy levels were determined from emission spectra. Observation of edge emission spectrum variation with temperature yielded information concerning the shift in emission energies as the crystal warmed up. An energy model was devised by arranging these measured energy levels into a logical pattern.

Related Work

A similar study performed on cadmium sulfide crystals at the Wright-Patterson Air Force Base Aeronautical Research Laboratory demonstrated the feasibility of this experiment (Ref 8). The energies of cadmium sulfide fluorescence were identified, and, by observation of energy changes with temperature, it was possible to devise a model which would account for cadmium sulfide edge emission. It was this work which prompted the study of zinc selenide.

II. Theory

Included in Section II are qualitative discussions of the band theory of solids and of crystal emission. Their application to zinc selenide completes this section of the report.

Band Theory of Solids

A crystal is composed of a group of uniformly arranged atoms bound together by electrostatic forces. If the spacing between atoms is large, possible electron energy levels in the crystal will be just those available in the individual atoms. However, when the lattice spacing is reduced, Coulomb interaction between atoms separates the single-atom energy levels into a huge number of distinct levels. These levels are so closely spaced that they can be regarded as a continuous distribution of energies and are called "allowed bands."

Figure 2.1 illustrates the separation of atomic energy levels into allowed bands as the lattice separation is decreased. Also shown are the "forbidden-energy regions" which contain no available electron energy levels. Rather than depicting a specific material, this diagram indicates general features of the energy bands. For this example, at the 1s energy level the nearest neighbor distance, R, is large enough so that the electron interaction with neighboring atoms is slight and there is no noticeable separation of levels. Also, as the atomic levels increase, the allowed bands become larger and eventually overlap (3s and 3p bands).

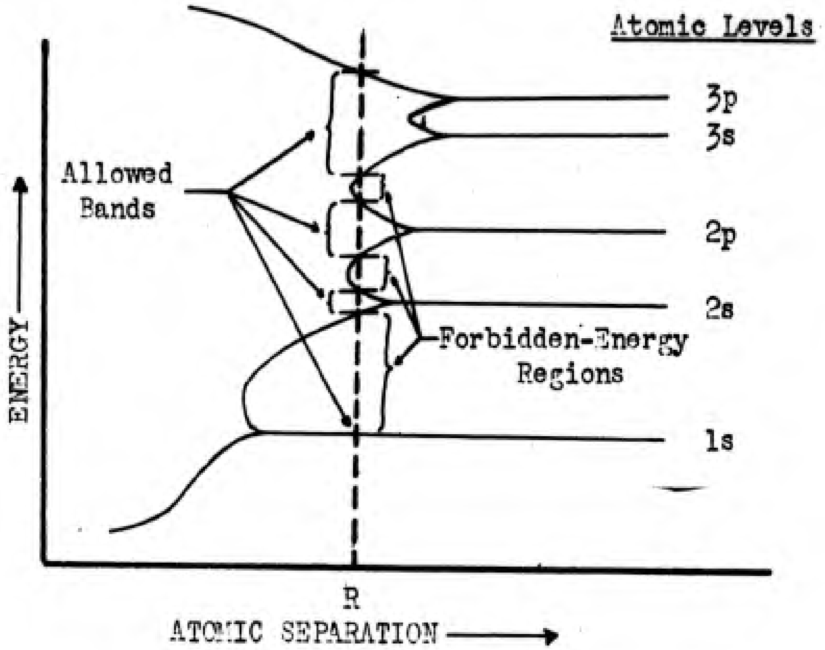
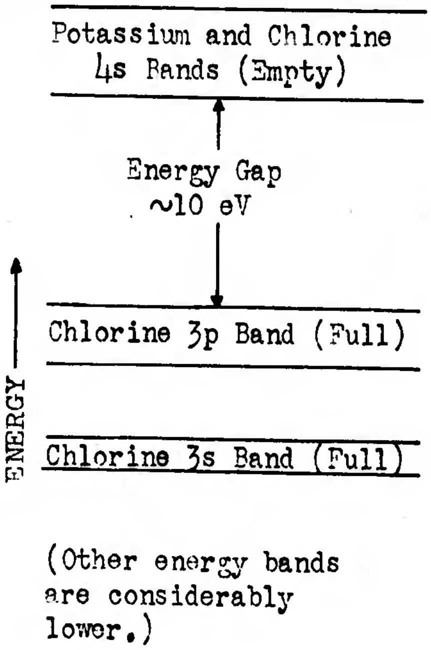


Fig. 2.1 Illustration of Energy Levels as a Function of Atomic Separation. The bands are shown for separation R. (From Ref 4:379)

Insulators. Electrical insulators are characterized by completely-filled energy bands which are separated from completely-empty bands by a large forbidden-energy region. The highest-energy filled band is called the "valence band" and the next higher empty band is called the "conduction band." Application of an electric field to an insulator does not result in current flow because there are no available energy levels to which the valence-band electrons can be accelerated, and the unoccupied conduction band is unaffected by the field.

Figure 2.2 illustrates the energy band structure of potassium chloride which is a good insulator. The



Distribution of Electrons

KCl - 36 Electrons

Element	Band	Electrons/Atom
K	1s	2
Cl	1s	2
K	2s	2
Cl	2s	2
K	3s	2
Cl	3s	2
K	2p	6
Cl	2p	6
K	3p	6
Cl	3p	6
		Total: 36

Fig. 2.2 Illustration of Potassium Chloride Energy Bands and Tabulation of Electron Distribution.

(From Ref 10:250)

36 electrons associated with this molecule completely fill the 1s, 2s, 3s, 2p and 3p bands of both elements and there is approximately a ten electron volt energy gap to the next available energy band which is vacant (Ref 10:250). Since there is a sizeable energy gap with no partially-filled bands, KCL meets the requirements of an insulator.

Conductors. The identifying characteristic of conductors is the availability of unoccupied energy levels in an energy band which contains electrons. An electric field applied to such a crystal is able to accelerate electrons to unoccupied states and electrical conduction results. Unoccupied energy levels exist if an energy band is only partially filled or if adjacent empty bands overlap completely-filled levels.

Sodium, with its eleven electrons, is an example of a conductor. The 1s and 2s levels each require two electrons per atom to complete the bands while six electrons from each atom are used to fill the 2p band. There remains only one electron from each atom for the 3s band which could accommodate two electrons per atom. Since the 3s band is only partially filled, sodium is a conductor of electricity. Also, for sodium, the empty 3p band overlaps the 3s band providing additional unoccupied states for conduction (Ref 10:250).

Beryllium provides an example of conduction because of band overlap. The four electrons of each atom completely fill the 1s and 2s bands leaving the 2p states empty. These completely filled and completely empty bands are characteristic of insulators except that in this case the 2p band overlaps the 2s providing unoccupied energy levels so that electrical conduction can occur.

Semiconductors. The term "semiconductor" is used to describe materials which exhibit electrical conductivity between that of insulators and that of conductors. There are two classifications of semiconductors known as intrinsic semiconductors and impurity semiconductors.

Intrinsic semiconductors are pure crystals distinguished by a narrow energy gap between the valence and conduction bands. At low temperatures these crystals behave as insulators, but at higher temperatures thermal energy can excite electrons into the conduction band which then allows electrical conduction.

Impurity semiconductors are materials whose electrical properties have been altered by the presence of vacancies or interstitials in the lattice or by the incorporation of another chemical element into the crystals. These impurities are called "donors" or "acceptors." A donor introduces occupied levels near the conduction band so that electrons can be readily excited into the conduction band while an acceptor introduces vacant levels near the valence band so that valence electrons can be excited into the acceptor level.

Emission

Some semiconductor materials exhibit luminescence when excited by irradiation with light or bombardment with particles. The crystal absorbs incident energy and re-emits it as light. If the emission ceases within less than a micro-second after excitation stops, the process is called "fluorescence" while the term "phosphorescence" is used to describe more persistent emission.

Fluorescence. Fluorescence can be simply explained as follows. Radiation-energy incident on the crystal ejects electrons from the filled bands to the conduction band. When these excited electrons return almost instantaneously to the valence band, they are accompanied by the emission of photons. This fluorescence may be either equivalent to or less than the energy of transitions made by electrons returning to lower energy levels.

Phonons. In addition to emitting photons, electron transitions from the conduction-to-valence bands may contribute to crystal-lattice vibrations. These elastic waves are quantized so that the vibrational energy of the lattice can change only by discrete units called "phonons."

Fluorescence may then appear as a series of emission-energies. The highest energy corresponds to that electron transition for which no lattice interactions occur, and each succeeding emission energy is decreased by a multiple of the phonon energy as more crystal vibration occurs.

Fundamental Absorption Edge. The minimum incident-energy which a crystal can absorb is called the "fundamental absorption edge." This energy corresponds to the value of the energy gap between the valence and conduction bands. Greater energies can be absorbed, but the fundamental absorption edge describes the minimum of a wide range of energies that can be absorbed.

Edge Emission. Edge emission, as the name implies, is energy emitted as a result of electron transitions from levels located near the fundamental absorption edge. These impurity energy levels lie within the semiconductor forbidden band and allow transitions from levels below the conduction-band to the valence-band and from the conduction-band to levels above the valence-band. Therefore, edge emission is of slightly lower energy (longer wavelength) than the fundamental absorption edge.

Application to ZnSe

Zinc selenide is a II - VI semiconductor with 64 electrons per molecule. The 1s, 2s, 2p, 3s, 3p, 3d, and 4s atomic energy levels of both zinc and selenium are filled. Also, the 4p level of selenium contains four electrons.

When these elements are combined to form zinc selenide, the two zinc 4s electrons complete the selenium 4p energy levels. In the crystal, then, there is an energy gap between the selenium 4p and zinc 4s bands. These bands correspond to the valence and conduction bands respectively (Ref 2). When irradiated with ultraviolet light at low temperatures, zinc selenide crystals fluoresce. They exhibit predominantly green and yellow emission. The remainder of this report is concerned with an experimental analysis of this zinc selenide fluorescence.

III. Experimental Apparatus

This section is composed of brief descriptions of experimental apparatus used during the study of zinc selenide edge emission. It is presented to assist the reader in relating titles used in this report to the associated equipment.

Crystals

Zinc selenide crystalline structure is zinc blende which consists of two interpenetrating face-centered cubic lattices. Crystals used in this experiment were grown and furnished by the Aeronautical Research Laboratory of Wright-Patterson Air Force Base. They were high-purity zinc selenide crystals grown from the vapor phase (Ref 9).

These yellow rod-like crystals grew in flat, randomly oriented clusters. For this experiment several clusters were mounted on a 1/4 inch diameter glass rod to form a composite (approximately 5 x 3 x 0.2 mm) crystal. Rubber cement was used to secure the zinc selenide crystals two inches from one end of the 15-inch rod. This ZnSe-to-glass bonding was capable of withstanding temperature variations from 4.2°K to room temperature.

Dewars

A 16-inch long quartz Dewar was used to contain either liquid nitrogen or liquid helium during low temperature experimentation. This double-walled, 1 1/2-inch inner-diameter by 2 1/2-inch outer-diameter, "vacuum bottle" was evacuated to about 2 x10^{-7} millimeters of mercury. The zinc selenide was suspended near the bottom of the Dewar by inserting the glass-rod crystal-mounting and centering it with a styrofoam spacer at the top as shown in figure 3.1. The entire Dewar was closed at the top with a vented stopper.

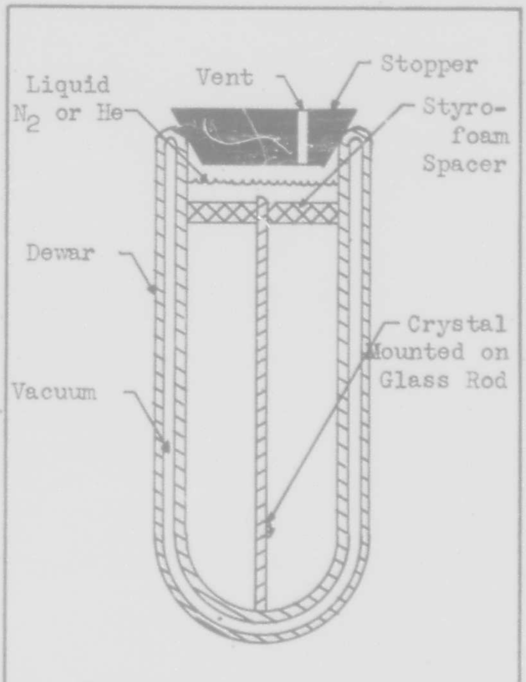


Fig. 3.1 Diagram of Crystal Mounted in Dewar.

When the crystal was immersed in liquid helium a large liquid-nitrogen-filled Dewar (19 inches long by 3- inch inner-diameter by 4- inch outer-diameter) was used to surround the quartz Dewar. This double-Dewar arrangement reduced the rate of helium evaporation so that the crystal could be maintained at 4.2°K for more than two hours.

During experimentation, Dewars were clamped to a ringstand for support. A Sunbeam hairdryer was used as a defroster to prevent ice formation, on the outer surface of the outer Dewar, from obscuring the crystal.

Photographic Film

Kodak Royal X Film and Kodak Type 103-0 Photographic Plates were used in this experiment. Royal X is an extremely fast film with a sensitivity range extending through the visible spectrum. The 103-0 plates have a uniform sensitivity in the range of 2200 Å to about 5500 Å.

Spectrographic Equipment

CENCO Spectrograph. The CENCO model spectrograph was equipped with a 15,000 lines/inch grating. This spectrograph had a dispersion of 16 Å/mm and a wavelength range of 2350 to 7000 Å.

Bausch and Lomb Spectrograph. A two-meter Bausch and Lomb dual-grating spectrograph was used in this experiment. Dispersion capabilities were 4 Å/mm with the 1200 lines/mm grating and 8 Å/mm with the 600 lines/mm grating.

Densitometer. A NSL (National Spectrographic Laboratories, Inc.) Spec Recorder, designed for spectral analysis, coupled with a Bristol strip-recording potentiometer was used to transfer spectral intensities from film to paper for ease of energy determination. This densitometer had a variable traverse speed so that emission-wavelength separation could be controlled for ease of identification.

Monochromater. A Bausch and Lomb grating monochromater with an IP28 photomultiplier coupled to an x-y plotter facilitated observation of individual emission wavelength intensities. Variations in intensity and wavelength of emission were recorded by this device as the crystal temperature changed.

IV. Experimental Procedures

Zinc selenide edge emission at $4.2^{o}K$ and $77^{o}K$ was examined. These emission temperatures were obtained after a cluster of zinc selenide crystals (5 x 3 x 0.2 mm) had been allowed to reach equilibrium temperature while immersed either in liquid helium ($4.2^{o}K$) or liquid nitrogen ($77^{o}K$). A quartz Dewar, as described in Section III, was used to contain the reference-temperature liquid. Liquified helium and nitrogen were selected as low-temperature references because they represented fairly standard values for solid state analysis, the liquids were readily available, and their stability minimized cryogenic handling problems.

This study of edge emission can be separated into four distinct experimental phases:

1. Selection of crystals
2. Location of the edge
3. Determination of emission energies
4. Observation of emission variation with temperature.

The following experimental procedures, performed in a room darkened to eliminate extraneous light sources, were used to accomplish each phase.

Selection of Crystals

Some zinc selenide crystals under ultraviolet-light irradiation exhibit a greater intensity of fluorescence than others. Since spectrographic analysis is enhanced by high intensities, many crystals were examined for fluorescence and only the brightest were selected for further experimentation. Selection was accomplished by placing several crystals at a time into a liquid nitrogen bath, irradiating them with ultraviolet light, and choosing the crystals which appeared brightest to the eye.

Location of the Edge

The fundamental absorption edge was obtained by a reflection experiment. T. S. Moss has explained theoretically by a classical oscillator analysis (Ref 6:15-23), the variation of reflectivity with frequency of incident radiation. Figure 4.1 illustrates the dependence of reflectivity on frequency. In this example, ω corresponds to the angular velocity of the impressed force or incident radiation and ω_0 to the resonant angular velocity of the oscillator.

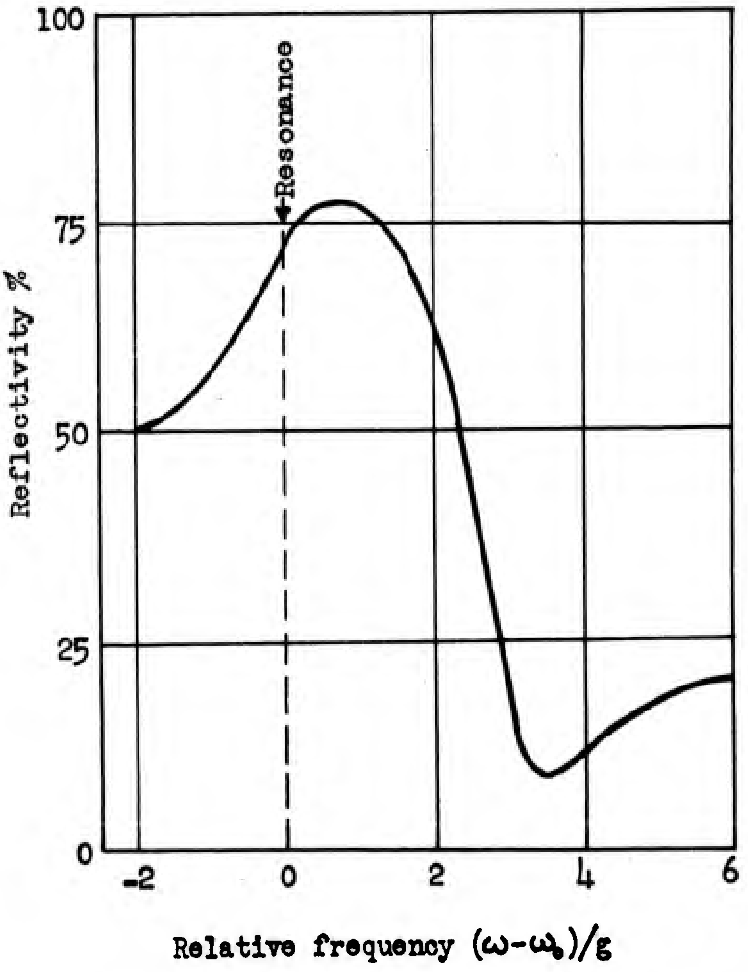


Fig. 4.1 Theoretical Frequency Dependence of Reflectivity for a Classical Oscillator.

(From Ref 6:23)

Note that, as the wavelength of incident radiation increases, relative frequency decreases, and the reflectivity passes through a distinct minimum, after which it exhibits a sharp rise to the maximum value. In general, the steepest portion of this sharp rise is linear, and the low-wavelength limit of the linear region corresponds to the fundamental absorption edge (Ref 6:43).

Light from a zirconium continuous-energy source was reflected from the crystal into a Bausch and Lomb two-meter, linear dispersion, grating spectrograph, and the resulting spectrum was recorded on a Kodak Type 103-0 Photographic Plate. These reflection spectra were photographed for ZnSe crystals at 4.2°K and 77°K using 15 minute exposure times. Either a mercury-arc or a helium-arc spectrum was exposed on each plate for wavelength identification purposes. These plates were then analyzed with a NSL densitometer which recorded, on a strip chart, variations in film exposure intensity over the spectrum.

Reflection spectra for zinc selenide were characterized by a very sharp decrease to the minimum reflected intensity. This easily distinguished "reflection-peak" (minimum intensity) wavelength was determined by linear interpolation between two known calibration lines. When converted to energy this gave the value of the fundamental absorption edge.

Determination of Emission Energies

Figure 4.2 is a schematic diagram of the experimental setup used to determine emission energies. A H100-SP4 mercury lamp was used as a source of ultraviolet radiation to excite the zinc selenide crystal to fluorescence. The irradiation was filtered to remove visible light so that only crystal-emission would appear in the 3900 to 8100 angstrom wavelength region. A glass, condensing lens acted as a collector to focus fluorescent emission on the grating of a spectrograph.

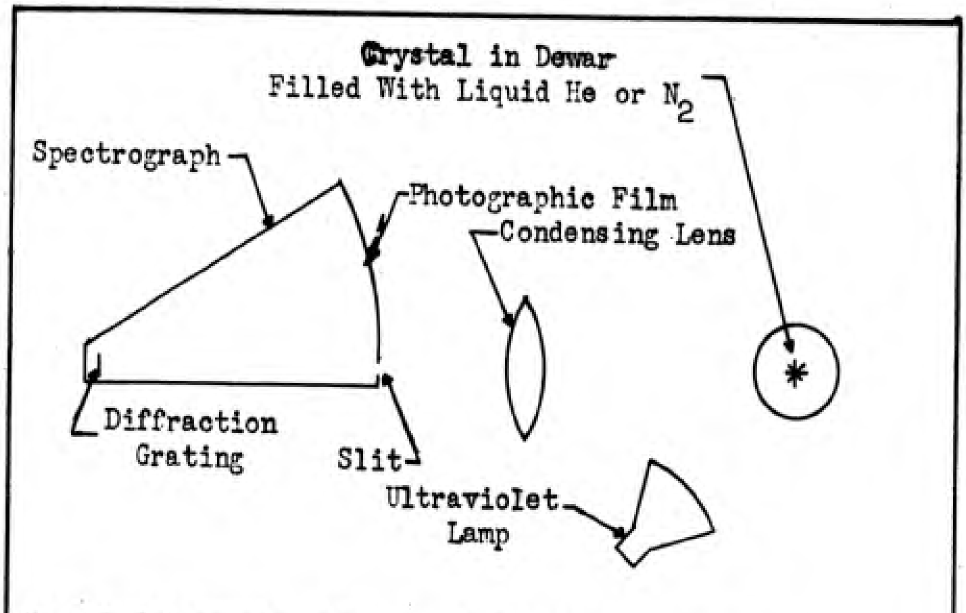


Fig. 4.2 Schematic Diagram of Apparatus Used to Determine Emission Energies.

Initial experimentation involved use of a CENCO Grating Spectrograph with a linear dispersion of 16 Å/mm. Use of this spectrograph with Kodak Royal X film permitted visualization of nearly the entire visible spectrum and therefore located emission wavelengths which merited more detailed study.

Based on results obtained with the CENCO apparatus, the Bausch and Lomb two-meter grating spectrograph with a linear dispersion of 4 Å/mm was used to photograph the edge emission in the vicinity of 4500 Å. Kodak Type 103-0 Photographic Plates were used to record the emission spectrum obtained with this larger grating.

Zinc selenide emission spectra at 4.2°K and 77°K were photographed on both the CENCO and Bausch and Lomb spectrographs. Exposure times varied from 60 to 90 minutes with a 1000 micron spectrographic slit width for each emission spectra. A mercury spectrum, for calibration, was exposed over the emission spectra.

The photographs were analyzed with a densitometer. CENCO film intensities were recorded on a strip-chart at a traverse speed of 11 mm/min. while an 18 mm/min. traverse speed was used with the Bausch and Lomb plates. Identification of emission wavelengths was accomplished by linear interpolation between known mercury lines. Fluorescent emission energies were obtained by conversion of these wavelengths to corresponding energy values.

Variation of Emission with Temperature

In order to investigate the change in the fluorescence as the crystal was warmed from 4.2°K to 77°K, the following experiment was performed. The zinc selenide crystal was attached with silver paint to an aluminum rod which was immersed in liquid helium, all of which was contained in the inner Dewar of a double Dewar arrangement. The liquid helium was allowed to evaporate from the inner Dewar, and as a result the crystal temperature increased gradually from 4.2°K to 77°K. A Bausch and Lomb grating monochromater

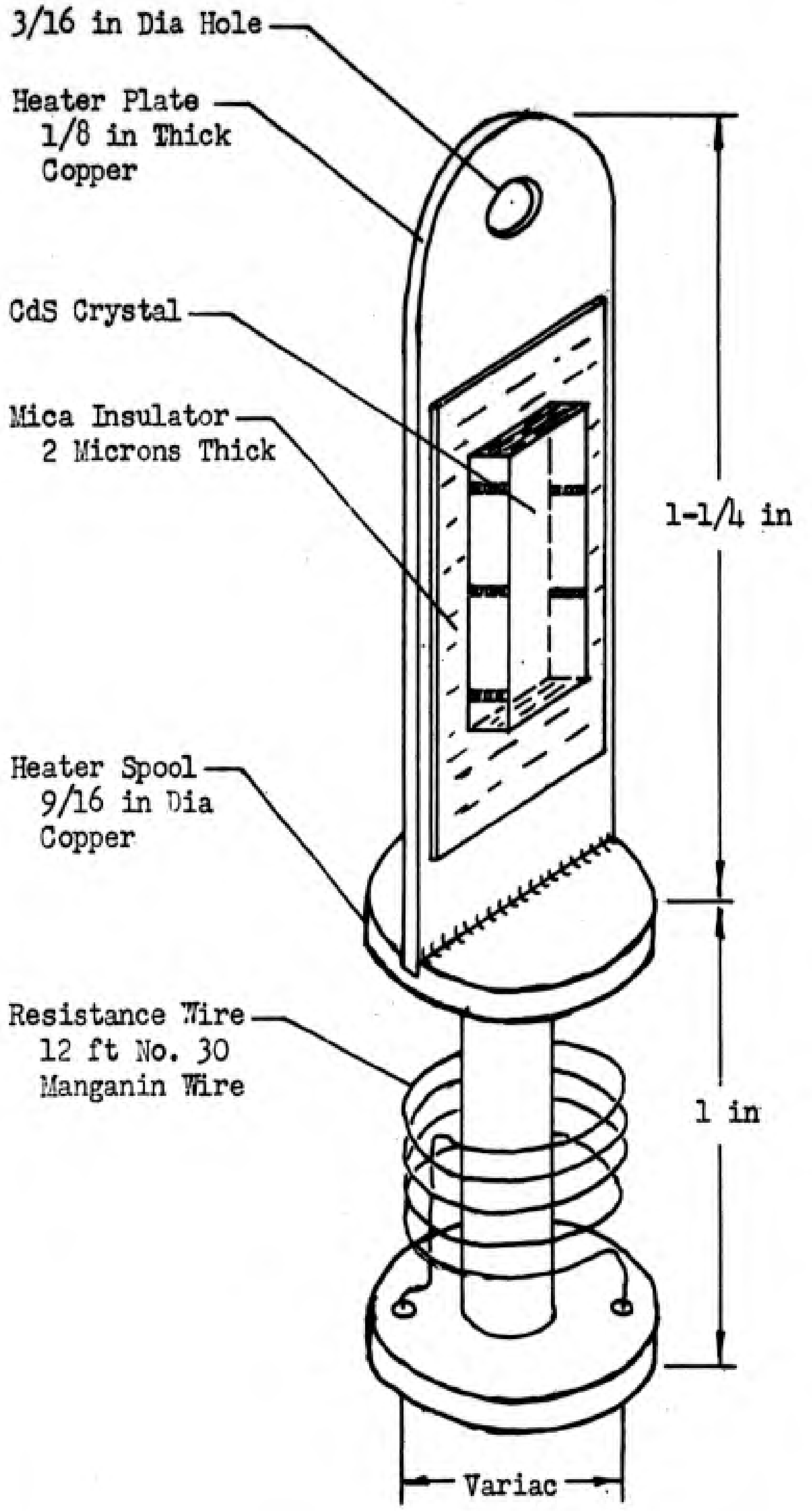


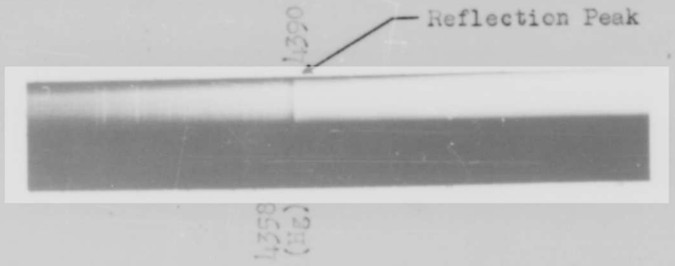
Fig. 6 - Heater assembly. This drawing illustrates the important details and dimensions of the heater assembly.

using an IP28 photomultiplier tube was used to monitor the positions of prominent emission lines as the temperature increased. A copper-constantan thermocouple fastened to the aluminum rod adjacent to the crystal was used to record the changing temperature. The temperature measurements were not taken at equilibrium conditions; consequently a temperature lag between thermocouple and crystal may have existed.

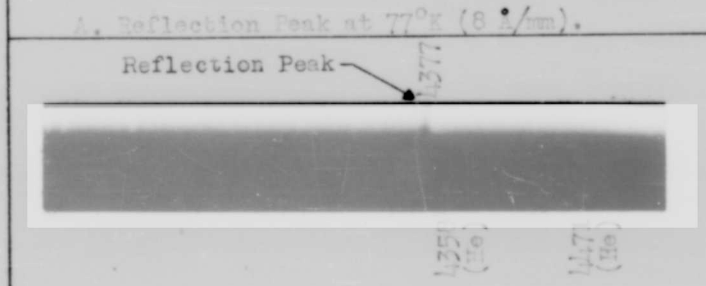
V. Results

Fundamental Absorption Edge

Figure 5.1 contains photographs of the zinc selenide reflection spectra. The calibration spectrum was photographed below the reflection spectrum in each case. The fundamental absorption edge was found to decrease with temperature. Measured wavelengths of 4377 and 4390 Å were converted to:



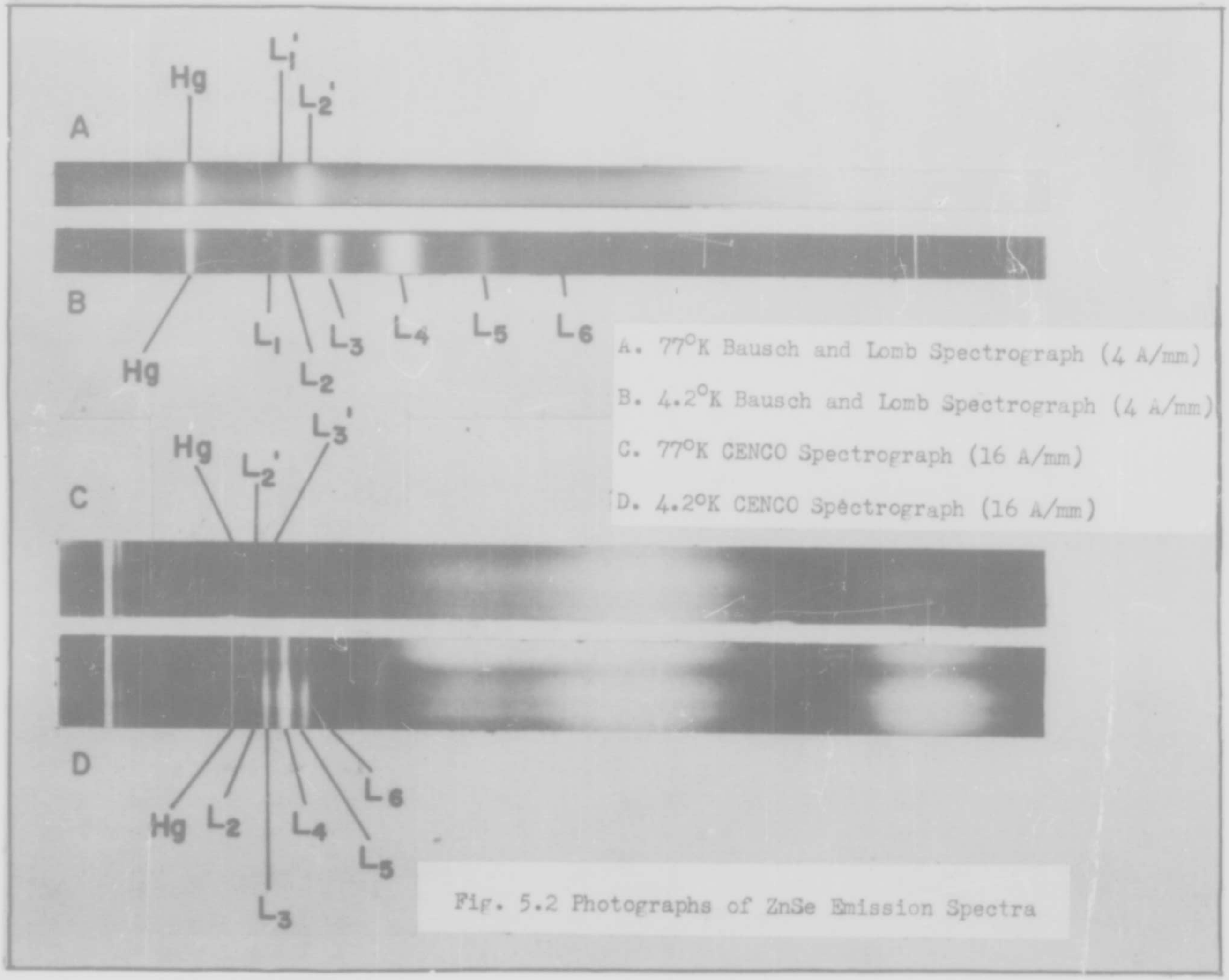
A. Reflection Peak at 77°K (8 Å/mm).



B. Reflection Peak at 4.2°K (4 Å/mm).

Fig. 5.1 Photographs of ZnSe Reflection Spectra. The reflection peak was observed to increase in wavelength (decrease in energy) with temperature.

1. $2.8\bar{3}19$ eV at 4.2°K
2. $2.8\bar{2}35$ eV at 77°K



A. 77°K Bausch and Lomb Spectrograph (4 A/mm)

B. 4.2°K Bausch and Lomb Spectrograph (4 A/mm)

C. 77°K CENCO Spectrograph (16 A/mm)

D. 4.2°K CENCO Spectrograph (16 A/mm)

Fig. 5.2 Photographs of ZnSe Emission Spectra

Marple, Aven, and Segall (Ref 5:19) have reported 2.80 eV

Edge Emission

Photographs of emission spectra are presented in Figure 5.2 facing this page. Densitometer traces were used to determine the wavelengths observed in each case.

The three broad emission bands, visible in photographs C and D which were taken on the CENCO spectrograph, peak at about 4950, 5365, and 6140 Å with no significant wavelength shift between 4.2 and 77°K. Since these broad bands are not part of the edge emission, they have not been thoroughly investigated. However, the energies lie within the band gap and it is speculated that the levels are probably very broad. Other experimenters have observed that broad bands also appear in zinc sulfide when foreign atoms such as silver or copper are introduced (Ref 10:314).

Figure 5.3 facing page 21 is a condensed drawing of the densitometer traces of edge emission obtained from spectra photographs A and B which were taken on the Bausch and Lomb two-meter spectrograph. The wavelengths and their corresponding energy values which were determined from these densitometer traces are tabulated in Table V.I. Note that the energy difference between lines L_3 through L_7 correspond quite well with the zinc selenide phonon energy of 0.027 eV which was reported by Marple, Aven, and Segall (Ref 5:19).

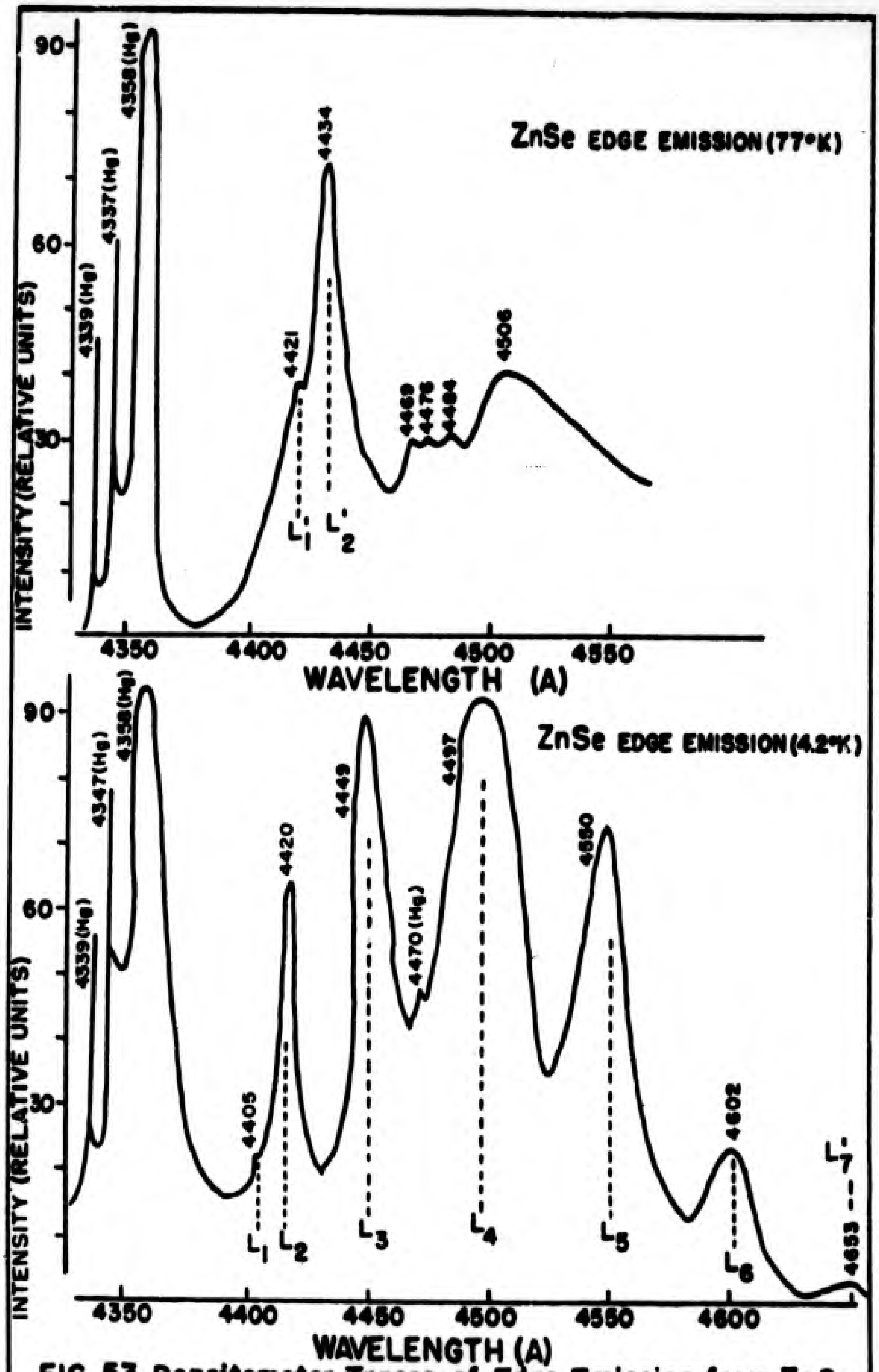


FIG. 5.3 Densitometer Traces of Edge Emission from ZnSe Crystals at 77°K and at 4.2°K

Table V.I

Observed ZnSe Edge Emission

4.2°K				77°K			
Line	Wave-length (Å)	Energy (eV)	Energy Difference (eV)	Line	Wave-length (Å)	Energy (eV)	Energy Difference (eV)
L_1	4405	2.8138		L'_1	4421	2.8038	
			0.0095				0.0072
L_2	4420	2.8043		L'_2	4434	2.7966	
			0.0183				0.0230
L_3	4449	2.7860			4469	2.7736	
			0.0297				0.0044
L_4	4497	2.7563			4476	2.7692	
			0.0321				0.0051
L_5	4550	2.7242			4484	2.7641	
			0.0308				0.0133
L_6	4602	2.6934			4506	2.7508	
			0.0296				
L_7	4653	2.6638					

Emission Versus Temperature

In Figure 5.4 facing page 22, relative intensity is plotted against wavelength of emission for temperatures between 4.2 and 77°K. This data was obtained with the Bausch and Lomb monochromater. Lines L_1 and L_7 could not be resolved, but L_2 is observed to increase in wavelength with temperature and apparently becomes L'_2 at 77°K.

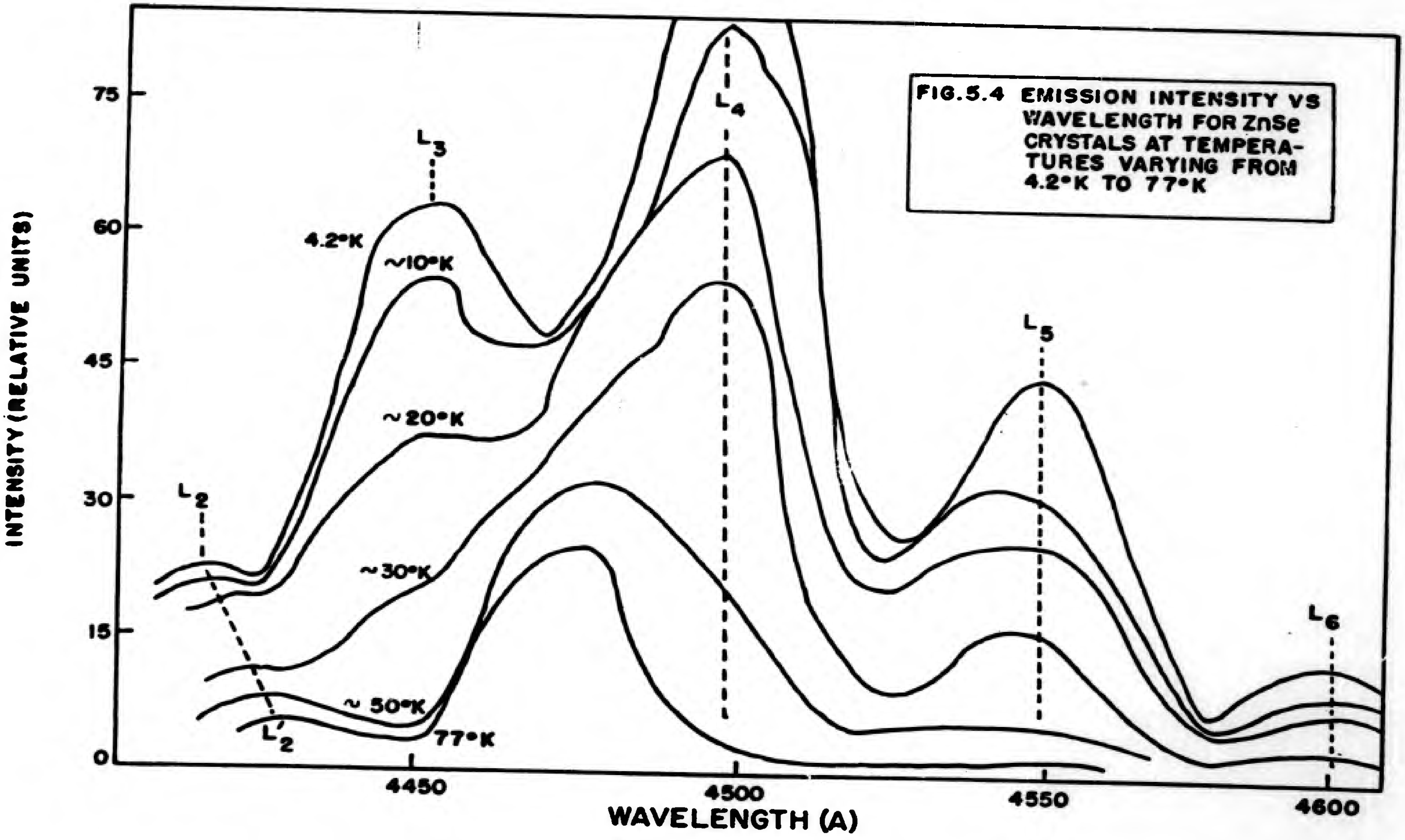


FIG.5.4 EMISSION INTENSITY VS WAVELENGTH FOR ZnSe CRYSTALS AT TEMPERATURES VARYING FROM 4.2°K TO 77°K

The presence of a 4470 Å mercury line which became prominent as temperature increased prevented resolution of line L_3 above 4.2°K. It was therefore not possible to determine whether L_3 shifted to higher wavelengths or just decreased in intensity. The remaining lines, L_4 through L_6, diminished in intensity and vanished as the temperature increased.

VI. Analysis of Results

Based on the results of this experiment, an energy model which accounts for zinc selenide fluorescence is proposed. This section of the thesis presents a brief discussion of accuracy of results and describes the energy model.

Accuracy

Since dispersions of the grating spectrographs used in this experiment were not perfectly linear, a small error may exist in the magnitudes of emission wavelengths which were determined by linear interpolation between known mercury spectrum lines. In an effort to check the accuracy of emission wavelength determinations, the wavelengths of known mercury lines were calculated by interpolation between the 4339 and 4916 Å lines of the calibration spectrum. Each of these checks agreed within 2.5 angstroms of the accepted values published in the "MIT Wavelength Tables" (Ref 1).

As a result of these calculations, the error in calculated emission wavelengths is estimated to be less than ± 3 Å. Differences between the wavelengths of closely-spaced emission lines are more accurate than individual line measurements because any error in linear dispersion was incorporated into the magnitude of each line and was cancelled out by subtraction.

Energy Model

The fundamental absorption edge served as a measure of the band gap at 4.2 and 77°K. This band gap was observed to decrease as temperature increased. With this information available, the densitometer traces of edge emission (Fig. 5.3) were examined to see if there was a comparable shift in emission energies with temperature. It was found that the decrease in energy with temperature could account for line L_2 shifting to L_2' and, with a slight correction, it could also account for L_1 shifting to L_1'.

To check the energy shift, the emission was observed at intermediate temperatures. It was verified (Fig. 5.4) that line L_2 shifted to longer wavelengths. Line L_1 could not be resolved with the monochromater to actually observe the decrease in emission energy with temperature.

Examination of Table V.I revealed that for edge emission at 4.2°K, lines L_3 through L_7 were each separated by approximately the zinc selenide phonon energy. Line L_3 was therefore selected as emission which was representative of an electron energy-transition, and L_4 through L_7 were considered as the same transition decreased in energy by lattice interactions.

Figure 6.1 illustrates the proposed energy model

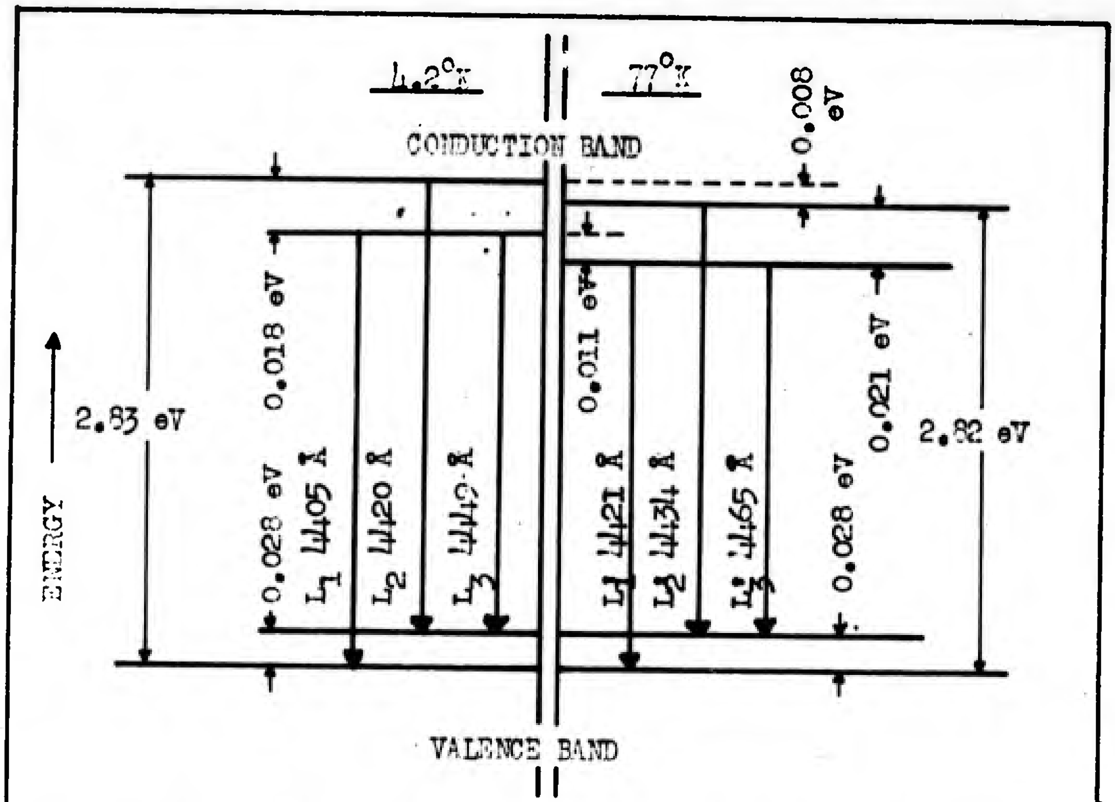


Fig. 6.1 Proposed ZnSe Edge Emission Energy Model. Line L_3' was not observed.

which accounts for zinc selenide edge emission. At 77°K a 4465 Å emission wavelength, L_3', was predicted to complete the symmetry of the model. The densitometer trace (Fig 5.3) indicated emission in this region, but it could not be resolved because of the presence of a nearby mercury line. The prominence of this mercury line in the monochromater data (Fig. 5.4) also prevented observation of a wavelength shift in line L_3 as the crystal temperature increased above 4.2°K.

The presence of a 4506 Å line at 77°K shown in Figure 5.3 supported the prediction of the existence of line L_3'. The separation between these wavelengths is approximately that corresponding to the phonon energy so that the 4506 Å line could be explained as the L_3' transition reduced by a phonon interaction.

At 4.2°K, energy levels within the band gap were located 0.018 eV below the conduction band and 0.028 eV above the valence band. The band gap decreased at 77°K and the energy level near the conduction band was also lowered. It should be noted that whereas the energy model chosen to explain the zinc selenide edge emission locates an energy level closer to the conduction band than to the valence band, a mirror reflection of these levels about the middle of the forbidden-energy gap would also account for this fluorescence. In the latter case, the energy level near the valence band would increase with temperature. The experimental evidence does not distinguish between these two choices, but the proposed energy model does account for all of the observed edge emission.

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Vita

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