FUNDAMENTAL RESEARCH IN SOLID STATE ENERGY CONVERSION PROCESSES

CENTER FOR SPACE RESEARCH

and

Semiconductor Materials and Devices Group
Department of Electrical Engineering

and

Center for Materials Science and Engineering

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Cambridge 39, Massachusetts

Semiannual Technical Summary Report No. 6
December 1, 1965 to July 1, 1966

on

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INTRODUCTION

This is the sixth semiannual technical summary report of the research program entitled "Fundamental Research in Solid State Energy Conversion Processes". The report covers research on fundamental processes involved in optical behavior of solids and associated with photovoltaic energy conversion.

The work on HgTe-CdTe heterostructures, which has been previously reported, is nearing completion. The photovoltaic properties seem to be limited by the presence of undesired p-n junctions in the structure. Our present work is directed toward an understanding of the devices we have made and it is this phase which is nearly complete. It would seem that any further work must involve much better control of the metallurgical properties and the future course of this work is uncertain.

The study of $Cd_xZn_{1-x}Sb$ alloys is proceeding. Apparatus has been assembled to measure free carrier absorption in the infrared region. We hope to be able to obtain a better understanding of the band structure from the results of these experiments.

The remaining two projects are involved with electro-optic effects in semiconductors which we have previously studied by other means, CdTe and CdS. The preliminary experiments on these materials indicate that this will be a useful tool for understanding these materials.

George S. Almasi

CHAPTER I

GRADED-ENERGY-GAP HETEROSTRUCTURES

As mentioned in the last progress report[1], one of the unexpected properties of the HgTe-CdTe heterostructures prepared during this study is a photovoltage which is a strong exponential function of photon energy. At that time a model was tentatively assumed in which the graded-energy-gap region was in series with a p-n junction at the large-gap (CdTe) end; this junction collects a certain fraction of the excess carriers generated in the graded-gap region. This model was supported by the results of some copper-electroplating experiments on the devices. Since that time, several other approaches have been investigated in an effort to verify or disprove this model.

I-V CHARACTERISTICS

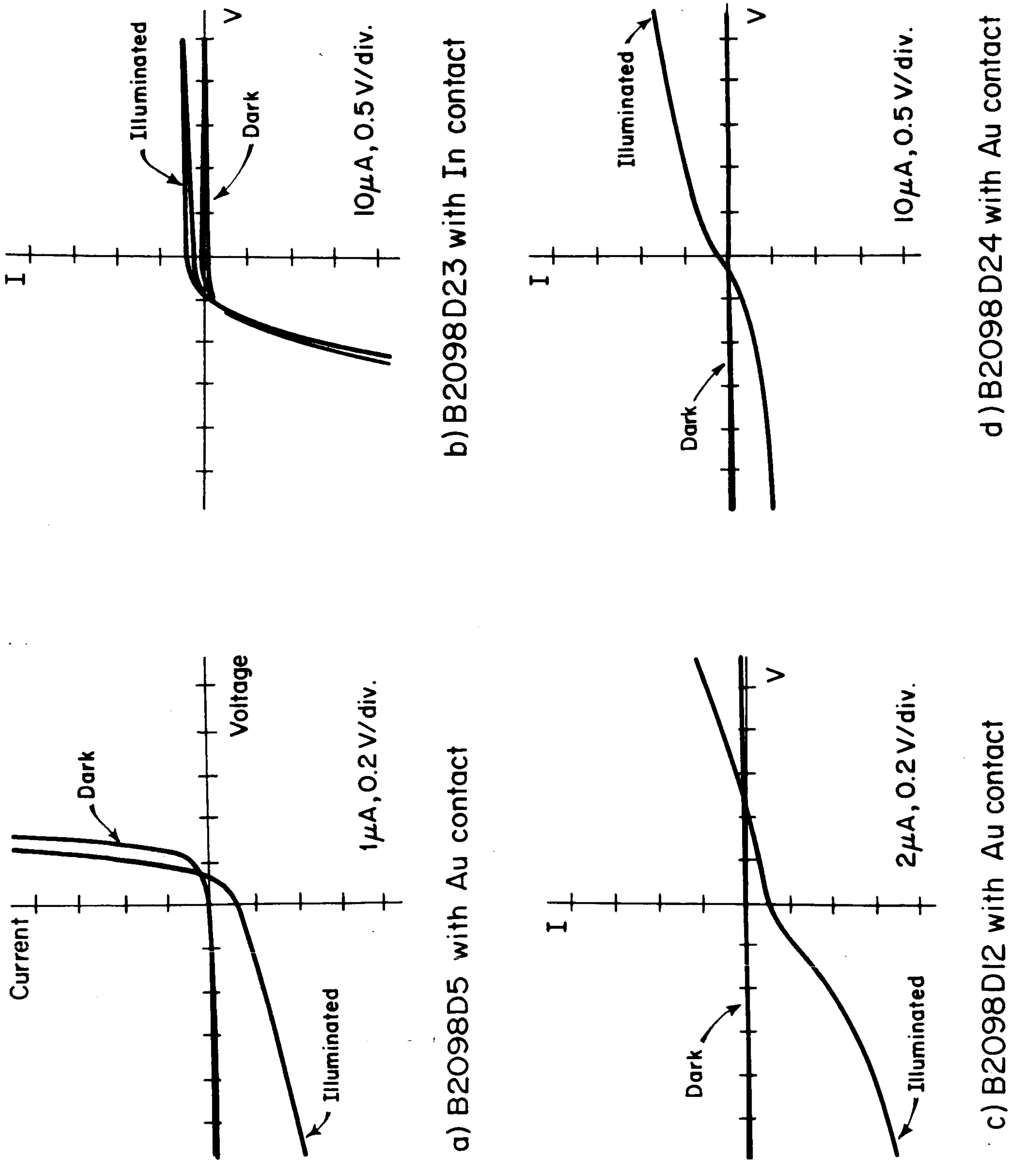
The current-voltage characteristics of a number of samples were measured at 300°K using a Tektronix Model 575 transistor curve-tracer. DC methods were used where greater precision was required. Nearly all of these samples show a rectifying I-V curve which is sensitive to photon energies below the bandgap of CdTe.

It is difficult to make an ohmic contact to the CdTe face of the samples, and therefore one must be very careful to separate out the rectification at the contact from the rectification associated with the CdTe-HgTe interface. Fortunately, it is possible to change the direction in which the CdTe contact rectifies by using either indium or gold contacts. In addition, experiments were performed on the photovoltage arising between two contacts on the CdTe face, and in no case was there any appreciable sensitivity to light with energy below the CdTe bandgap. Thus by using both CdTe-filtered and unfiltered light as well as several different contacts per sample, it is possible to separate out the contact rectification.

The four types of behavior observed for CdTe-filtered illumination are shown in Fig. 1. (Only data from samples with the same response to filtered and unfiltered light are shown.) The curves (c) and (d) are the same for both indium and gold contacts, and furthermore, the behavior is the same for filtered and unfiltered light, which indicates that in these samples there is a second junction in the CdTe, but not near the surface, in addition to the junction near the CdTe-HgTe interface.

CAPACITANCE MEASUREMENTS

Voltage-dependent capacitances were found in a number of



a) B2098D5 with Au contact

b) B2098D23 with In contact

c) B2098D12 with Au contact

d) B2098D24 with Au contact

Fig. 1 I-V Characteristics of CdTe-HgTe Devices Under CdTe-filtered Illumination the devices, although the multi-junction structure present in most of them makes the exact interpretation of the voltage behavior difficult. Measurements were made using a Boonton Model 75B-S8 direct capacitance bridge operating at 1 Mc.

The C-V curve of the sample whose I-V curve is given in Fig. 1a is shown in Fig. 2a. Again voltage is positive with respect to the CdTe. It can be seen that the capacitance decreases for the reverse-bias polarity indicated by the I-V curve.

If it is assumed that the junction is strongly asymmetric and that therefore most of the depletion-layer width change occurs on one side of the junction, then the equation derived by Schottky[2]

$$\frac{d(1/C^2)}{dV_{24}} = \frac{8\pi}{eN_{A,D}\varepsilon}$$

can be used to infer the doping variation on that side of the junction. This is shown in Fig. 2b, where it has been assumed that the dielectric constant is position-independent and equal to the CdTe value of $11\varepsilon_o$. The calculated doping densities are within an order of magnitude of the value obtained from Hall measurements on the sample before diffusion ($p=4.8 \times 10^{12} cm^{-3}$).

It was observed in passing that the capacitances were quite photosensitive both in the biased and unbiased conditions, and that the effect of illumination was to increase the capacitance.

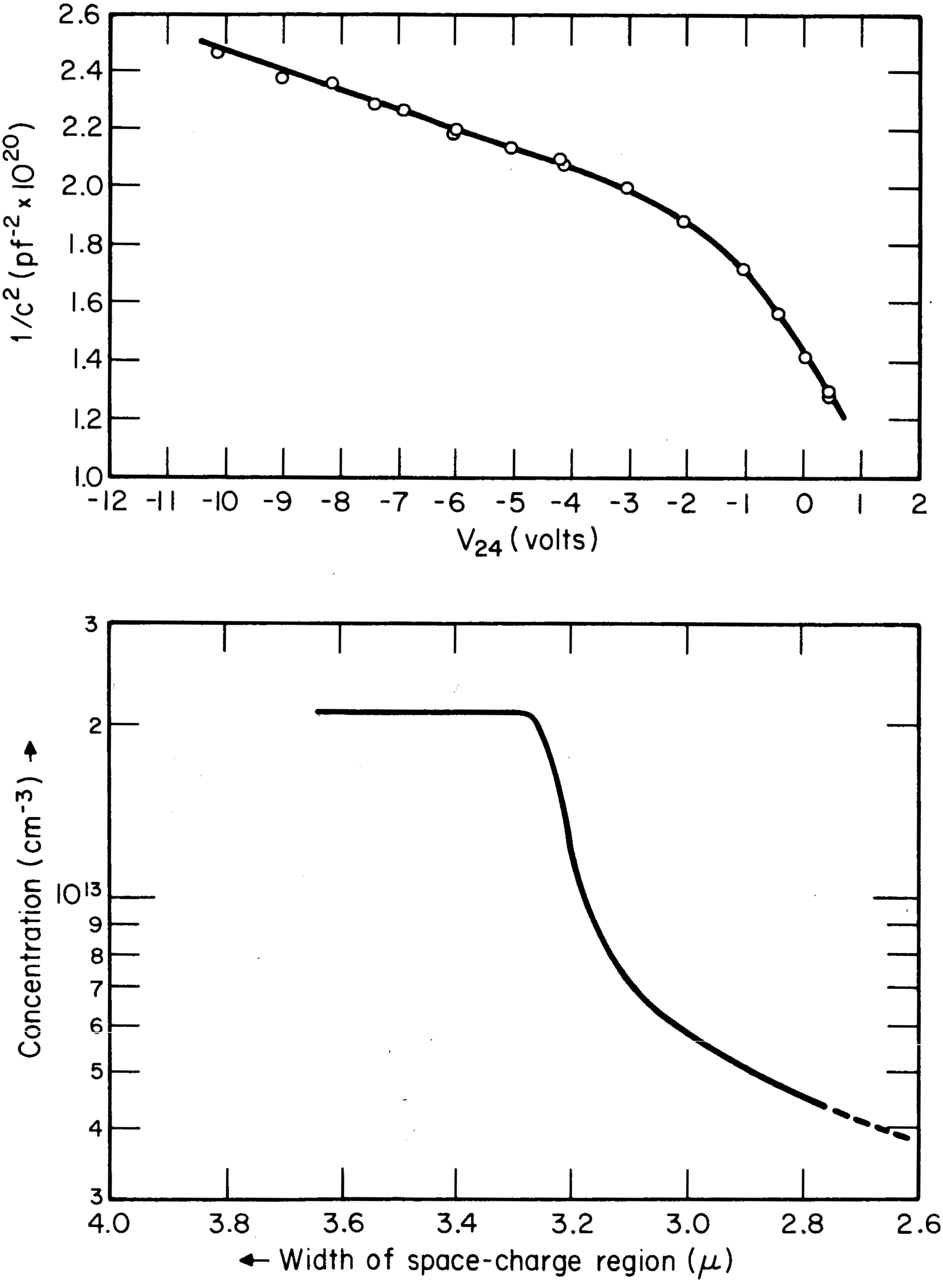


Fig. 2 Capacitance-Voltage Behavior and Deduced Impurity Distribution

ANALYSIS

The model for the graded gap outlined in an earlier progress report[3] has been generalized and extended to include the effects of diffusion as well as drift of minority carriers, monochromatic radiation, and finite absorption coefficients. The excess carrier density in a photoexcited graded-gap region adjacent to a p-n junction is now being calculated, with the final aim of obtaining an expression for the spectral behavior of the photocurrent for the model under discussion.

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Alan W. Carlson

CHAPTER II

CADMIUM-ZINC ANTIMONIDE SOLID SOLUTIONS

Growth of single crystal regions of $Cd_xZn_{1-x}Sb$ with x equal to 0.2 and 0.3 has recently been achieved. Attempts to extend the method for growing ZnSb, that of maintaining a 20 atomic per cent excess of Sb in the molten region to avoid a peritectic region in the ZnSb phase diagram, to this composition range had previously failed. Similarly attempts to extend the method used for CdSb, that of using a stochiometric composition in the molten region, had also failed. The recent, successful results were obtained by reducing the excess Sb concentration in the molten zone as more Cd was introduced. A 15 atomic per cent excess of Sb was used for $x = 0.2$ and a 10 atomic per cent excess was used for $x = 0.3$.

Experiments with composition analysis by various methods have shown that wet chemical analysis is the most accurate and practical method to use. Both x-ray fluorescence and density measurements proved to be of questionable accuracy. Polarographic methods were also investigated and found to be unsuitable. It is planned to determine composition crudely by the crystal growth records and to determine the composition accurately by destructive wet analysis of samples after measurements have been made on them.

ZnSb and CdSb have orthorhombic crystal lattices. Unlike cubic crystals, these compounds possess many anisotropies in the absence of a magnetic field. For both compounds, the electrical conductivity and the refractive index are tensors diagonal in the crystallographic axes. This leads to interesting electrical and optical effects. Optically the crystals are biaxial, i.e., they possess two optic axes. Being somewhat transparent in the infrared, the crystals will exhibit infrared interference phenomena analogous to that exhibited by transparent birefringent crystals in the visible region.

The determination of the effective masses of holes in ZnSb, CdSb, and their solid solutions is essential for an understanding of their properties. Presently the state of the literature is uncertain with regard to the effective masses of the end compounds, ZnSb and CdSb. Several conflicting values for these parameters have been reported. An investigation was made to determine a method for obtaining the effective masses in a way different from those that have already been used by others. Faraday rotation seemed to be a reasonable method to use until investigation of the theory revealed otherwise. The anisotropy of the dielectric constant produces an anisotropy in displacement current which completely obscures the effect of the magnetic field. Only an extremely small rotation proportional to the square of the magnetic field would be observed.

The three independent effective masses of a general, zero-centered ellipsoid may be determined from free carrier absorption measurements for semiconductors of orthorhombic symmetry. This is not possible for cubic materials where the free carrier absorption is isotropic. To extract effective masses from free carrier absorption data it is necessary to know the refractive indices, the carrier concentration and information about the scattering parameters. This auxilliary data can be obtained by additional optical and electrical measurements on the samples.

A study of the ZnSb-CdSb system through free carrier absorption has been undertaken. A laboratory spectrometer has been outfitted with silver chloride transmission polarizers for this purpose. An absorption coefficient proportional to wavelength squared, characteristic of free carrier absorption, has been observed for the b and c axis of ZnSb in the range of 6 to 15 microns. To date this has been the only sample investigated. The refractive index as a function of wavelength has been determined for the b and c axes of ZnSb by observation of interference fringes with light polarized along each axis and between crossed polarizers. Presently, electrical conductivity and the Hall effect are being measured on samples of ZnSb cut along these axes. The resulting data will be correlated with the other information to yield effective mass parameters m_b^* and m_c^* for ZnSb. Then similar measurements will be made on the a axis of ZnSb, the three axes of CdSb and the three axes of various compositions of the mixed crystals.

Clifton G. Fonstad

CHAPTER III

ELECTRO-OPTICAL EFFECT MEASUREMENTS IN CADMIUM TELLURIDE

INTRODUCTION

Recent literature shows that the energy band structure of cadmium telluride is not well understood and is the subject of much discussion[1,2,3]. The major question concerns whether the conduction-valence band gap is direct or indirect. Magneto-resistance[4], cyclotron resonance[2], optical absorption[1,3], photovoltaic effect, infrared Faraday rotation, and infrared-reflection[2] measurements conflict as to which model, direct or indirect band gap, fits the data best although the direct model is gaining favor and is supported by several recent measurements of optical absorption and piezoresistance[2], and by the only published energy band calculation for cadmium telluride[5]. Several questions also exist as to the exact energies of several higher inter-band transitions observed in optical-reflectance measurements on cadmium telluride[6]. The peaks in the data curves are, in these cases, broad and/or quite obscure and thus the energies of the photons involved in the transition are somewhat uncertain. A final question about cadmium telluride concerns a point raised by Conley[3] dealing with which phonons are involved in the exciton absorption at the fundamental absorption edge. He has observed the transition to the exciton accompanied by the annihilation of a longitudinal optical phonon but suggests that a second process involving a transverse optical phonon also occurs.

HISTORY OF ELECTRO-OPTICAL EFFECTS

The Franz-Keldysh effect--the change of the optical absorption coefficients of a semiconductor because of the presence of an electric field[7]--and electroreflectance--its counterpart in reflection and the change of the optical reflection coefficient--offer powerful tools for investigating semiconductor energy band structures because they are differential techniques. Whereas, for instance a new absorption process will appear as a change in the slope of the absorption coefficient when plotted against photon energy, the same process will appear in Franz-Keldysh data as a peak or series of peaks which are more easily identified and more accurately located than the slope change. By studying the temperature and electric field dependences of the position and magnitude of the peaks and the number of peaks it is possible to distinguish between possible absorption processes. For example, a direct allowed band-to-band transition shows very strong electro-optic effects while indirect or direct unallowed transitions show much smaller effects. Exciton absorption shows symmetrical Franz-Keldysh peaks with a characteristic temperature dependence.

Franz-Keldysh effect measurements have been used to study the optical-absorption edges of, for example, Si[9], Ge[10], GaAs, CdS, and TiO_2[11] revealing a large amount of previously unobserved structure, and recently electroreflectance measurements have been used to study absorption structure above the fundamental absorption edge in Si[12], Ge[13], GaAs[8], HgTe, InSb, HgSe, InP, and GaSb[14]. No data for any electro-optical measurements on cadmium telluride have been published although Cardona has reported making some room temperature electroreflectance measurements[15].

In view of the successful use of electro-optical effect studies in other semiconductor materials and because of the failure of many experimental tools to yield conclusive results concerning the energy band structure of cadmium telluride, it was decided to use both the Franz-Keldysh effect and electroreflectance to study optical absorption processes in cadmium telluride in an attempt to gain additional, more conclusive evidence concerning the energy transitions mentioned previously.

Franz-Keldysh effect measurements are limited to photon energies where the absorption coefficient is below 200 cm^{-1} and thus do not permit a study of absorption processes occurring above the absorption edge as do reflection measurements but they are more easily analyzed, are more readily performed on the available equipment, and are a very powerful tool. Electroreflectance measurements have the advantage of being effective at energies well above the absorption edge and thus allowing a more complete spectrum study but they present data analysis problems that make drawing ready conclusions difficult.

SAMPLES FOR EXPERIMENTATION

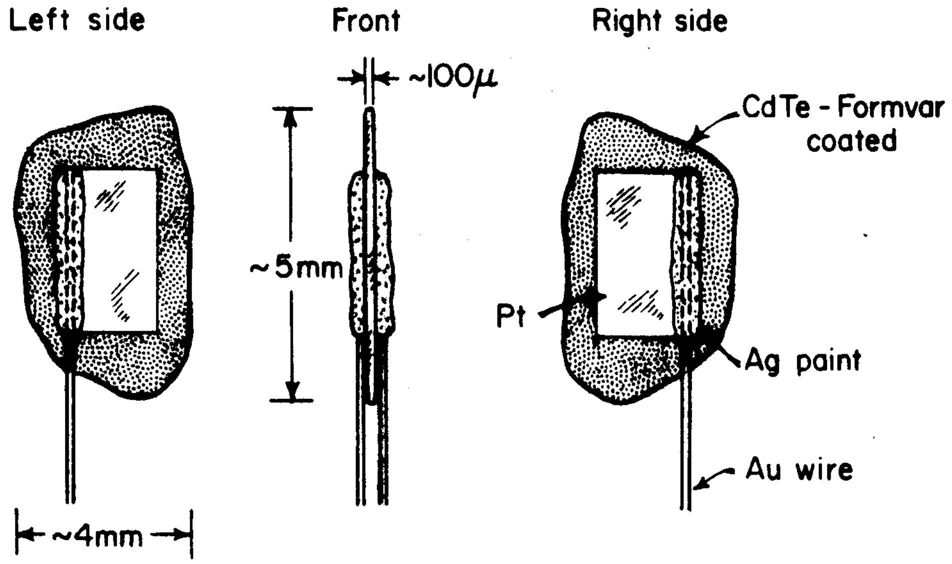
The cadmium telluride used in the experiments was grown by George Almasi in this laboratory[3,16]. The samples are single crystals of high purity. Six samples from three different ingots were obtained and prepared for use.

Transmission measurement, i.e., Franz-Keldysh, samples must necessarily be thin, <100 microns, and, because a high and uniform electric field must be maintained in them with negligible heating, they must have high resistivities,$<5 \times 10^2$ ohm-cm. The (initially) low resistivity of the samples was due to an excess of either cadmium (n-type) or tellurium (p-type) in the crystals; by annealing the samples at 650°C for 24 hours in the presence of additional pulverized cadmium telluride and in an evacuated Vycor tube a better stochiometric balance was obtained and the resistivites were increased. Evaluation of the samples after the annealing was complicated by the difficulty of making ohmic contacts to cadmium telluride and by the lack of any extra material to make special geometry samples. Two resistivity measurements, one ac and one dc, were found to be usable; in both the samples were polished on two parallel surfaces to give a flat "disk" about 1 cm in diameter and 2 mm thick. In the ac measurement the samples were coated with Formvar, an insulating varnish, and rectangular platinum electrodes were plated on the flat faces. By measuring the impedance between the platinum electrodes and considering the structure as a lossy capacitor the bulk resistivity is obtained. In the dc measurement a four point technique for measuring the resistivity of irregularly shaped disks was used[17]. Four ohmic contacts were put on the edges of the sample either by ultrasonically soldering on indium (best on n-type) or by depositing gold areas from a gold chloride solution (best on p-type). Accurate measurements of the resistivities were not obtained but the results obtained were sufficient to allow the selection of three samples of adequate resistivity. These were commercially polished to 100 microns (thickness) or less. They were then chemically etch-polished 2-1/2 minutes in a 3:7 solution of concentrated sulfuric acid and saturated potassium dichromate solution to remove 12 - 15 microns from each surface. They were then coated with formvar and thin, transparent platinum electrodes were plated on the faces. A gold wire was attached to each platinum electrode with silver paint to complete the structure,

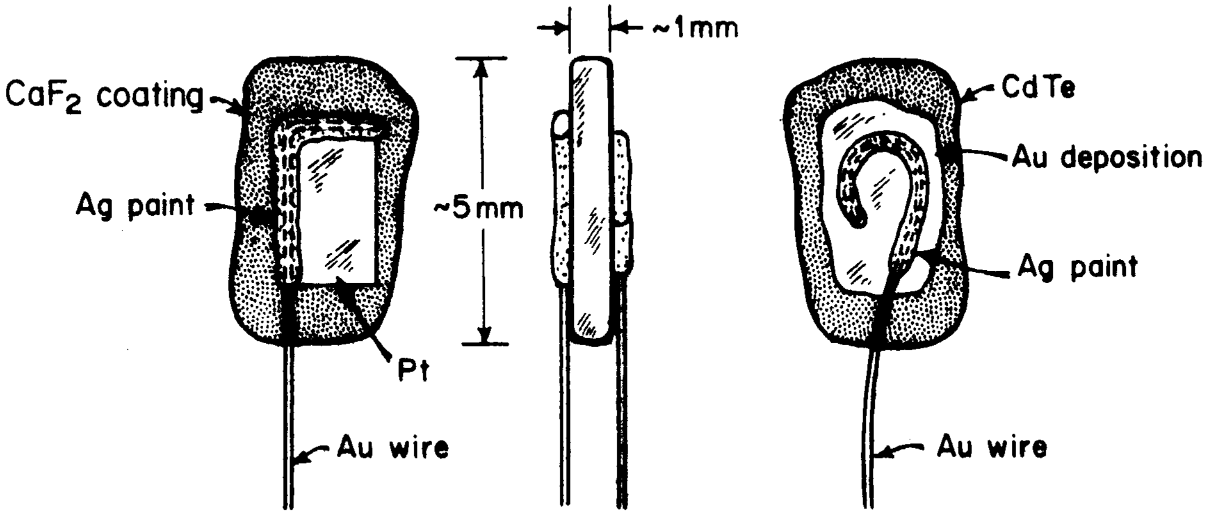
Fig. 3a. This parallel plate geometry is similar to that used by Yacoby on silicon[9]. The Formvar prevents the injection of carriers into the high resistivity sample yet this thin insulating layer is effectively shorted when a high frequency voltage signal is applied to the sample between the platinum electrodes so that all of the voltage (and, thus, the field) falls across the cadmium telluride.

Electroreflectance samples were designed differently so that measurements would be made at room temperature and so quantitative analysis of reflection data could be performed readily (Note: transmission samples could be used except that even with their increased resistivities they cannot be used at room temperature and they are not readily adapted to the evaluation of reflection data). A high field is needed only at the sample surface so a properly biased rectifying or blocking contact on the reflecting surface will create a depletion layer there and high field without any heating of the sample even if the resistivity is low.

Cardona has had success with other semiconductors using a semiconductor-electrolytic solution interface as a rectifying contact on the reflecting surface. This is an ideal structure because the light is essentially reflected from a bare cadmium telluride surface but in all of the attempts made to imitate this with the available samples leakage currents at the contact



a) Transmission sample



b) Reflection sample

Fig. 3 Sketches of Samples

were high, resulting in rapid corrosion of the cadmium telluride surface. Instead, a blocking contact geometry was developed; it consists of a layer of calcium floride evaporated on a etch-polished sample face and a thin platinum electrode evaporated on the calcium floride. A gold area deposited on the back face of the sample makes ohmic contact to the cadmium telluride (see Fig. 3b). Properly biasing the sample with respect to the platinum area creates, with about 10 volts bias, fields of from 10^4 to 10^5 volts/cm at the surface. The major problem with this structure lies in the interpretation of the reflection and electroreflection data obtained; it is hard to isolate the optical constants of the cadmium telluride itself. This present geometry with electrodes and dielectrics on the sample surface makes analysis of the reflection data complicated, and a careful set of measurements made at each stage in the fabrication of a sample is necessary to determine the thickness and optical constants of each layer. While this procedure has not been entirely worked out, it is feasible but complicated and there is hope of simplification.

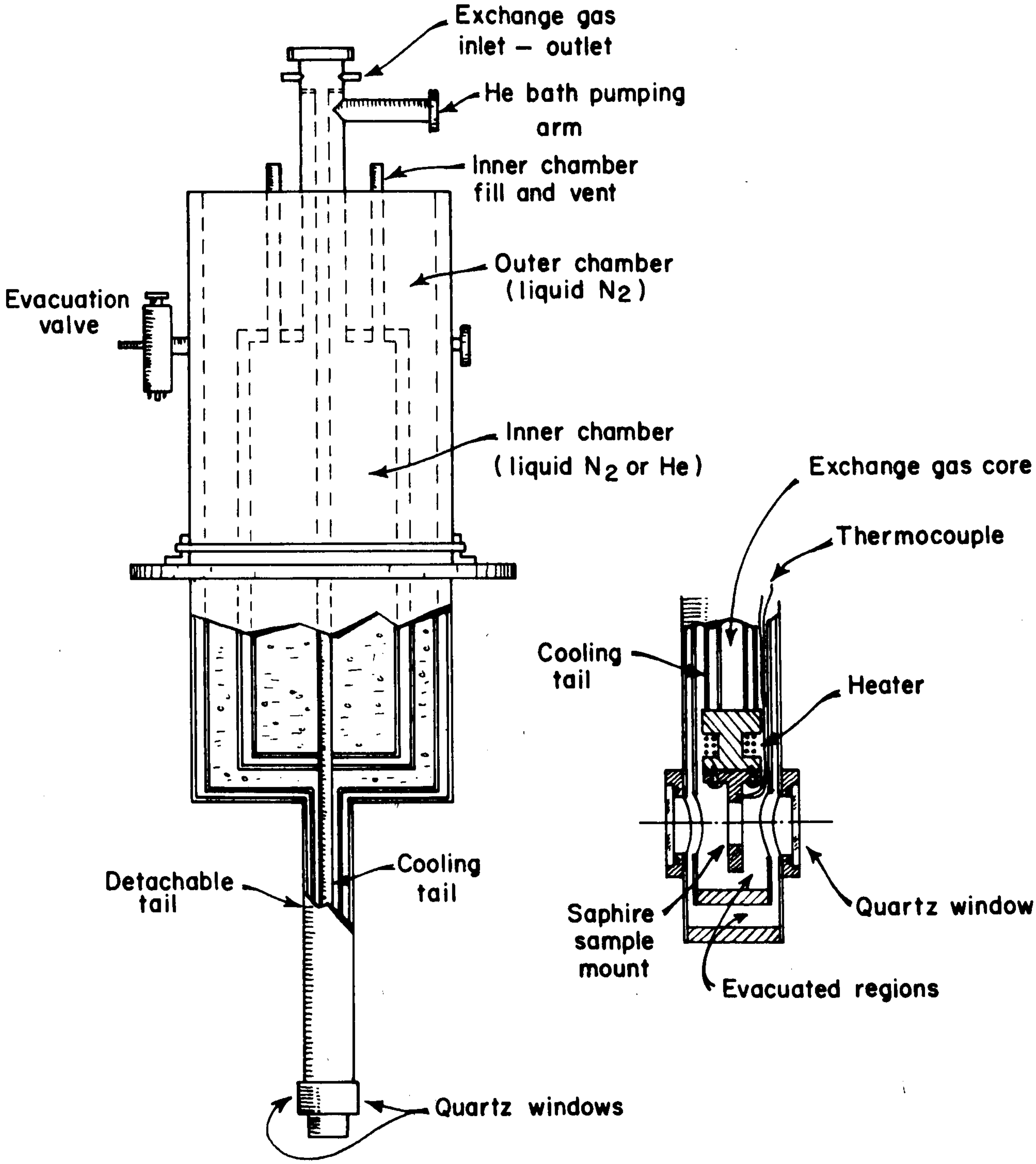
EXPERIMENTAL APPARATUS

Much of the basic apparatus required for electro-optical measurements has been assembled by Professor Yacoby and has been described previously[9]. Only a brief description of the apparatus with specific attention to modifications necessary for use on cadmium telluride will be given here. The basic units in the experimental set-up are the samples and their mounts, the light source and optics, the electric field source, and the detection system.

Franz-Keldysh measurements are being performed at low temperatures, <150°K, because the samples do not have sufficient resistivity at higher temperatures to prevent excessive heating and because much of the phonon-exciton structure is unobservable by high temperatures. This requires a special dewar for a sample holder; Fig. 4 shows this dewar and a detail of the sample mount. With the dewar and its heater the sample temperature can be varied from 4.2°K to near room temperature with good control.

The sample mount for electroreflectance measurements, on the other hand, is designed for room temperature use and to allow easy removal and repositioning of the sample. The sample is attached to a glass microscope slide and the slide is fitted into a special holder, where it can be raised and lowered vertically, can be rotated accurately, can be easily removed and re-inserted without disturbing any position settings, and is stable. The mount also has mounting posts for polarizors, lenses, and/or the photomultiplier tube.

The light source for both series of measurements is a Perkin Elmer model 112 double-pass monochromameter (in addition,



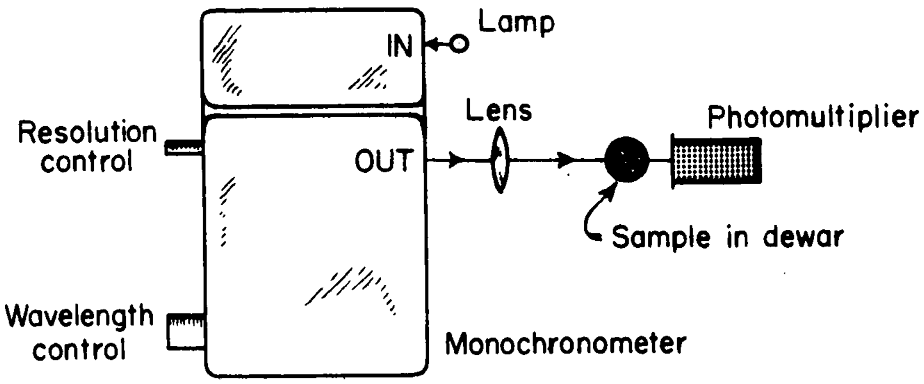
a) Dewar

b) Detail of sample mount section

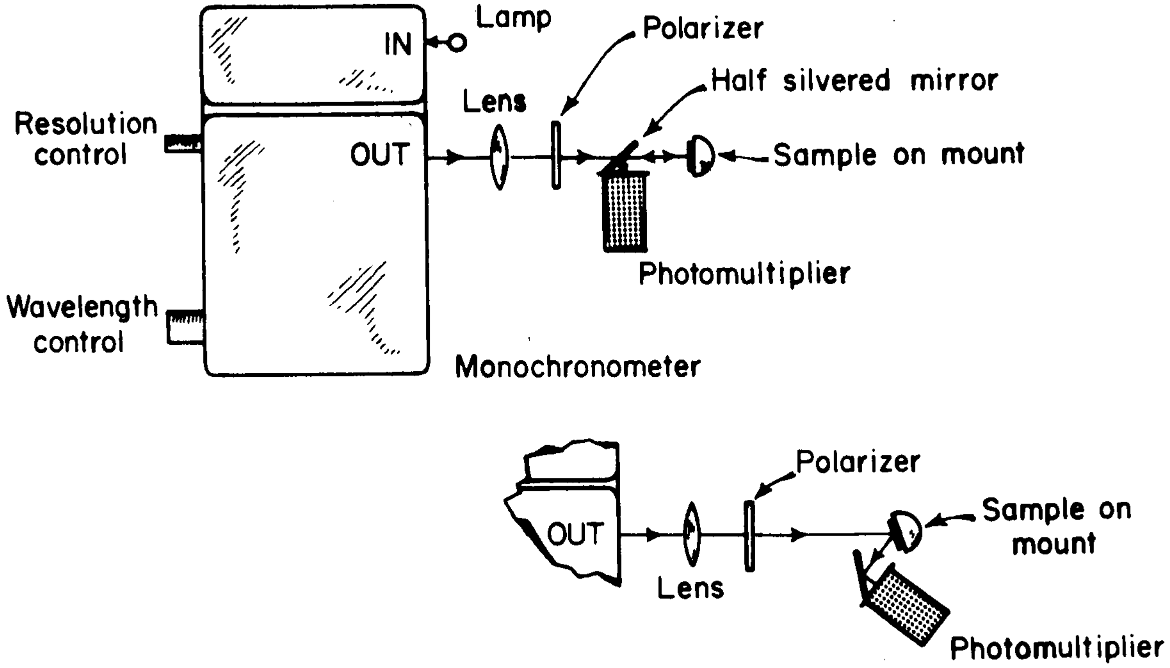
Fig. 4 Dewar for Transmission Measurements a model 99 grating monochromameter is available if increased resolution is required). The monochromameter is set to give a near monochromatic light beam which is directed through a lens and focused on the sample. For transmission measurements a photomultiplier tube, RCA 7102, is placed directly behind the sample; for reflection a half-silvered mirror gathers the beam reflected off the sample and deflects it onto a photomultiplier tube, RCA 1702 or RCA 931A depending on the energies of interest. A layout schematic is shown in Fig. 5.

The voltage signal to create the electric fields inside the samples is obtained, for reflection, from a General Radio Model 1217-C Pulse Generator--it is a 400 cps square pulse of up to 15 volts. For transmission a higher voltage--up to 300 volts--is required and the circuit of Fig. 6 is used to obtain the waveform also shown in that figure. Note that in both cases the field is created in the sample in an on-off pulse shape at 400 cps. This then means that the photomultiplier tube output will have a 400 cps component proportional to the change in the light absorbed or reflected when the field is applied.

This 400 cps signal is detected using a synchronous detection system. A small computer, much like a spectrum analyzer, is used in this system to allow long data accumulation times

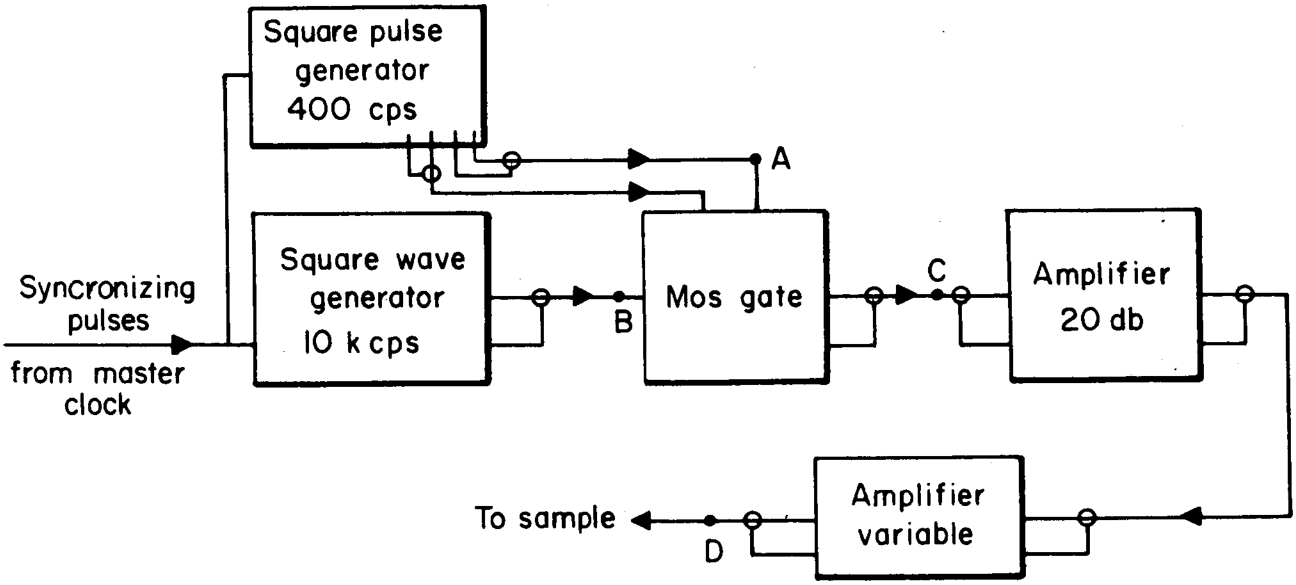


a) Transmission

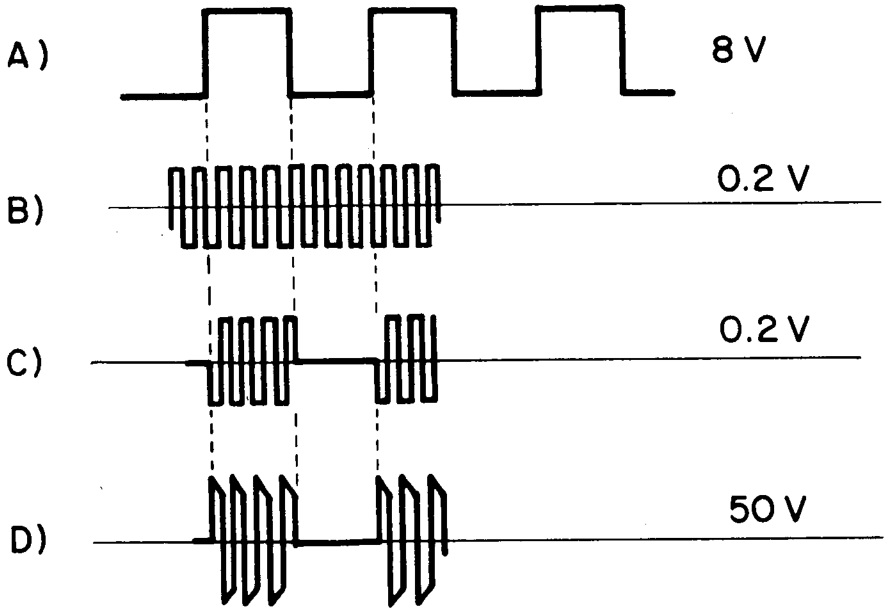


b) Reflection - upper for normal incidence, lower for $\theta = 0°$

Fig. 5 Optical Layout Schematics



a) Block diagram



b) Voltage waveforms at points in circuit

Fig. 6 Electric Field Supply for Transmission Measurements thus improving the signal-to-noise ratio while eliminating drift problems because many quick sweeps of the light energy spectrum, as opposed to one slow sweep, can be made. The general operation of the system has been described previously[9] and only a block diagram, Fig. 7, is presented here. Essentially, the light transmitted through or reflected off the sample is detected by a photomultiplier and the initial stages filter and amplify this output sending any 400 cps signal present to the computer. The computer, by adding and subtracting counts to its memory proportional to the magnitude of its input signal and by doing so at 400 cps in exact synchronism with the electric field on the sample (the variable phase shifter corrects for any phase shift in the amplifiers), performs the synchronous detection. Signals at other frequencies or not in phase with the electric field (e.g., due to sample heating) are treated as noise and are eliminated. Microswitches on the monochromameter spectrum scanning drum combined with a "bookkeeping" relay array allow the system to sweep a band of light energies many times, each time adding new data to previous data while keeping the energies separate. A master clock provides overall synchronization. Data from the computer can be displayed on a cathode ray tube and photographed, and/or read onto punched paper tape and then to punched cards for digital computer processing.

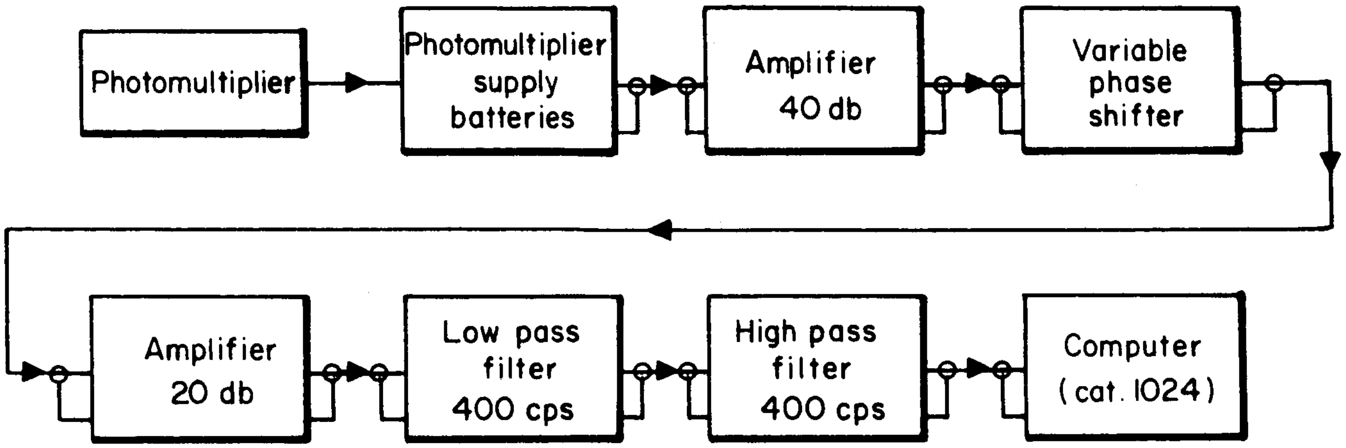


Fig. 7 Block Diagram of Synchronous Detector

EXPERIMENTS IN PROGRESS

Experimental techniques have been developed for each set of measurements--Franz-Keldysh and electroreflectance--and a brief description of what type of experiment is being or has been performed will be given below. Future work is also outlined. The results obtained thus far are tentative and too incomplete to be reported at this time.

Room temperature electroreflection measurements have been made on one sample using the arrangement of Fig. 5. Measurements were made on a complete structure where the calcium floride and platinum thicknesses were unknown so analysis of the data quantitatively was impossible, but it could be determined that there was an electro-optical effect. It was possible with our optical arrangement to investigate the region from 1.2 to 3.5 electron volts--this covers the optical-absorption edge and several higher interband transitions. Only at the absorption edge was an effect seen. Presently, work is not being done on electroreflection measurements, but it will be continued later with quantitative interpretation of the data and a more detailed search of the higher energy region looking for possible structure.

Present work is concentrating on Franz-Keldysh measurements. A strong effect has been observed and work is proceeding on determining its true shape and fine structure, its temperature dependence, and its field strength dependence. This work will be continued and checked on other samples from different ingots.

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H. St Onge

CHAPTER IV

ELECTROPHOTOLUMINESCENCE IN CdS

INTRODUCTION

The success of the Franz-Keldysh effect[1,2] as an efficient technique of investigation of the fundamental optical properties of solids has suggested the possibility of studying the effect of an electric field on the fluorescence of semiconductors.

The experimental investigation of the effect of a strong electric field on the luminescence of CdS is under way. The purpose of the study is to make a measurement of the change in the width, position and amplitude of the emission lines with the emphasis put on the study of an intrinsic emission of CdS, namely the "blue" exciton recombination lines.

EXPERIMENTAL INVESTIGATION

In an attempt to observe emission from the bulk of the crystal, numerous difficulties have been encountered in finding a way to apply a high electric field. The contradiction between a bulk measurement, which requires light excitation in the high photoconductivity region, and the application of a high electric field has not been solved.

As a first attempt we hoped to find an experimental compromise using a simple Keldysh-like configuration for the contacts: two blocking contacts on each surface. The low resistivity needed to observe the fluorescence with good resolution ruled out this possibility.

We found it was practically impossible to create a large enough depletion region in the CdS by using a blocking contact and an ohmic contact. Presumably the continuous generation of carriers creates a nonequilibrium situation in the depleted region.

We are now considering the emission from the surface of the sample. This approach is now giving satisfactory results.

SAMPLE CONFIGURATION

By shining light of high energy on the sample, i.e., where the absorption coefficient is very large, it is possible to limit the region of carrier generation to a small layer on the surface of the sample. The surface resistivity will decrease considerably leaving the bulk resistivity practically unchanged from the dark resistivity. Between two ohmic contacts very close to each other one can obtain a fairly high resistance and thus be able to apply voltages large enough to create on the surface the necessary high electric fields. The sample geometry is shown in Fig. 8.

Thin single crystals of thickness varying between 25 and 100 microns are available. The surfaces are either naturally

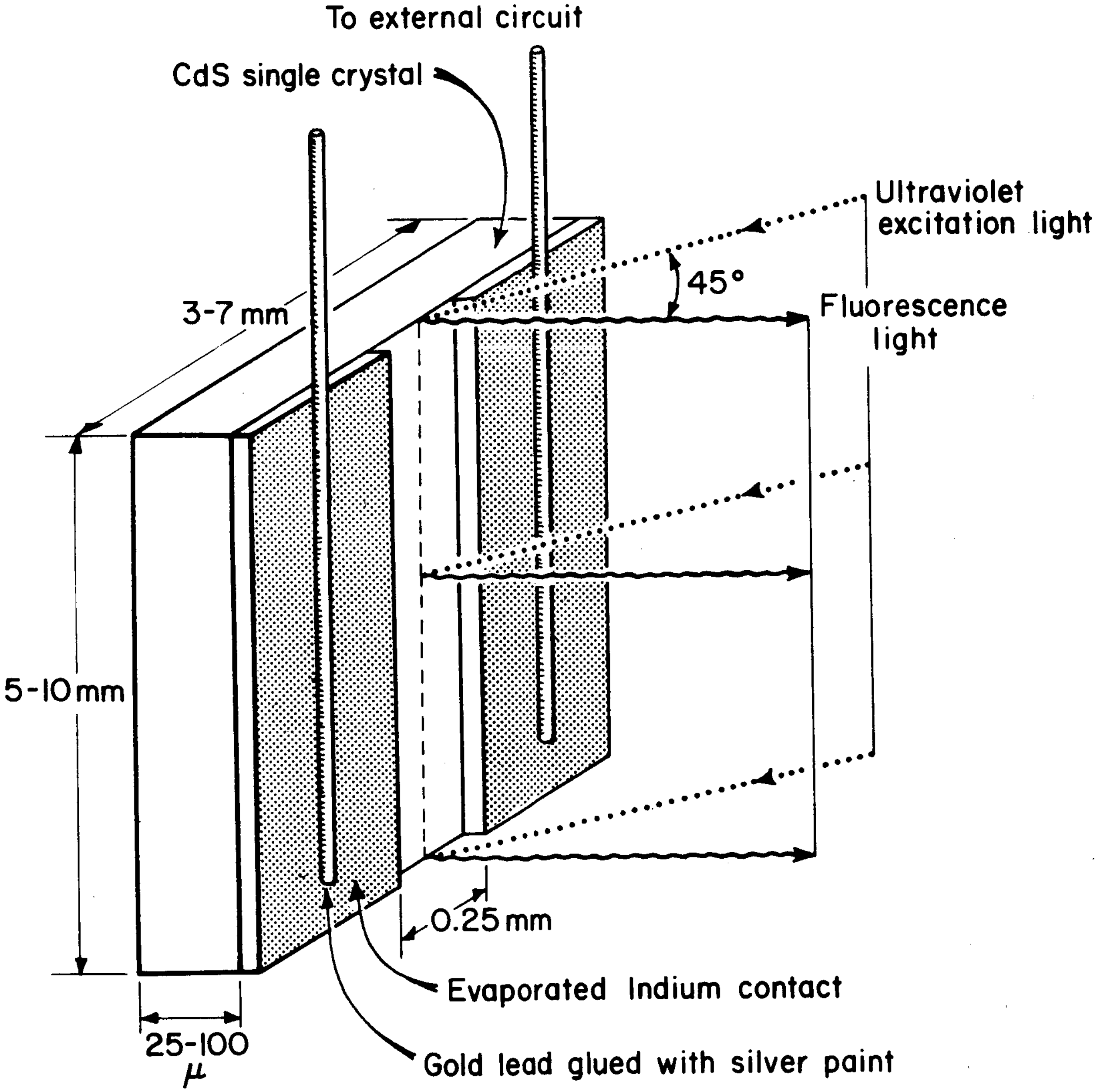

Fig. 8 Sample Geometry

polished directly from the growth, or are mechanically polished. Ohmic contacts are obtained by evaporation of indium on the surface of the sample. Small gold wires are then glued to the indium by silver paint.

MEASUREMENT OF THE ELECTROPHOTOLUMINESCENCE

A high pressure mercury arc and the Corning filter 7.60 produce the narrow-band light excitation around 3600 Å. A gas-exchange optical dewar especially equipped with a 360° quartz window holds the sample. The emitted light is then analyzed through a high-resolution grating spectrometer. An RCA 931-A photomultiplier cooled to liquid nitrogen detects the light signal. The signal from the photomultiplier is filtered and amplified and sent to a special-purpose computer which acts as a synchronous detector. In reference 3 a detailed analysis of such a detection system is given.

The voltage applied to the sample has the basic frequency of the detection system (440 cps). In order to avoid heating effects in the sample the electric field has the form of a narrow pulse at a repetition frequency of 440 cps. The synchronous detection gives directly the change in fluorescence caused by the electric field. The data appears at the computer as the change in emission as a function of wavelength. A mechanical chopper is used to measure the emission spectrum in the absence of a field.

Figure 9 gives a block diagram of the electrophotoluninescence measurement.

PRELIMINARY RESULTS

The first samples to be investigated were impurity doped crystals. These crystals showed a very strong emission in the green region at 77°K almost exactly where the known "green" emission of CdS usually occurs[4,5]. The fluorescence appears as a wide peak with no structure; nothing has been observed in the blue region where the exciton lines should be seen[6].

The absence of structure in the green emission can be understood by the presence of impurities; although nothing is known about the doping of the crystals, a study by Uchida[7] strongly suggests that doping can easily cause the disappearance of a structure which is easily resolved in a pure crystal.

The mechanical polish of the crystal could explain the absence of a blue emission. It has been shown that the exciton lines disappear after a mechanical polish but after proper etching they can reappear. No attempts were made to improve the surface condition on account of difficulties with the ohmic contacts. An investigation at helium temperature did not yield the interesting changes which have been observed in pure crystals[6], where lowering the temperature enhances considerably the blue emission.

The electro-effect was measured for the green emission.

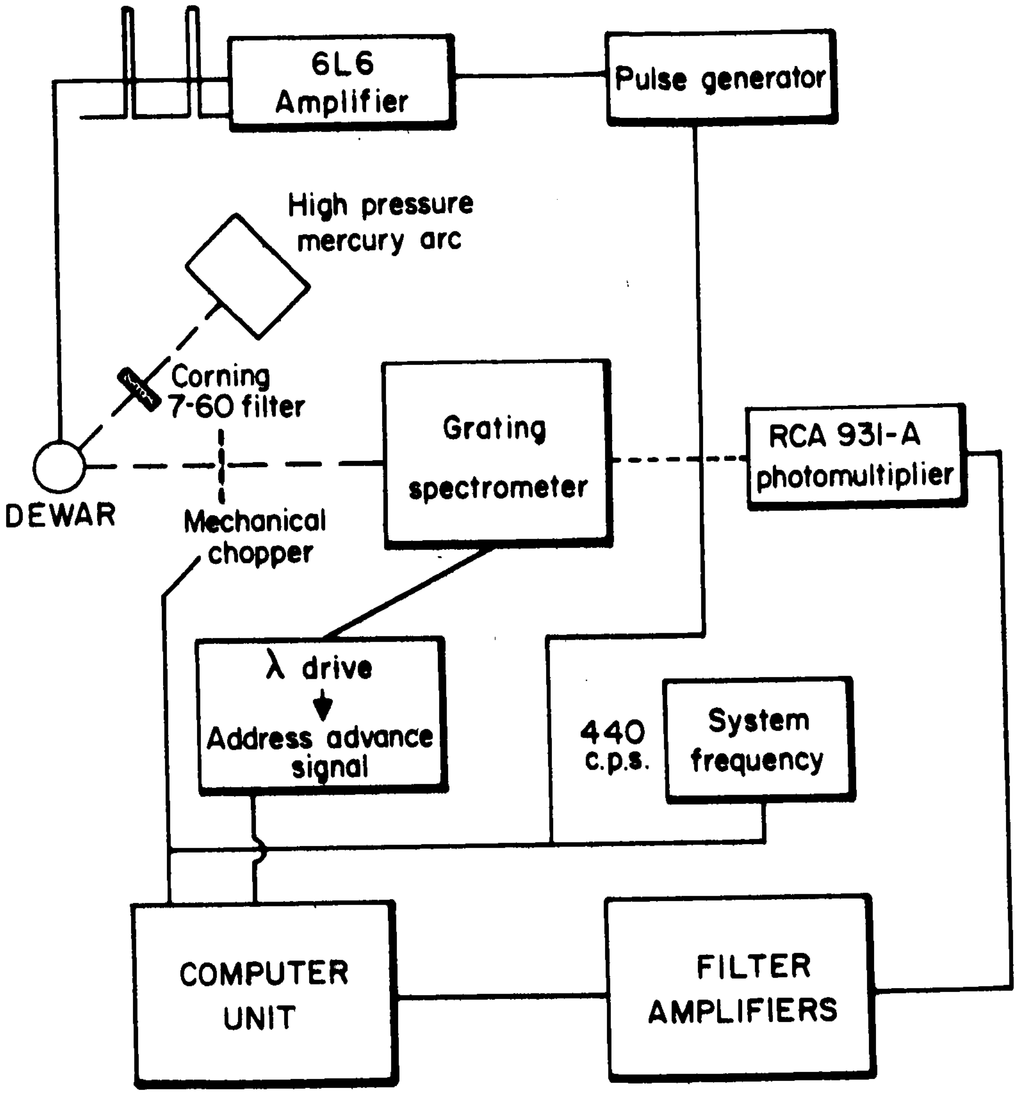

Fig. 9 Measuring and Detecting System

We found an extremely small enhancement of the emission for fields of 10^4 volts/cm. The spectrum of the change in fluorescence follows exactly the emission spectrum. The temperature effect appeared to be important and thus made the interpretation very difficult. A more elaborate investigation to distinguish the true field effect could be made but the availability of new high purity crystals led our investigation toward these new samples.

These crystals are naturally polished and are presumably of very high purity. The luminescence was measured with no contacts on the sample. Very promising results were obtained. The crystals show blue, green, and orange fluorescence. The structure found in the blue emission is very similar to that observed by Thomas and Hopfield[6] and is believed to be the intrinsic exciton recombination. Contacts are now being prepared for an investigation of the electrofluorescence effect.

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