1.0

1.1

1.25

4.5
5.0
5.5

2.8

3.2

3.6

4.0

1.4

2.5

2.2

2.0

1.8

1.6

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

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IMPURITY STUDIES IN SINGLE CRYSTAL CADMIUM SULFIDE

Lawrence C. Greene

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December 1979

TECHNICAL REPORT AFML-TR-79-4104

Final Report for Period 1966 - 1974

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This technical report has been reviewed and is approved for publication.

LAWRENCE C. GREENE
Project Engineer

FOR THE COMMANDER

G. EDWARD KUHL, Chief
Laser and Optical Materials Branch
Electromagnetic Materials Division

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Crystal Growth
Spectra

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In cadmium sulfide crystals an easily observed and measured phenomenon is the low temperature bound exciton emission spectrum. The spectral lines are sharp, and their wavelength can be measured with considerable precision. The spectral position of the lines in a magnetic field can tell us much about the symmetry and structure of the center. The purpose of this work was to establish a relationship between the bound exciton spectra and defect or impurity structure of the crystal. A line associated with a neutral donor and a pair of lines ——> over

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associated with an ionized donor were found for the very purest material. A neutral donor was found for crystals equilibrated in hydrogen, and a pair of ionized donors for material equilibrated in hydrogen sulfide. Lithium doped crystals showed several pairs of ionized donor lines as well as a large number of characteristic neutral donor lines. Silver doping produced a large number of characteristic lines, but the nature of the associated centers has not been established. Sodium showed many characteristic lines, some associated with neutral donors, some with ionized donors, as well as lines clearly associated with complex structures. Potassium and rubidium both showed characteristic ionized donor lines.

FOREWORD

This report summarizes research performed at the Aerospace Research Laboratories on the exciton spectra of cadmium sulfide in its relationship to the defect structure. It was performed between 1966 and the termination of the cadmium sulfide research in 1974 under work unit 78850105. The results have been presented at various society meetings but were never published. In this technical report the papers have been assembled in chronological order. The writing may seem abrupt but keep in mind that the papers were prepared for oral presentation.

This work was performed at the Solid State Physics Research Laboratory, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio. Dr. Lawrence C. Greene was the principal investigator for this work unit. The preparation of the technical report was performed at the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 45433.

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SECTION I

INTRODUCTION

1.   GENERAL

Cadmium sulfide is a direct gap semiconductor having an energy gap
of 2.42 eV at room temperature and should be capable of producing
injection luminescence near 5100Å. Cadmium sulfide is freely soluble
in all proportions with both zinc sulfide and cadmium selenide in the
solid phase, so that one would expect a spectral range of injection
luminescence from 3390Å to 7100Å using the alloys.

Indeed such luminescence has been produced by electron beam injection,
but to obtain usable devices one needs injection through a junction.
Usable junctions have not been produced on these materials because low-
resistivity p-type material has never been produced. The work reported
here addresses the question why we have not been able to produce low
resistivity p-type cadmium sulfide and whether it can ever be produced
and if so, how?

The dopants expected to produce low-resistivity p-type cadmium
sulfide are the monovalent metals: lithium, sodium, silver, copper, and
perhaps potassium and rubidium. These elements are expected to enter the
cadmium sulfide structure in the substitutional mode and should then be
acceptors. Experience has shown that when any of these dopants is in-
corporated into cadmium sulfide, high-resistivity n-type material is
produced except under the most extreme conditions. Even where p-type
cadmium sulfide has been obtained its resistivity has been so high that
type identification by thermoelectric or Hall effect methods has been,
at best, uncertain, and the dominant carrier has been identified from
emission spectra.

Pure, defect-free cadmium sulfide would be expected to have a
resistivity comparable to that of sulfur or glass, but in practice the
best quality n-type crystals may have resistivities of the order of an
ohm-cm. Some of this low resistivity may very well be due to residual
aluminum incorporated in the substitutional mode but there is no doubt

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that a large part is due to the presence of large concentrations of n-type
native defects, particularly interstitial cadmium. All of this makes a
study of impurity centers by means of the traditional Hall effect and
resistivity techniques impractical.

We have chosen to study both defect and impurity centers by means of
the photoluminescence emission that they produce when excited by
radiation of suitable energy. This technique is particularly effective
for cadmium sulfide for several reasons. A first reason is that cadmium
sulfide is a direct gap material and hence produces bound exciton emission
with high efficiency and this emission is in the spectral region from
4500A to 6000Å, which is particularly convenient to study. A second
reason is that aside from the water soluble materials, cadmium sulfide
is about the easiest crystal to grow and in addition it can be grown in a
platelet form having nearly perfect surfaces. Such surfaces can produce
bound exciton lines whose only broadening results from basic processes
such as lifetime.

2. FREE EXCITONS

The low temperature photoluminescence spectra of cadmium sulfide
near the band edge exhibit well-developed structure consisting of many
sharp lines and broad bands. In cadmium sulfide, which normally
crystallizes in the hexagonal (wurtzite) structure, the sharp lines
have been attributed to the radiative decay of free excitons and of
excitons bound to localized donor or acceptor defects.

If a semiconductor or insulator crystal is excited with radiation
of sufficient energy, an electron will be raised from a filled or valence
band to an empty or conduction band. When this process occurs, a hole
with an effective positive charge is left behind. The recombination of
the electron and the hole is a low probability transition because of
momentum conservation. The electrons and the holes must recombine through
some more probable transition involving a defect state.

One such transition mechanism is the exciton. When an electron
approaches a hole sufficiently close to begin to interact, momentum

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conservation does not permit it to fall directly into the hole. Instead the electron falls into a permitted, hydrogen-atom like orbit around the hole. Such a combination of an electron and hole is a free-exciton. A free-exciton is unstable and will be annihilated by the recombination of the electron and hole, but with a rather long lifetime. When this re-combination occurs the energy may be emitted as a spectral line. Since the exciton is free to move about in the lattice, it will have kinetic energy as well as binding energy. This kinetic energy causes a broadening of the emission line.

3. BOUND-EXCITONS

A bound-exciton is a hydrogen-atom like combination of an electron and a hole, bound in a hydrogen-molecule like or a hydrogen-molecule-ion like combination with a defect or impurity in the lattice. Such bound-excitons can be formed by several different mechanisms. If the crystal is excited by radiation of above band gap energy, free excitons are formed. These free excitons can be trapped by lattice defects with a trapping time that is much less than their decay time. Also, it is believed that under such irradiation the carriers may bind to the defect separately. For example, a neutral donor might bind a hole in a hydrogen-molecule-ion like configuration. This complex would then trap an electron by coulomb attraction to form a hydrogen-molecule like configuration. If the energy of the exciting radiation is less than bandgap, but resonant with the bound exciton decay energy, it can excite the bound exciton directly.

When the electron and the hole in the exciton recombine the total energy must be released by some mechanism. All or part of the energy may, for example, elevate an electron or hole from the binding center into an excited state or even far into the conduction or valence band. Part of the energy may be absorbed by the lattice in the form of phonons. The mechanism in which we are most interested here is that in which the total energy is emitted as a photon, the bound exciton emission.

Cadmium sulfide is a direct gap semiconductor. This means that the electron in the minimum of the conduction band and the hole in the maximum

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of the valence band both have zero momentum. Since the bound exciton is localized near a defect, its hole and electron are associated with this minimum and maximum (Figure 1). In this situation there is no problem of momentum conservation to prevent the hole and the electron from recombining and so the bound exciton is annihilated with a very short lifetime unless the recombination is forbidden by selection rules. Where the transition is allowed, the lifetime is so short as to appreciably broaden the emission line.

Γ_7

2.582 eV

Γ_9 OR A

0.016 eV

Γ_7 OR B

0.057 eV

Γ_7 OR C

$\underset{\sim}{k} = 0$

BAND EXTREMA IN CdS
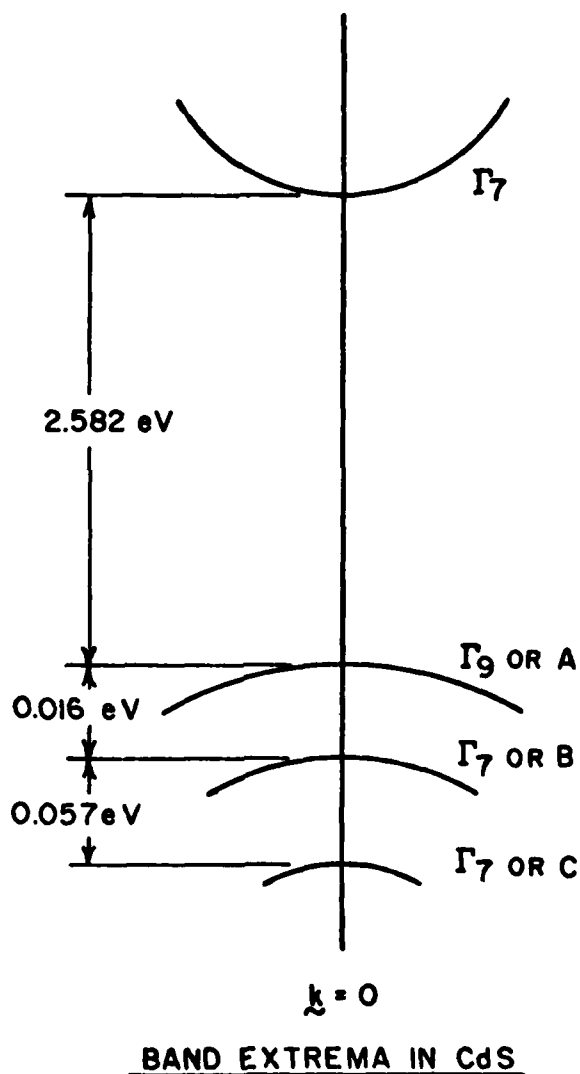
Figure 1. Schematic Diagram of the Ground and Excited States of the Bound Exciton Transitions

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When an exciton localized on a defect or impurity collapses, the energy is emitted in a series of lines called a phonon assisted series. The dominant or zero phonon line will have an energy equal to the total bound exciton energy; the other lines of the series will have such an energy diminished by one or more longitudinal phonon energies. It is possible, then, to find the binding energy of the bound exciton by sub-tracting the energy of its zero phonon line from the energy of the free exciton line. The exciton binding energy depends on the donor or acceptor binding energy and hence is different for each different donor or acceptor. It would seem possible, then, to identify a given impurity by its bound exciton spectrum, and this is indeed the subject of this study. With cadmium sulfide the difficulty lies in the fact that the active impurities in which we are most interested produce not one, nor a few, but many such lines. Furthermore, these lines vary in relative intensities from specimen to specimen according to growth or annealing conditions. This indicates that the impurity is present not merely as simple interstitials and substitutionals, but in many more complex modes.

4. LINE SPLITTING IN A MAGNETIC FIELD

Bound-excitons are complexes in which excitons are bound to neutral or charged donors or acceptors. In crystals such as cadmium sulfide, which have a direct band gap, these bound excitons are observed as sharp absorption and emission lines at wavelengths longer than that of the free exciton. In hexagonal cadmium sulfide free electrons occupy an S-like $J = 1/2\Gamma_7$ band, and free holes from the top valence band occupy a P-like $J = 3/2\Gamma_9$ band (Figure 1). The neutral donors or acceptors are doublet states $(S=1/2)$ and this is also true of the bound exciton complexes since the paired electrons or holes must have antiparallel spins. Parallel spins would result in instability just as in the hydrogen molecule system. Figure 2 shows in a schematic form the structures of donors and acceptors and their bound-exciton complexes. It is the transition between the upper bound-exciton state and the lower donor or acceptor state that is responsible for the sharp-line bound-exciton emission.

5
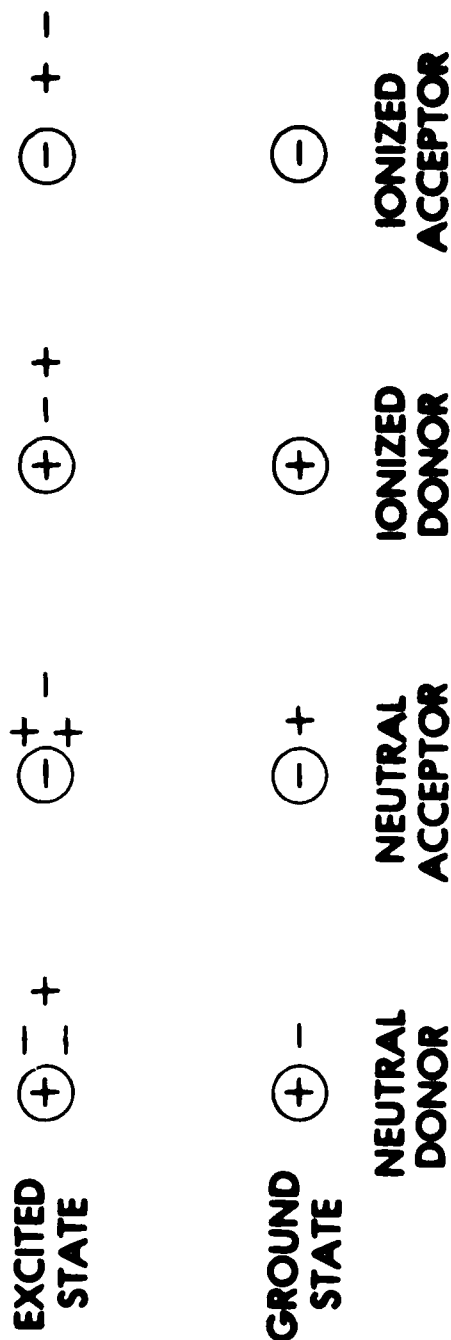
Figure 2. Ground States and Excited States of an Exciton Bound
to Neutral and Ionized Donors, and Neutral and Ionized
Acceptors, Shown Schematically

In a magnetic field the states associated with the neutral centers will split with a g value equal to that of the odd particle as shown in Figure 3. The electron has a g value of - 1.78, a value which is independent of θ, the angle between the c-axis and the magnetic field vector. The hole, on the other hand, has a g value given by

$$g_h = g_h|| \cos \theta$$

where

$$g_h|| = g_h \text{ for } \theta = 0 \text{ i.e. } c \ || \ H$$

For the free hole, $g_h|| = 1.15$, but for a bound hole $g_h||$ may have quite different values depending on its state of binding.

It can be seen from Figure 3 that there should be four transitions and this is true for $\theta \approx 0$ or $\theta \approx 90°$. For $\theta = 0$, selection rules allow only one transition for the exciton bound to a neutral donor and two for the exciton bound to a neutral acceptor. For $\theta = 90°$ it has been shown (Reference 1) that $g_U = g_L$ and hence the splittings in the upper and lower states are equal and only two lines are seen. These lines separate linearly as magnetic field intensity increases.

In an exciton bound to an ionized center (Figure 3) there occurs an exchange interaction between the unpaired hole and the unpaired electron. This results in a zero field splitting of the excited state and a nonlinear fourfold splitting in a magnetic field. Since the ground state has no free carriers, there is no ground state splitting. Such a configuration leads to two lines for H = 0 and in general four lines for H ≈ 0. However for $\theta = 90°$, that is H⊥C, only the two H = 0 lines are seen. These lines separate nonlinearly with increasing magnetic field as shown in Figure 4.

5. PREPARATION OF MATERIAL

The cadmium sulfide crystals used in this study were of the platelet form. Such platelets grow under dynamic conditions in which cadmium sulfide is vaporized at a suitable temperature and then transported in a flow of inert gas to a region of suitable temperature for deposition. The crystals grow free of physical constraints being attached to the growth
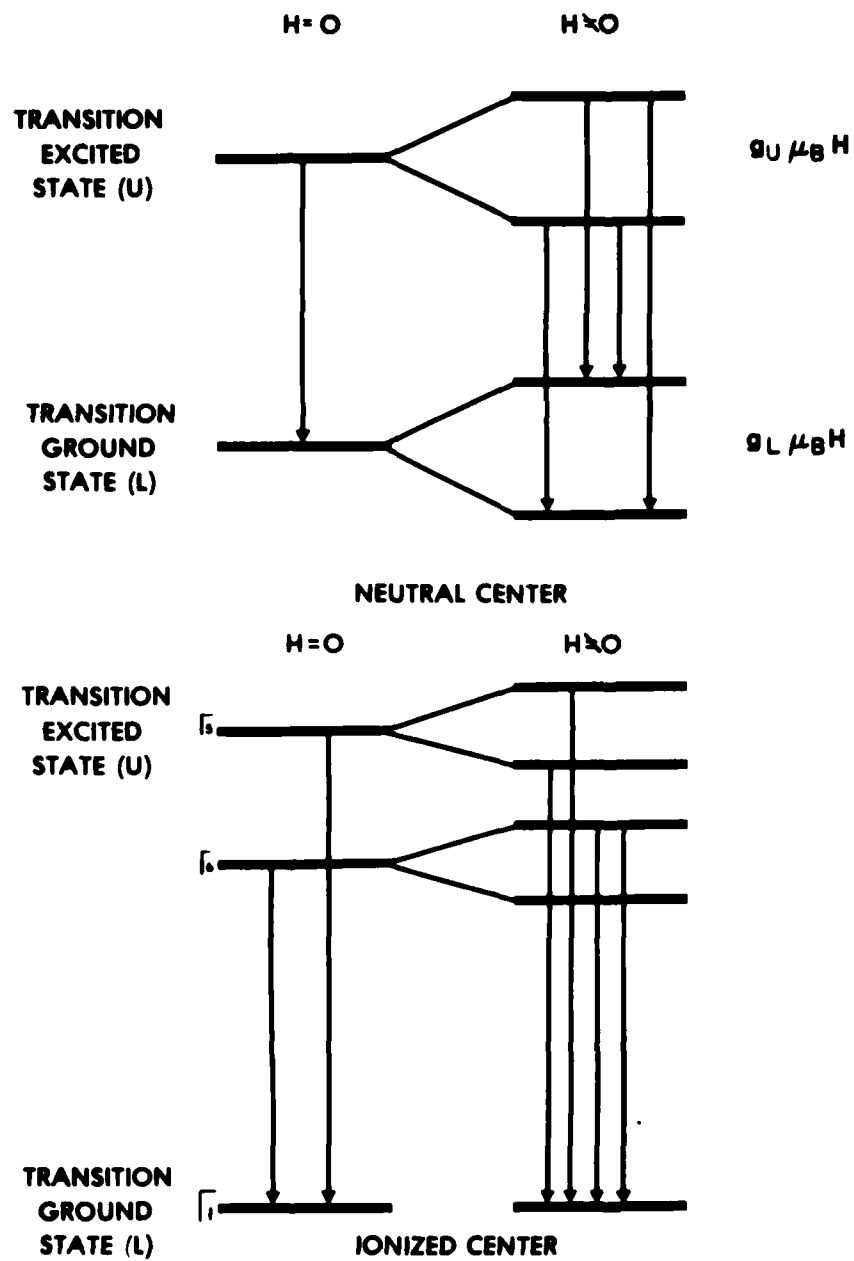
Figure 3. Energy Level Diagrams for Excitons Bound to Neutral and Ionized Centers Showing Line Splitting in a Magnetic Field

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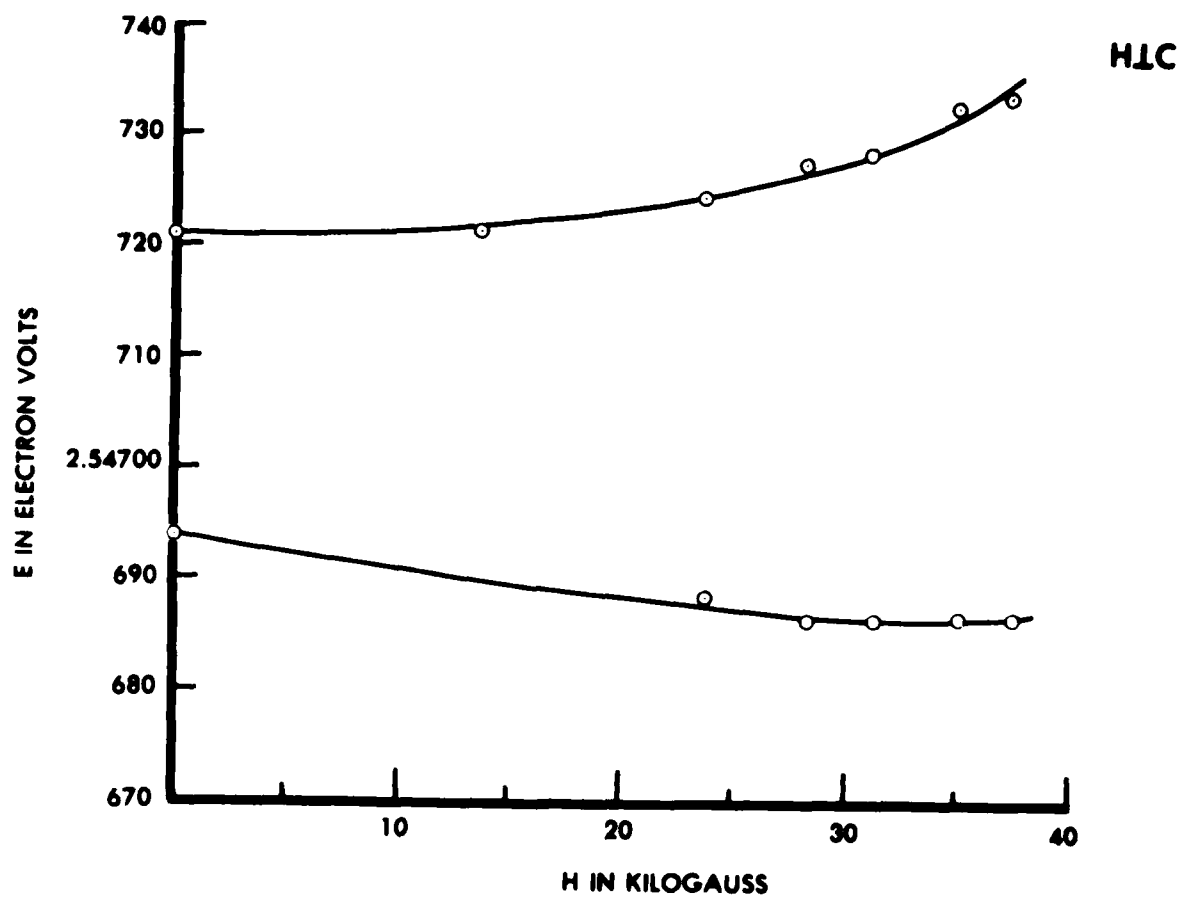
Figure 4. Magnetic Field Dependence of the Spin-Exchange
Splitting of the Lines from an Exciton Bound to an
Ionized Donor with $H \perp c$. The lower line is the Γ_6 line
and the upper line is the Γ_5 line

chamber only by an edge or corner. The result is that the crystals are remarkably free of strains resulting from physical constraints and from impurities picked up from the quartz on which it is grown. Furthermore, the surfaces are grown surfaces and display a very high degree of surface perfection, a factor that is necessary for exciton emission studies. A photograph of a collection of these platelet type crystals is shown in Figure 5.

The furnace used for the growth of these crystals consisted of porous firebrick, the inner bricks being cut so as to form a chamber with a square cross section (Figure 6). Silicon carbide resistance heaters are used horizontally in pairs, above and below the crystal growing tube. Three separately controlled heating zones make it possible to maintain a desired temperature profile such as the one in Figure 7. An exterior view of the assembled furnace is shown in Figure 8 and the control panel assembly is shown in Figure 9. Figure 10 shows the power and gas control system.

The growing chamber itself consists of a mullite cylinder with pyrex joints cemented to its ends. Inside the mullite cylinder is a quartz cylinder open at one end and with an exhaust vent at the other. The charge and dopant boats are placed near the open end of the quartz tube, from which position they can be pushed into the hot zone at the proper time. Each boat contains a thermocouple well. The thermocouple tubes leave the furnace through rubber glands so that they can be used for positioning the boats. The progress of the crystal growth can be observed through a glass window cemented over a hole in the end of the cap.

In operation the boats are loaded with weighed quantities of raw material and dopant and positioned as in Figure 6. In this section we are discussing cadmium sulfide, but the procedures are equally applicable to the growth of platelets of cadmium selenide, zinc sulfide, and antimony trisulfide. Argon, which is used as the carrier gas is introduced into the outer tube of the growing chamber through a side-arm stopcock. The gas passes the full length of the surface chamber (but not to the end of the furnace as is erroneously shown in Figure 6) before entering the
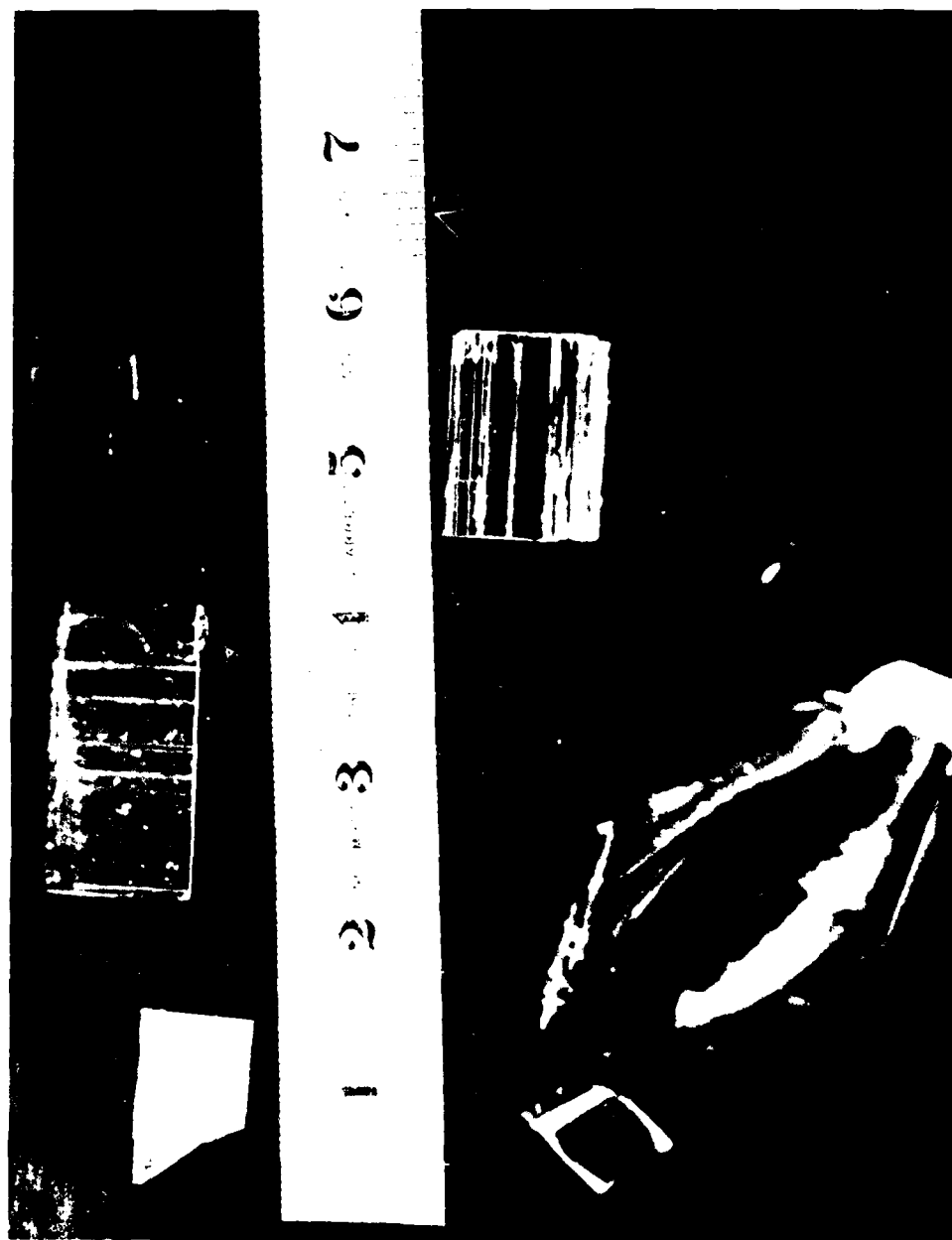
Figure 5. Cadmium Sulfide Platelets Grown by the Dynamic Vapor Phase Transfer Method
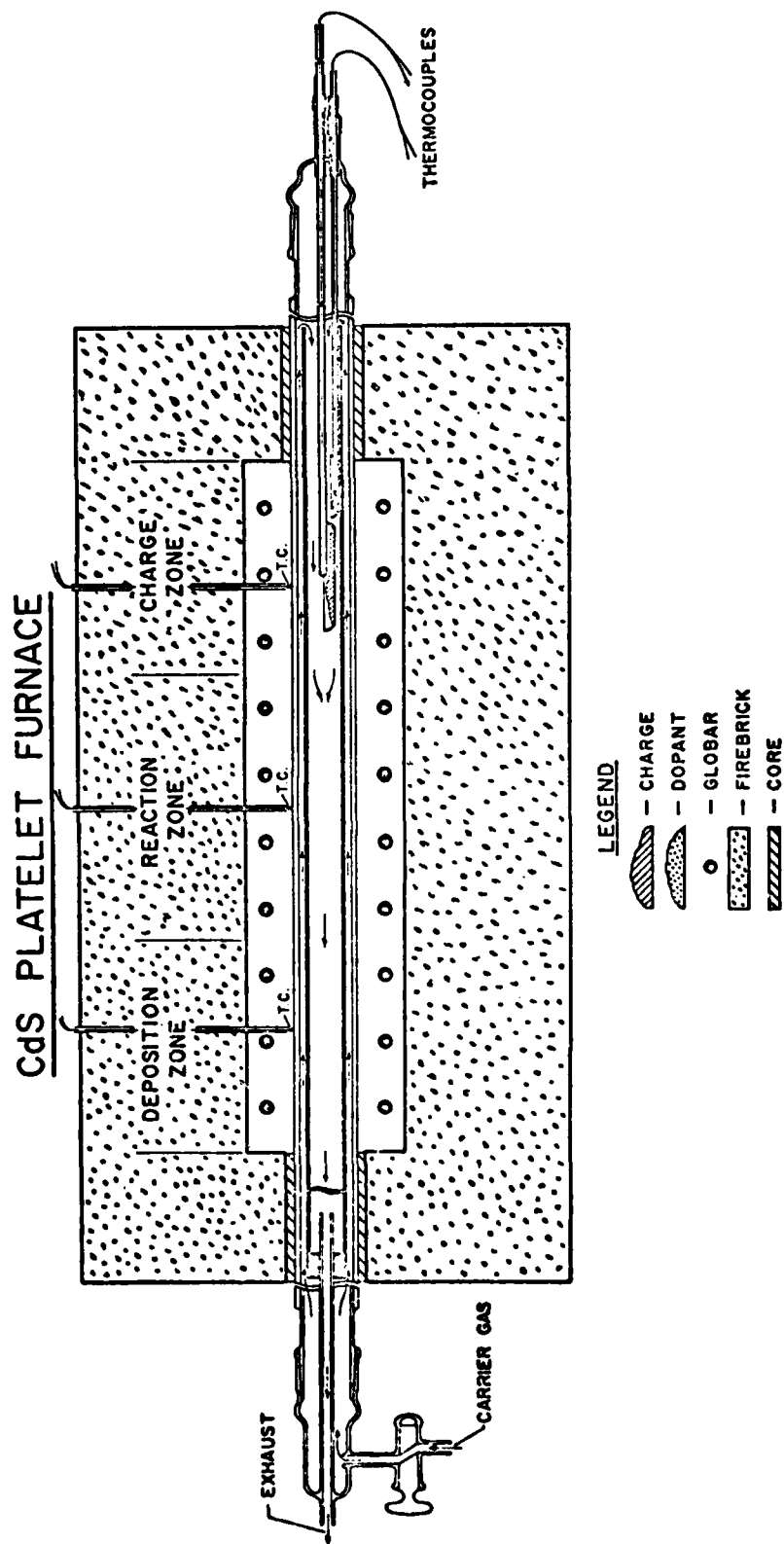
Figure 6.   Cross-Sectional Diagram of the Furnace Used for
            Dynamic Vapor-Phase Transfer Method
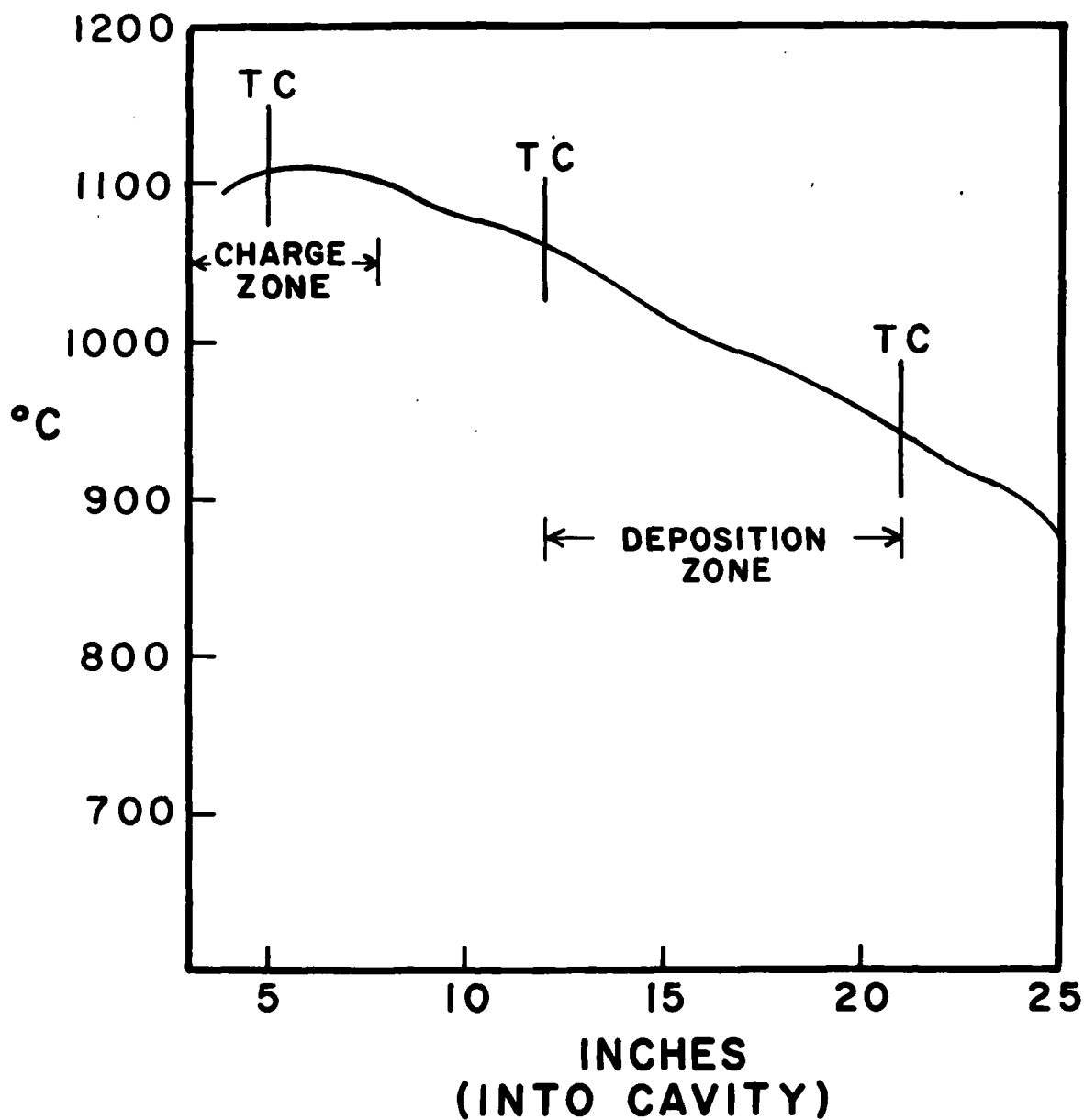
Figure 7. Typical Temperature Profile Used in the Dynamic
Vapor-Phase Transfer Method
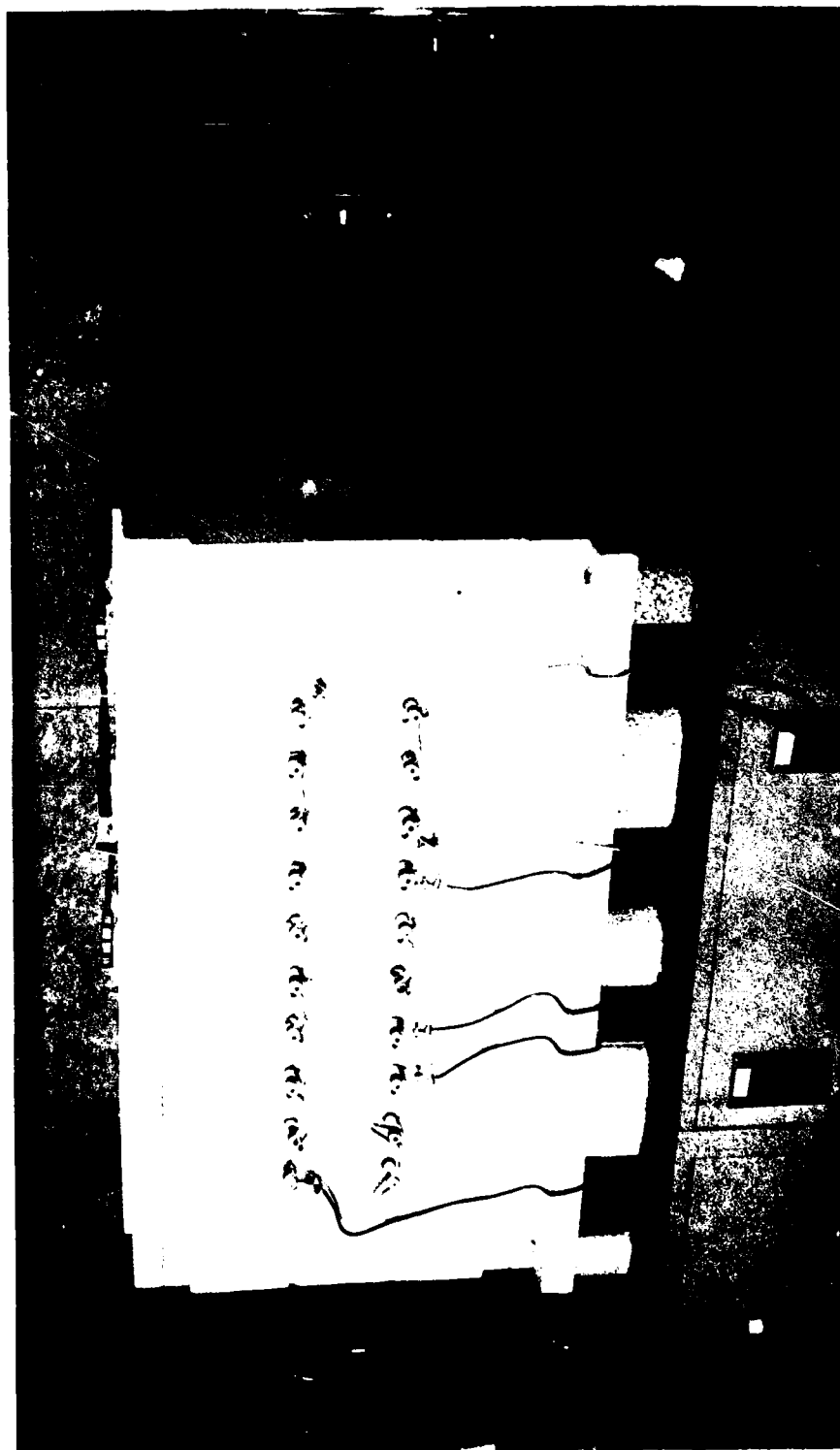
Figure 8. Exterior View of Furnace Used for the Dynamic Vapor-Phase Transfer Method

Figure 9. View of Control Instrumentation Used in Vapor-Phase Furnace
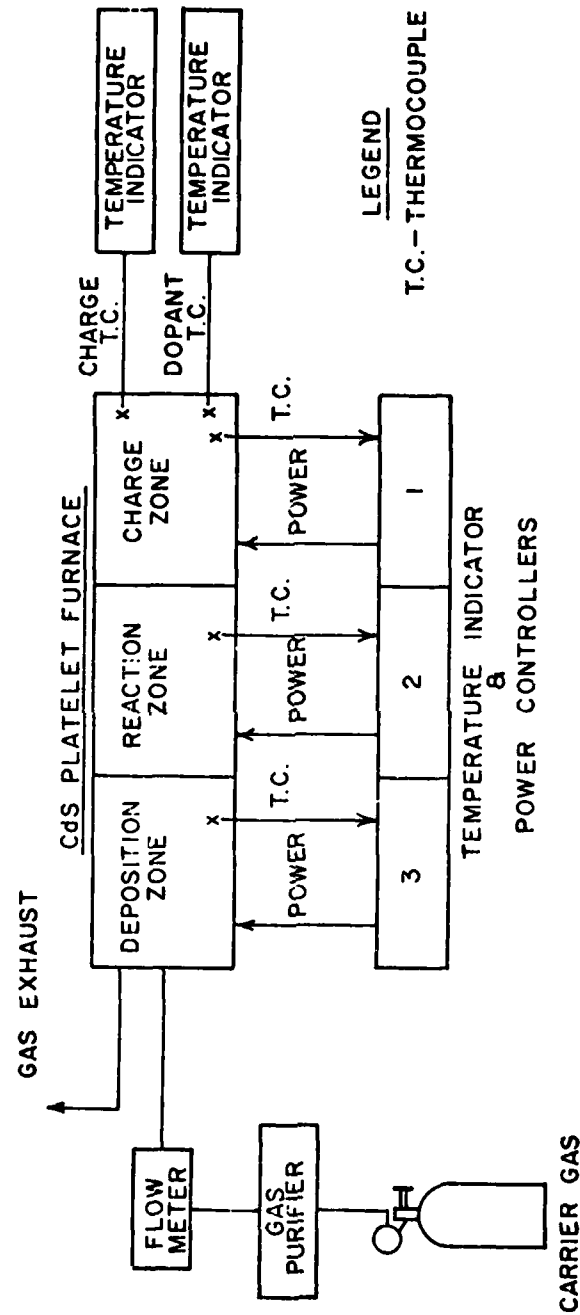
Figure 10. Schematic Diagram of Power and Carrier Gas Control in Vapor-Phase Furnace

growing chamber to assure temperature equilibrium. The cadmium sulfide
and dopant vapors are picked up by the hot carrier gas and transferred to
a region of a temperature suitable for deposition.

Doping may be done by one of several different procedures. In the
case of silver or copper the powdered metal is added directly to the
cadmium sulfide charge. Dopants whose vapor pressure is appreciably
greater than that of cadmium sulfide are put in a separate dopant boat
at a lower temperature and transferred simultaneously. The alkali metals
require an exception to this procedure, since cadmium sulfide platelets
will not grow well in the presence of these elements. We have doped
successfully with lithium, sodium, potassium, and rubidium by growing
the crystals first in a suitable temperature region and then passing
the dopant vapor over the crystals for a short period of time.

6. MEASUREMENTS

Emission measurements were made on the as-grown surfaces. Specimens
were chosen that were uniform in appearance so as to be less likely to
contain strains, and that were free from striations. The specimens were
fastened to the specimen-holder with fine filaments of rubber cement at
one end to minimize strains. The crystals were immersed in liquid
helium which could be pumped if necessary. The spectra were analyzed
with a Baird-Atomic 2-meter grating spectrograph with a reciprocal dis-
persion of 0.7Å/mm in the third order. The luminescence was excited with
the radiation from a 500-watt Osram high pressure mercury lamp suitably
filtered to remove interfering wavelengths. Calibration of the film was
accomplished by superimposing lines from a neon lamp filtered to remove
the dominant red emission.

SECTION II

EXPERIMENTAL RESULTS

1. RED FLUORESCENCE OF CdS:Ag

PHONON ASSISTED STRUCTURE
IN THE RED FLUORESCENCE OF CdS:Ag

Lawrence C. Greene
1966

In the fluorescence spectra of CdS, phonon assistance seems to be the rule rather than the exception. At low temperatures the spectral region from 4850A to 5100Å shows a very complex array of primary and phonon assisted lines which are believed to originate from excitons bound to various defect and impurity centers. The phonon assisted green bands lying between 5100A and 6000Å have been very extensively studied. Several series of these have been seen, some associated with simple lattice defects, others with specific impurities. These bands are without doubt the result of bound to bound and free to bound transitions. The phonon most frequently seen in these spectral regions is the longitudinal optical phonon whose value is usually quoted to be 0.038ev.

We have looked for phonon assistance in the red band of silver doped CdS. This band has been shown (Reference 2) to be associated with the transition of a hole from the valence band to a center about 0.4ev below the conduction band. The specimens used were plates cleaved from bulk crystals. These crystals were grcwn from a charge of pure CdS powder to which a small amount of elemental silver powder had been added. They were grown by a vapor phase technique commonly used in this laboratory (Reference 3).

In Figure 11 is shown a densitometer trace of the red band photographed at 4.2°K. A very weak structure can be seen. Vertical lines have been drawn .0375ev (to the nearest 5Å) apart on each side of the central peak at 6060Å. It·is seen that these lines follow the structure very closely, indicating certainly that the structure is associated with the longitudinal optical phonon, possibly superimposed on a broad unstructured band.

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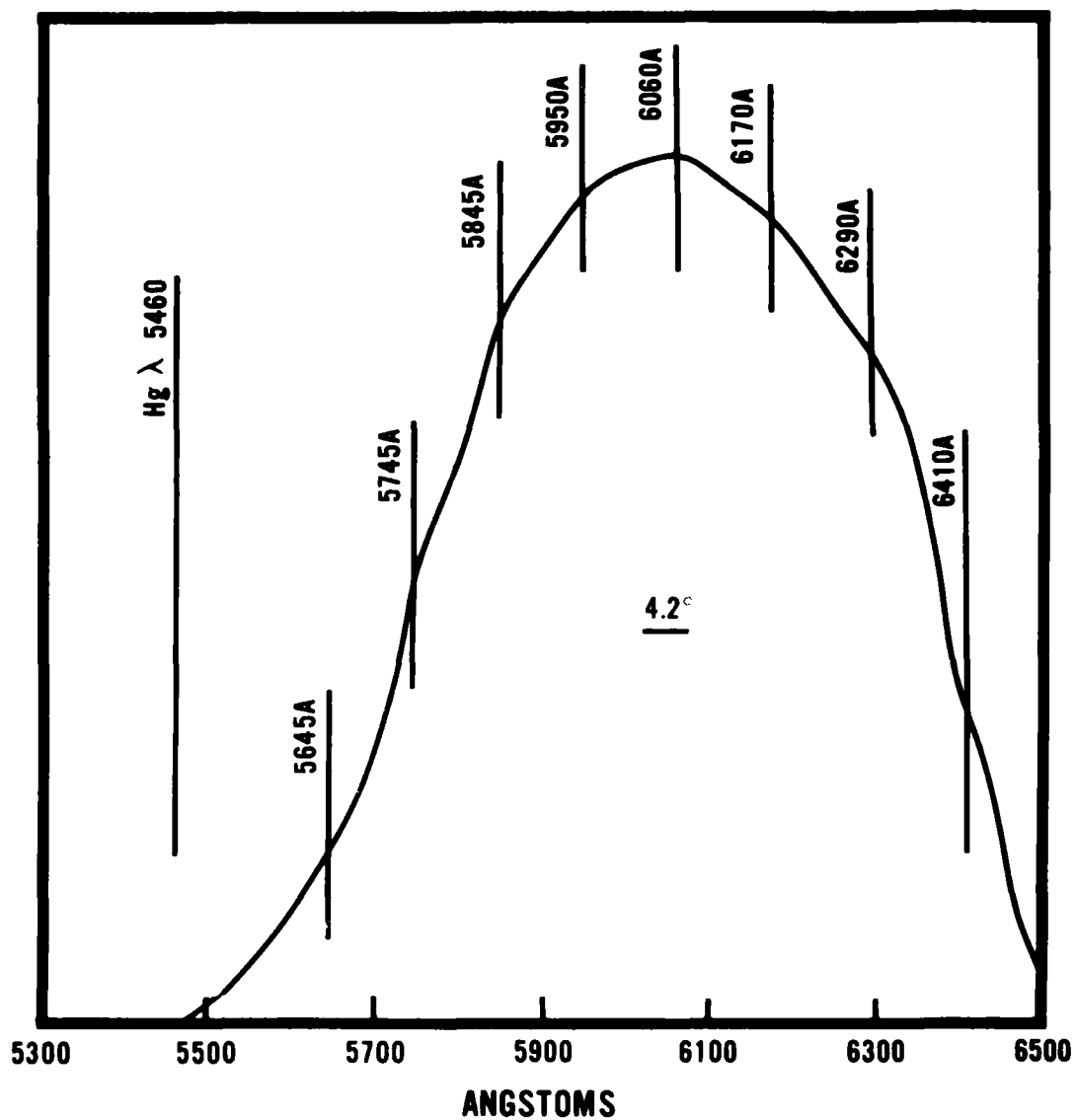
Figure 11. Densitometer Trace Showing the Red Band in CdS:Ag
The vertical Lines are spaced at 0.0375 eV intervals
from the central peak at 6060Å.

2.   GREEN EMISSION IN CdS:Cl

GREEN EDGE EMISSION BANDS
IN CHLORINE DOPED CADMIUM SULFIDE

Lawrence C. Greene, David L. Kingston
and Lake W. Croft

This paper discusses the effects of doping CdS with a non-isoelectronic impurity; in this case, chlorine. There are many possible phenomena that could be considered, but this discussion will be limited to the low temperature fluorescence, near the band edge.

With such doping one might look for a number of effects. One would certainly look for new lines - lines not seen in pure material. These might result from band-to-center or from center-to-center or possibly from bound-exciton transitions involving the chlorine center.

In addition to these new lines one might also expect to see pronounced effects on the native defect spectrum. Some of these native lines may be strengthened as a result of an increased density of a defect induced by the presence of the foreign ion; other lines weakened because of the suppression of another defect.

Finally, a known line may be strengthened or weakened not by a change in density of the causitive defect, but by a change in charge state as the result of compensation processes.

The purpose here is to discuss an example of each of these effects as seen in a specimen of chlorine doped cadmium sulfide.

The cadmium sulfide crystals used in this study were of the platelet type grown in an inert carrier. The doping was carried out during the growth by introducing CdCl vapor into the carrier. Analyses of crystals grown under these conditions indicate a chlorine content of about 100 parts per million.

Figure 12 shows a typical emission spectrum of chlorine doped cadmium sulfide at 4.2°K. The first effect to be considered will be the emission directly associated with the presence of the chlorine in the lattice.

At 4905A a broad line is seen. Although not shown in Figure 12, lines which may be the first and second phonon wings have also been seen. These lines are not seen in pure CdS. The line width and wavelength indicate a transition involving a shallow center, in this case the chlorine donor.

The second effect will involve a native defect induced by the presence of the substitutional chlorine. Here we see a series of broad bands. These are green edge emission bands. It can be shown that there are four well defined series of such bands in pure CdS at 4.2°. However, it may be replaced by the so-called high temperature series, as the temperature is increased. This series has its zero phonon peak at 5140A at 77°.

We know from defect chemistry equations and from the vast body of knowledge available from phosphor research that, unless a compensating impurity is introduced, the presence of substitutional chlorine in the cadmium sulfide lattice must be attended by compensating cadmium vacancies. We propose then that the Y_a series of edge emission bands is associated with the cadmium vacancy.

The third effect to be discussed is associated with a change in charge state of a native defect. It has become almost axiomatic that the edge emission series are accompanied by a very narrow line, or pair of lines at about 4888A. These are the I_1 lines. They are known to arise from the decay of an exciton bound to an acceptor; presumably the same one associated with the green series. In this group of crystals these lines were either absent or very weak. In the presence of the shallow chlorine donors, it will be expected that acceptors will be ionized rather than neutral, so that I_1 may not appear, even though the Y_a series is present.
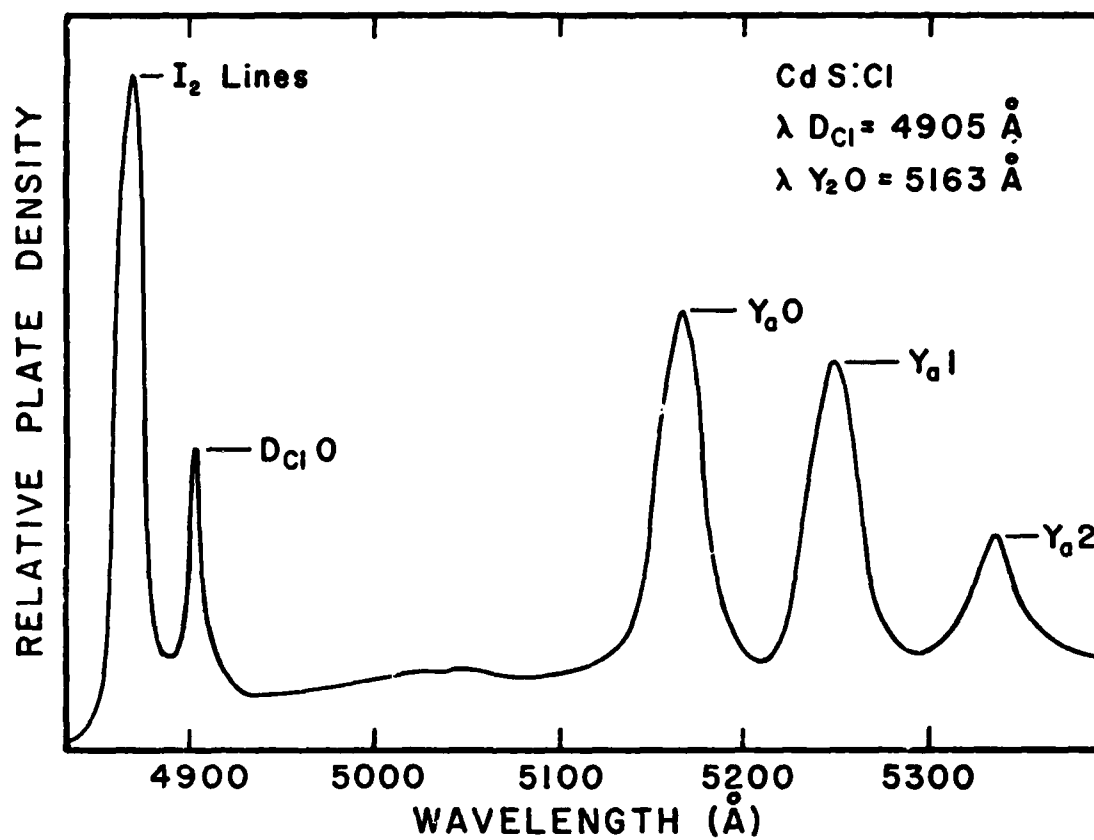
Figure 12.   Emission Spectrum of CdS:Cl (4.2K)

Now lets tie all of this together into a model. For this purpose
we will propose a modification of the Reynolds-Pedrotti energy level
diagram (Figure 13).

We will put the shallow chlorine donor here. The native donor
level usually seen in such a diagram is gone, suppressed by the
presence of the chlorine donors. For this reason the center-to-
center transitions involving this level are not seen in the chlorine
doped crystals.

The lower acceptor level is associated with the high temperature
on X_a bands; the upper one with the low temperature or Y_a bands.
When both of these levels are present Y_a is replaced by X_a as the
temperature increases because of thermal reequilibration of charge
occupancy between the two levels.

Kulps sulfur overlap experiment has shown that the X_a level
is associated with a sulfur interstitial, hence an acceptor. Therefore,
the Y_a level should also be an acceptor, presumably a cadmium vacancy
as already proposed.

Now what about the missing I_1 line. I_1 will certainly be
associated with the neutral state of one or the other of these
acceptors. Which one? We don't know.*

We have demonstrated three distinct effects associated with
the presence of the chlorine; a direct effect, the 4905A chlorine
band; then two indirect effects; the Y_a bands resulting from induced
cadmium vacancies, and the absence of the I_1 lines as a result of
charge compensation of native acceptors.

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*It is now well known, of course, that the I_1 line at 4888.52A is
associated with lithium and at 4888.22A with sodium, both present in
the substitutional mode (1978).
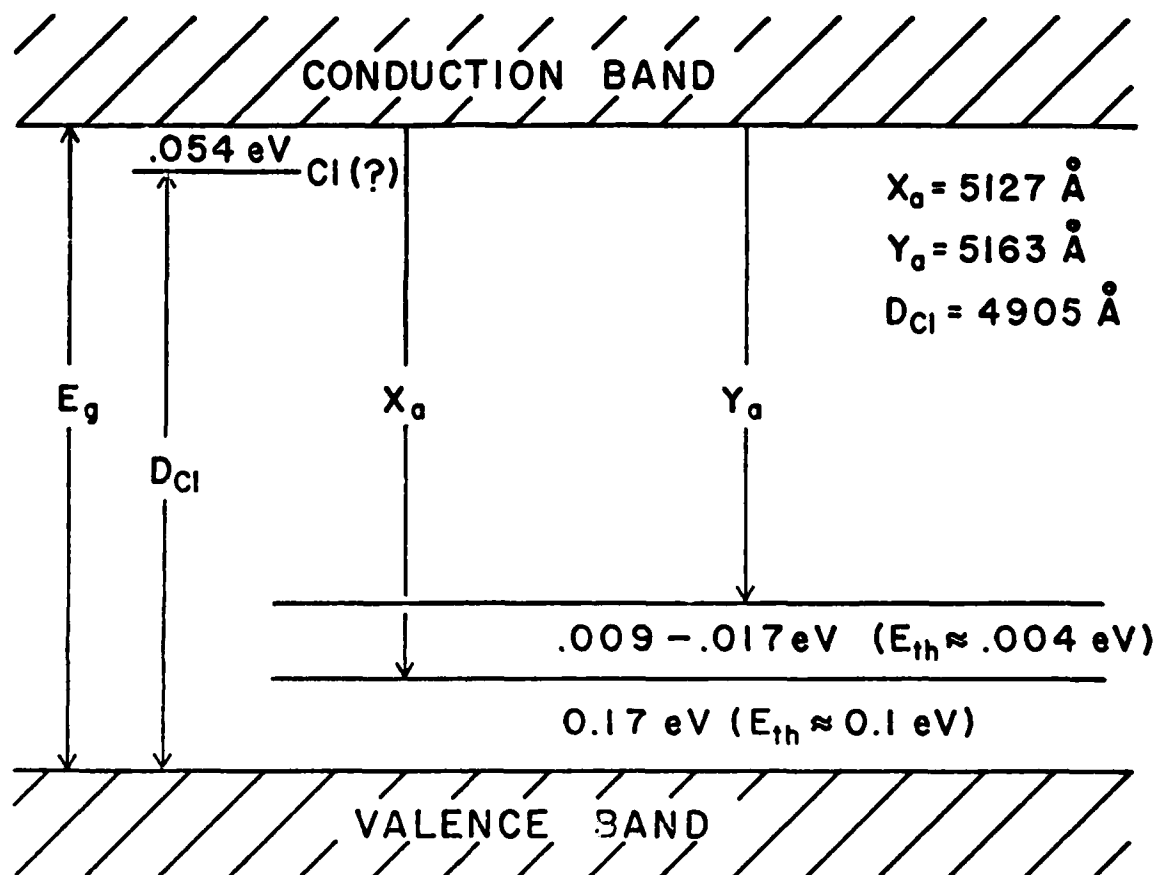
Figure 13. Energy Level Diagram for the Edge Emission Bands in CdS:Cl

3.   EMISSION LINES IN UNDOPED CdS

A STUDY OF THE 4928 AND 5005Å LINES
IN THE LOW-TEMPERATURE EMISSION OF CADMIUM SULFIDE

L. C. Greene, D. L. Kingston and L. W. Croft

The part played by excitons and exciton-phonon interactions in the optical properties of CdS has been the subject of intensive study for a considerable period of time. Rather recently a number of writers have reported at length on intrinsic emission processes. Particularly the radiative recombination of a free exciton with the simultaneous emission of longitudinal phonons has been reported and a detailed study of the line shapes, widths and relative intensities carried out. While studying the exciton emission from pure cadmium sulfide at low temperatures, Bliel and Broser (Reference 4) observed a pair of lines, which they interpreted to be the 1LO and 2LO wings of the intrinsic exciton line. These lines appeared at 4928Å and 5005Å at 4.2K. Gross and his co-workers (Reference 5) and later Segal and Mahan (Reference 6) have made theoretical studies with results which seem to justify this assumption quite convincingly.

In our studies of the low temperature fluorescence spectra of CdS as related to the conditions of growth, we have found empirical relationships among some of the emission lines which we feel must be given serious consideration before final decisions are made.

The emission spectrum of CdS at 4.2°K is often seen as a complex array of lines and bands (Figure 14). This figure shows some of the lines that are most frequently seen. This specimen also shows several of the edge emission band series at longer wavelengths. Here, we see the lines at 4928Å and 5005Å, which have been designated as the first
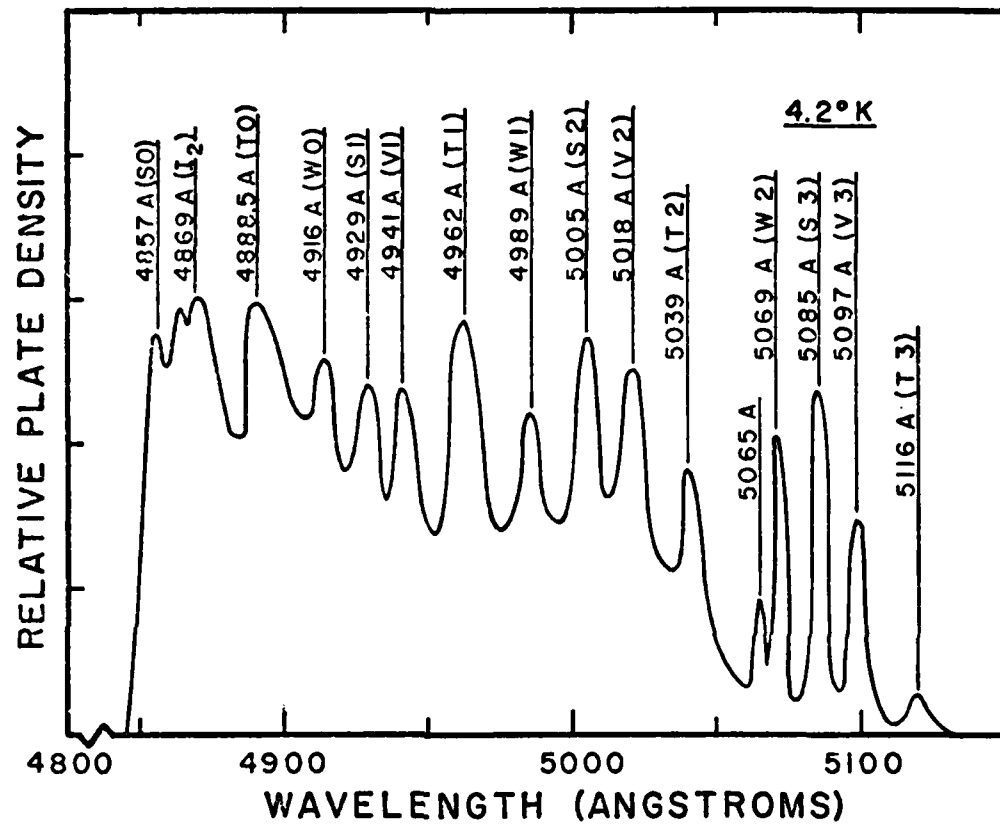
Figure 14. Emission Lines from CdS of Uncontrolled Defect
Structure

and second longitudinal optical phonon replicas of the intrinsic exciton. For convenience we call them S1 and S2. Most of these lines are commonly referred to as "impurity" lines because they are associated with defects in the crystal lattice. By controlling the defect structure of the crystal it is possible to control the appearance or nonappearance of many of them.

This crystal, for example, was very carefully annealed in an inert atmosphere (Figure 15). All of the "impurity lines" except these three disappeared. These are the I_{2B} and I_{2C} lines which are known to be associated with the decay of excitons bound to a neutral donor, possibly the sulfur vacancy, and the line at 4866Å associated with an ionized donor. This specimen showed no other defect lines at any exposure.

The complex of lines shown in Figure 14 can also be resolved into groups of co-occurring lines, the various phonon-assisted series. For example, one well-known group consists of I_1 and its replicas, one of which is shown here (Figure 16). This series appears particularly prominent in CdS crystals that are lightly doped with sodium and sulfur. We also see the intrinsic exciton line but the S1 and S2 lines are completely suppressed by the sodium.

In Figure 17 two dominant series are seen. We call these the V series with lines at 4867, 4941, and 5018Å and the W series with lines 4916 and 4989Å. These assignments are made entirely on the basis of co-occurrence, that is, the lines of each series are always seen together.

The purpose in showing these spectra is to show how the complex emission line spectra of cadmium sulfide can be separated into groups of lines that always occur together and hence may be assumed to arise from a common process.

27
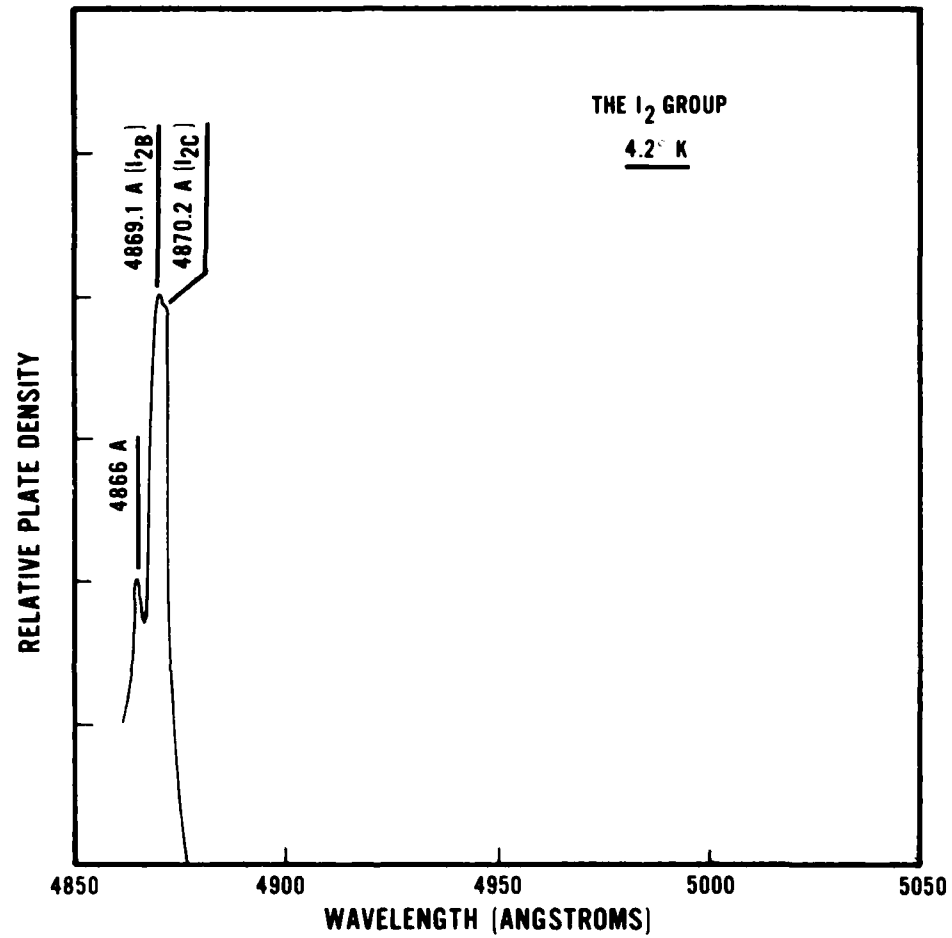
Figure 15.   Emission Lines from a CdS Crystal Annealed in an
Inert Atmosphere
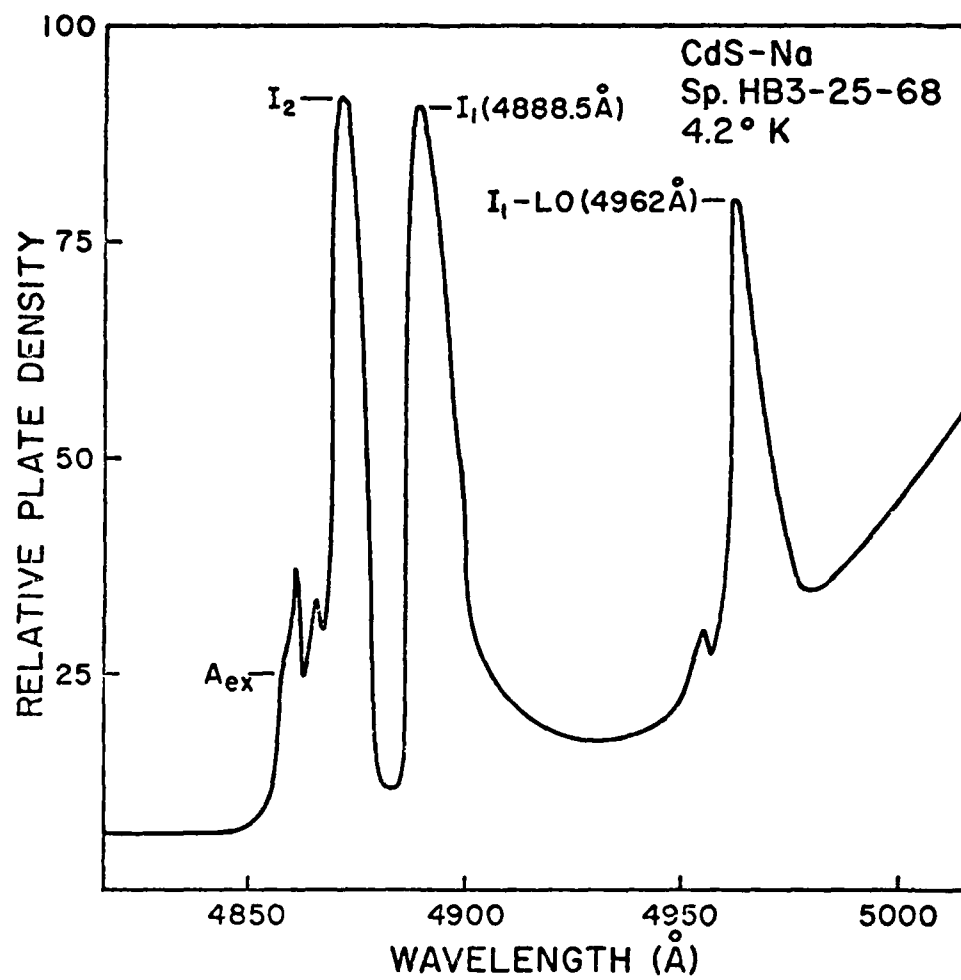
Figure 16. Emission Spectrum from CdS Showing the I_1 Series
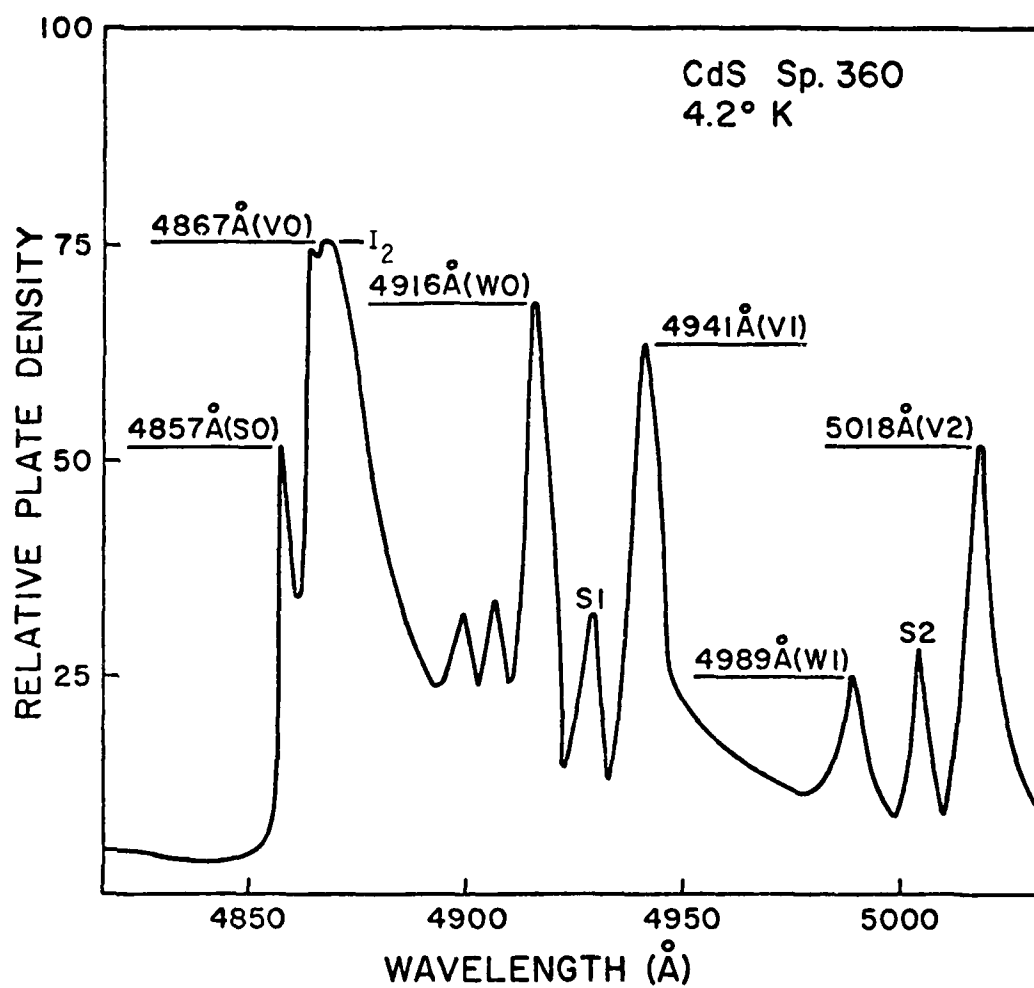
Figure 17. Emission Spectrum from CdS Showing the V and W Series

One such group of lines, always seen together and very easily suppressed or enhanced in the growth furnace is one we have chosen to call the "S" series (Figure 18), and of course you will immediately recognize S1 and S2 as the lines assumed to be the phonon wings of the intrinsic exciton line.

In the literature these lines are described as "weak", but in crystals such as this one they may dominate the line spectrum. The relative strength of the lines may, perhaps, be better appreciated when one observes that at the exposure used here the intrinsic exciton line is not seen at all. In this figure, attention is called to the broad line labeled S0 at 4857A. This line is polarized predominantly $E \perp C$. It is not to be confused with the Γ_6 exciton line at the same wavelength. The Γ_6 line is much narrower and is polarized $E \parallel C$. Where the two occur together they are very clearly separated with a polarizer.

Now the important thing about this S0 line is that it always accompanies S1 and S2. In the many hundreds of cadmium sulfide crystals which we have studied, the three lines have always occurred together, and it is for this reason we have classified S0 with S1 and S2. These S lines are very sensitive to the defect structure of the crystal and can be greatly enhanced or completely suppressed in the growth furnace. This certainly suggests that the lines should not be classified with the intrinsic exciton emission but rather with the defect or impurity emission.

To summarize, our purpose has been to show that from a strictly empirical standpoint there seems to be no relationship between the intrinsic exciton line and the S1 and S2 lines, and that there is a very clearly observed relationship between the S0 line at 4857A and these lines of such nature that one cannot avoid the conclusion that the three arise from a common process.
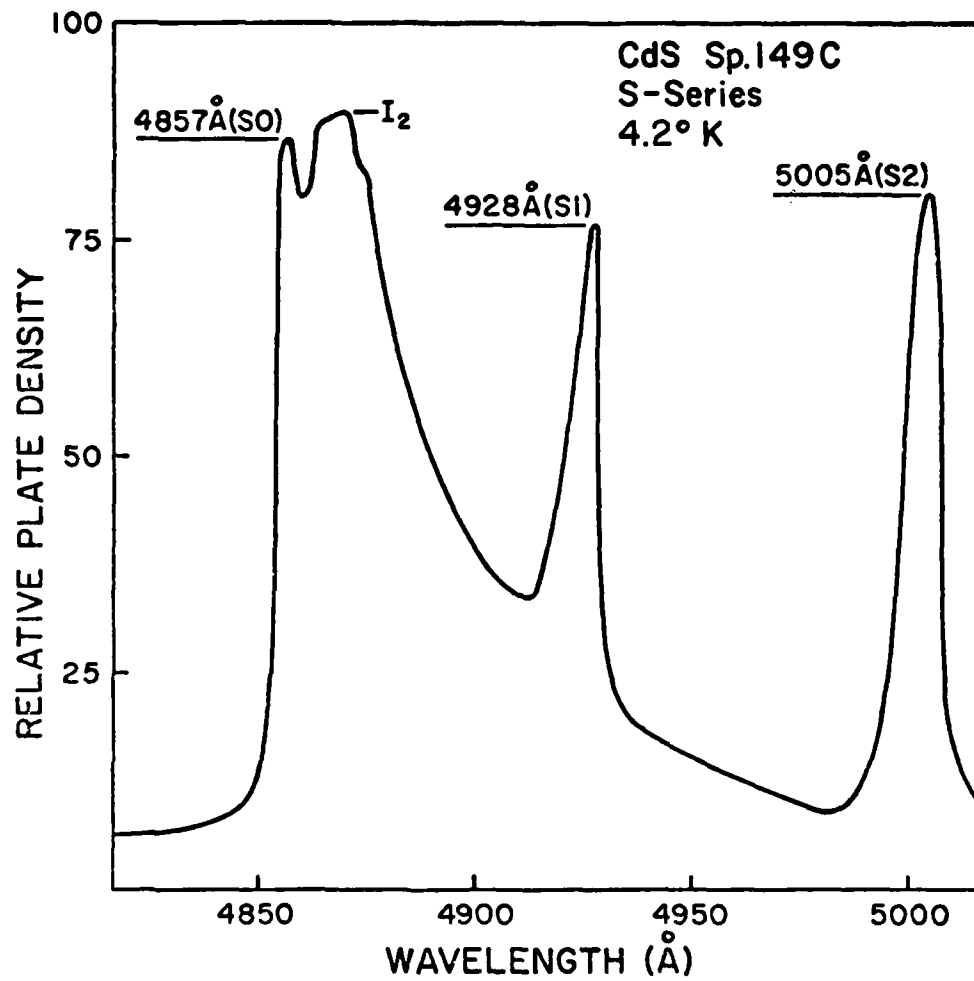
Figure 18.   Emission Spectrum from CdS Showing the S Series

4.   EXCITON LINES IN CdS:Cl

BOUND EXCITON LINES IN THE LOW TEMPERATURE
EMISSION SPECTRA OF HALOGEN DOPED CADMIUM SULFIDE CRYSTALS

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
at Stanford University Dec. 28-30, 1970

When sulfur doped cadmium sulfide crystals are equilibrated at
900°C in an inert atmosphere, the low temperature emission line spectrum
is that characteristic of excess cadmium. On the other hand, when
fluorine or chlorine doped cadmium sulfide crystals are equilibrated
under the same conditions, the line spectrum is that to be expected
from crystals equilibrated with sulfur or hydrogen sulfide.

Figure 19 shows the bound exciton spectrum from a cadmium sulfide
crystal equilibrated with cadmium sulfide vapor at 800°C. The dominant
lines are the I_5 line at 4869.14Å and a line at 4866.6Å. It is known
that the I_5 line arises from the decay of an exciton bound to a
neutral donor. It has been proposed that this donor is a substitutional
halogen, but there seems to be no correlation between the intensity
of this line and the halogen concentration in the lattice. We feel
that the line is more probably associated with an anion vacancy.
Less is known about the 4866.6Å line, but it may very well be associated
with the decay of an ionized donor, probably the same donor responsible
for I_5. This spectrum is quite reproducible in undoped crystals.

Figure 20 shows the bound exciton spectrum from a cadmium sulfide
crystal equilibrated with cadmium sulfide vapor and cadmium vapor at
900°C. A new line appears at 4869.8Å. This line arises from the
decay of an exciton bound to a neutral donor, probably an interstitial
cadmium.

Figure 21 shows the spectrum from a crystal equilibrated at 900°
with cadmium sulfide vapor and hydrogen sulfide. This spectrum contains
unidentified donor lines at 4867.1Å and 4868.8Å, and I_5 line and a

CdS UNDOPED
SOAKED 800°
18hr QUENCHED

I₅ 4869.14 A

4866.6 A
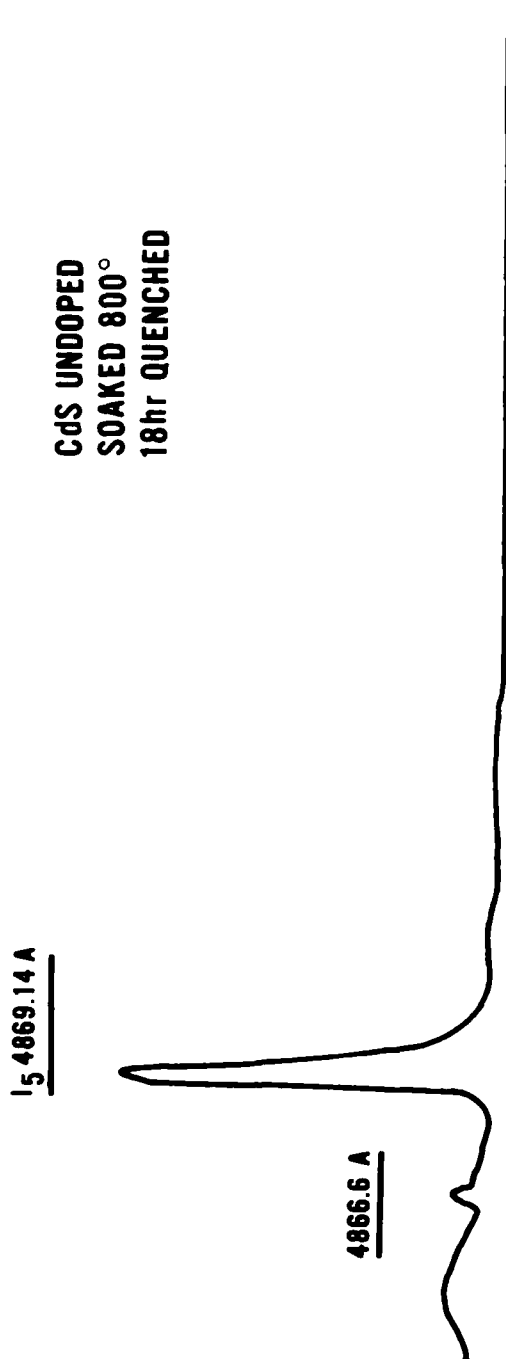
Figure 19. Bound Exciton Emission Spectrum of Undoped CdS Soaked 800°C
for 18 Hours and Quenched

34
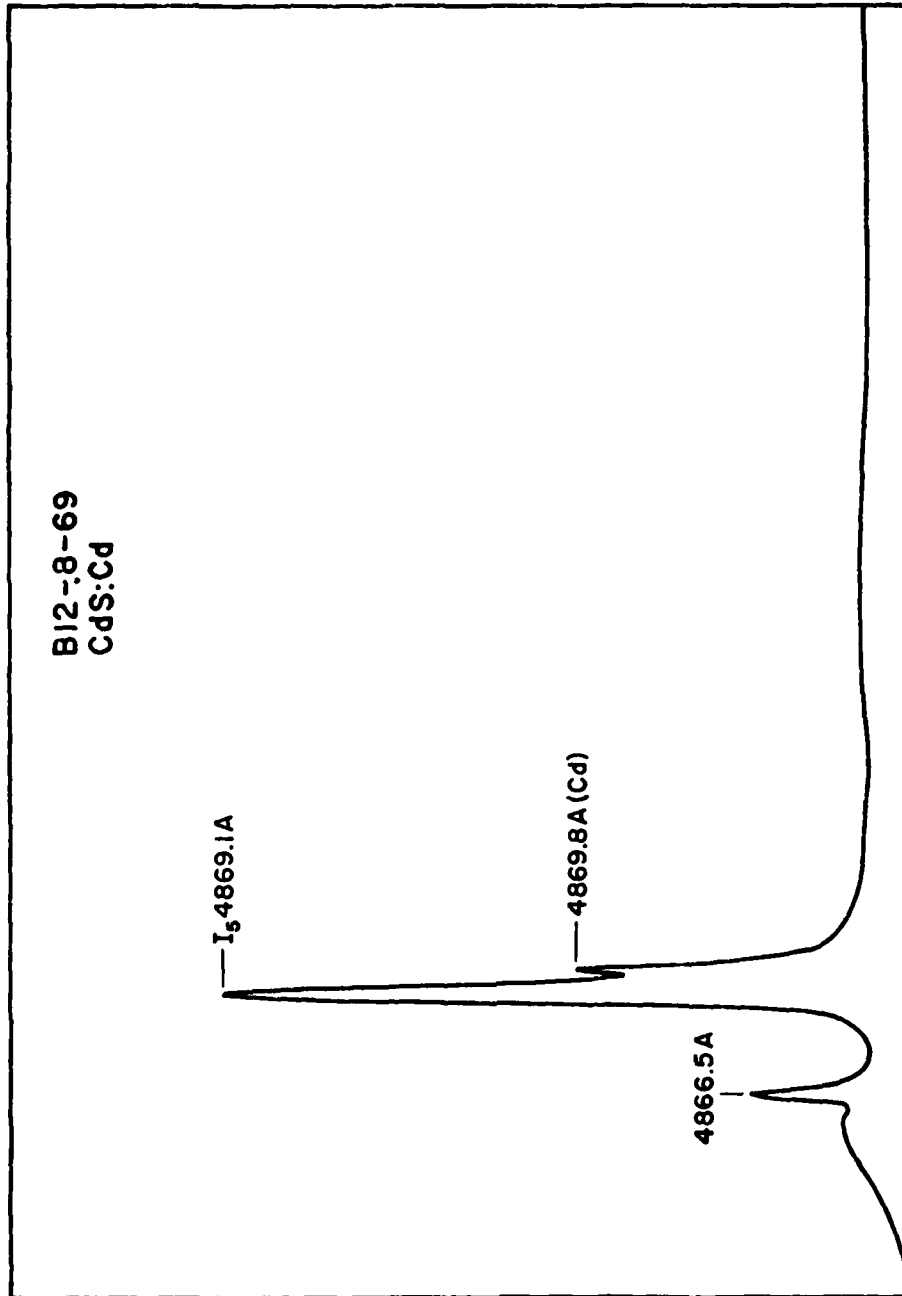
Figure 20. Bound Exciton Emission Spectrum of Cadmium Sulfide Equilibrated with Cadmium Sulfide Vapor and Cadmium Vapor at 900°C
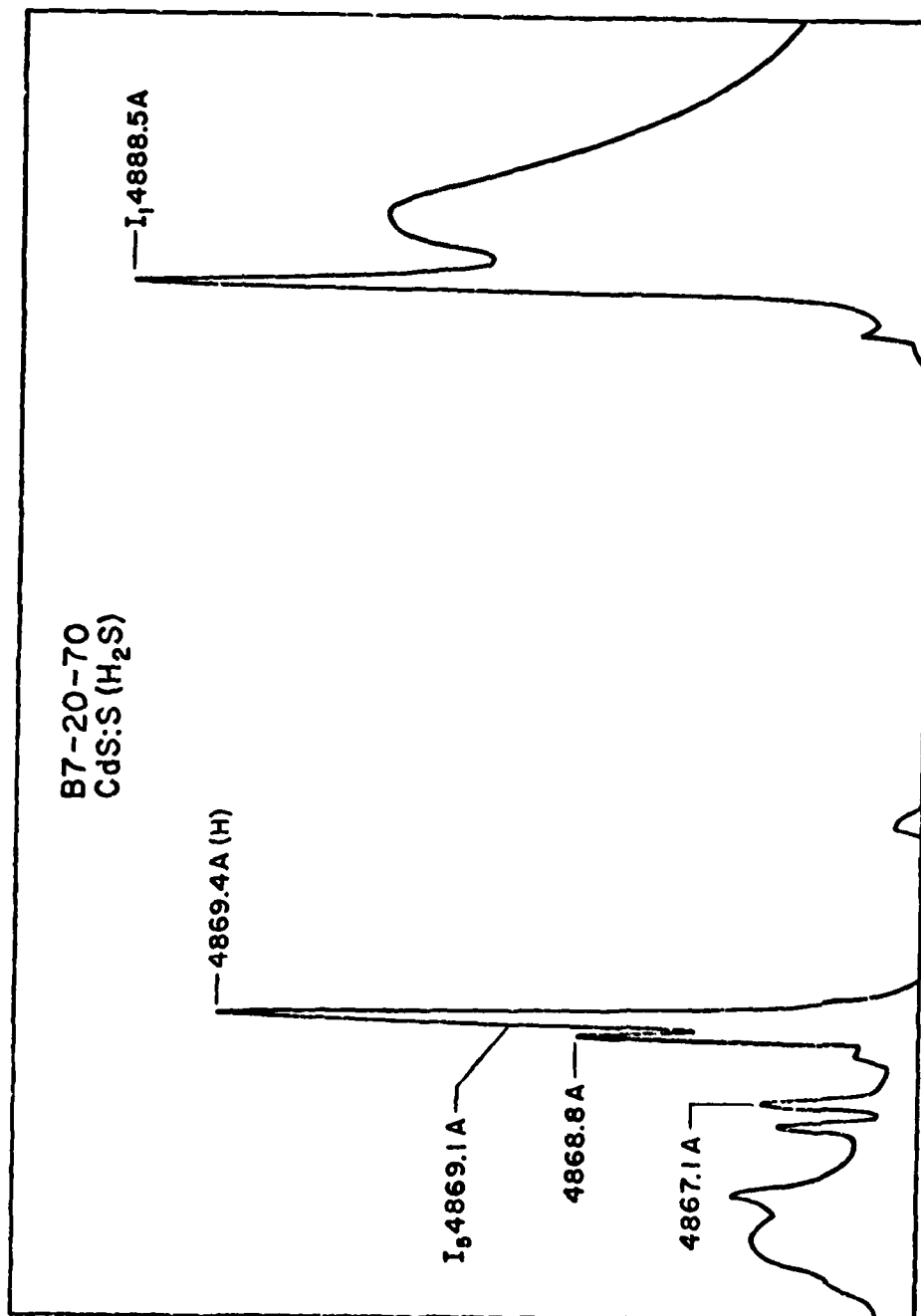
Figure 21. Bound Exciton Emission Spectrum of Cadmium Sulfide Equilibrated with Cadmium Sulfide Vapor and Hydrogen Sulfide

36

dominant donor line at 4869.4Å which is associated with hydrogen. It also shows lines characteristic of sulfur doping, the I_1 line at 4888.5Å and its acoustic phonon. This I_1 line, which appears predominantly in sulfur doped crystals, is a neutral acceptor line and was presumed to be associated with a sulfur interstitial. However, it is now known to be associated with a lithium in a substitutional position. In the presence of the excess sulfur the interstitial lithium, which is present in the best material, undergoes a site transfer interaction with the lattice cadmium.

Figure 22 shows the spectrum from a cadmium sulfide crystal lightly doped with chlorine. Dominant lines are the I_5 line and donor lines at 4870.4Å and 4871.0Å which seem to be associated with the halogen. Also present are the I_1 line associated with substitutional lithium, and its acoustic phonon. The formation of the I_1 center in the chlorine doped cadmium sulfide certainly results from a different mechanism than that used to explain its presence in the sulfur doped material. The centers are probably the result of a controlled defect (Koch-Wagner) compensation mechanism. A weak band shows as a *hump* on the long wavelength side of the donor exciton group at 4872Å. This is certainly a free-to-bound transition from a shallow donor, probably the chlorine substitutional. It has an ionization energy of about 39meV.

Figure 23 shows the spectrum of a crystal somewhat more heavily doped with chlorine than that shown in Figure 22. The 4870.4Å chlorine line is present but the 4871.0Å line is apparently obscured by the greatly increased 4872Å free-to-bound transition band. There is also a new band almost directly overlapping the I_1 acoustic phonon. We have had no opportunity to study this band further.

To resolve the question whether the I_1 center is really induced by the presence of the chlorine, a chlorine doped cadmium sulfide crystal was equilibrated in cadmium sulfide vapor with a 3% partial pressure of cadmium vapor. Equilibration of undoped crystals in the presence

37
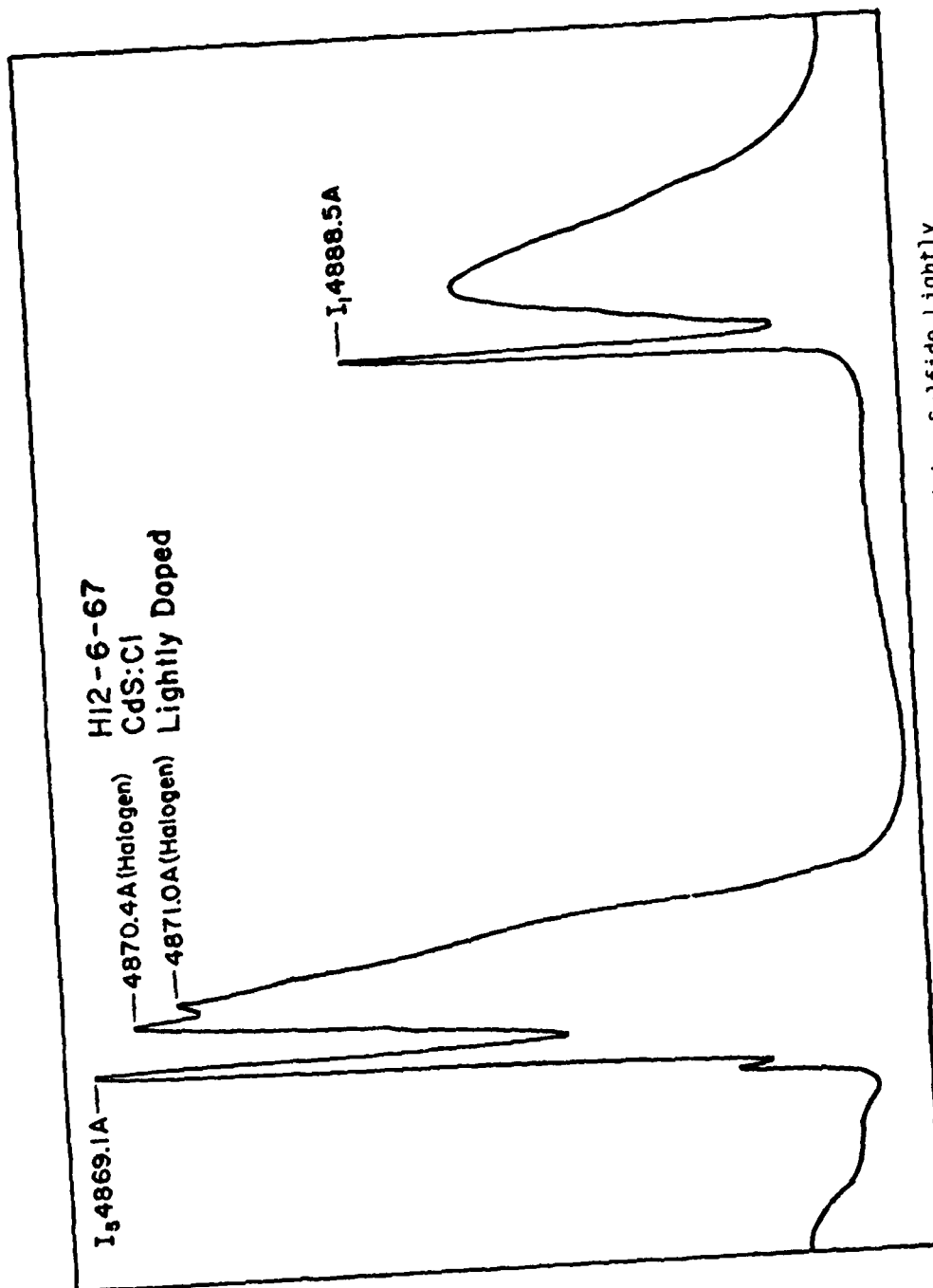
Figure 22. Bound Exciton Spectrum of Cadmium Sulfide Lightly
Doped with Chlorine
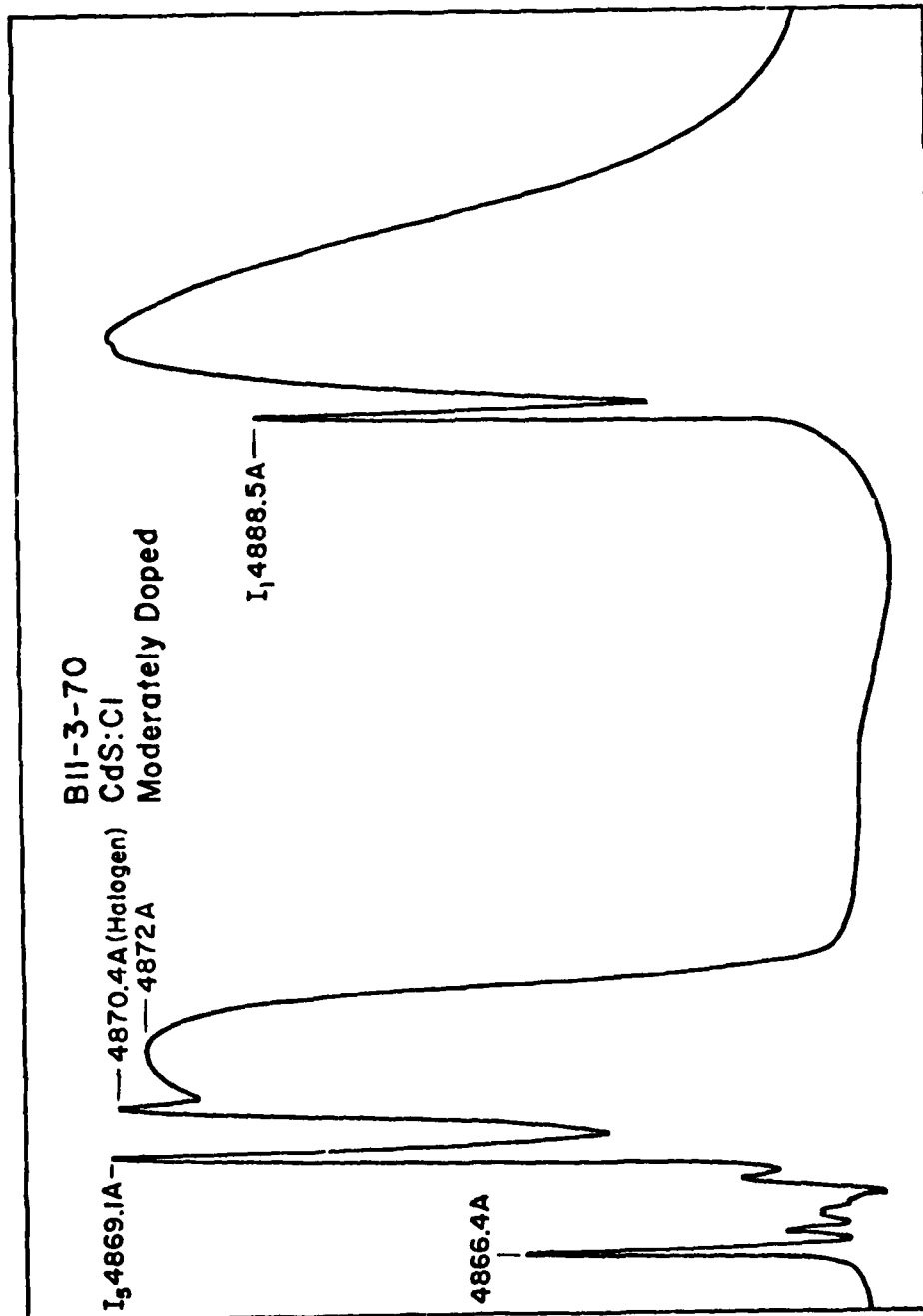
Figure 23. Bound Exciton Spectrum of Cadmium Sulfide Moderately
Doped with Chlorine

of cadmium vapor always suppresses the I_1 center by means of the reverse
of the site exchange interaction which produces them in the presence
of sulfur vapor. Figure 24 shows the spectrum from such a specimen.
There is a characteristic cadmium line at 4869.8Å and the chlorine
line at 4870.4Å, but the I_1 line and its acoustic phonon are still
dominant.

The fact that we can retain the I_1 center in the presence of
excess cadmium makes possible the study of the I_1 line under varying
cadmium excess concentrations. Figure 25 shows the spectra of three
CdS:Cl crystals containing successively increasing amounts of excess
cadmium. The I_5 donor line is seen to broaden and shift to higher energy.
This is a well-known phenomenon which is associated with coulomb
screening due to the presence of the high concentration of donors. In
addition we see a similar broadening and shifting of the I_1 acceptor
line, a phenomenon not previously seen.

In summary, we find that the presence of the dopant, chlorine,
in cadmium sulfide stabilizes the I_1 center even in the presence of
considerable excesses of cadmium in the lattice. This makes it pos-
sible to study the I_1 acceptor line in the presence of such excess
cadmium.

5. EXCITON LINES IN CdS:Ag

<div align="center">

THE BOUND EXCITON LINES ASSOCIATED
WITH SILVER CENTERS IN CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
in Seattle, Washington August 1971

</div>

When high purity cadmium sulfide crystals are carefully equilibrated
in an atmosphere containing one of the component elements, strong bound
exciton emission lines are produced, which are characteristic of the
component used. Similarly, if the crystals are equilibrated in an
atmosphere containing a monovalent metal, a group of dominant lines
characteristic of that metal are produced.
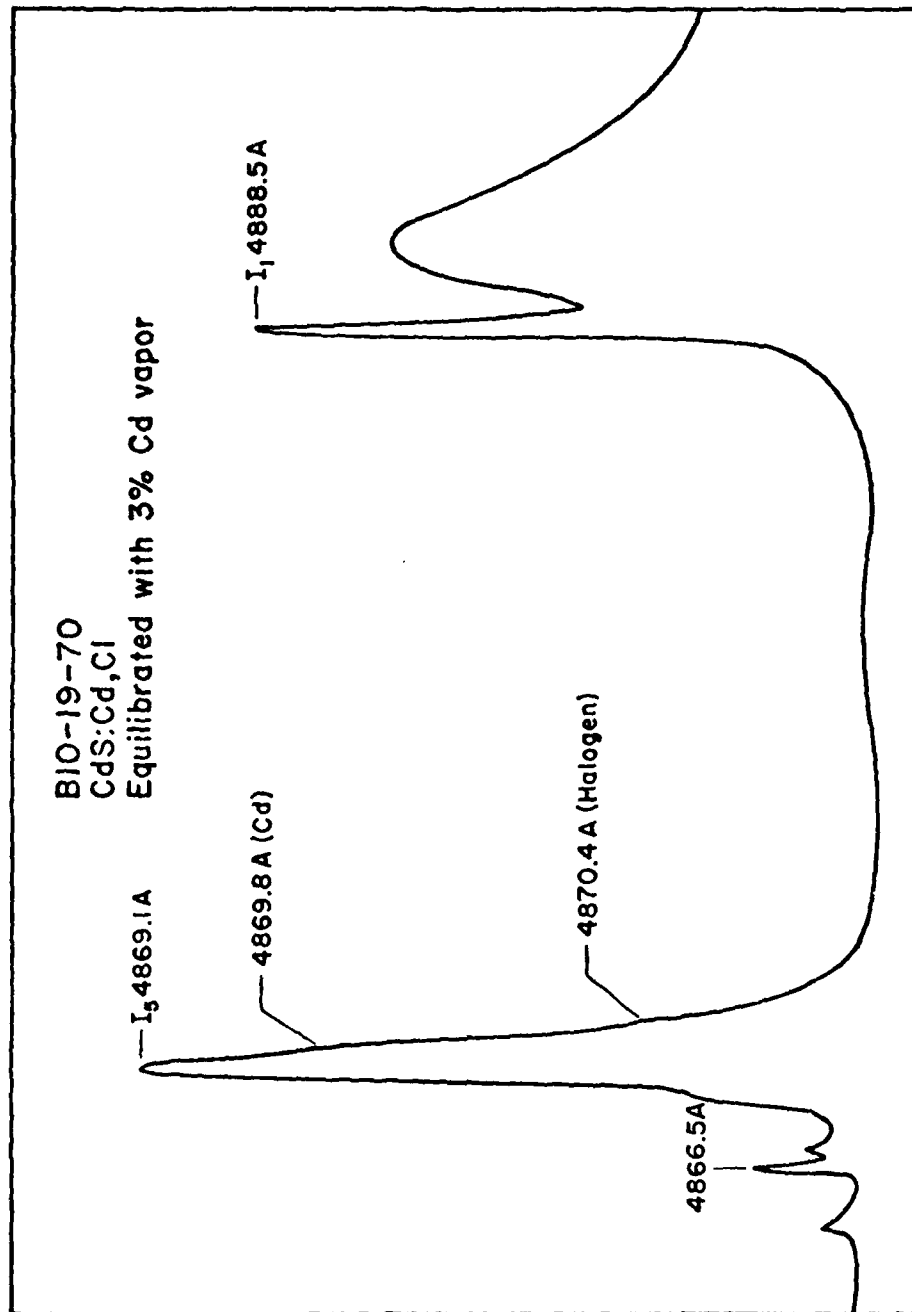
Figure 24. Bound Exciton Spectrum of CdS:Cl Equilibrated in 3% Cadmium Vapor
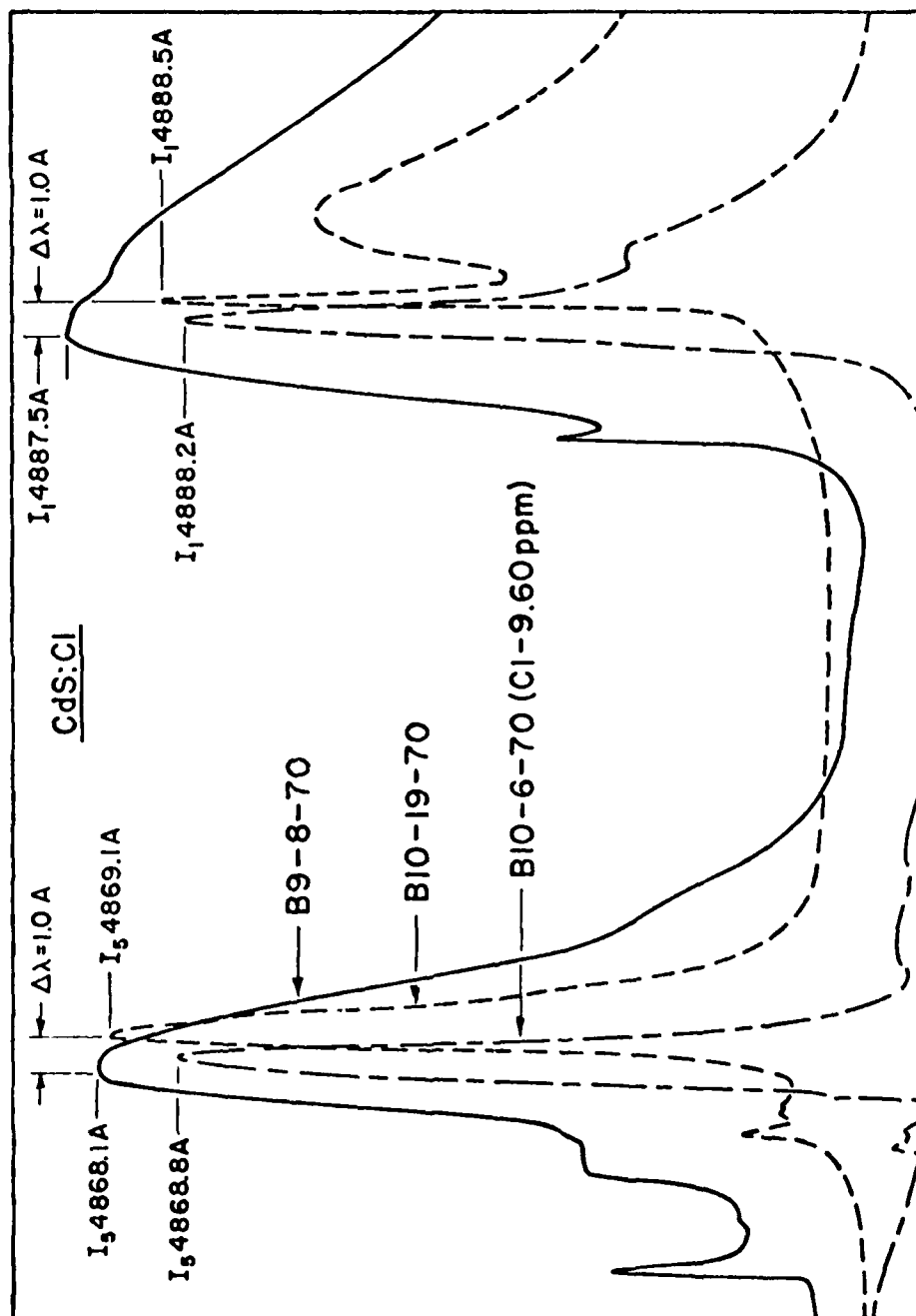
Figure 25. Bound Exciton Spectrum of CdS:Cl with Varying Concentrations of Excess Cadmium

Figure 26 shows the bound exciton emission spectrum of a cadmium sulfide crystal equilibrated in an atmosphere consisting of argon with an equilibrium partial pressure of cadmium sulfide vapor and additional cadmium vapor. The lines shown arise from the decay of neutral donors. The acceptor region of the spectrum is not shown because there are no acceptor lines. The 4867.9Å and 4869.02Å lines are associated with donors involving sodium, probably as sodium interstitials. Sodium is the predominant impurity in "high purity" cadmium sulfide. The lines at 4869.12Å(I_5) and the line at 4869.72Å are associated with excess cadmium either as sulfur vacancies or as cadmium interstitials. The line at 4869.32Å is unidentified.

Figure 27 shows a cadmium sulfide crystal containing approximately 1.2ppma of silver. This spectrum contains several interesting features. On the short-wavelength side of the group of lines we find two pairs of lines, one pair at about 4867.82Å and another pair at about 4868.12Å. These have not been seen except in silver doped crystals. The 4868.42Å line is associated with residual sodium and the 4869.22Å line with lithium. The remaining longer wavelength lines are all associated with silver. It is to be noted that, even though there is only 1.2ppma of silver, the silver lines dominate the spectrum. The line at 4869.82, which is a silver line, has a weaker companion with a separation comparable to those of the 4868.12Å and 4867.82Å pairs. The 4870.36Å line, which is a sodium line, has a closely spaced pair of lines to the long wavelength side, which are silver lines. All of these line groupings have separations too small to be explained as the spin-exchange splitting seen in exciton lines from ionized donors. Zero field split lines cannot arise from simple neutral donors in cadmium sulfide, so if the pairs seen in such CdS:Ag spectra are, indeed, true doublets they most probably are associated with complexes. These might be a silver interstitial with a silver substitutional, pairs of silver interstitials or substitutionals, silver in one mode of incorporation with sodium in another, or even sodium and silver in the same mode.

The large number of lines which are seen in the silver doped crystals becomes explainable when one considers the large number of possible combinations in such complexes.

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P12-22-70
Cd S UNDOPED
UNCERTAINTY ±0.02 A

4869.12 A ───   ─ 4869.32 A

4869.02 A ─

4867.9 A ─   ─ 4869.72 A
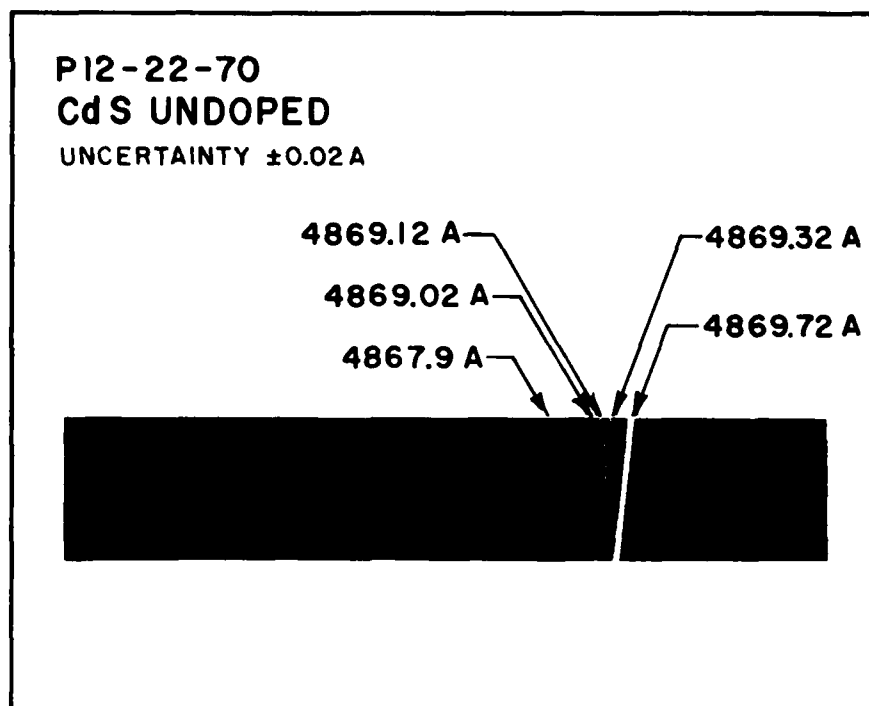
Figure 26. Bound Exciton Spectrum of Undoped CdS
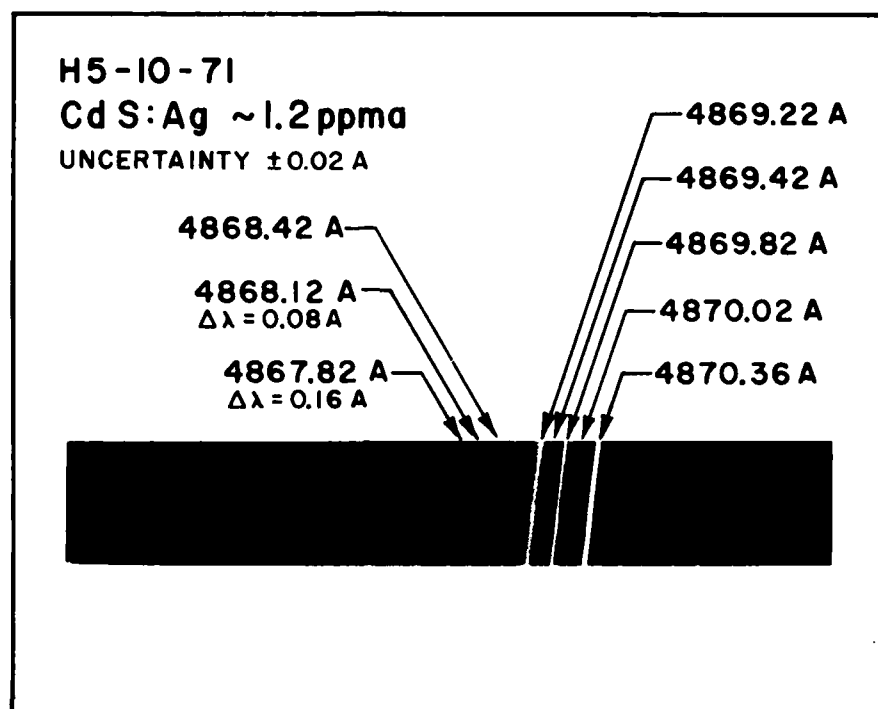
Figure 27. Bound Exciton Spectrum of CdS:Ag

6.   DONOR LINES IN CdS:Na

DONOR LINES ASSOCIATED WITH BOUND-EXCITONS
IN SODIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
in San Francisco, 31 Jan-3 Feb 1972

When high purity cadmium sulfide crystals are carefully equilibrated
in an atmosphere containing the vapor of one of the component elements,
strong bound-exciton lines are produced in the low temperature emission,
which are characteristic of the component. Similarly, if the crystals
are equilibrated in an atmosphere containing sodium vapor, a group of
dominant lines characteristic of the sodium are produced. One of these,
I_1(Na) at 4888.20Å, which is an acceptor line arising from the decay
of an exciton bound to a center associated with substitutional sodium,
has been extensively studied (References 7, 8). There are, in addition
to the I_1(Na) acceptor line, many donor lines which have not been
previously studied.

Figure 28 shows the bound exciton spectrum of the donor centers in
high purity cadmium sulfide. Mass spectrographic analysis showed 0.66ppma
sodium, with lithium not detected. This crystal had been carefully equil-
ibrated in argon with an equilibrium partial pressure of cadmium sulfide
vapor at 900°C. At low exposure two lines are seen, I_5(Cd) at 4869.13Å
and a weaker line at 4866.48Å. At increased exposure other lines appear.
One of these is 4868.42Å, a sodium line. A sharp line also appears at
4866.98Å. The lines at 4866.48Å and 4866.98Å are a zero field split doub-
let. They are the Γ_5 and Γ_6 exciton lines from an ionized donor, split
by spin-exchange interaction. The stronger line, the Γ_5, is from an
allowed transition and is lifetime broadened. The weaker line, Γ_6, is
from a nominally forbidden transition with a long decay lifetime, and hence
is much sharper than the Γ_5 line. Zeeman studies have confirmed these
assumptions.
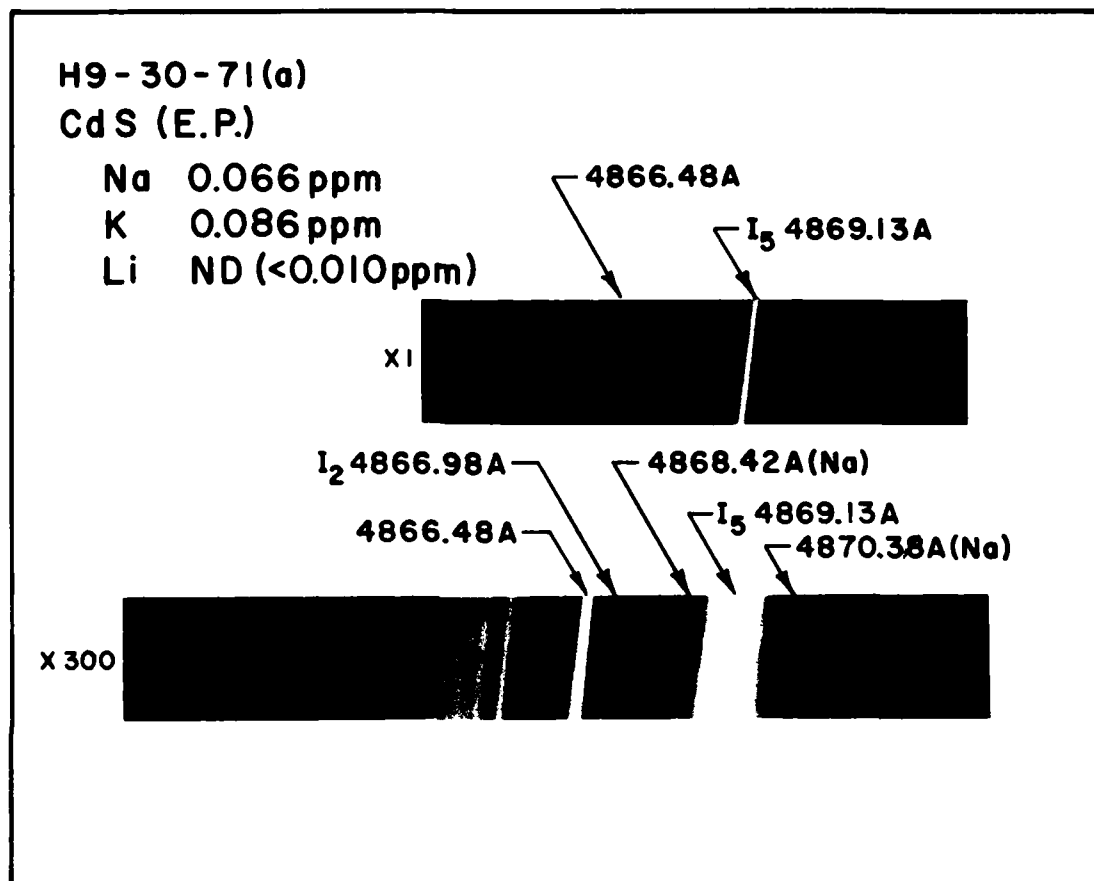
Figure 28. Bound Exciton Spectrum of a High Purity CdS Crystal

The dominant line in the spectrum of the undoped cadmium sulfide was the I_5(Cd), a donor, presumably associated with a sulfur vacancy, but possibly with a cadmium interstitial. Figure 29 shows a spectrum from a cadmium sulfide crystal doped with 8ppma of sodium. Particularly noteworthy is the very strong line I_5(Na) at 4869.02Å. This line, line I_5(Cd), is associated with a neutral donor, very probably a sodium interstitial. A line also occurring predominantly in sodium doped cadmium sulfide is seen at 4870.38Å.

It is interesting that a third line also appears in the I_5 group. This is I_5(Li) at 4869.22Å which is seen in Figure 30 as a member of the very closely spaced I_5 trio.

Figure 31 shows two exposures from a cadmium sulfide crystal containing 10.4ppma of sodium. In the short exposure the I_5(Cd) and I_5(Na) lines dominate the spectrum. These are the neutral donor lines. The ionized donor lines associated with excess cadmium are also seen at 4866.48Å and 4866.98Å. At 4866.22Å and 4866.71Å there are a pair of lines which very clearly are associated with an ionized donor. This donor involved sodium and we presume that it is a sodium interstitial.

In summary, it is seen that sodium doped cadmium sulfide shows exciton emission lines from neutral donors at 4868.42Å, 4869.02Å, and 4870.38Å, and a zero field split pair of lines from an ionized donor at 4866.22Å and 4866.71Å.

7. DONOR LINES IN CdS:Li

DONOR LINES ASSOCIATED WITH BOUND EXCITONS IN LITHIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society in Atlantic City, 27-30 March 1972

When high purity cadmium sulfide crystals are carefully equilibrated in an atmosphere containing the vapor of one of the component elements, strong bound-exciton lines are produced in the low temperature emission, which are characteristic of the component. Similarly, if the crystals
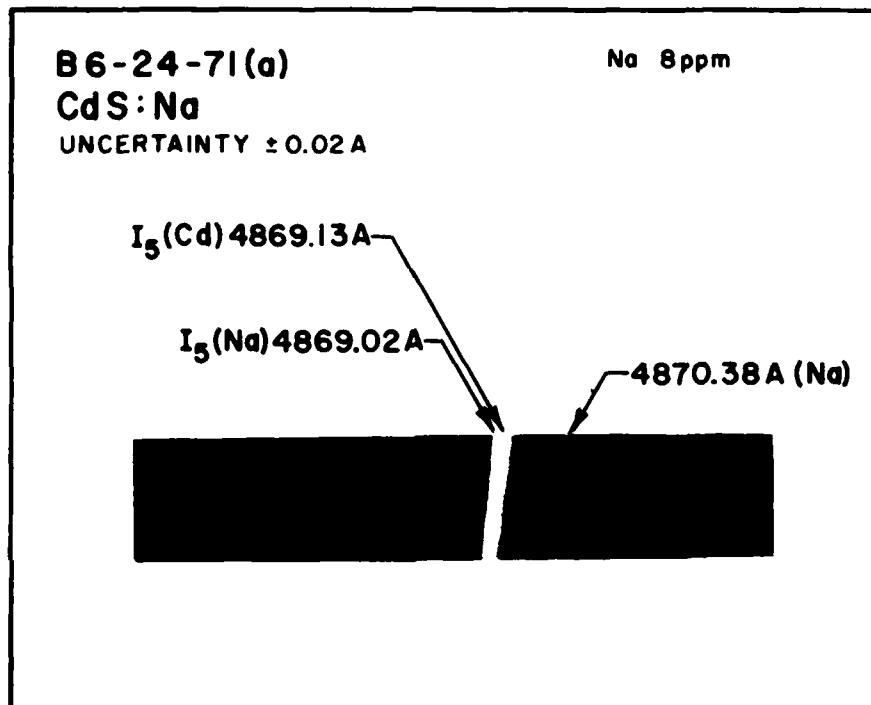
Figure 29. Donor Lines in CdS:Na Showing the I_5(Na) Line and the Na Line at 4870.38Å
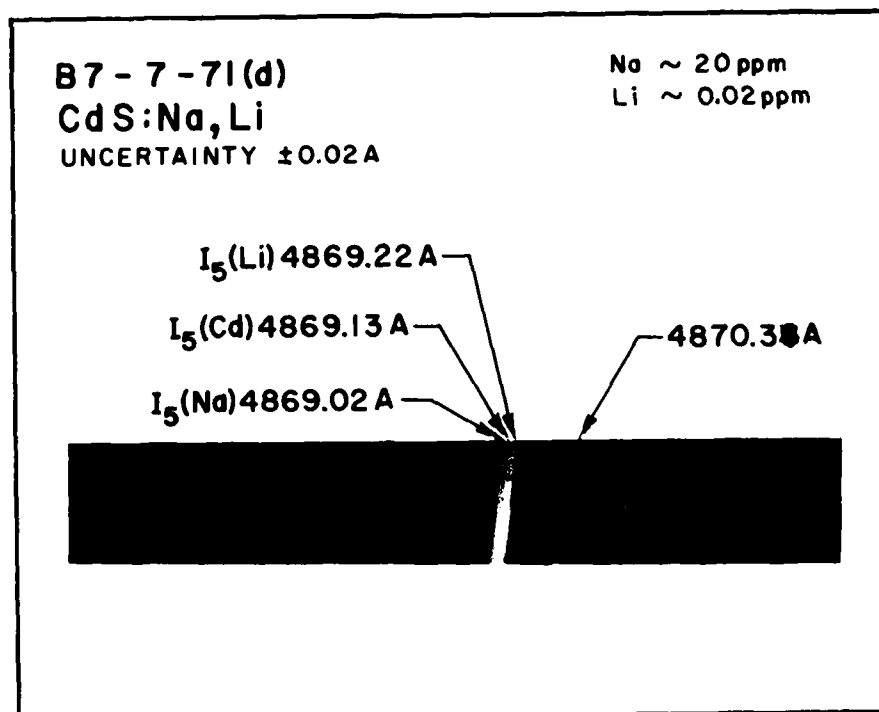
Figure 30. Donor Lines in CdS:Na Showing the I_5(Cd), I_5(Na), and I_5(Li) Trio of Lines

50
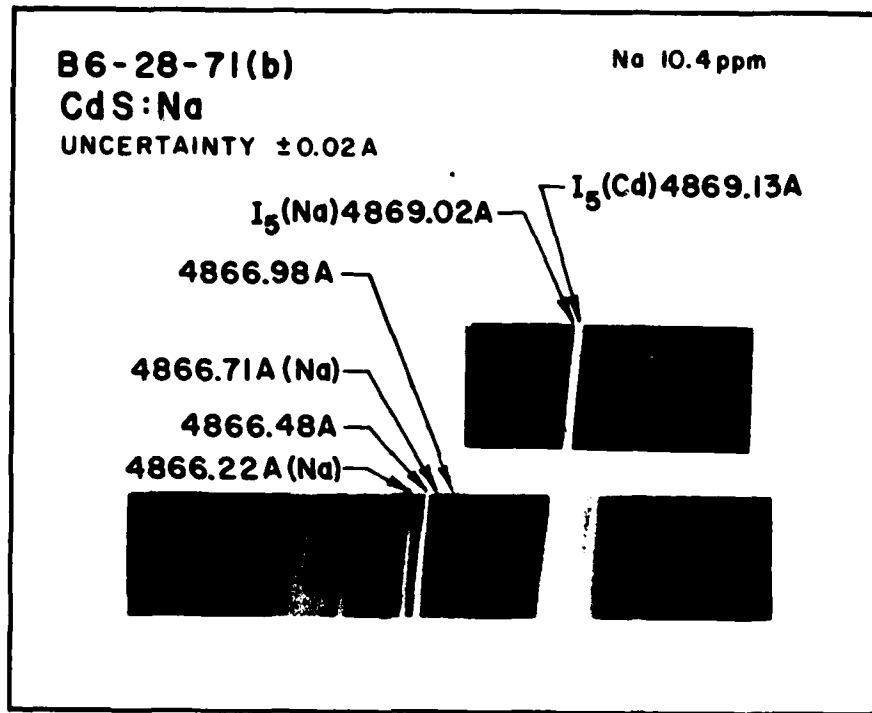
Figure 31.   Donor Lines in CdS:Na Showing the Ionized Donor Lines
Associated with Sodium

are equilibrated in an atmosphere containing lithium vapor, dominant lines characteristic of lithium are produced. One of these is the well known $I_1(Li)$ acceptor line (References 7, 8). This line is seen only in crystals that have been equilibrated in an atmosphere containing sulfur. In addition to the acceptor line, the presence of lithium in the cadmium sulfide lattice produces many donor lines which have not been previously studied.

Figure 28 shows the bound exciton spectrum of the donor centers in a high purity cadmium sulfide crystal. Mass spectrographic analysis showed 0.066ppma sodium, with lithium not detected. The crystal has been carefully equilibrated in argon with an equilibrium partial pressure of cadmium sulfide vapor at 900°C. At low exposure two lines are seen, $I_5(Cd)$ at 4869.13Å and a weaker line at 4866.48Å. At increased exposure other lines appear. One of these is 4868.42Å, a sodium line. A sharp line also appears at 4866.98Å. The lines at 4866.48Å and 4866.98Å are a zero field split doublet. They are the Γ_5 and Γ_6 exciton lines from an ionized donor, split by spin-exchange interaction. The stronger Γ_5 is from an allowed transition that is lifetime broadened. The weaker Γ_6 line is from a nominally forbidden transition with a long decay lifetime, and hence is much sharper than the Γ_5 line. Zeeman studies have confirmed these assumptions.

The exciton spectra of lithium doped cadmium sulfide are not as reproducible as those from the high purity crystals. Two crystals from the same run may show spectra, which at first, appear to be quite different. However, after one has studied many crystals, dominant lines are found, which are clearly associated with the lithium. To lessen the confusion that would attend the displaying of the very complex spectra normally seen, we have chosen four spectra, each of which shows a few of the dominant lithium donor lines.

Figure 32 shows the exciton spectrum of a well equilibrated specimen containing 2.1ppma of lithium. It shows three dominant lines: a lithium line at 4868.35Å, the $I_5(Li)$ at 4869.22Å, and a line at 4869.72Å which has been seen in some pure material and has been ascribed to a
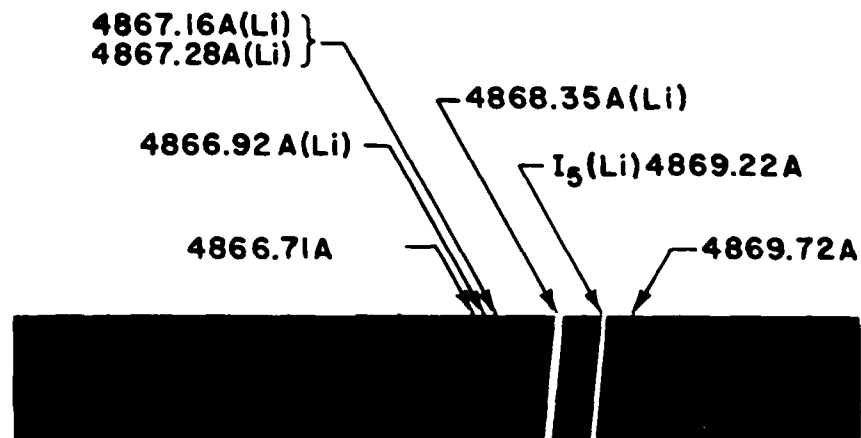
Figure 32. Donor Lines in CdS:Li Showing Lower Energy Neutral Donors

cadmium excess defect. It is noted that, with the exception of the
4869.72Å line, and the 4866.71Å line, which is a sodium line, there are
no lines that are ever seen in cadmium sulfide that is not doped with
lithium. Particularly, the $I_5(Cd)$ line, which is always dominant in
high purity material, is not present.

Figure 33 shows the spectrum from a crystal taken from the same
furnace run as in Figure 32. Its dominant neutral donor lines are about
the same. However, this specimen shows a pair of lines at 4864.5Å and
4865.02Å that is very clearly the zero-field split doublet from an
ionized donor. Such a splitting results from the spin-exchange inter-
action involving the unpaired electron in the ionized-donor exciton
complex. The strong, broad line is the Γ_5 and the weaker, sharp line,
the Γ_6 transition. Such a doublet associated with an excess cadmium
defect was seen in Figure 28, and a similar doublet has been reported as
being associated with an ionized interstitial sodium donor (Reference 9).

Figure 34 shows two strong lithium lines not seen in the previous
spectra. These are at 4869.95Å and 4870.91Å. These are among the lower
energy neutral donors. The strongest line at 4870.38Å has previously
been assigned to a sodium donor. Its presence shows a lack in the "sodium
free" lithium used for doping. It is interesting to note that the appear-
ance of the broad 4870.38Å line and the sharp 4870.91Å line is just that
for an ionized donor pair. Also the line separation of 0.26meV is just
the energy separation of the other ionized donor pairs. However, one
would not expect ionized donor pairs at such low energies. No Zeeman
studies have been made to resolve the question.

Figure 35 shows a group of lithium donor lines at somewhat greater
energy. The neutral donor lines are the single line at 4868.26Å and a
pair at 4867.16Å and 4867.29Å. The lower energy neutral donor lines seen
in the previous figures do not appear. 4867.16Å and 4867.29Å, when seen,
always appear together. This would indicate that they may be a true
doublet. A simple neutral point defect cannot show such an energy split-
ting. This leads to the probability that the center is an axial defect
with a symmetry lower than that of a simple point defect allowing a
splitting of the lines in the crystalline field.
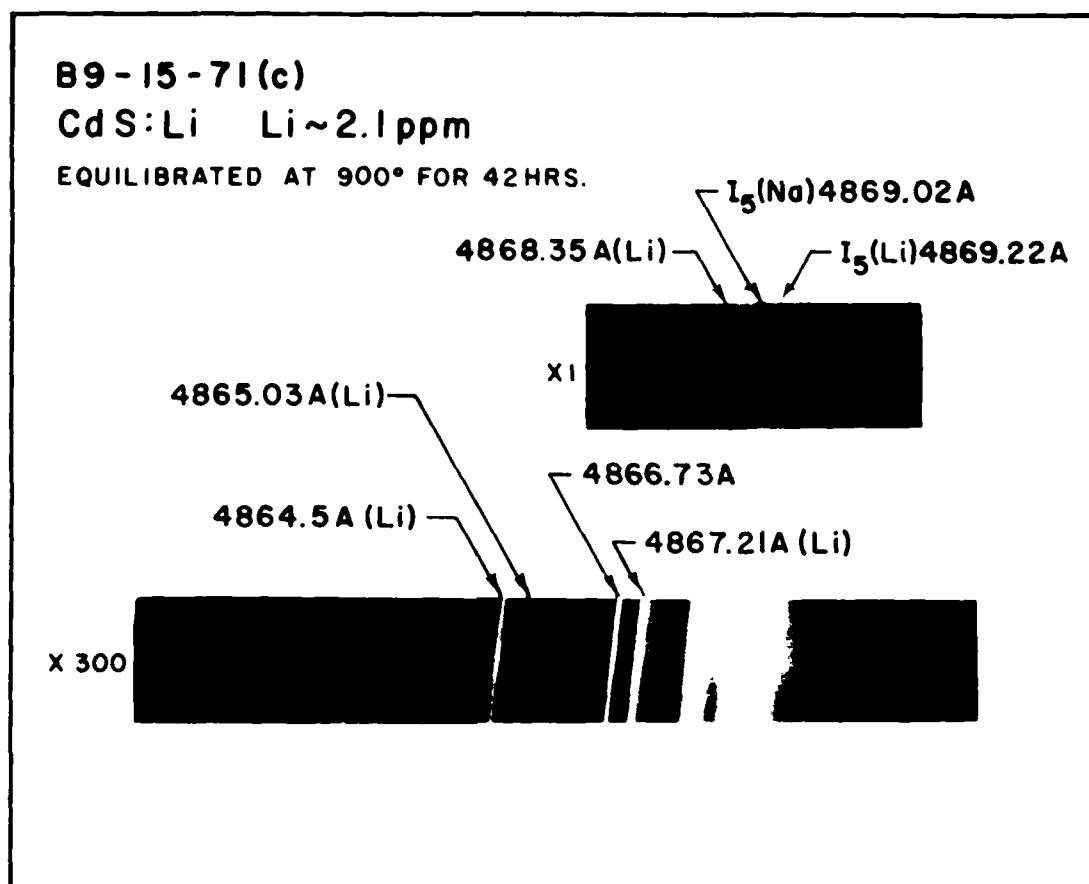
Figure 33.   Donor Lines in CdS:Li Showing Lower Energy Ionized
Donor
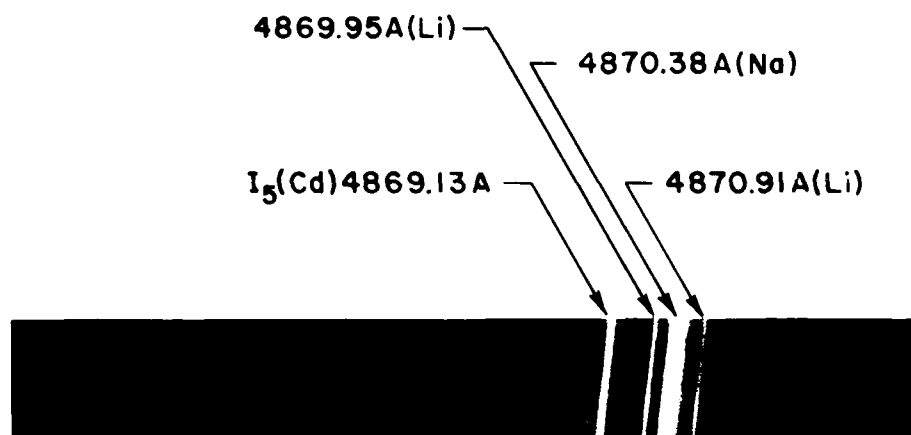
Figure 34. Donor Lines in CdS:Li Showing Dominant 4870.38Å Line

H2 - 29 - 72 (g)

Cd S : Li

EQUILIBRATED AT 900° FOR 30 MIN.

4864.80A(Li) — 4867.16A(Li)

4864.30A(Li) — 4867.29A(Li)

4868.26A(Li)
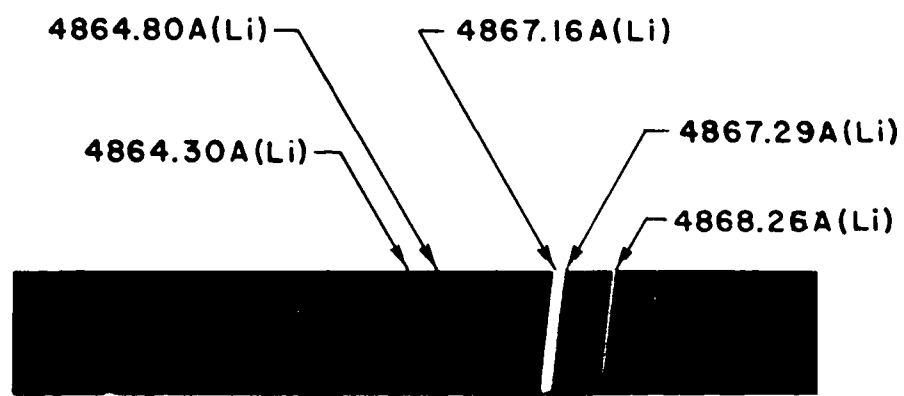
Figure 35. Donor Lines in CdS:Li Showing Higher Energy Neutral
Donors and Ionized Donor

The pair of lines at 4864.30Å and 4864.80Å are obviously a spin-exchange split doublet from an ionized donor, but a different donor from that seen in Figure 33.

From these figures it is seen that lithium in cadmium sulfide produces a number of dominant neutral donors and at least two ionized donors in the exciton spectra. It is also interesting to note that the lithium causes a suppression of most of the lines seen in pure or otherwise lightly doped crystals. This phenomenon may possibly be associated with the high ionic mobility of the lithium, which would allow it to drift rapidly through the lattice until immobilized in the proximity of another defect to form a complex center. This, of course, would also explain the origin of the large number of different dominant centers, many of which must certainly be complexes.

A notable exception is the 4870.38Å in Figure 34. This line is seen in many nominally pure crystals, in many sodium doped crystals, and in some lithium doped crystals, and has been previously ascribed to sodium. The fact that the line appears in some, but not all, of both sodium doped and lithium doped crystals and is so dominant in this particular specimen leads to the belief that both lithium and sodium are involved, that is, it is a lithium-sodium complex.

8.   DOUBLETS IN CdS:Na EXCITON SPECTRA

DOUBLETS IN THE BOUND EXCITON EMISSION
SPECTRUM OF SODIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
at Albuquerque, New Mexico 5-7 June 1972

When high purity cadmium sulfide crystals are carefully equilibrated in an atmosphere containing the vapor of one of the component elements, strong bound-exciton lines are produced in the low temperature emission, which are characteristic of the component. Similarly, if the crystals are equilibrated in an atmosphere containing sodium vapor, dominant lines

characteristic of the sodium are produced. One of these lines is the well known acceptor I_1(Na) line at 4888.22Å which is known to be associated with a sodium interstitial (References 7, 8). The I_1(Na) center is unstable and the line is rarely seen even in crystals that are known to contain sodium. Sodium in the cadmium sulfide lattice also produces many donor lines. Some of these have been discussed in a previous paper (Reference 9).

Figure 36 shows the helium temperature bound exciton spectrum from a nominally pure cadmium sulfide crystal. The low exposure spectrum shows a line at 4866.48Å and the I_5 line at 4869.13Å. These are two lines that seem particularly characteristic of the highest purity material. The 4866.48Å line is from the allowed Γ_5 transition from an ionized donor, and the I_5 line is from a neutral donor. The donor, which is assumed to be the same for both lines, is probably a cadmium excess defect. The high exposure line shows a sharp line at 4866.98Å. This is from the Γ_6 transition, which is nominally forbidden, from the ionized donor. The 4866.48Å and 4866.98Å lines are the components of a zero field split doublet. The splitting results from the spin-exchange interaction involving the unpaired electron in the ionized donor-exciton complex.

The drawing shows two lines that are obscured by overexposure in the high exposure spectrum. These are the lines at 4869.32Å and 4869.72Å. They are seen in high purity cadmium sulfide crystals, but not consistently. They also do not appear consistently in association with any dopants that we have studied. We believe that these lines are associated with complexes involving native defects. Such centers would be more dependent on growth conditions than the simple defects, and hence would be less reproducible.

Figure 37 shows the spectrum of a cadmium sulfide crystal doped with sodium. This spectrum shows a pair of strong lines at 4867.91Å and 4868.16Å, and a weaker pair at 4868.41Å and 4868.62Å. These pairs are seen in most sodium doped cadmium sulfide crystals and are certainly associated with the sodium. If we pair a strong line with a weak line instead of a strong line with a strong line, we have two pairs that look
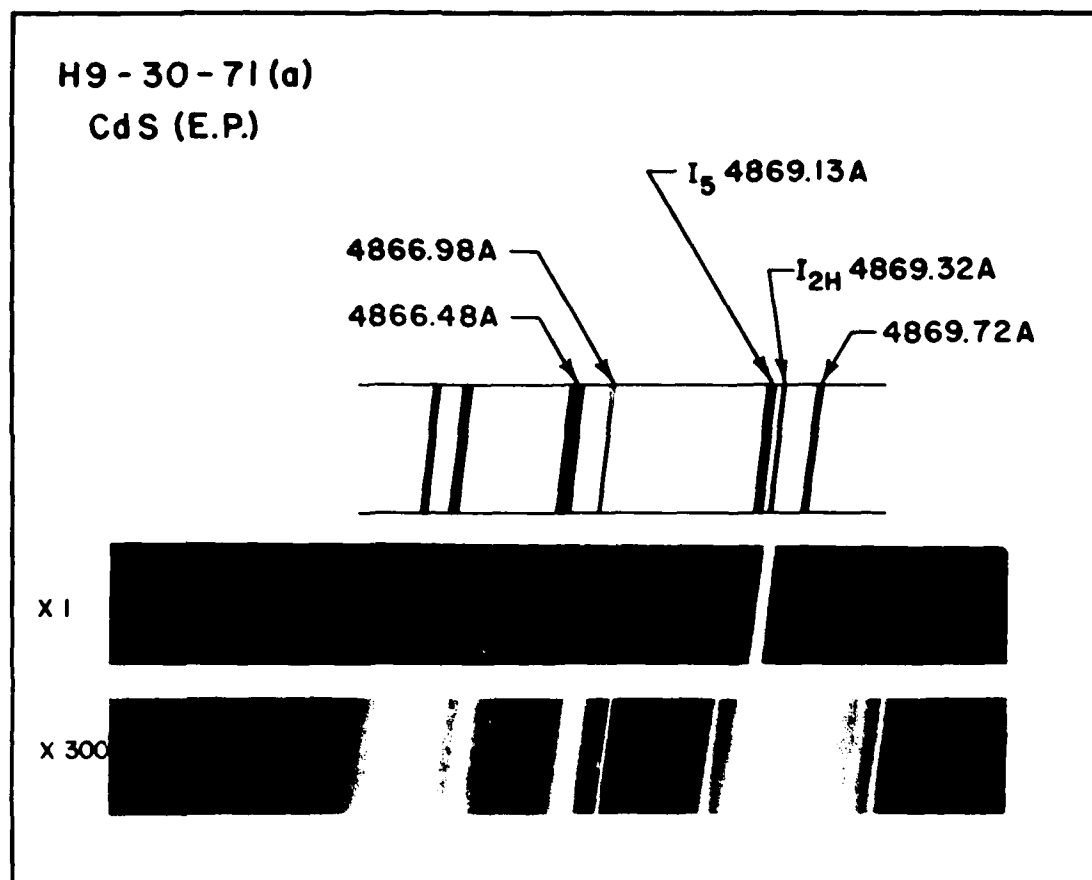
Figure 36. Donor Lines in High Purity Cadmium Sulfide
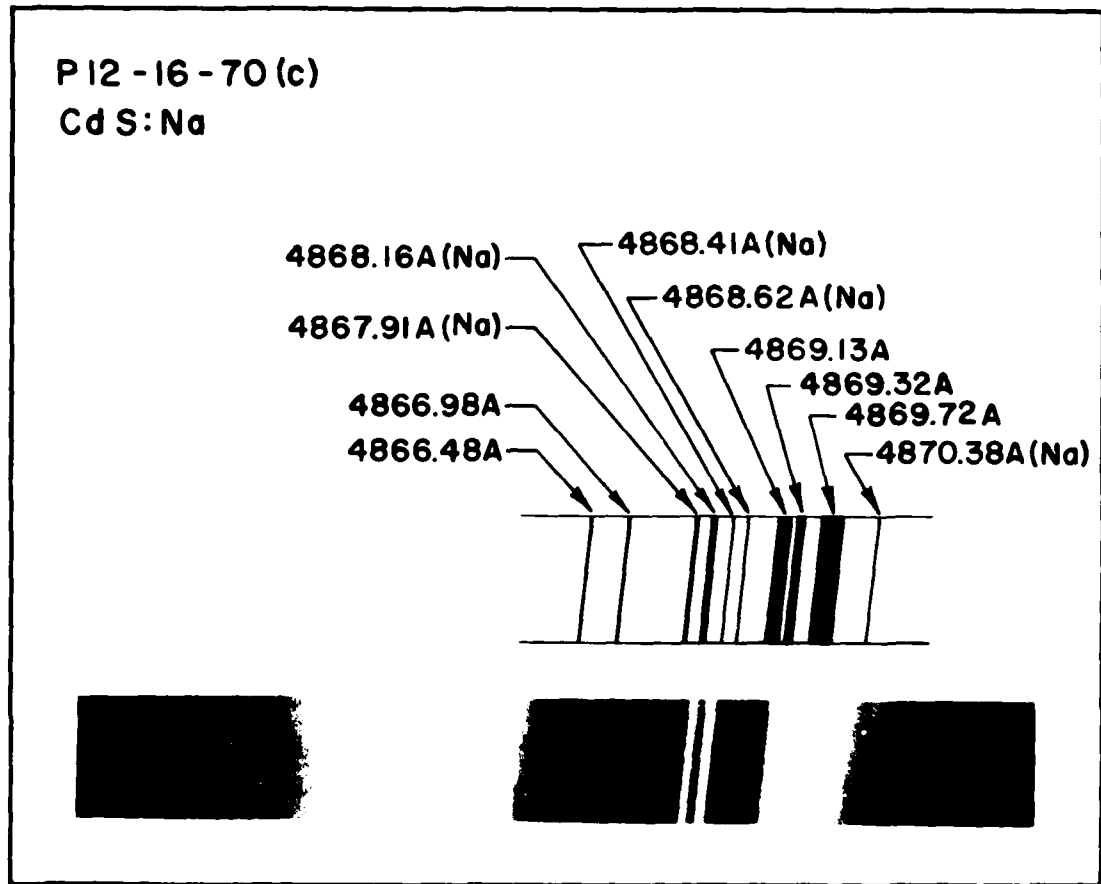
Figure 37. Donor Lines in Sodium Doped Cadmium Sulfide Showing
Doublets 4867.91Å, 4868.16Å, 4868.41Å, and 4868.62Å

very much like the ionized donor pair in Figure 36, and have about the same separation of 0.26meV. In a previous paper (Reference 9) we described an ionized donor doublet in sodium doped cadmium sulfide, which appears at 4866.22Å and 4866.71Å. We believe these lines to be associated with a sodium interstitial. These two doublets, if indeed they are from ionized donors, are most likely associated with complexes involving sodium interstitials.

A dominant pair of lines in sodium doped cadmium sulfide is the I_5 pair at 4869.02Å and 4869.13Å (Figure 38). This pair is not a true doublet, since we never see the line at 4869.02Å except in sodium doped crystals, while the line at 4869.13Å is seen in the purest crystals.

Figure 39 shows four doublets in the region of lower energy neutral donors. These doublets have been seen only in sodium doped crystals. The energy separations of the doublets range from 0.05meV to 0.07meV. These values are too small to come from spin-exchange splitting. True, zero field split doublets cannot be associated with a simple point defect such as a sodium interstitial. However, they can be associated with axial defects such as Na_i-V_{cd}, Cd_i-Cd_{Na}, or Na_i-Cd_{Na}. The data that we have do not make possible any further conjecture about the structure or composition of the centers.

9. MONOVALENT METALS IN CADMIUM SULFIDE

FURNACE DOPING OF CADMIUM SULFIDE CRYSTALS WITH MONOVALENT METALS IN RELATIONSHIP TO THE BOUND EXCITON SPECTRA

Lawrence C. Greene and Henry A. Wilson

Very high purity crystals of cadmium sulfide which have been well equilibrated show a very simple low-temperature emission spectrum in the spectral region associated with bound excitons. Five lines appear to be associated with the undoped crystal. These are 4866.48Å, 4866.98Å, 4869.13Å, 4869.32Å, and 4869.72Å. Other lines may be seen but these may be shown to
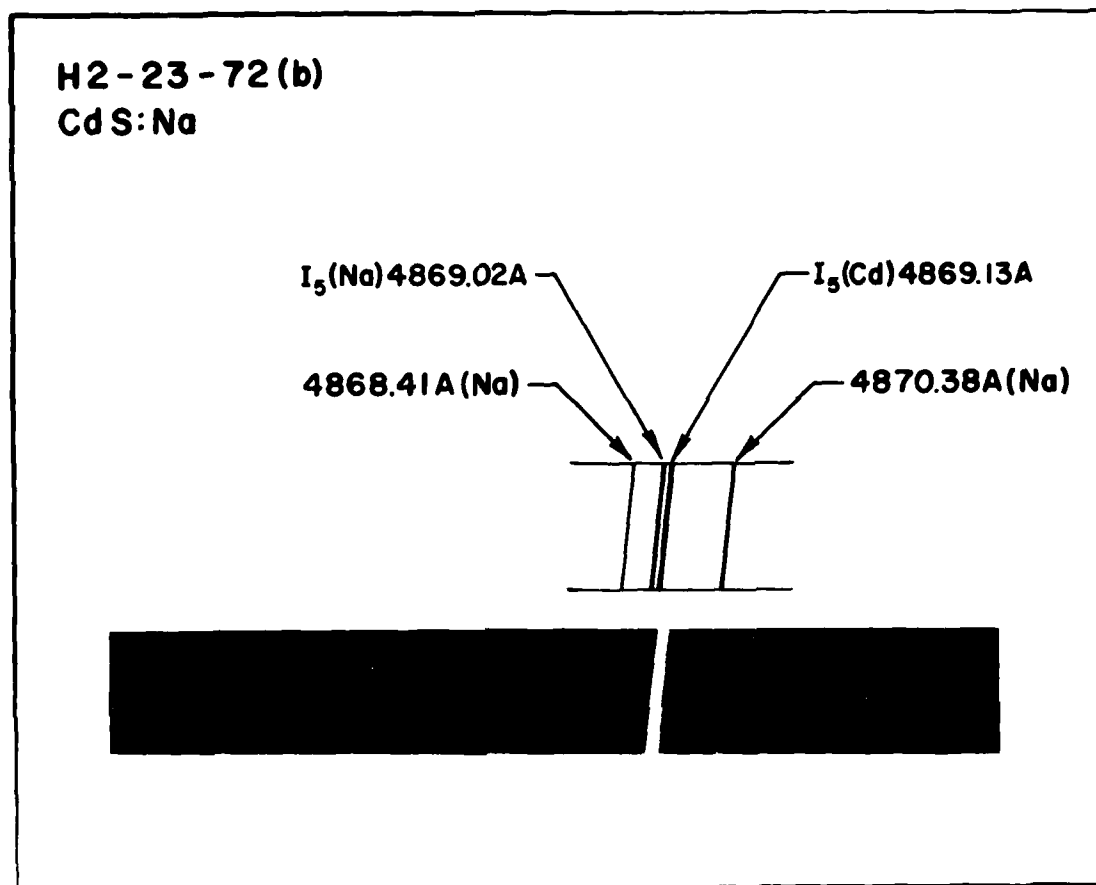
Figure 38.   Donor Lines in Sodium Doped Cadmium Sulfide Showing
             I_5 Pair
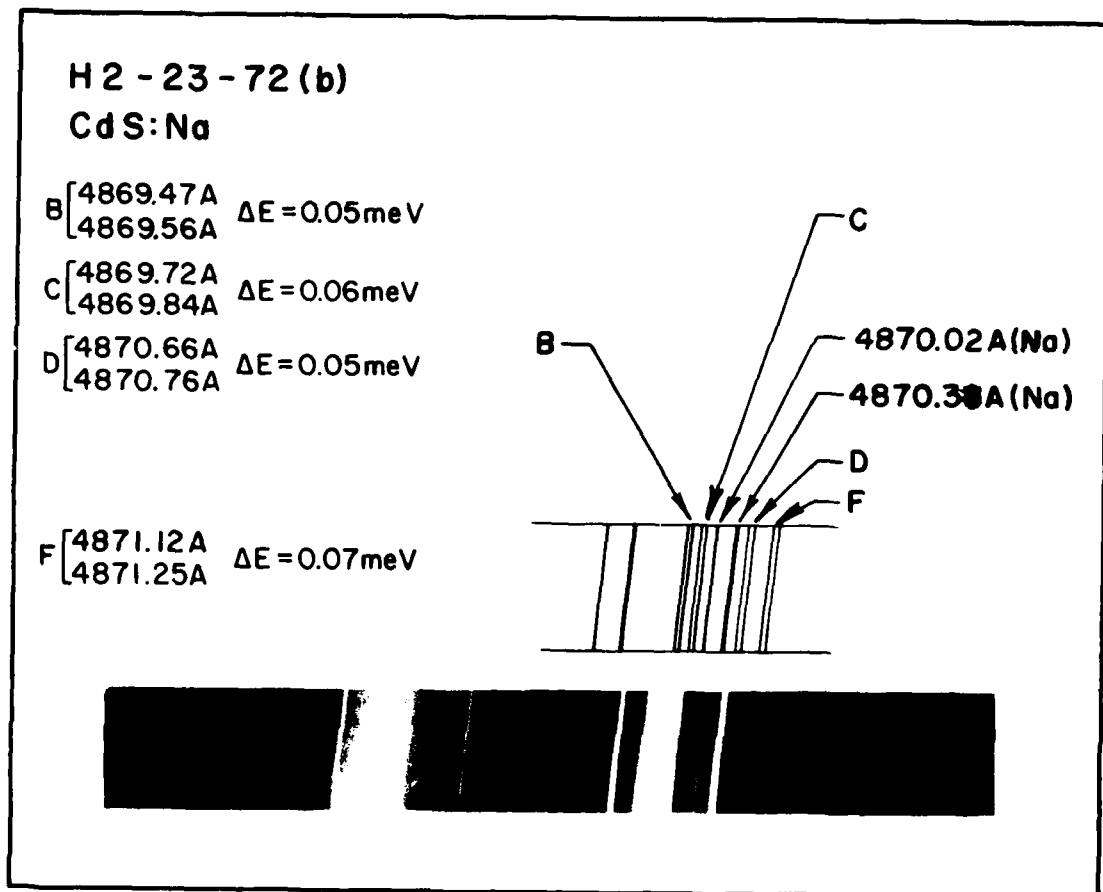
Figure 39.   Donor Lines in Sodium Doped Cadmium Sulfide Showing
Closely Spaced Doublets Near 4870.38Å Line

be associated with chemical impurities. Three monovalent metals in particular are considered in this paper: lithium, sodium, and silver. The crystals were grown, doped, and equilibrated in a system described by Greene and Geesner (Reference 10). The lithium doping was accomplished by passing lithium vapor over the crystals after growth had been completed. Bound exciton lines in the donor region of the spectrum associated with lithium are 4864.5$\overset{\circ}{A}$, 4865.03$\overset{\circ}{A}$, 4866.92$\overset{\circ}{A}$, 4867.28$\overset{\circ}{A}$, 4868.35$\overset{\circ}{A}$, and 4869.22$\overset{\circ}{A}$ as well as the well known I_1(Li) acceptor line at 4888.52$\overset{\circ}{A}$. Sodium doping was accomplished by passing sodium sulfide vapor over the crystals. There are more than 30 dominant donor lines associated with sodium, the most characteristic being 4866.21$\overset{\circ}{A}$, 4866.71$\overset{\circ}{A}$, 4868.14$\overset{\circ}{A}$, 4868.42$\overset{\circ}{A}$, 4869.02$\overset{\circ}{A}$, and 4870.38$\overset{\circ}{A}$. Silver doping was accomplished by adding silver powder to the cadmium sulfide charge. As with the sodium, there are a large number of donor lines associated with the silver. Characteristic silver lines are 4865.64$\overset{\circ}{A}$, 4865.78$\overset{\circ}{A}$, 4867.74$\overset{\circ}{A}$, 4868.08$\overset{\circ}{A}$, 4869.26$\overset{\circ}{A}$, and 4870.61$\overset{\circ}{A}$. In all three cases the appearance of particular lines is critically dependent on the furnace procedures.

In any crystal growing investigation most important aspects are quality and purity. The problem of purity can be particularly difficult. Often it is not easy to know whether we are really growing purer crystals or just contaminating our material. We need a fast, simple, and inexpensive method of following our progress. In early studies of the elemental semiconductors this was well accomplished by simple electrical measurements to determine carrier concentrations or donor and acceptor ionization energies. In the compound semiconductors these are less useful since they tell us very little about the fundamental nature of the defects and this is the information we need to feed back to the crystal grower.

In our laboratory there has been for many years a strong interest in exciton phenomena in the II-VI compounds and especially in cadmium sulfide. Cadmium sulfide has a particular rich bound exciton spectrum and it is natural that we should turn to such phenomena to seek an answer to the problem. In this section we propose to show some of the

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possibilities of this approach by discussing the bound exciton spectra of three particularly active impurities in cadmium sulfide: lithium, sodium, and silver.

The crystals used were thin platelets grown by an inert gas transport process. The technique and furnace configuration are well known. The crystals were doped and equilibrated in the growth chamber. The exciton emission spectra were made with the crystal immersed in pumped helium at below 2K.

In Figure 36 we see the dominant bound exciton lines in an undoped cadmium sulfide crystal. The spectrum is dominated by the well-known I_5 line at $4869.13\mathring{A}$. A second separate strong line appears at $4866.48\mathring{A}$. Increased exposure brings out lines at $4866.98\mathring{A}$, and $4869.72\mathring{A}$. With increased equilibration temperature the I_{2H} line at $4869.32\mathring{A}$ becomes very strong. The spectrum of undoped cadmium sulfide is then largely characterized by these five lines.

Figure 40 shows spectra from two lithium-doped crystals. The upper spectrum is from a crystal equilibrated at 900° for 30 minutes. Atomic absorption analysis averaged over the run shows about 1.6ppm lithium. There are five lines all characteristic of lithium, but the closely spaced pair near $4867\mathring{A}$ and the line at $4868.27\mathring{A}$ will be most important for identifying lithium. It is noteworthy that none of the undoped lines appear here, not even the I_5 line.

In the lower spectrum the crystal has been equilibrated at the same temperature for 42 hours. It has about the same concentration of lithium. Now another strong line appears very near the position of the undoped I_5 line. We call this the $I_5(Li)$ line. Then there are four dominant lines which identify lithium. These lines are in the region of the spectrum usually considered associated with excitons bound to donors. The well-known $I_1(Li)$ acceptor line is also very strong in these specimens, but it is not a good line for determining the presence or absence of lithium.
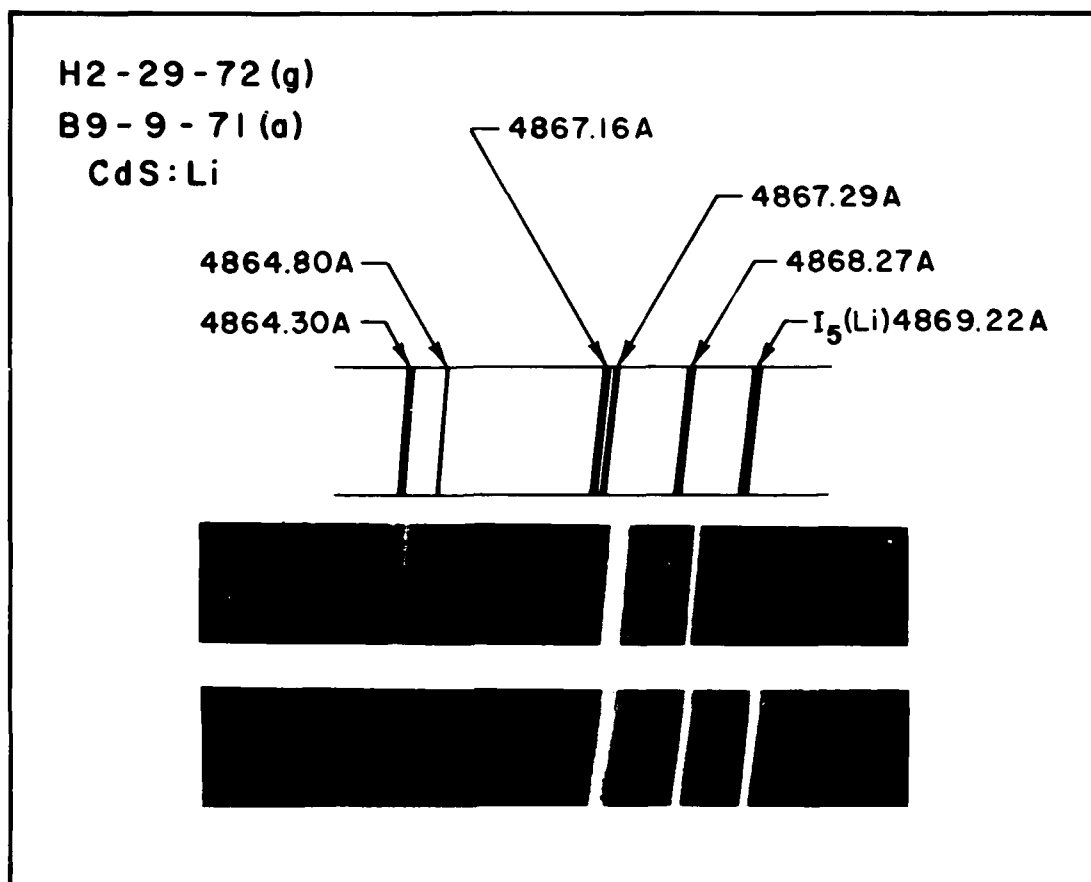
Figure 40. Bound Exciton Spectrum of CdS:Li Showing Character-
istic Lithium Lines

In Figure 41 we have the spectra of two crystals doped with sodium. The upper spectrum is from a crystal containing about 10.4ppma of sodium. It is characterized by three pairs of lines. The three dominant lines seen in the undoped crystal appear here: the lines at 4866.48$\overset{\circ}{A}$ and 4866.98$\overset{\circ}{A}$ and the I_5(Cd) line at 4869.13$\overset{\circ}{A}$. Paired with each of these is a characteristic sodium line: lines at 4866.22$\overset{\circ}{A}$, 4866.71$\overset{\circ}{A}$, and the I_5(Na) line at 4869.02$\overset{\circ}{A}$. The crystal represented in the lower spectrum contained about 0.62ppma of sodium. Its spectrum is quite complex, but the lines at 4868.14$\overset{\circ}{A}$, 4868.41$\overset{\circ}{A}$, the I_5(Na) at 4869.02$\overset{\circ}{A}$ and the 4870.37$\overset{\circ}{A}$ are the most useful for identifying the presence of sodium.

To get an idea of the sensitivity of this method we will take another look at the undoped specimen in Figure 42 using greater exposure. Mass spectrographic analysis using electronic detection shows 66ppba of sodium. Two of the identifying lines at 4868.42$\overset{\circ}{A}$ and 4870.37$\overset{\circ}{A}$ stand out clearly.

Finally we take a brief look at silver doped cadmium sulfide in Figure 43. The study of silver doping has presented more of a problem because of interference from adjacent sodium lines. The apparent complexity of the spectrum is due to the presence of some of the sodium lines. We have separated out the silver lines in the drawing. The dominant silver line is the I_5(Ag) at 4869.26$\overset{\circ}{A}$. Other lines that are helpful in detecting silver are those at 4867.74$\overset{\circ}{A}$, 4868.08$\overset{\circ}{A}$, 4869.85$\overset{\circ}{A}$, and 4870.51$\overset{\circ}{A}$.

In Figure 44 we bring the data together in tabulated form showing the dominant characteristic bound exciton emission lines of undoped and doped cadmium sulfide.
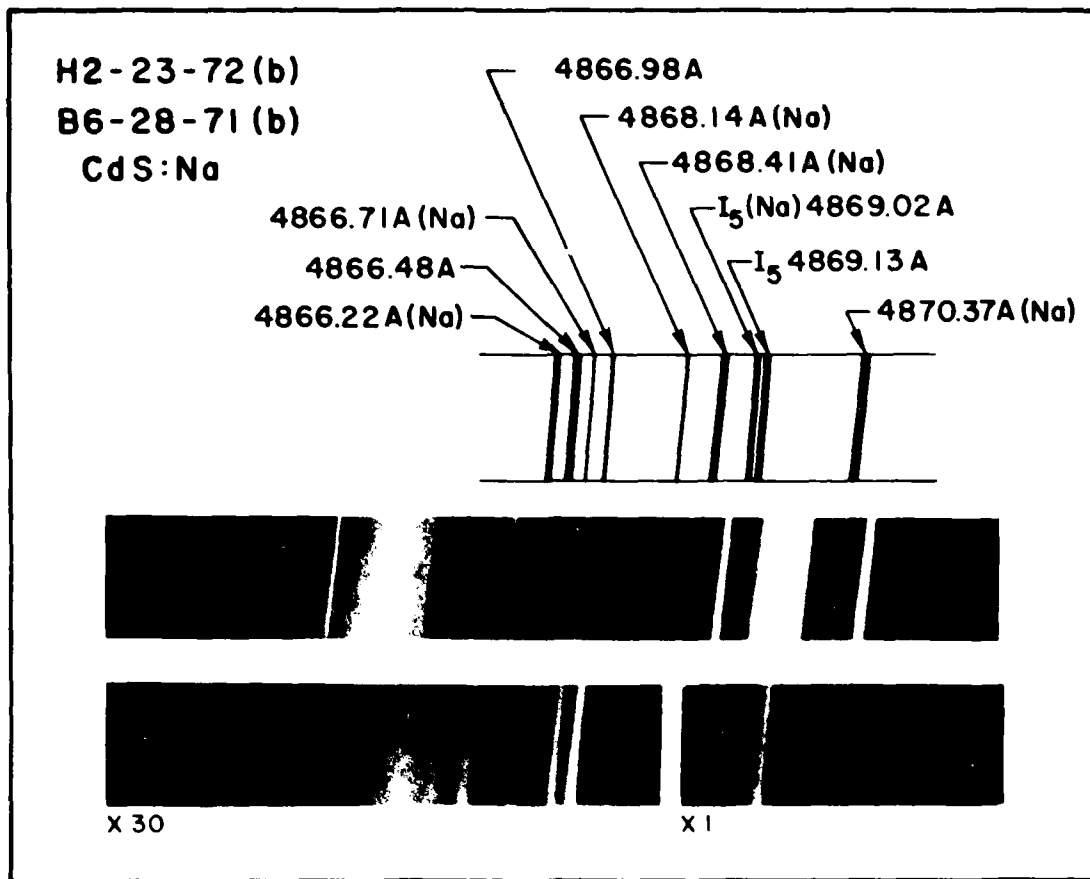
Figure 41. Bound Exciton Spectrum of CdS:Na Showing Characteristic Sodium Lines
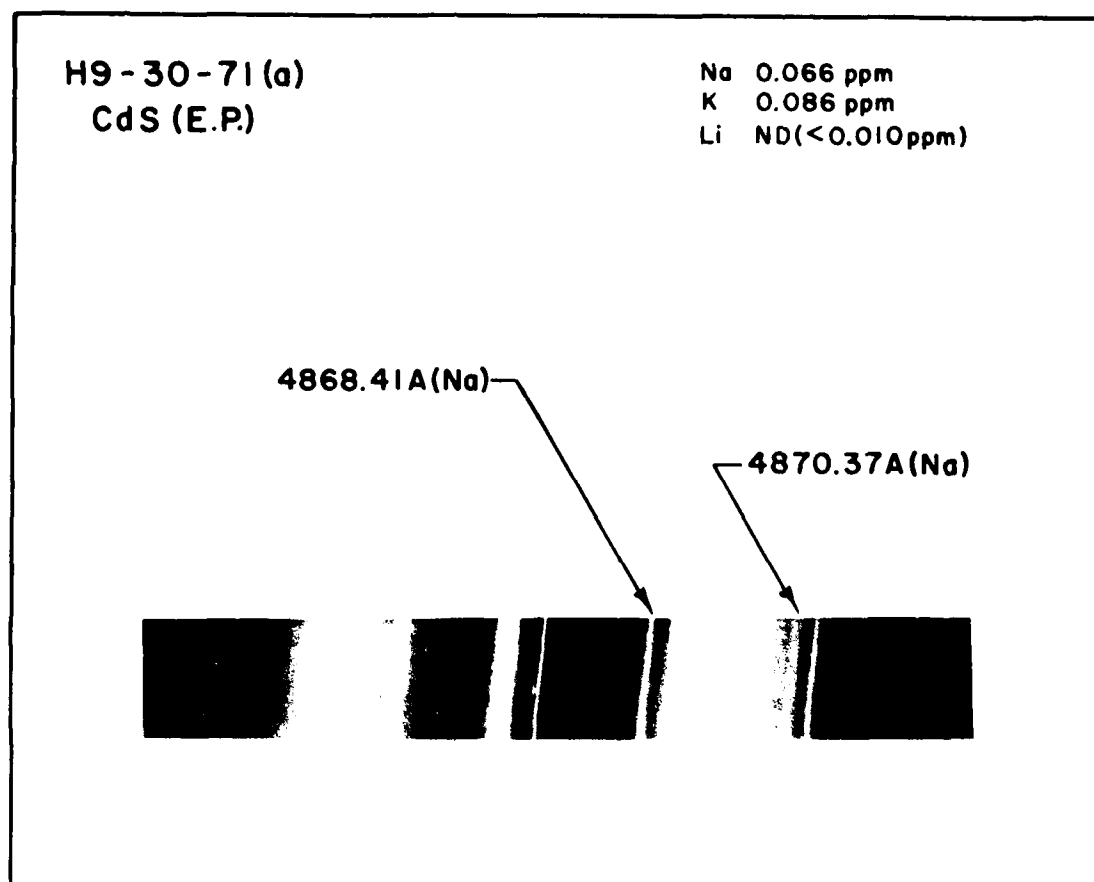
Figure 42. Bound Exciton Spectrum of High Purity Cadmium
Sulfide Showing Residual Sodium Lines
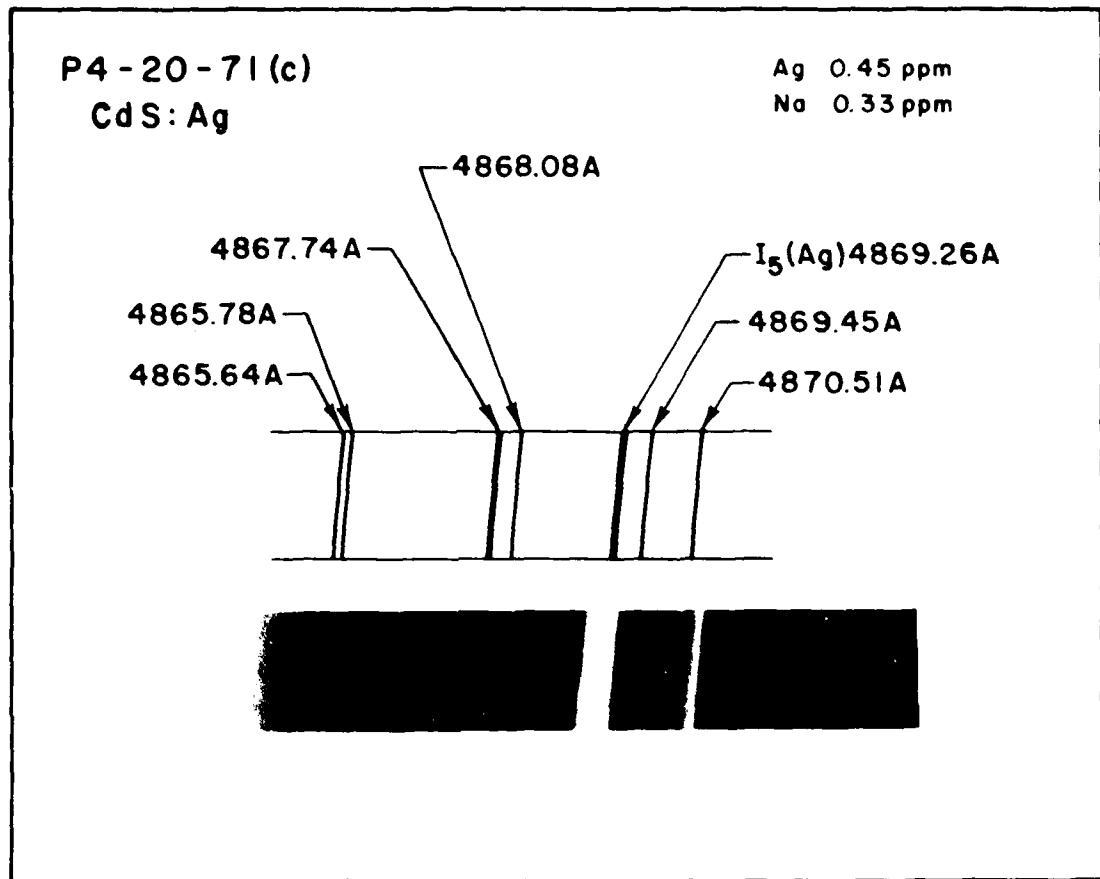
Figure 43. Bound Exciton Spectrum of CdS:Ag Showing Character-
istic Silver Lines

UNDOPED	LITHIUM	SODIUM	SILVER
	4864.30 A		
	4864.80 A		
			4865.64 A
			4865.78 A
		4866.22 A	
4866.48 A			
		4866.71 A	
I_2 4866.98 A			
	4867.16 A		
	4867.29 A		
			4867.74 A
			4868.08 A
		4868.14 A	
	4868.27 A		
		4868.41 A	
		I_5(Na)4869.02 A	
I_5 4869.13 A			
	I_5(Li)4869.22 A		
			I_5(Ag)4869.26 A
I_{2H} 4869.32 A			
			4869.45 A
4869.72 A			
		4870.37 A	
			4870.51 A

Figure 44. Tabulation of Characteristic Bound Exciton Lines in
Cadmium Sulfide Doped with Monovalent Metals

10. ZEEMAN SPLITTING OF SODIUM LINES

ZEEMAN SPLITTING OF CHARACTERISTIC SODIUM LINES
IN THE BOUND EXCITON SPECTRUM OF CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
at Los Angeles 27-29 December 1972

The bound exciton emission spectrum of well equilibrated, undoped cadmium sulfide is dominated by three lines: I_5 at 4869.13Å, J_2 at 4866.98Å, and J_3 at 4866.48Å. I_5 has been extensively studied and is known to arise from an exciton bound to a neutral donor (Reference 11). J_2 and J_3 are believed to be the spin-split doublet arising from an ionized donor, probably the same donor responsible for I_5. J_3 arises from the Γ_5 to Γ_1 transition in Figure 45. This is an allowed transition with a short lifetime. The line is strong and lifetime broadened. J_2 arises from the Γ_6 to Γ_1 transition, which is a nominally forbidden transition. The line is weak and very sharp. In a magnetic field, I_5 splits linearly, and if the H vector is perpendicular to the c-axis of the crystal, only two lines are seen. This splitting is seen in the drawing in Figure 46. Figure 45 shows the splitting of an ionized donor in a magnetic field with $\theta \neq 90°$ and with $\theta = 90°$. It is seen from these diagrams that when $H \perp c$ there are two lines but in this case the line separation is not zero for H=o, and the lines do not split linearly. With these facts in mind it becomes possible to distinguish between neutral donor lines and ionized donor lines on the basis of their splitting in a magnetic field as is shown in Figure 46.

When cadmium sulfide crystals are doped with sodium, a large number of characteristic lines may be produced. Several of the lines most useful for identifying sodium are shown in Figure 47. The characteristic neutral donors are $J_6(Na)$ at 4868.42Å, $I_5(Na)$ at 4869.02Å and, $J_7(Na)$ at 4870.37Å. Two lines also appear among the ionized donors: $J_3(Na)$ at 4866.21Å and $J_2(Na)$ at 4866.71Å.

Figure 48 shows these neutral and ionized donor lines in zero field and in fields of 12.2kG and 31.4kG with H perpendicular to c. It is seen that $J_6(Na)$, $I_5(Na)$, and $J_7(Na)$ all split like I_5 and hence it is shown
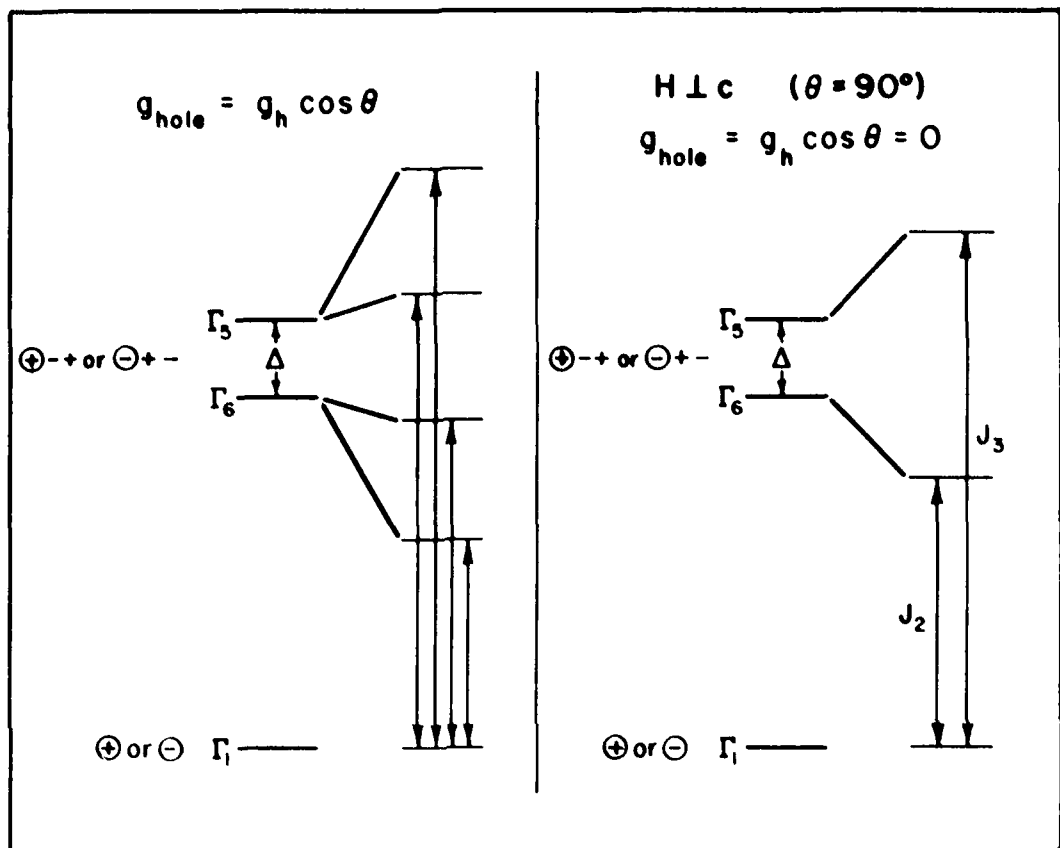
Figure 45. Zeeman Splitting Diagram for Ionized Donor in Cadmium Sulfide
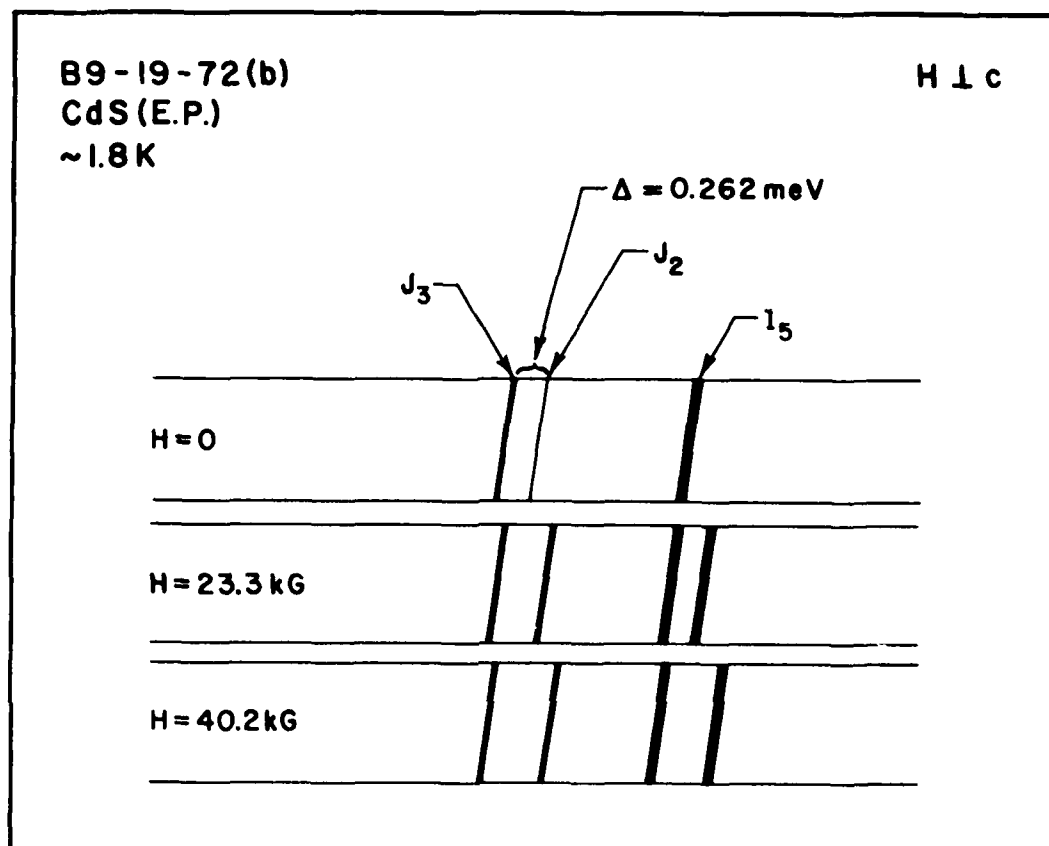
Figure 46. Neutral and Ionized Donors in Pure Cadmium Sulfide, Showing Zeeman Splitting
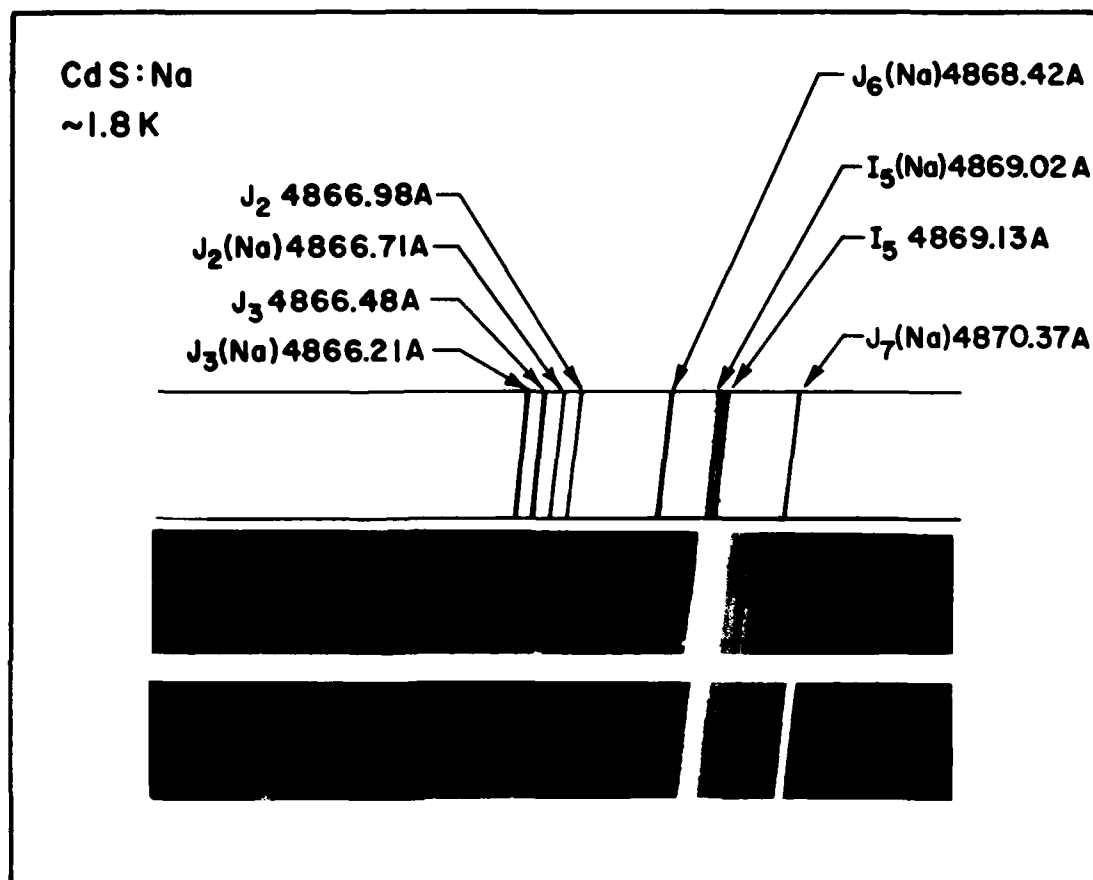
Figure 47.   Characteristic Sodium Lines in Bound Exciton
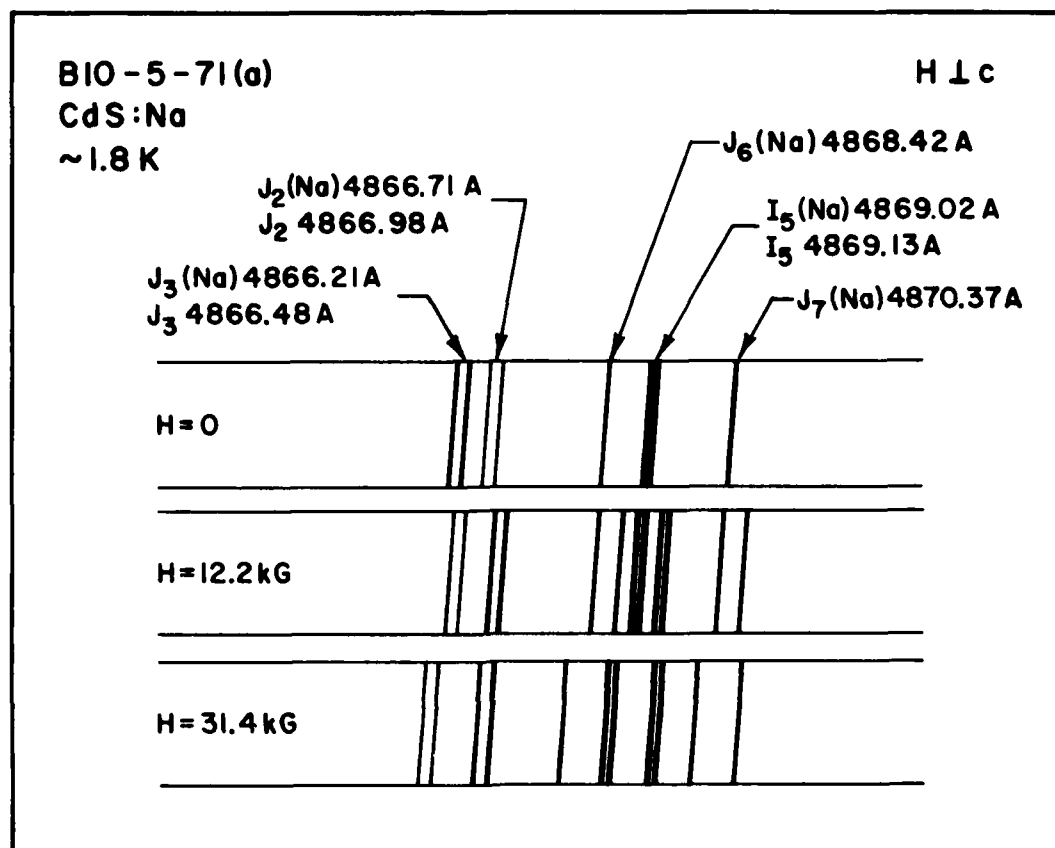Spectrum of Cadmium Sulfide

Figure 48.   Neutral and Ionized Donors in Sodium Doped Cadmium
Sulfide, Showing Zeeman Splitting

that we were correct in our assumption that these lines are associated
with neutral donors. J_3(Na) and J_2(Na) split like J_3 and J_2 and therefore
we may conclude that they are associated with an ionized donor. This
donor is probably a sodium interstitial.

11. ZEEMAN SPLITTING OF POTASSIUM LINES

ZEEMAN SPLITTING OF CHARACTERISTIC POTASSIUM LINES IN THE BOUND EXCITON SPECTRUM OF POTASSIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

Presented before the American Physical Society
San Diego, 19-22 March 1973

Figure 36 shows that the bound exciton emission spectrum of high
purity cadmium sulfide that has been well equilibrated is dominated by
three lines. The strongest of these is the I_5 line. This line has been
extensively studied and is known to be associated with the decay of an
exciton bound to a neutral donor. The other lines at shorter wavelengths
are the J_2 and J_3 lines. These lines appear with different relative
intensities in different crystals and in the very best crystals J_2 may
not be seen at all. One might be tempted to conclude that the two lines
arise from different centers. The appearance of the pair, however, with
the shorter wavelength line broad and more intense and the longer wave-
length line weaker and very sharp is that seen in the decay of an exciton
bound to an ionized center. The two lines arise from a spin exchange
splitting into Γ_5 and Γ_6 components. The Γ_5, from which J_3 arises, is
lifetime broadened. The Γ_6 decay is nominally forbidden so the J_2 is
normally very sharp. Other studies verify this assignment. For example,
decreasing the excitation intensity causes an increase in the relative
intensity of J_2. In a magnetic field J_2 is also intensified and the
lines separate as one would except for an exciton bound to an ionized
center. In cadmium sulfide an ionized center binding an exciton must
be a donor.

The first spectrum in Figure 49 is from a sodium doped cadmium
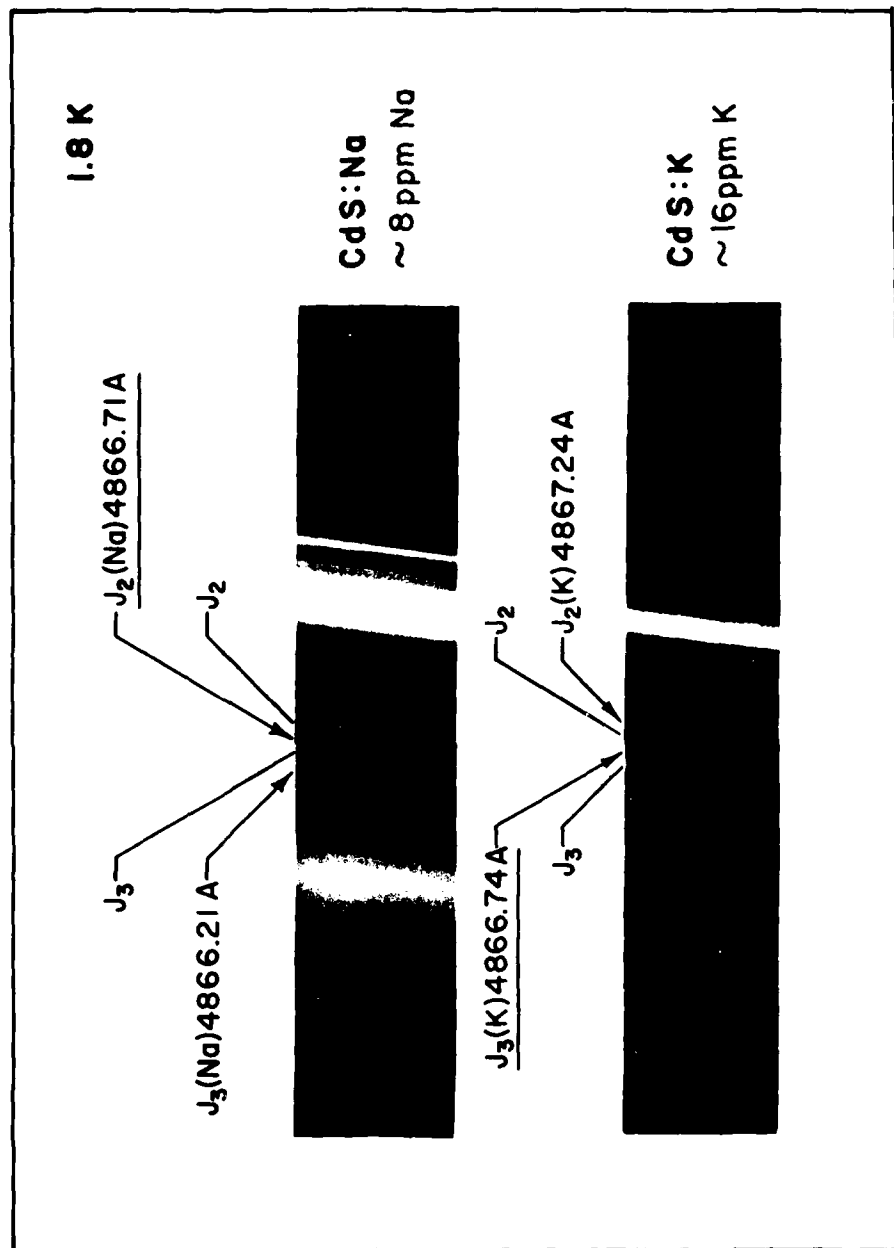sulfide crystal. This spectrum shows the J_2 and J_3 lines seen in Figure 36,

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Figure 49. Ionized Donors in Sodium and Potassium Doped Cadmium Sulfide

but also a second pair of lines: $J_2(Na)$ at 4866.71Å and $J_3(Na)$ at 4866.21Å.
The $J_2(Na)$ and $J_3(Na)$ pair have the same separation as the J_2 and J_3 lines,
that is 0.026meV. Previous studies have shown that both pairs of lines
show Zeeman splittings consistent with their assignment as being associated
with ionized donors. In the case of $J_3(Na)$ and $J_2(Na)$ it is assumed that
the donor is the sodium interstitial.

The second spectrum in Figure 49 is from a potassium doped crystal.
Here we see a group of four lines that looks just like the ionized donor
quartet in the sodium doped crystal. However, measurement of the line
wavelengths shows that we have J_2 and J_3 along with two lines at longer
rather than shorter wavelengths. We tentatively call these $J_3(K)$ at
4866.74Å and $J_2(K)$ at 4867.24Å. The line separation for this pair is the
same as for the others but a clear assignment is more difficult because
the line we have called $J_3(K)$ in the lower spectrum does not differ sig-
nificantly in wavelength from $J_2(Na)$ in the upper spectrum. If our assign-
ment is correct, the sodium line, $J_2(Na)$, which is a Γ_6 line, and the
potassium line, $J_3(K)$, which is a Γ_5 line will behave differently in a
magnetic field.

Figure 50 shows the emission spectra of the three types of crystals
in a magnetic field with $H \perp C$. In each spectrum each pair of lines splits
as predicted for an ionized donor. In the middle spectrum $J_2(Na)$ behaves
like a Γ_6 exciton, that is it moves to longer wavelength. In the lower
spectrum $J_3(K)$, at nearly the same wavelength, behaves like a Γ_5 exciton;
it moves to shorter wavelength-that is most of it does. We see that a
small component has moved to longer wavelength like $J_2(Na)$ and this shows
us that there is a residual sodium contamination in the crystals. This
weak $J_2(Na)$ could not be seen except in a field.

We see in these spectra that the J_2 or Γ_6 lines are stronger than the
J_3 or Γ_5 lines, in contrast to what was seen in the spectra in Figure 49.
This is brought about by a lifting of the selection rules by the magnetic
field. This phenomenon makes it possible to see impurity lines that are
otherwise hidden in the background in high purity crystals. The top
spectrum in Figure 50 shows the spectrum of a very high purity crystal,
essentially the same as the one shown in Figure 36, but in a magnetic
field of 40.2kG. $J_2(Na)$ and $J_2(K)$ are seen, one on each side of the
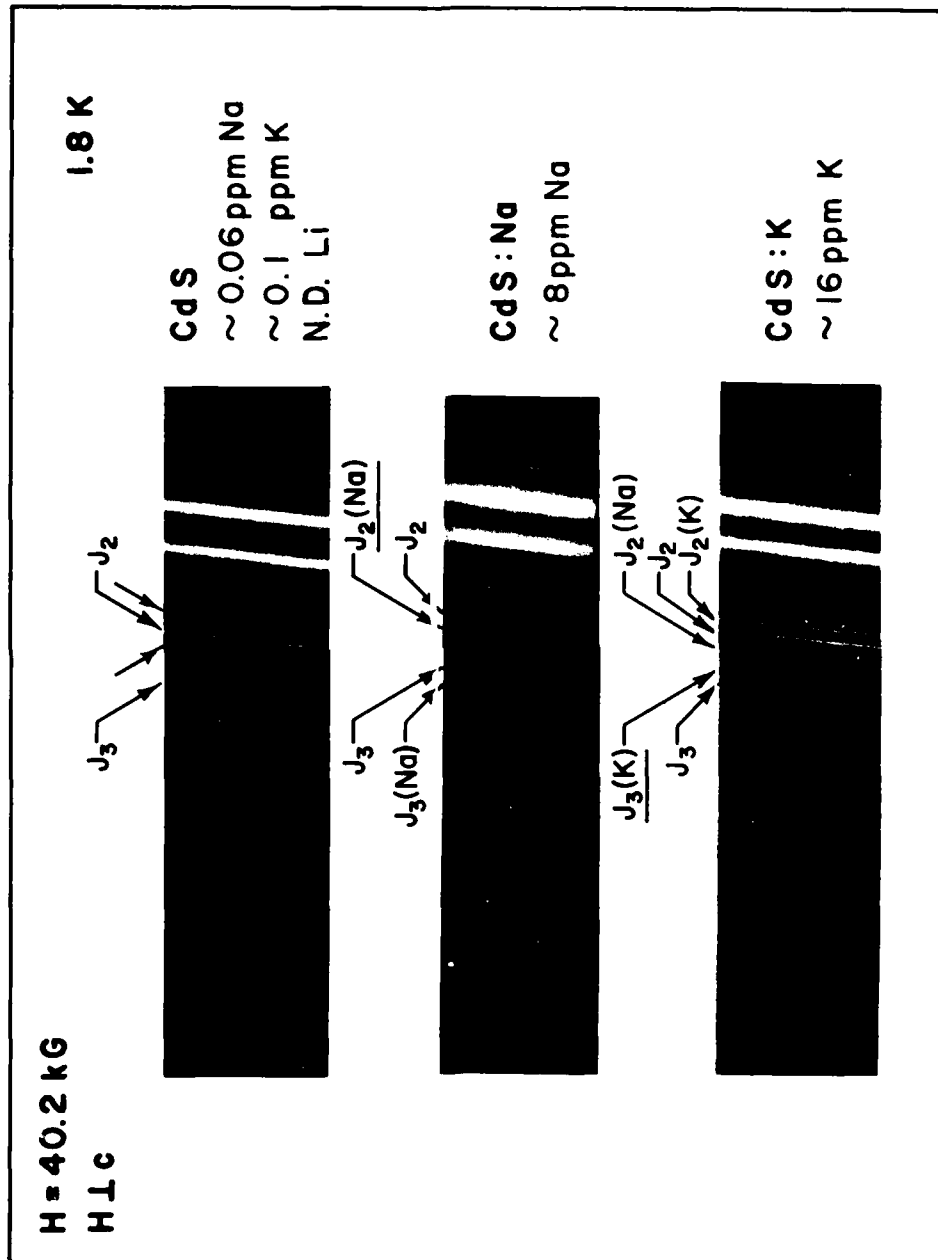strong J_2 line.

Figure 50. The Splitting of Ionized Donors in Sodium and Potassium Doped Cadmium Sulfide in a Magnetic Field

Although the ionized donor pair associated with the potassium donor
are seen clearly in these specimens, no neutral donor lines or acceptor
lines were seen that could be associated with the presence of potassium
in the lattice.

12. ZEEMAN SPLITTING OF RUBIDIUM LINES

CHARACTERISTIC IONIZED DONOR LINES IN THE BOUND
EXCITON SPECTRUM OF RUBIDIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

The bound exciton emission spectrum of high purity cadmium sulfide
is dominated by three lines (Figure 36). The strongest of these is the
I_5 line, a line which is well known to be associated with the decay of
an exciton bound to a neutral donor. The others are the J_2 and J_3 lines.
The appearance of these lines is of particular importance. J_3 is rela-
tively much stronger and broader. This combination of a fat line and
a skinny line, closely spaced, is characteristic of a spin exchange split
pair arising from the decay of an exciton bound to an ionized donor.
The J_3 line comes from an allowed transition and is lifetime broadened.
The J_2 line, which comes from a nominally forbidden transition, is much
weaker and very sharp. This assignment for these lines has been con-
firmed by magnetic field measurements.

Figure 49 shows the spectrum of a crystal lightly doped with sodium.
A second pair of lines appears at shorter wavelengths. These are J_2(Na)
and J_3(Na). They are indicated by the arrows in the upper spectrum.
Here again we see the intensity and line-width relationships as in
Figure 36. And again Zeeman studies confirm that this is an ionized
donor pair. In the lower spectrum we see lines from a potassium doped
crystal. Here we have a quartet of lines that look like the lines in the
sodium doped crystal. However, measurements of wavelengths show that
two of these lines are different and these are indicated by the arrows.

Again the new pair of lines $J_2(K)$ and $J_3(K)$ is shown to be an ionized donor pair. In each of these three pairs the lines are separated by about a half an angstrom (0.26meV).

We have seen a pair of ionized donor lines associated with an unknown center, possibly a cadmium interstitial and two such pairs associated with the alkali metals, sodium and potassium. When it comes to doping cadmium sulfide with heavier alkali metals the literature is discouraging. However, we tried to dope with rubidium and a completely unfamiliar line appeared in this same spectral region (Figure 51). This new line has the appearance of a sharp-line member of an ionized donor pair. If this is what it is, then the broad line member would have to be at about the same wavelength as J_2. When we look at J_2 we see that the line there is indeed very broad, not at all like the J_2 lines in the previous figures. It is easy to conclude that we actually have here another ionized donor pair, $J_2(Rb)$ and $J_3(Rb)$ at 4867.47Å and 4866.98Å, with $J_3(Rb)$ overlapping J_2. Of course, we're guessing. However magnetic field measurements will tell us if the guess is right or wrong. In Figure 52 the specimen is in a field of 24 kilogauss 90° to the c-axis. The line at the J_2 position has clearly split, but this splitting does not come from any kind of a degeneracy. Rather the lines come from two different centers; they have different symmetries so they separate in the field. The $J_2(Rb)$ behaves like the J_2 line, and the $J_3(Rb)$ behaves like the J_3 line. Figure 53 shows the magnetic field dependence of the four lines.

The $J_3(Rb)$ and $J_2(Rb)$, then are clearly the components of a spin-split doublet, and since they are seen only in rubidium doped crystals, we feel justified in our assumption that they are, indeed, associated with the rubidium, probably as an interstitial. We found no other donor lines that could be attributed to rubidium, nor did we observe a rubidium I_1 acceptor line.

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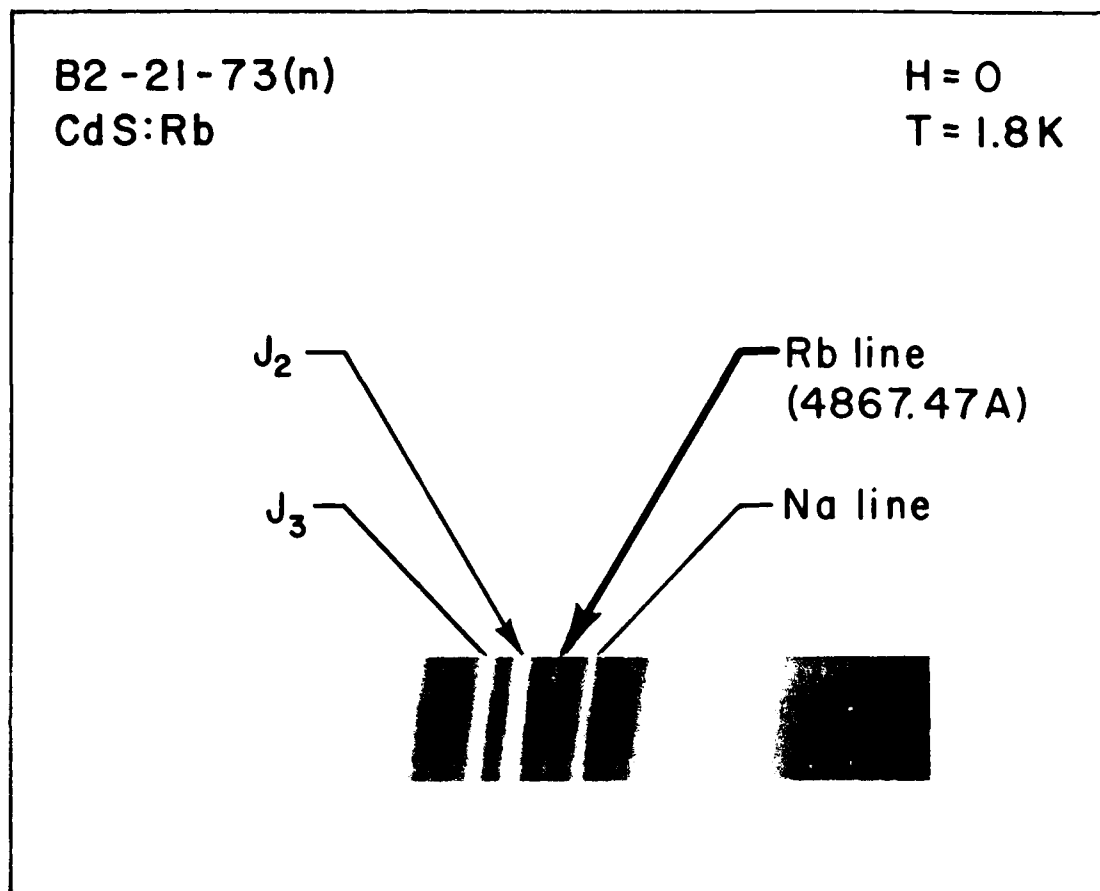
Figure 51.   The Bound Exciton Spectrum of CdS:Rb Showing the J_2(Rb)
Line at 4867.47Å and the J_3(Rb) Line Superimposed on
the J_2 Line at 4866.98Å
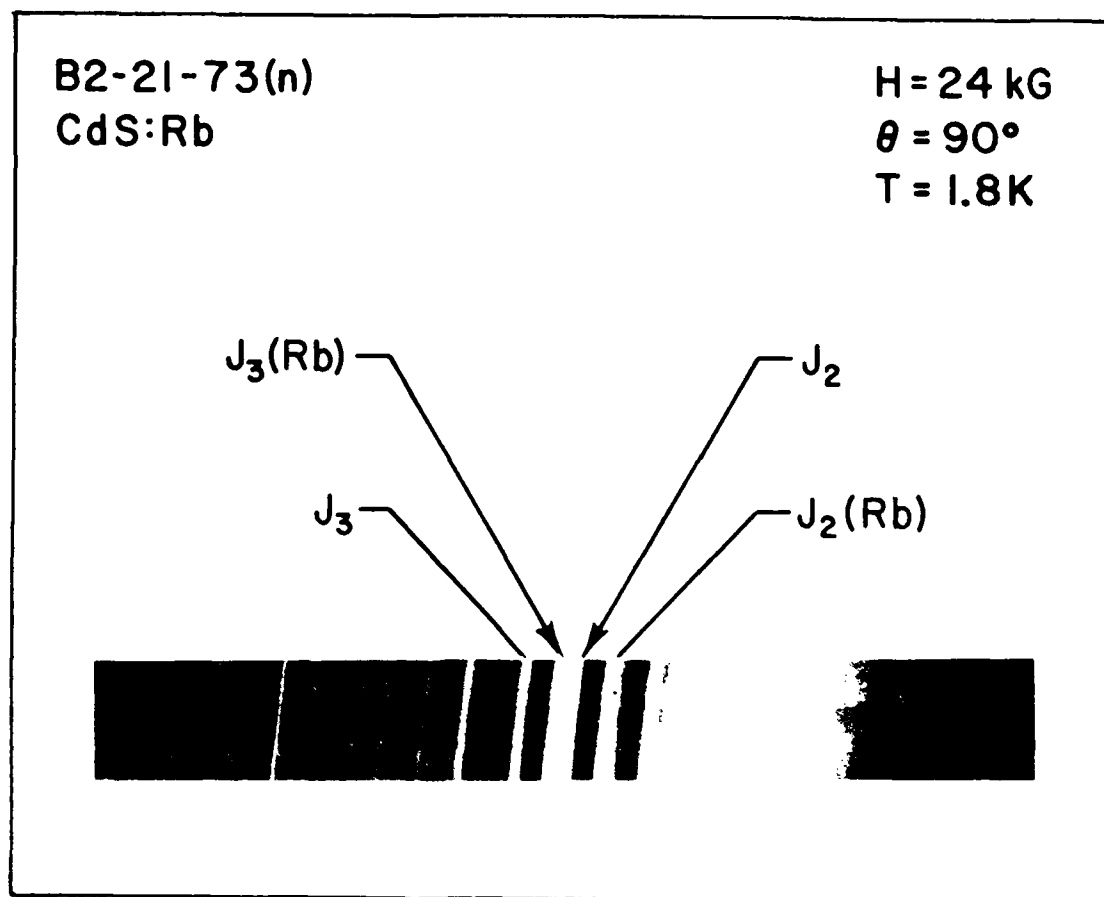
Figure 52. The Bound Exciton Spectrum of CdS:Rb Showing the Magnetic Field Splitting of the $J_3(Rb)$ and $J_2(Rb)$ Lines

1.0
1.1
1.25
2.8 2.5
3.2 2.2
3.6
4.0 2.0
1.8
1.4 1.6
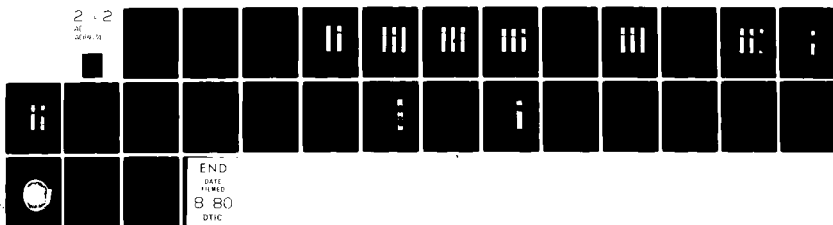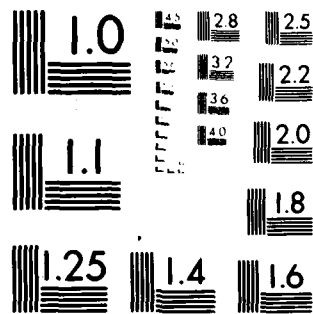
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A
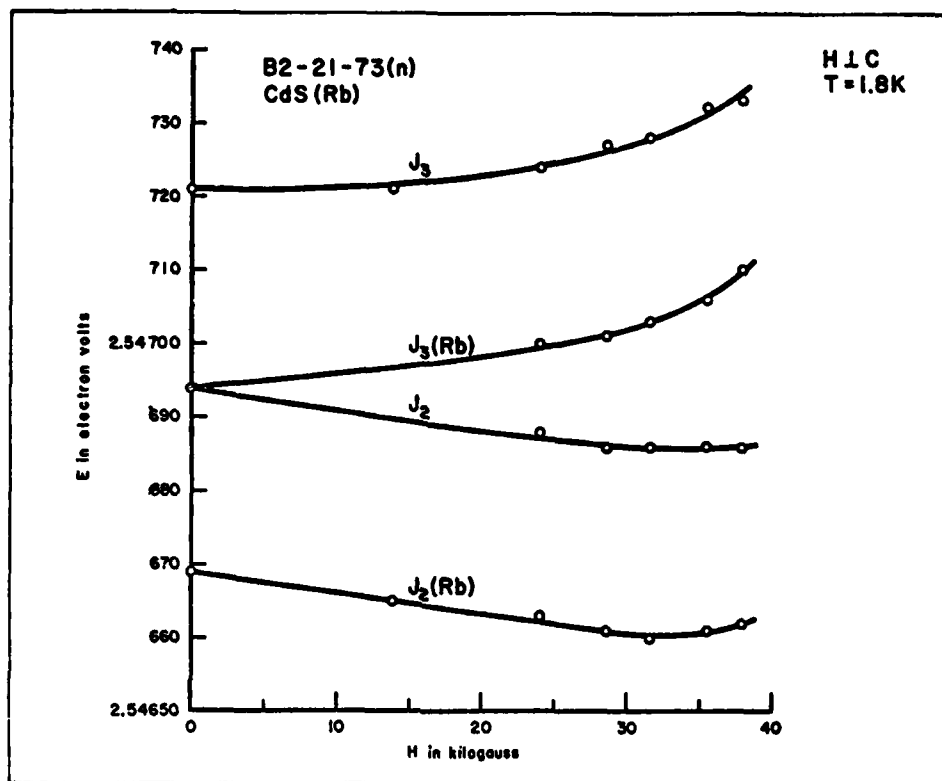
Figure 53. Magnetic Field Dependence of J_2, J_3, J_2(Rb), and J_3(Rb) Lines

13. CdS GROWN IN H_2S AND H_2

THE EFFECT OF EQUILIBRATION IN HYDROGEN SULFIDE AND IN
HYDROGEN ON THE BOUND EXCITON SPECTRA OF CADMIUM SULFIDE

Henry A. Wilson and Lawrence C. Greene

From the very beginning of cadmium sulfide crystal growth studies,
very little attention has been given to the effects of the growth atmos-
phere itself on the defect structure of the crystals. Variously, nitrogen,
hydrogen sulfide, hydrogen, argon, and mixtures of these were used and
few have seemed concerned about the non-reproducibility of results. For
several years we have been studying induced defects in cadmium sulfide
using bound exciton emission spectra as a means of identification. In
this paper we will discuss several such spectral lines which seem to be
characteristic of crystals grown in a carrier containing either hydrogen
or hydrogen sulfide. All of these lines are associated with excitons
bound to donors. Particularly we want to discuss two such spectral lines
that are characteristic of crystals grown in argon-hydrogen sulfide and
argon-hydrogen mixtures separately.

The crystals used in this study were thin platelets grown by the
dynamic flow technique. To achieve improved reproducibility the crystals
were grown in pure argon, then equilibrated in a flow of the gas mixture
to be studied containing an equilibrium pressure of cadmium sulfide vapor.

The bound exciton emission spectrum of high purity cadmium sulfide
grown in a carrier consisting of pure argon is dominated by three lines
(Figure 36). The strongest of these is I_5 which is known to be associated
with the decay of an exciton bound to a neutral donor. The other two, J_3
and J_2 have been shown to be the zero field split pair associated with
the decay of an exciton bound to an ionized donor. These are the only
strong bound exciton lines which appear consistently in undoped argon-
grown crystals.

Figure 54 shows spectra from crystals equilibrated in an atmosphere to which hydrogen sulfide or hydrogen has been added. The upper spectrum is from a crystal equilibrated in the agron-hydrogen sulfide mixture, the lower from a crystal equilibrated in the argon-hydrogen mixture. In each spectrum there are three new lines. Two of these are common to both spectra. These common lines are the I_{2H} line at 4869.34Å and the J_4 line at 4869.73Å. In addition each spectrum has a line not seen in the other: K_4 at 4868.78Å in the hydrogen sulfide crystal and K_3 at 4868.18Å in the hydrogen crystal.

In Figure 55 the first spectrum is from a cadmium sulfide crystal equilibrated at 400°C in an argon - 10% H_2S mixture. The H_2S introduces no new lines. The weak lines to the left of I_5 seem unrelated to the H_2S, but rather result from very low level residual impurity in the cadmium sulfide powder. In the second spectrum the crystal was equilibrated at 600°C. Here I_{2H} and J_4 are strong indicating that these centers stabilize at relatively low temperatures. In the third spectrum the crystal was equilibrated at 950°C. K_4, I_{2H}, and J_4 are all strong; K_4 has then stabilized at a higher temperature than did I_{2H} and J_4. I_5 has disappeared as might be expected if the I_5 center is associated with excess cadmium.

In Figure 56 we see three specimens equilibrated at 900°C. The first spectrum with no H_2S is just the one we saw in Figure 36. In the second spectrum with 1% H_2S the K_4 line has reached dominant intensity and does not change measurably as we go to 10% H_2S. This tells us that although the K_4 center stabilizes at a fairly high temperature, its formation saturates at low H_2S pressure.

In Figure 57 the first spectrum is from a CdS crystal equilibrated at 400°C in an argon - 10% H_2 mixture. I_{2H} is present but neither K_3 nor J_4. In the second spectrum the crystal was equilibrated at 600°C. Here K_3 is present, indicating that the hydrogen K_3 center stabilizes at a much lower temperature than the hydrogen sulfide K_4 center. In the third spectrum the crystal was equilibrated at 900°C. K_3 seems little changed. We can conclude, then, that the formation of the K_3 center saturates at below 600°C.
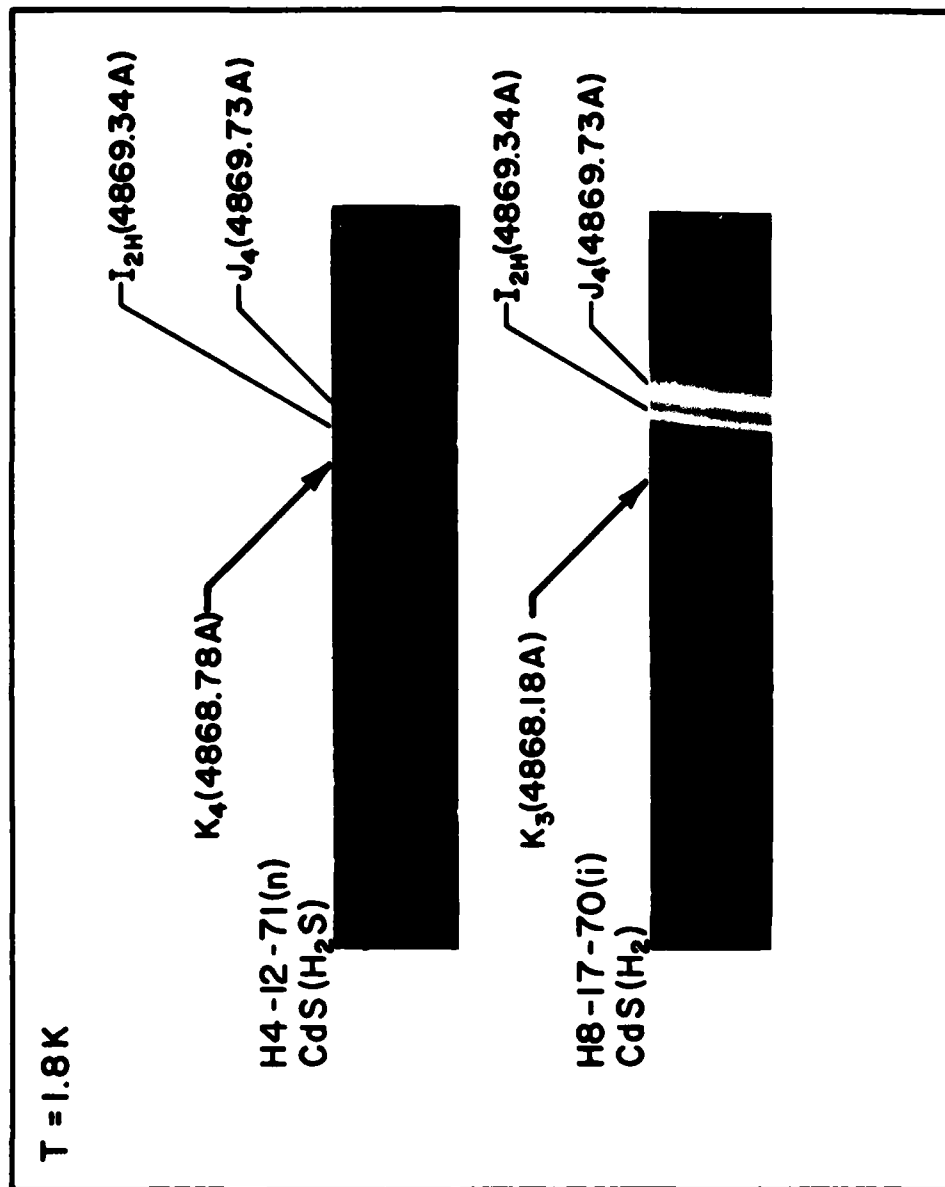
Figure 54. Bound Exciton Spectra of Cadmium Sulfide Crystals Equilibrated in Hydrogen Sulfide and in Hydrogen
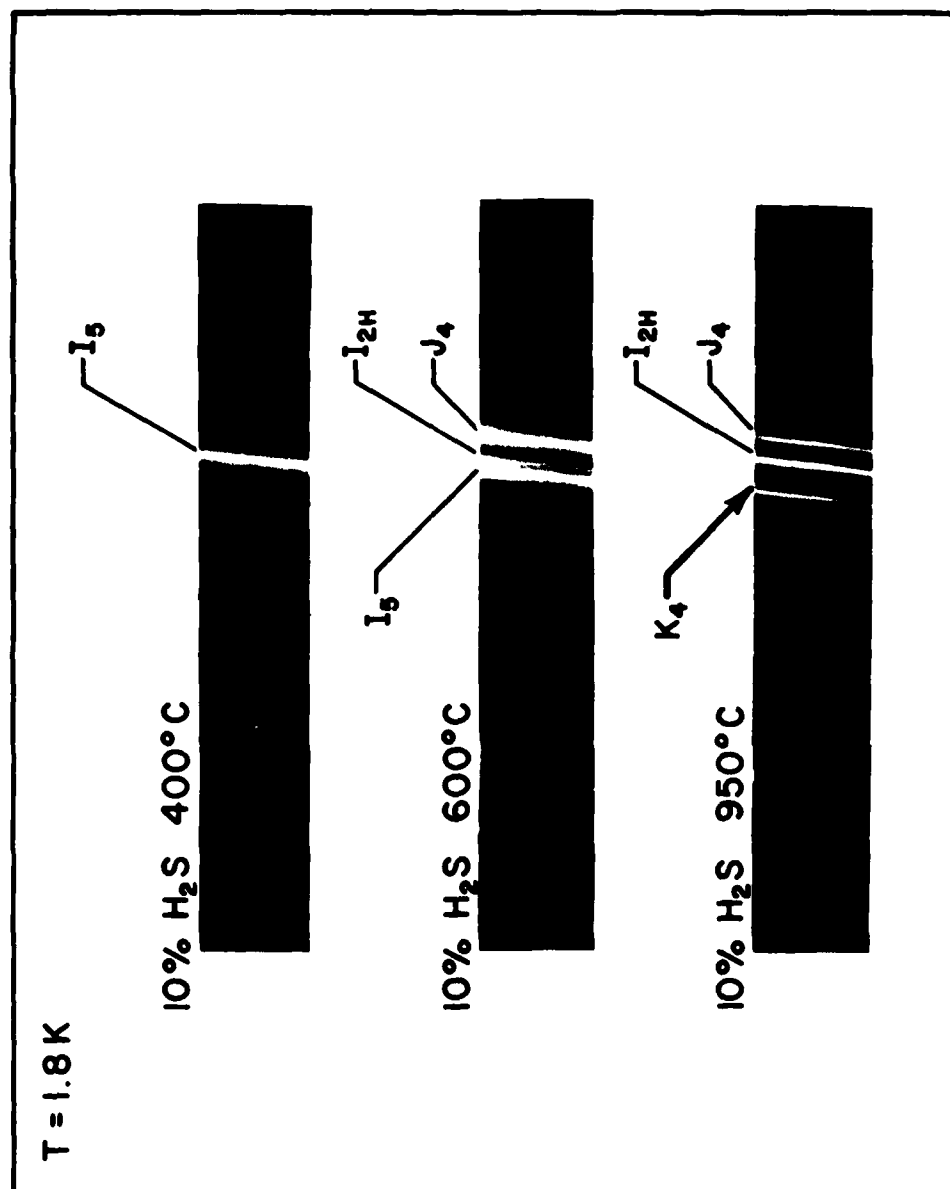
Figure 55. Spectra Showing the Temperature Dependence of the Formation of K_4, I_{2H}, and J_4 in the Presence of Hydrogen Sulfide
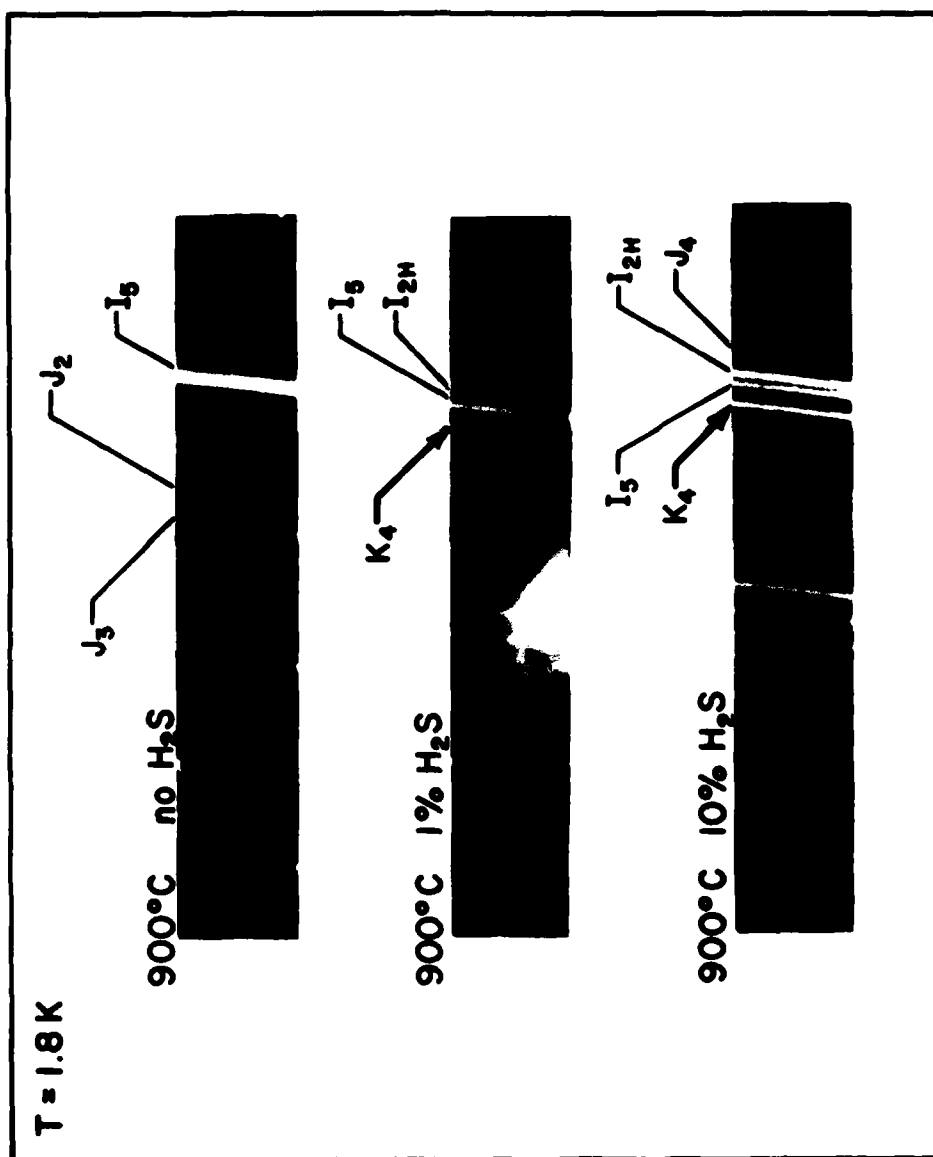
Figure 56. Spectra Showing Hydrogen Sulfide Concentration Dependence of K_4, I_{2H}, and J_4 Equilibrated at 900°C
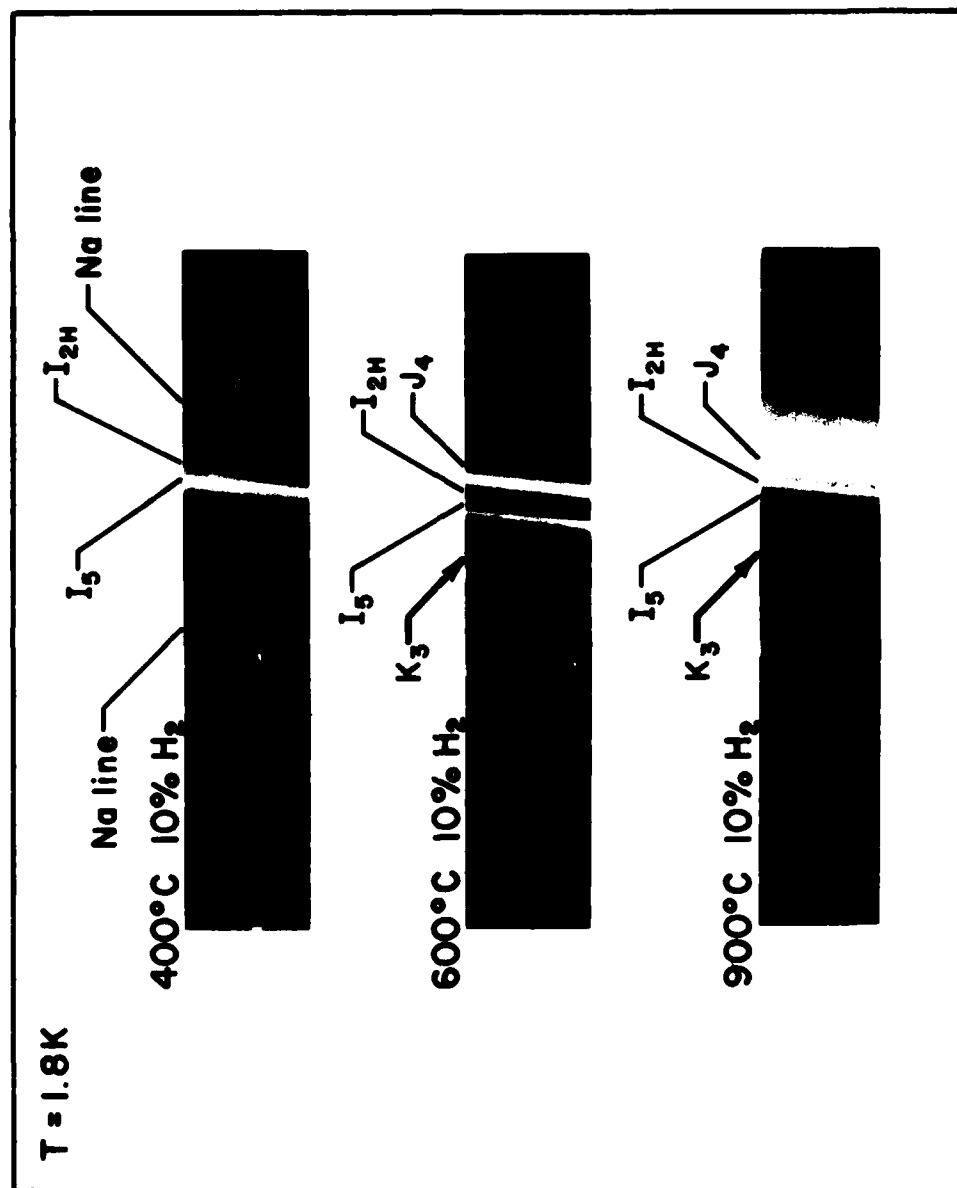
Figure 57. Spectra Showing the Temperature Dependence of the Formation of K_3, I_{2H}, and J_4 in the Presence of Hydrogen

In Figure 58 we see the effect of varying proportions of hydrogen in the equilibration gas. In the first spectrum no hydrogen was used. The lines are those characteristic of pure cadmium sulfide. In the second crystal 1% hydrogen was added. K_3 is seen to be present. In the third crystal 10% hydrogen was used. K_3 is no stronger than in the 1% crystal. We see, then, that K_3 saturates at low hydrogen pressure.

We have seen that the K_3 line is seen only in the hydrogen treated crystals. The K_3 center could be a hydrogen center or it could be a cadmium excess center such as a sulfur vacancy. If it is a sulfur vacancy then our assignment of the sulfur vacancy to the I_5 center was incorrect. This assignment was never anything but tentative.

The K_4 line was seen only in the hydrogen sulfide treated crystals. This indicates that sulfur is involved in the formation of the center. It cannot be a sulfur interstitial or a cadmium vacancy because all of these lines are donors. This leaves only complex centers to be considered.

The data available do not permit much speculation on the nature of the I_{2H} and J_4 center. They could be associated with hydrogen in the lattice. There is question whether ionic hydrogen would be stable in a substitutional position. The centers are too deep to be associated with simple interstitial hydrogen. Interstitial hydrogen, like interstitial lithium, would be expected to be very mobile and would very probably be trapped by other heavier defects to form defect complexes.

14. CHARACTERISTIC IONIZED DONOR LINES IN THE BOUND EXCITON SPECTRUM OF CADMIUM SULFIDE EQUILIBRATED IN THE PRESENCE OF HYDROGEN

Lawrence C. Greene and Henry A. Wilson

For several years we have been involved in a study of the defect and impurity structure of cadmium sulfide using the low-temperature bound exciton emission spectra as a tool for identification. Such spectra are particularly sensitive to the presence and nature of the defects. In high purity cadmium sulfide the bound exciton spectrum is
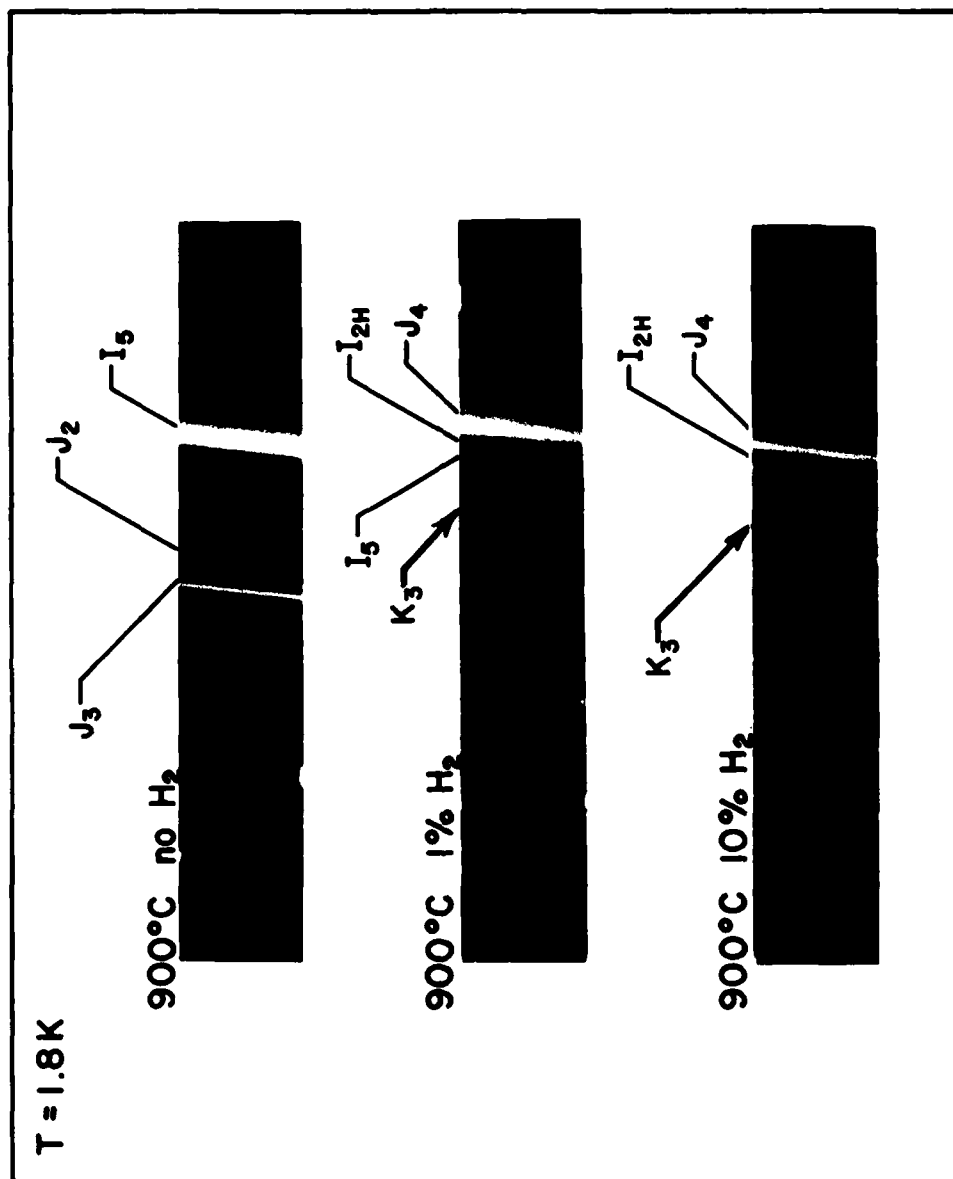
Figure 58. Spectra Showing the Hydrogen Concentration Dependence of the Formation of K_3, I_{2H}, and J_4 Equilibrated at 900°C

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dominated by three lines (Figure 36). One of these, I_5, is known to arise from the decay of an exciton bound to a neutral donor. The others, J_3 and J_2, are the spin exchange split doublet arising from the decay of an exciton bound to an ionized donor. The chemical nature of this center is not known, but it would probably be a good guess to call it a cadmium interstitial.

When cadmium sulfide is doped with an alkali metal a second very similar pair of lines appears. In Figure 59 the first spectrum is from a crystal doped with sodium. The J_3 and J_2 lines are present along with this second pair, $J_3(Na)$ and $J_2(Na)$. Both pairs of lines have the same spacing. The second spectrum is from a potassium doped crystal. Again we have a second pair of lines $J_3(K)$ and $J_2(K)$. In the third spectrum from a rubidium doped crystal, $J_3(Rb)$ and $J_2(Rb)$ appear with $J_3(Rb)$ lying on top of J_2. These assignments have been verified by Zeeman measurements.

In the preceding section we have discussed several lines that seem to result from the presence of hydrogen in the growth or equilibration phases of the crystal preparation. One of these was K_3 and this is the line we want to consider more closely (Figure 60). All of the lines which we have studied previously in this region of the bound exciton spectrum were neutral donor lines.

Therefore, it came somewhat as a surprise when we put a crystal in a magnetic field to see this line split like an ionized donor. In Figure 61 the upper spectrum is with zero field. We see the broad line component, K_3, which comes from an allowed transition, but the sharp line component arising from a nominally forbidden transition does not appear. In the lower spectrum the crystal is in a magnetic field just strong enough to lift the forbiddenness and the second component, which has been labeled K_2, is comparable in strength to K_3. Once we knew what to look for we were able to see the K_2 line in a zero field spectrum and to measure its wavelength, but we have not been able to prepare a figure that would show it.
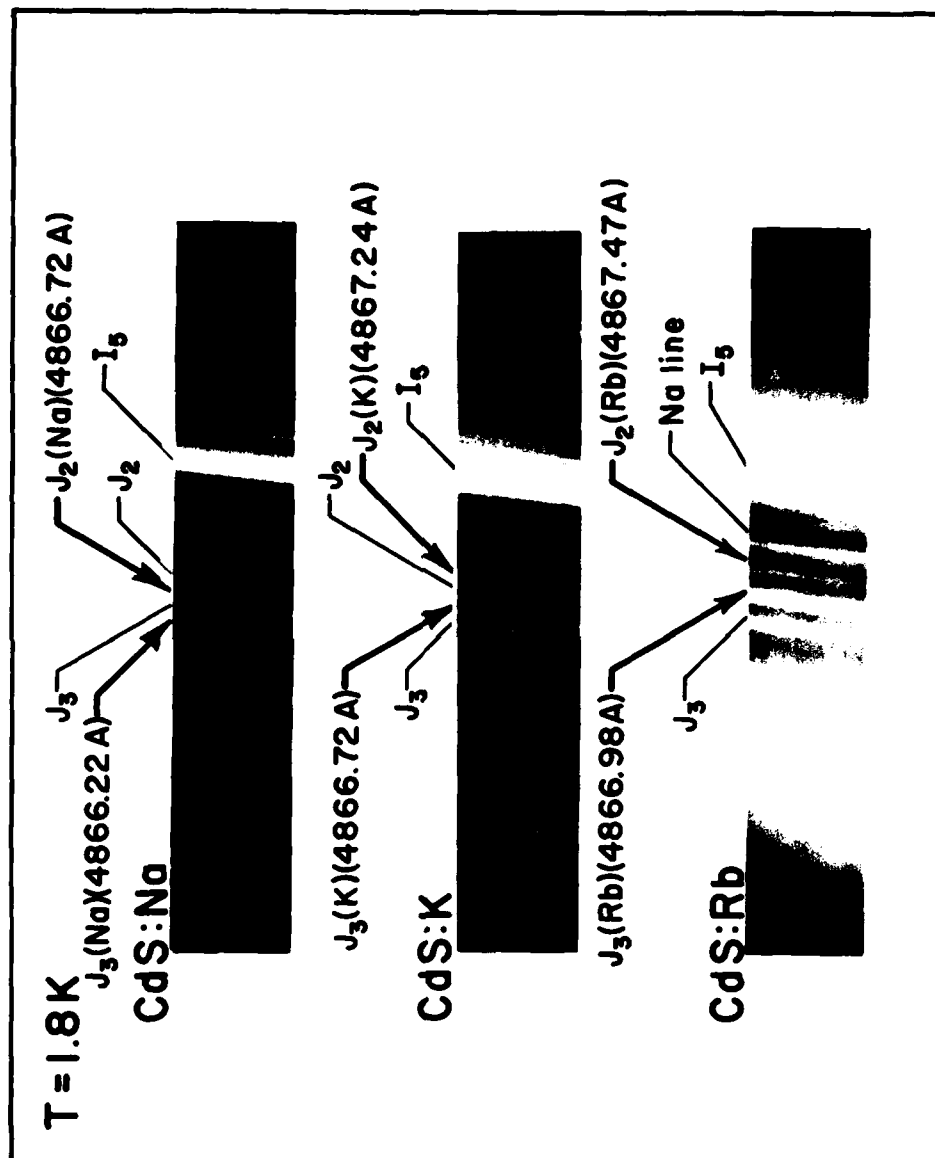
Figure 59. Spectra Showing the Ionized Donor Lines for CdS:Na, CdS:K, and CdS:Rb
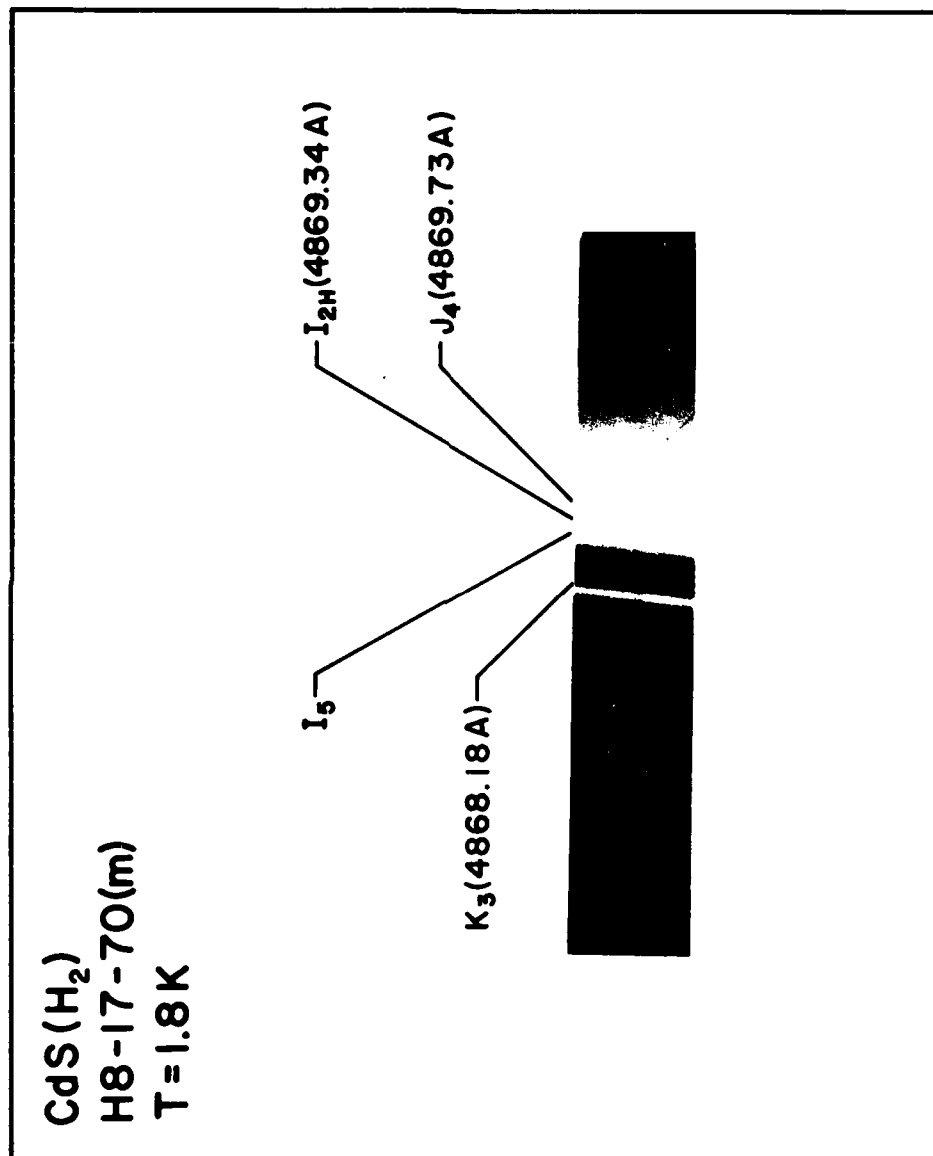
Figure 60. Spectrum Showing the K_3 Line in Cadmium Sulfide Equilibrated in an Atmosphere Containing Hydrogen
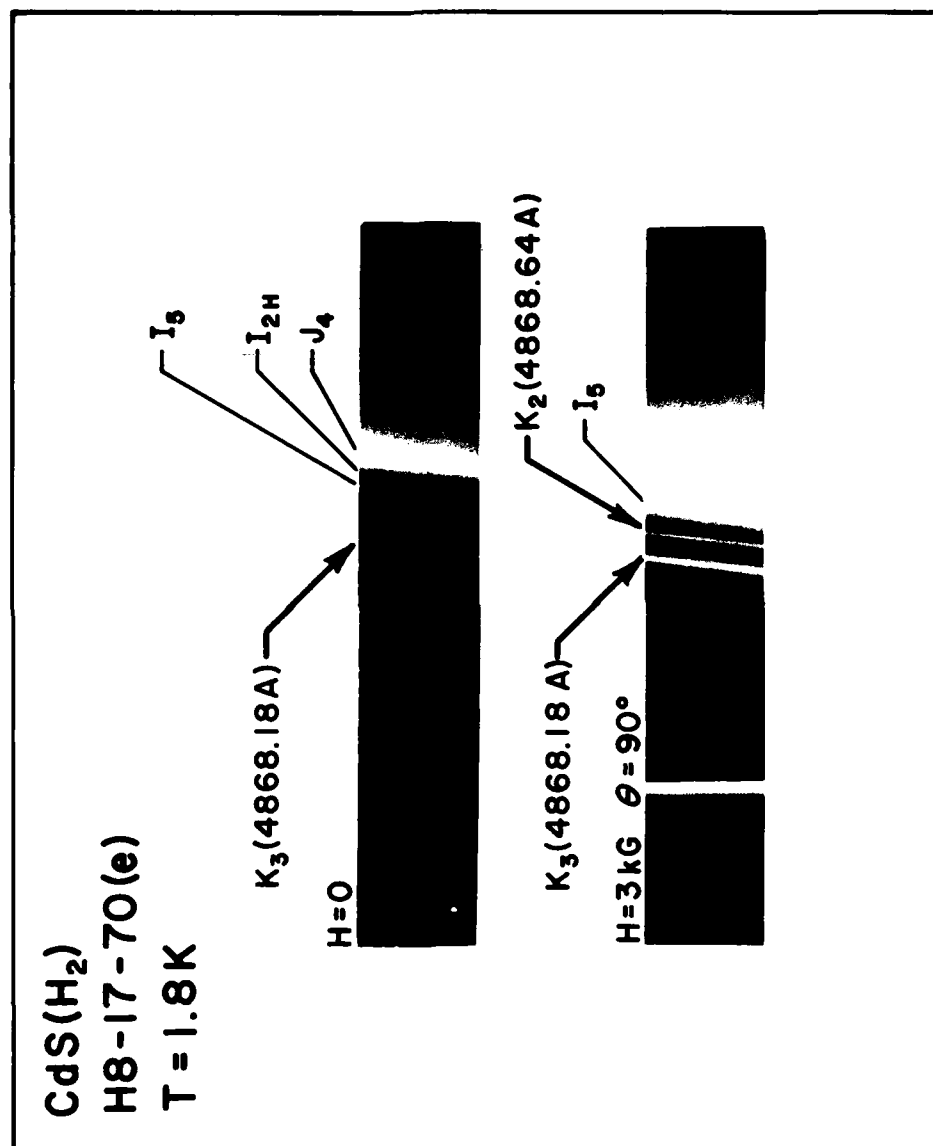
Figure 61. Spectrum Showing the K_3 Line in Zero Field and in a Field of 3kG with $\theta = 90°$

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In Figure 62 are shown relationships between line splitting and magnetic field for the J_2, J_3 pair and for the K_2, K_3 pair with $H{\perp}c$. The nonlinear relationship is characteristic of the ionized donor. It is interesting to note that the K_2, K_3 curve very nearly parallels the J_2, J_3 curve for its entire length, but is separated from it by about two hundreds of a milli-electron volt.

In Figure 63 we have plotted exciton binding energy against crystal ionic radius for the three alkali metal J_3 centers. In doing this we have assumed that the centers are simple interstitials. The three points lie on a fairly good straight line. The fourth point shows where we might expect a J_3 line for cesium. On such a plot as this the K_3 line would appear at the top as indicated by the arrow. If this were a simple interstitial it would have an ionic radius near 2.4A. There is no singly ionized cation with such a large ionic radius. We will have to consider some other kind of center. In a crystal equilibrated in the presence of hydrogen, one will certainly expect sulfur vacancies, and this would be a logical choice. However, we feel that the most probable choice is a hydrogen ion bound to another defect to form a complex donor.

15. IONIZED DONOR LINES IN CdS:Li

CHARACTERISTIC IONIZED DONOR LINES IN THE BOUND EXCITON SPECTRA OF LITHIUM DOPED CADMIUM SULFIDE

Lawrence C. Greene and Henry A. Wilson

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at Salt Lake City 12-14 June 1974

For several years we have been involved in a study of the defect and impurity structure of cadmium sulfide using the low-temperature bound exciton emission spectrum as a tool for identification. Such spectra are particularly sensitive to the presence and nature of the defects. In high purity cadmium sulfide the bound exciton spectrum is dominated by three lines (Figure 36). One of these, I_5, is known to arise from the decay of an exciton bound to a neutral donor. The others, J_3 and J_2, are
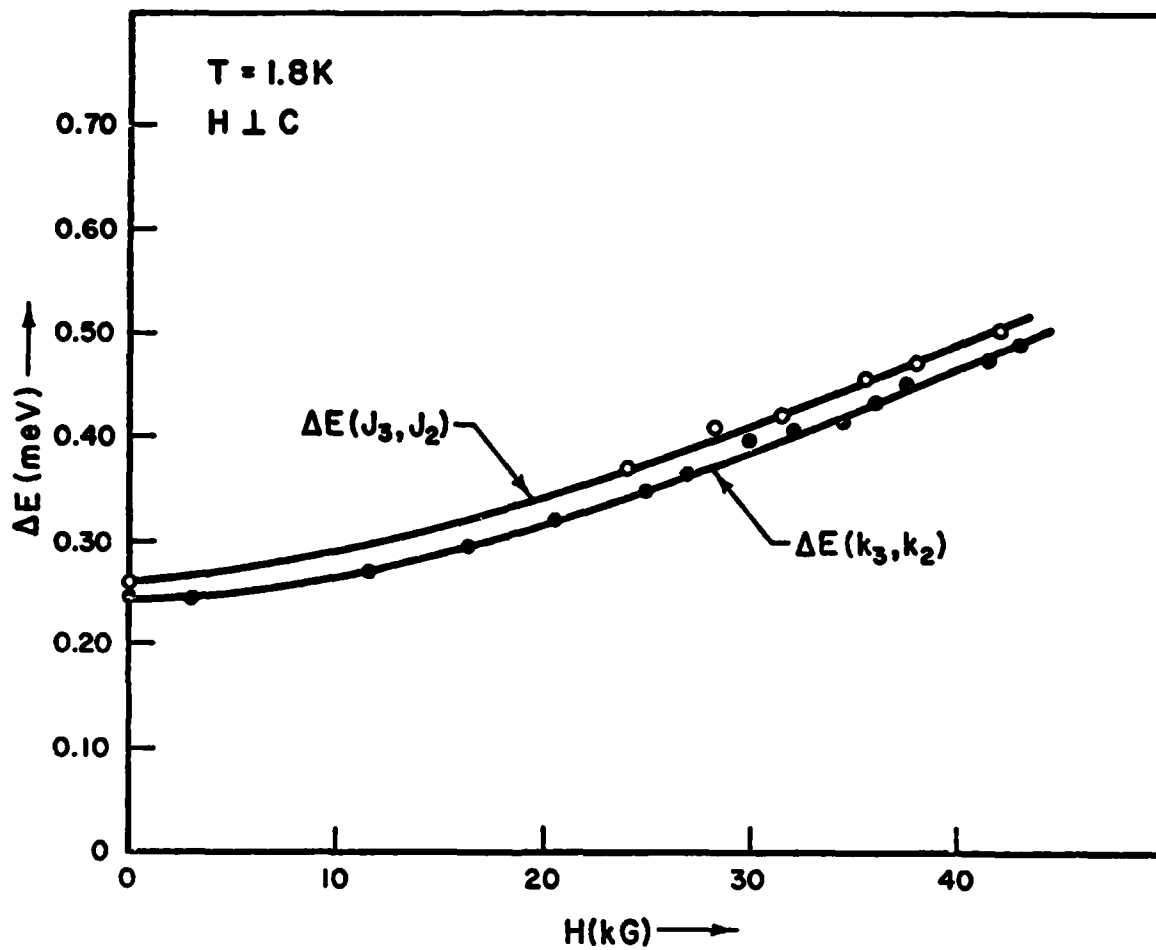
Figure 62. Line Splitting of the J_3, J_2 Doublet and of the K_3, K_2 Doublet as Functions of the Magnetic Field with $\theta = 90°$
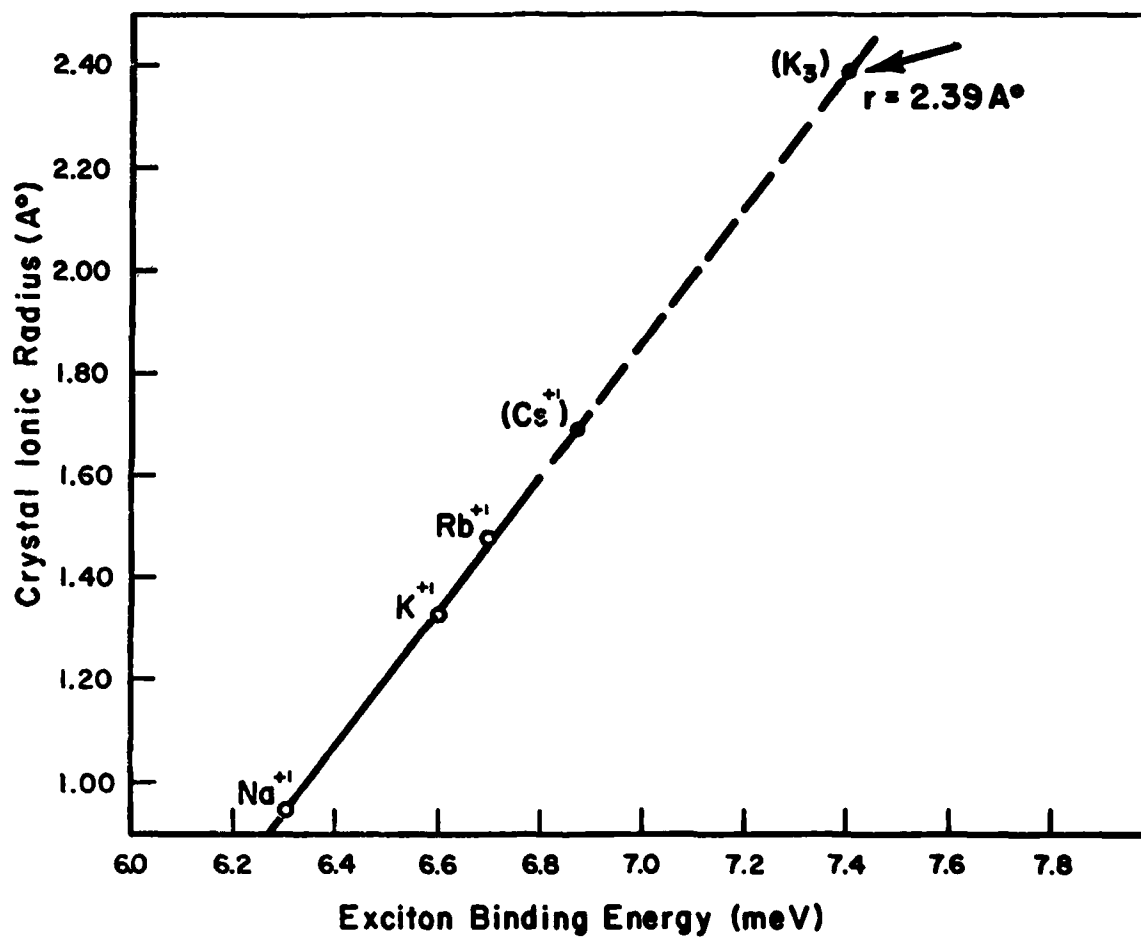
Figure 63. Exciton Binding Energy in Cadmium Sulfide as a
Function of Crystal Ionic Radius for Na, K, and Rb,
Showing Projected Ionic Radius for K_3

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the spin exchange split doublet arising from the decay of an exciton bound to an ionized donor. The chemical nature of this center is not known, but it would probably be a good guess to call it a cadmium interstitial.

When cadmium sulfide is doped with an alkali metal a second very similar pair of lines appears (Figure 59). The first spectrum is from a crystal doped with sodium. The J_3 and J_2 lines are present along with this second pair, $J_3(Na)$ and $J_2(Na)$. Both pairs of lines have the same spacing. The second spectrum is from a potassium doped crystal. Again, we have a second pair of lines $J_3(K)$ and $J_2(K)$. In the third spectrum from a rubidium doped crystal, $J_3(Rb)$ and $J_2(Rb)$ appear with $J_3(Rb)$ lying on top of J_2. The Zeeman studies confirm that these are spin exchange split lines arising from ionized donors.

In Figure 64 we have plotted exciton binding energy as a function of crystal ionic radius for these three alkali metal J_3 centers. In doing this we have assumed that the centers are simple interstitials. The three points lie on a fairly good straight line. Above the rubidium point we have indicated a point where we might look for a cesium J_3 line. However, we haven't found such a line and we really don't expect to. Below the sodium point we have indicated a point where we might expect to find a lithium J_3 line. We have studied many lithium doped CdS crystals but have never seen a line falling on the curve at this point. However, in the course of the studies we have identified a group of lines which clearly are associated with lithium, and are also clearly ionized donor lines, but they don't seem to belong to the Na-K-Rb series. These are indicated by the two isolated points at the left.

In Figure 65 we show a spectrum containing these lines. They appear very much like the lines in the previous figures except that there are two closely spaced pairs. There are two well resolved lines which have been designated as L_2 and L_2'. These are the Γ_6 or sharp lines from nominally forbidden transitions. Then there are two poorly resolved lines L_3 and L_3', which are the Γ_5 or broad lines from allowed transitions. The double pair shown here seems to be characteristic. In the specimens which we have studied, we have never seen either pair separately.
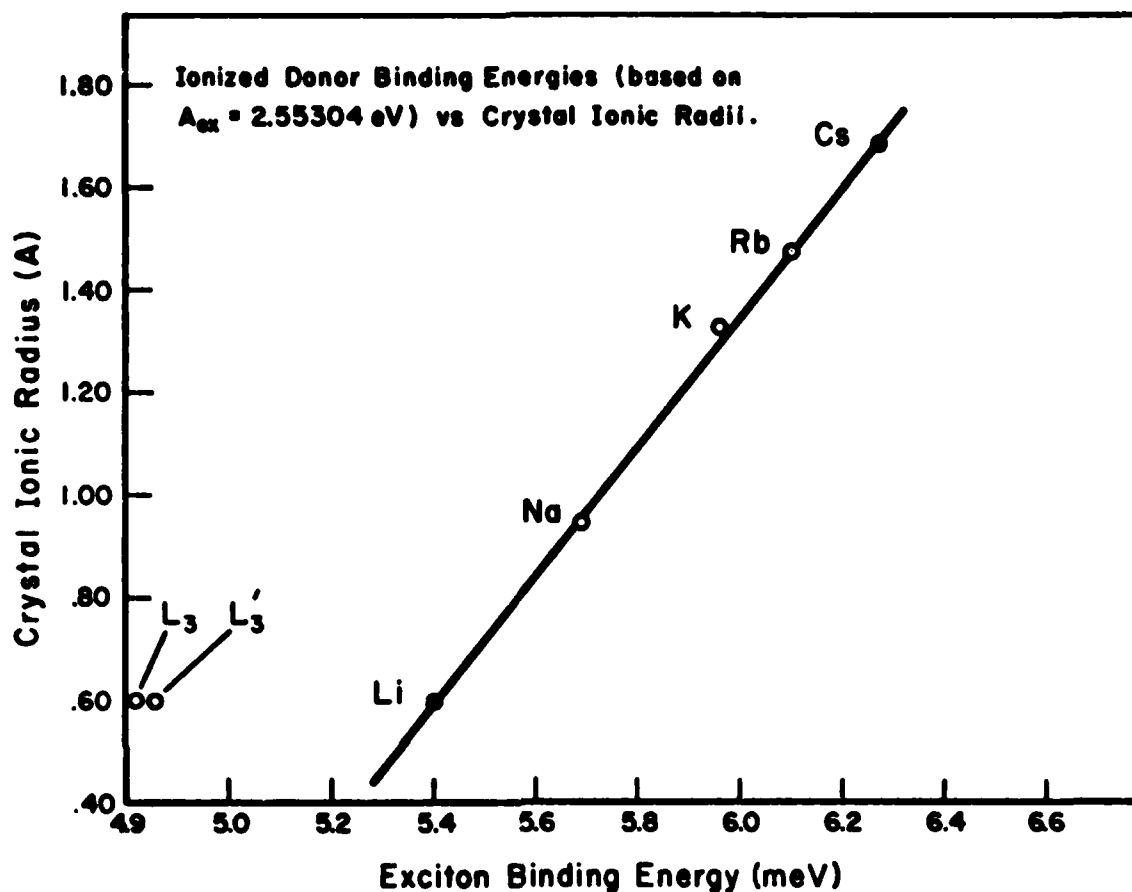
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Figure 64.   Exciton Binding Energy as a Function of Crystal
Ionic Radius for Na, K, and Rb, Showing Projected
Ionic Radius for an Ionized Donor Associated with
Interstitial Lithium

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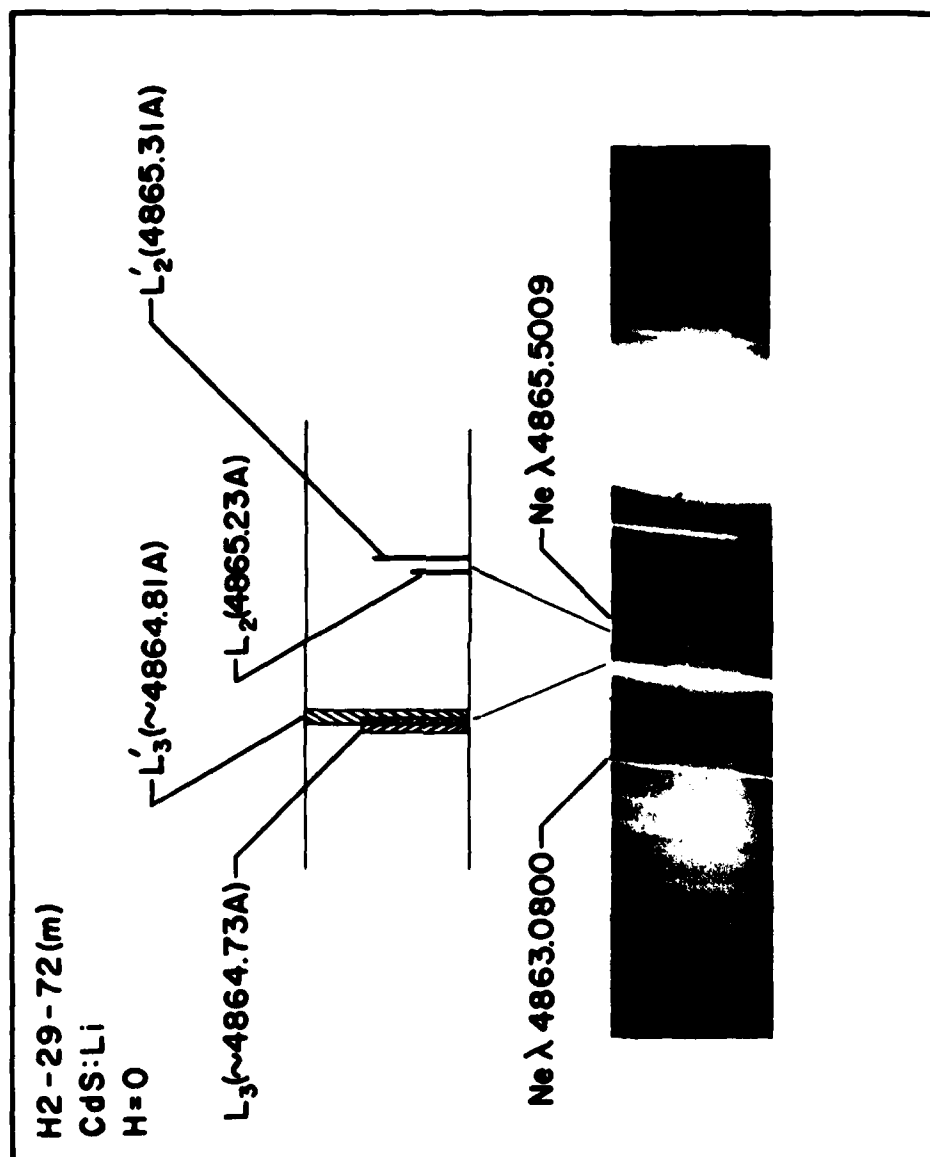
Figure 65. Ionized Donor Lines L_3, L'_3, L_2, and L'_2 Associated with Lithium

In Figure 66 we have the same specimen in a magnetic field of
40.6kG with the field perpendicular to the c-axis of the crystal. The
splitting seen here is just what we would expect if we have two ionized
donor pairs. The lines have not split but have separated, indicating
that there is already zero field splitting. Also the intensities of
the L_2-L_2' lines have increased considerably with respect to those of the
L_3-L_3' lines. This effect results from a relaxation of the selection
rules in the magnetic field. It is to be noted that there is no
observable change in the L_3-L_3' or L_2-L_2' separations.

Figure 67 shows the line splitting as a function of the field
intensity. The measurements were made for the L_2'-L_3' pair but the curve
applies equally well to the L_2-L_3 pair. Two things are to be noted.
First, the large zero-field splitting; second, the nonlinearity of the
relationship. Both of these are characteristic of emission from excitons
bound to ionized centers. However, there are still two possibilities.
Either we have two ionized donors with very nearly the same exciton
binding energies, or we have one ionized donor whose energy is split
by an unidentified perturbation. The material presented in this paper
is that which was available at abstract deadline time. Since that time
we have identified several other ionized-donor pairs clearly associated
with lithium. None of these fit into the Na-K-Rb series. Our conclusion
is that we are not looking at simple lithium interstitials, but rather
at lithium complexed with other defects. This is, of course, a well-
known phenomenon in other semiconductors.

H2-29-72(m)
CdS:Li
H=40.6kG
H⊥c

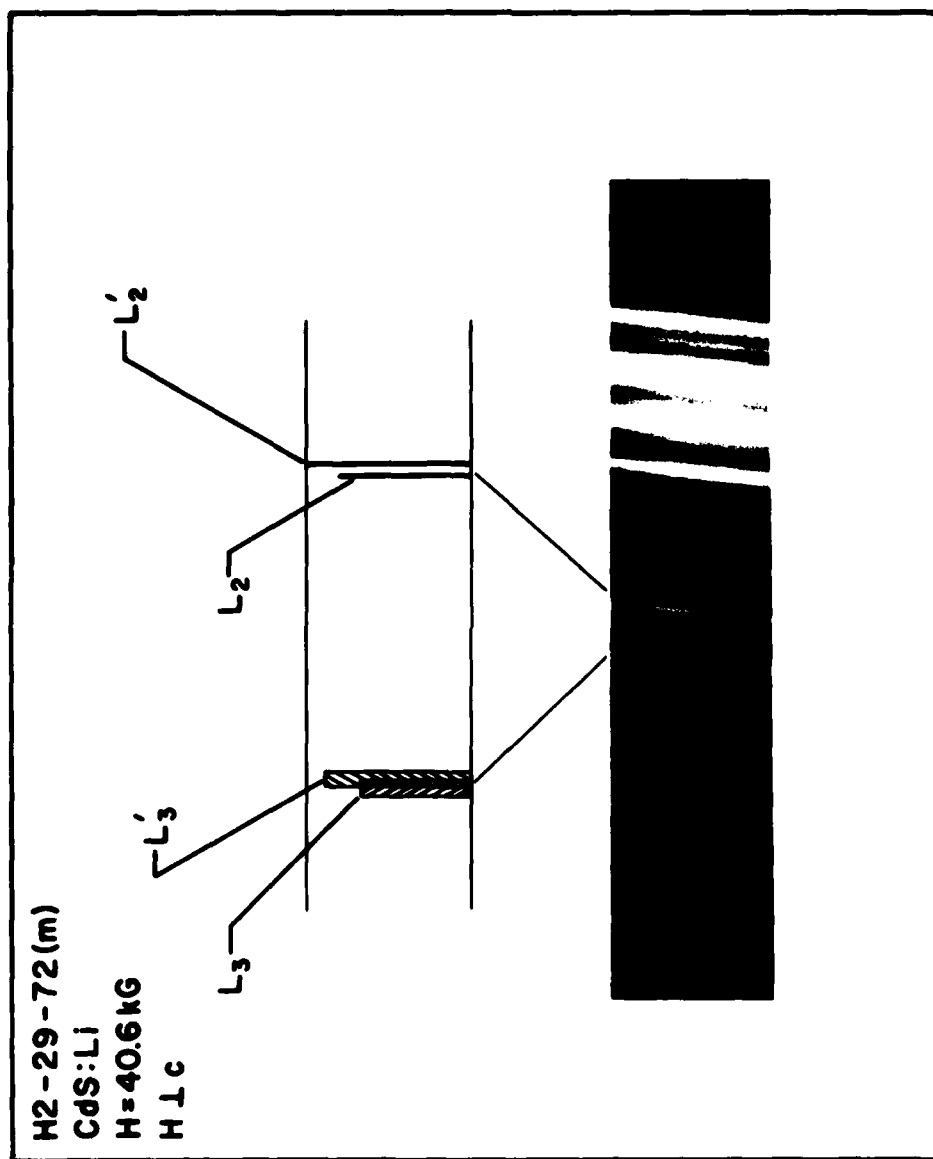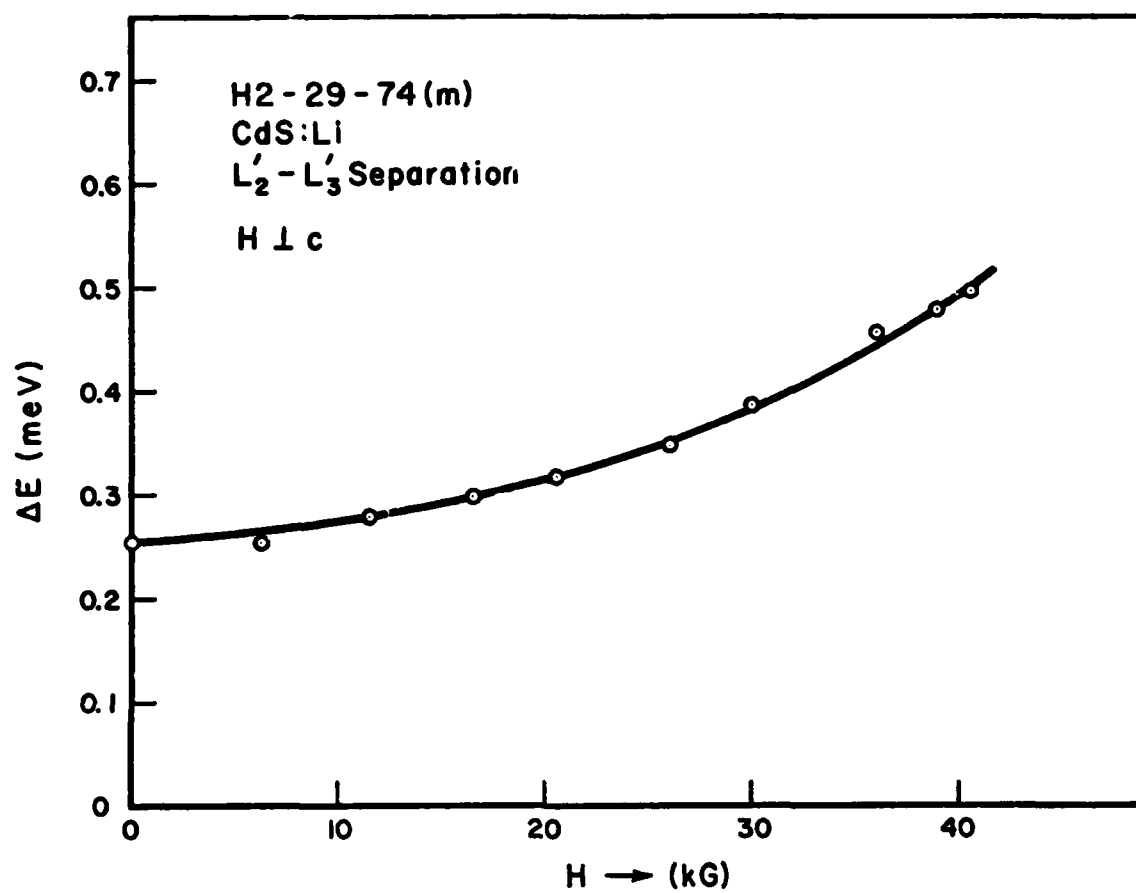Figure 66. Ionized Donor Lines L_3, L_3', L_2, and L_2' Split by a Magnetic Field with $\theta = 90°$

Figure 67. L_2' - L_3' Splitting as a Function of Magnetic Field
$\theta = 90°$

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SECTION III

CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS

We have used a crystal growing technique previously developed
(Reference 10) to grow platelet type cadmium sulfide crystals with
surfaces of sufficiently high perfection to allow the study of the
exciton emission spectra at low temperatures. We have identified
exciton emission lines associated with simple intrinsic and chemical
defects as well as with centers that are clearly not simple defects
but complexes.

There are more than 30 dominant exciton lines associated with
sodium, and probably as many associated with lithium and with silver.
Lines associated with potassium and rubidium were also identified.

We have established that the presence of these monovalent metals
can be determined qualitatively using this technique and we feel, that
with further study, a quantitative determination of the specific centers
involving the metals could be carried out.

Although our primary purpose in this study was to obtain purer
cadmium sulfide for a starting material, and to develop procedures for
growing purer crystals by monitoring contamination effects during crystal
growth, a secondary but important objective was to determine why it is
not possible to grow p-type crystals. It has always been presumed that
the monovalent metals, used as dopants, should give p-type conductivity.
In general, this has not been the case. A study of the spectra presented
in this report reveals that these metals go into cadmium sulfide to form
donors predominantly. In well equilibrated crystals such dopants go into
the cadmium sulfide lattice predominantly as interstitials or as com-
ponents of complexes which, whatever their forms, are also donors.

In unpublished work we did find that under extreme nonequilibrium
conditions, sufficient lithium would go into substitutional positions
so that the $I_1(Li)$ acceptor line would dominate the spectrum.

Thermoelectric probe studies showed that such crystals were p-type, but their resistivities were so high that really definitive conclusions could not be made.

It does seem clear from this work that a stable p-n junction will not be achievable. This means, of course, that junction devices using cadmium sulfide will have to depend on heterojunctions.

2. RECOMMENDATIONS

The practical value of this means of defect identification lies, not so much in the identification of the chemical impurity itself, but in determining its mode of incorporation. It is obvious that a qualitative determination of the presence of a given impurity such as sodium or silver will be relatively simple considering the large number of characteristic lines available. However, a quantitative determination would not be possible because the impurity will be shared among a great many different modes of incorporation, the relative densities of these centers will vary with variation in conditions of growth or heat-treatment.

However, it is to be noted, that the important factor in device fabrication, for example, is not the total amount of a given impurity, but the concentrations of the various active centers containing the impurity. If single crystal cadmium sulfide or cadmium selenide is to be used in a device, it will be necessary to develop heat treatment procedures that will produce the desired active centers and suppress those that are undesirable. Such a procedure cannot be monitored by standard analytical devices, but can be followed quite easily using bound exciton spectroscopy.

Much work, of course, remains to be done to make the technique quantitative for the centers, whether they are simple centers or complex centers. In the work presented in Part II very little correlation was made between the various spectral lines and the structures of the centers with which they were associated. Certainly if one is to gain an understanding of the relationship between the effects of the many centers on the device properties, it will be necessary to have a much more extensive comprehension of these structures.

Such an understanding will require much more extensive use of
Zeeman, uniaxial stress, and polarization effects to gain a better
picture of the symmetries and axial orientations of the centers. Thus,
in cadmium sulfide doped with any one of the active monovalent metals
it is not sufficient to ask whether it is substitutional or interstitial,
but one must determine how these simple defects are bound in the lattice
to other defects, and what energy levels or traps these complexes may
introduce. This, of course, means that when material of adequate quality
is available, the exciton spectra studies must be correlated with mobility,
lifetime, and infrared absorption studies.

If cadmium sulfide and the related II-VI compound crystals are to be
used for devices, much purification work remains to be done. Our studies
of impurity identification were carried out in association with con-
tractual work in purification (Reference 12). This work in purification
involved purifying the component elements by zoning and distillation, and
then reacting them in a quartz reactor. This produced a very high purity
material, particularly cadmium sulfide, which had been the most intensively
studied, but such cadmium sulfide was still several orders of magnitude
less pure than the presently available silicon.

It is clear that much work remains to be done in purification. As a
beginning the component elements themselves must be much more intensively
studied in order to determine more effective methods of purification. In
cadmium, for example, a thorough study should be made of the segregation
coefficients of the elements that seem likely to be active in the expected
applications. If unfavorable segregation coefficients are found, such as
for boron in silicon, then other approaches to cadmium purification should
be extensively studied. In particular fractional distillation, either
of the element itself or of suitable compounds should be considered.

Sulfur, although it can be zoned, probably will be more successfully
approached by distillation techniques. Such an approach may present
problems in the elemental sulfur because of its tendency to polymerize in
the liquid phase, but there might be many sulfur compounds with suitable
properties for successful distillation. Of course such compounds chosen

for distillation, both for cadmium and for sulfur, must be such as can be
converted to the element, or possibly directed to the desired compound
by means of reactions which will not, themselves, introduce contamination.

After the component elements have been suitably purified, they must
be reacted. This has been accomplished (Reference 12) in a quartz
reactor. In the very purest material there is clear evidence of com-
tamination from the quartz. It is possible that the Eagle-Picher
reactor (Reference 12) might be redesigned so that there is less contact
between the quartz and the reacted material. It is also possible that
such a reactor might be constructed so that the reacted material would
only come in contact with a super pure synthetic quartz. Another possi-
bility is the use of a reactor of the type used by Raytheon (Reference 13)
in the synthesis of CVD zinc selenide. This reactor is fabricated of
stainless steel and produces polycrystalline material of quite high purity.
Also to be considered might be a reactive deposition on a wire or rod
of a refractory metal.

Much work still remains to be done on crystal growth. Platelet type
crystals are the simplest and most economical to grow, and can be grown
with the least probability of contamination, and with the best structural
properties, since they grow without physical constraint, and contact the
growth chamber only at a corner or edge. However, their form and fixed
orientation may make them impractical to use.

Bulk crystals grown from the vapor phase would be the best choice
where it is desired to be able to machine the material into uniform chips.
The vapor phase technique is much more economical than melt growth since
it produces crystals of better quality with less contamination and there
is no size limitation. Single plates of cadmium sulfide have been grown
as large as six inches in diameter and two inches thick. Figure 68 shows
a crystal that is about three inches in diameter and one inch thick.
Furthermore, furnace fabrication and operation costs scale up about
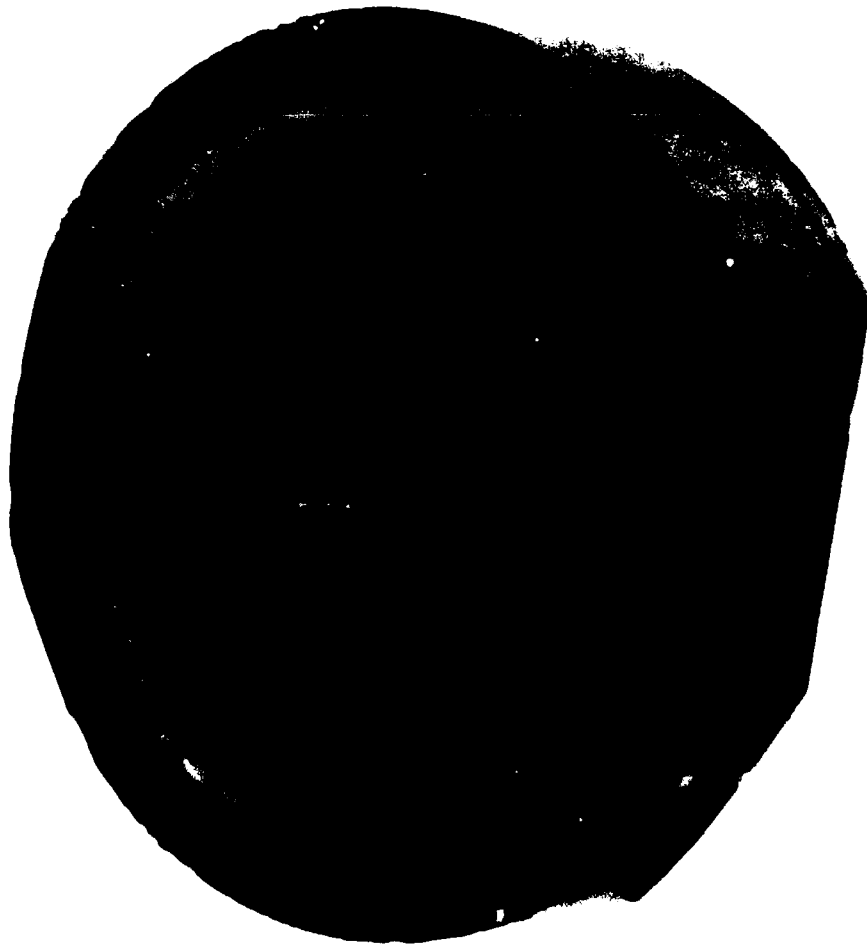linearly with furnace size.

Figure 68. Single Crystal of Cadmium Sulfide Grown by Static Vapor Phase Transfer. X2

The melt growth technique (Reference 12) is the most expensive of the three crystal growth techniques studied. It has another disadvantage in that the higher temperatures used produce greater concentrations of both chemical and physical defects. Furthermore, there are severe limitations on crystal size, with the cost of furnace fabrication scaling up far more than linearly with increase in size. The melt growth technique does have one advantage in that it makes possible the incorporation of dopants in the crystals, where the vapor pressure of the dopant may be too low to permit uniform incorporation in the vapor phase.

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