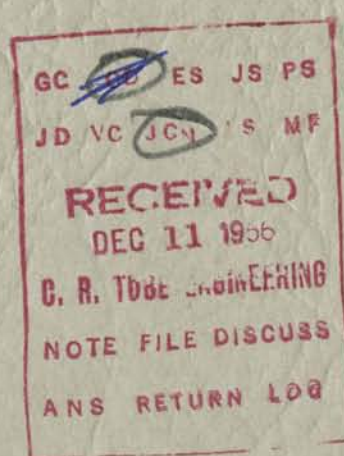


RB-78

**LOW FIELD ELECTROLUMINESCENCE
IN INSULATING CRYSTALS OF CdS**



**RADIO CORPORATION OF AMERICA
RCA LABORATORIES
INDUSTRY SERVICE LABORATORY**

RADIO CORPORATION OF AMERICA
RCA LABORATORIES
INDUSTRY SERVICE LABORATORY

RB-78

LOW FIELD ELECTROLUMINESCENCE IN
INSULATING CRYSTALS OF CdS

This report is the property of the Radio Corporation of America and is loaned for confidential use with the understanding that it will not be published in any manner, in whole or in part. The statements and data included herein are based upon information and measurements which we believe accurate and reliable. No responsibility is assumed for the application or interpretation of such statements or data or for any infringement of patent or other rights of third parties which may result from the use of circuits, systems and processes described or referred to herein or in any previous reports or bulletins or in any written or oral discussions supplementary thereto.

Low Field Electroluminescence In Insulating Crystals Of CdS

Green electroluminescence can be obtained from insulating crystals of CdS at low DC fields. The wavelength of the emitted light corresponds to the energy of the gap between the valence and conduction bands. The emission band and the optical absorption edge shift together with temperature. The emission of light is correlated with an abrupt increase in current through the crystal, and the intensity is proportional to it. The measured electric field in the region of the crystal where light is generated is approximately 1000 volts/cm. The pattern of the electroluminescence (beams) is deflected by an 8000 gauss magnetic field. The experiments can be explained by the hypothesis that conduction occurs because of injection of free carriers into the insulator by the electric field, electrons from the cathode and holes from the anode. The luminescence results from the recombination of the injected holes and electrons which have drifted into the bulk of the crystal.

Introduction

The conductivity of certain insulating CdS crystals can be profoundly increased by an electric field. At the same time, green (edge) electroluminescence can be obtained. This emission comes from a large region in the crystal (≈ 1 mm length) where the electric field is low.¹ This bulletin will show that conductivity is induced in the insulator by injecting electrons and holes from the electrodes and that the electroluminescence is produced by the subsequent radiative recombination of these carriers in the bulk of the crystal. It is believed that the crystals used were essentially uniform and that the only prominent barriers present were patches from which holes were injected at the anode. This hypothesis is in contrast with other published work^{2,3,4,5,6} in which only one sign of carrier (electrons) is assumed to be involved and in which excitation is attributed to impact ionization in a localized breakdown field.

CdS Crystals

The crystals examined were grown by the vapor phase technique by S.M. Thomsen, K.F. Stripp, C.J. Busanovich, and R.H. Bube.⁷ In most batches impurities were deliberately added at some stage of the preparation, although attempts were also made to obtain pure perfect crystals. The batches can be roughly divided into three classes:

1. Pure Insulating crystals with little photoconductivity.

2. Relatively less insulating crystals with high photoconductivity. Added impurities Cl and Cu.

3. Relatively conducting crystals with high photoconductivity. Highly doped.

TABLE I

Carrier Life Times

CdS Crystal	Life Time (sec.)	
	Majority	Minority
Photosensitive	$> 10^{-3}$	$< 10^{-11}$
Electroluminescent	$\sim 10^{-5}$	$\sim 10^{-6}$

The available data indicates that the crystals are N-type. Only pure and nonphotosensitive samples display green electroluminescence. There are only a few batches with these particular characteristics, and of these, one batch is appreciably better than the others. High photoconductivity in CdS is associated with a long electron life time and a short hole life time.⁸ The insensitive crystals which display electroluminescence have a relatively shorter electron life time and a longer hole life time.⁹ Table I indicates a probable range of the values of the electron and hole life times for crystals of these two classes.

Experiments

Current-Voltage Characteristic

For measurement of the current-voltage relationship and production of electroluminescence, the crystal is placed in the circuit illustrated in Fig. 1. Gallium electrodes spaced about 1 mm apart are applied on one face of the crystal. The electroluminescence is viewed with a low power microscope. A typical voltage-current (V-I) characteristic is shown in Fig. 2. When over 1000 volts is applied to a fresh crystal there is an abrupt increase in current and a drop in voltage across the crystal. Electroluminescence appears coincident with the increase in current, first as a few bright yellow electroluminescent (EL) spots at the anode, and then as beams of green light originating from the yellow patches and extending across the crystal. The number of yellow spots and associated green beams gradually increase during operation until the entire crystal is filled with green light, Fig. 3. There are no spots in the body of the crystal and appearance and the movement of the green beams indicates that the bulk of the crystal is uniform. In addition to the prominent green there is faint red radiation, the characteristics of which have not been determined.

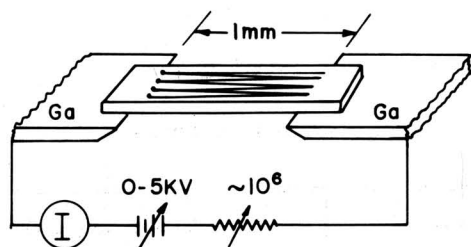


Fig. 1 - Experimental arrangement used to study CdS electroluminescence.

Spectral Distribution

The spectral distribution of the green light was measured by means of a Bausch and Lomb monochromator and detected with a multiplier phototube, having an S4 surface. Because of the dissipation of about 0.1 watt in the crystal by the current, the internal temperature of the crystal is not that of the surrounding atmosphere. In order to compare the location of the emission band with the optical absorption edge, both the emission and transmission were measured under the same operating conditions. Fig. 4 shows a series of curves giving the spectral distribution of the electroluminescence at several different ambient temperatures, and the corresponding transmission measurements. It is noted that the maximum electroluminescence and its shift with temperature correspond closely to the wavelength of the optical absorption

edge and to its temperature dependence. This correspondence indicates that the green electroluminescence is intrinsic recombination radiation (edge emission).

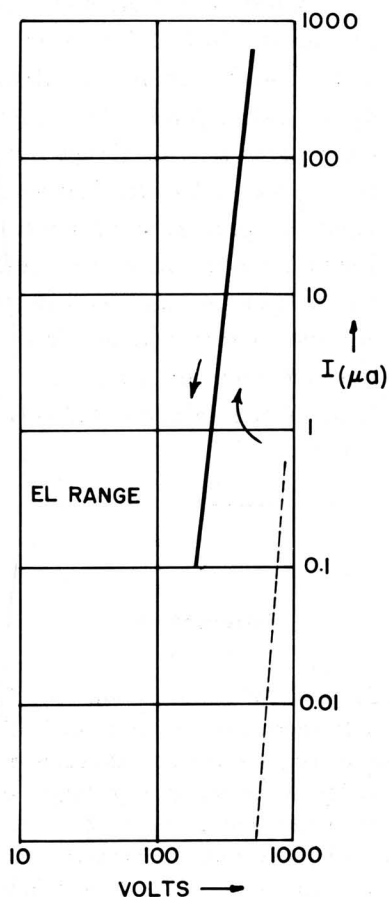


Fig. 2 - V-I characteristic of CdS in electroluminescent range.

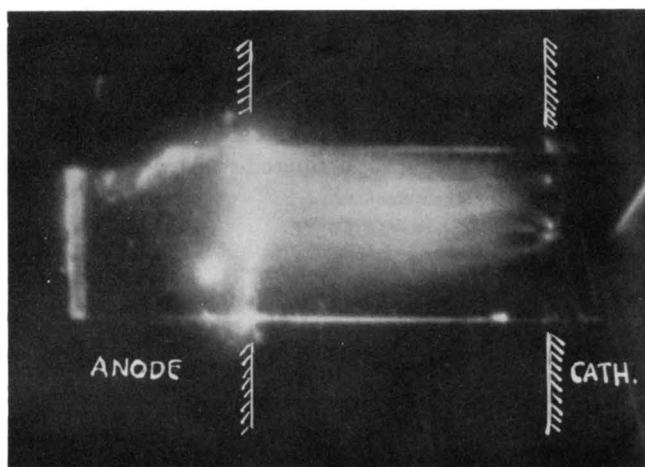


Fig. 3 - Photograph of electroluminescence from CdS. The over exposed region at the tip of the anode is an array of yellow (EL) spots. The spots at the tip of the cathode are not usually observed.

At liquid nitrogen temperature a double maximum is found in the electroluminescence. One peak corresponds

to the absorption edge, while the second one is at 5180 Å. The location of the short wavelength maximum relative to the peak at the longer wavelength and their relative amplitudes depend strongly on the current (temperature) being passed through the crystal. At temperatures below 90 degrees K prominent photoluminescence bands have been reported around 5180 Å.¹⁰ Apparently the same transition giving rise to the 5180 Å band is produced by both photons and by an electric field.

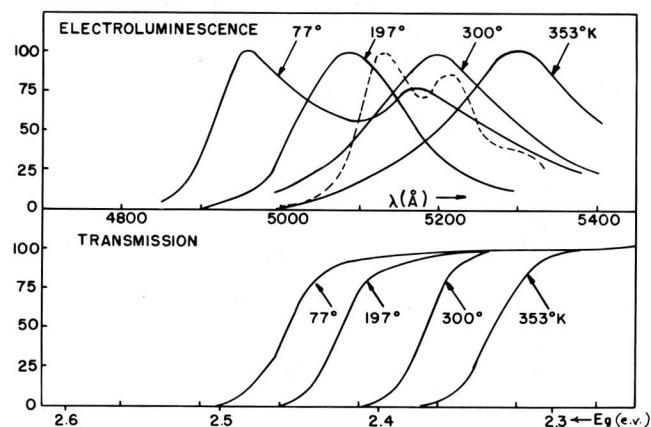


Fig. 4 - Spectral distribution of electroluminescence and corresponding optical transmission of CdS at indicated ambient temperature. The dotted curve shows the UV excited photoluminescence at liquid air temperature.

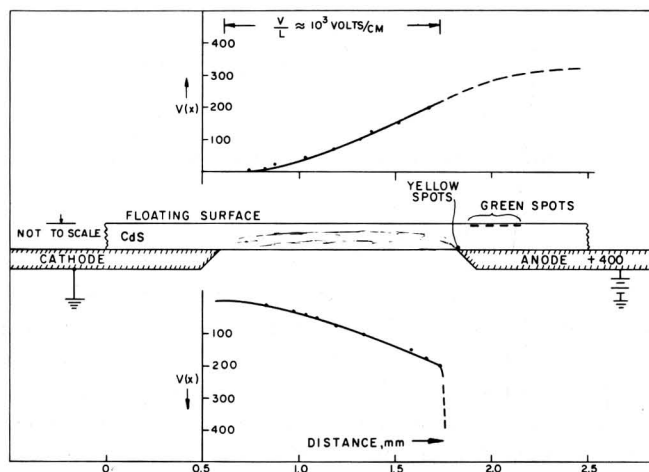


Fig. 5 - The distribution of potential $V(x)$ along an electroluminescent crystal.

Potential Distribution

The potential distribution along the surface of the crystal was measured with a fine wire probe and a high impedance electrometer. Fig. 5 is a plot of $V(x)$ along the top and bottom surface of the crystal under conditions giving green electroluminescence extending between the electrodes. The important features are: (1) The electric field at the cathode is low. (2) The field in the body of

the crystal where the green electroluminescence is emitted is relatively constant and low, being of the order of 1000 v/cm. (3) There is an abrupt change in potential in the region of the yellow patches. Though it is not possible to obtain a measurement of the voltage close enough to these regions to study the local field, it appears that the local field is higher here than in any other part of the crystal.

The Electroluminescence as a Function of Current

The intensity of the green radiation is proportional to the crystal current. The emitted power, as measured with a calibrated photomultiplier, is approximately 10^{-8} of the input electrical power. The conversion efficiency was not measured at low temperatures. There is, however, no appreciable diminution in the intensity of the green light when the crystal is operated in liquid air. On removing the electric field the electroluminescence decay time is less than 1 microsecond.

A-C Behavior

The a-c performance of the crystals is shown in Fig. 6. Consider a crystal with electrodes to which dc is first applied until electroluminescence is obtained and then removed. If a 60-cps voltage is now applied, it is found that at a particular voltage there is an abrupt increase in current and light is emitted. The light and the current are in phase, and the wave forms are identical. Current flows only during that part of the half cycle whose polarity corresponds to that of the dc initially applied. The crystal can be made to pass current in the opposite direction by reversing the d-c polarity and processing as before. Now current and light can be obtained during both half cycles, although the wave forms are not necessarily the same for each half cycle. In any case the yellow (EL) patches, described earlier, are always at the anode.

Electroluminescence can also be obtained in the absence of metallic electrodes by immersing the crystal in a dielectric medium between condenser plates. Here again, however, electroluminescence is found only if the crystal has previously been subjected to a high d-c field. The process by which the electrical properties of a crystal are altered by first applying a high voltage is called forming. In this particular case the specific action of the high field is thought to be confined to the region of the yellow patches at the tip of the anode.

Influence of a Magnetic Field

Haynes and Shockley describe an experiment in which the displacement of a beam of photoelectrons in

an $AgCl$ crystal was used to determine the mobility of the electrons in the crystal.¹¹ The displacement of the beam in traversing the crystal is given by the Hall angle, $\theta = 10^{-8} \mu H$, where μ is the mobility of the carrier, and H is the magnetic field strength. In CdS it is frequently possible to obtain isolated beams of green electroluminescence, most of which pass directly from electrode to electrode.* These beams are deflected in a properly oriented magnetic field. With 6000 oersteds applied, the angular displacement observed was approximately 6×10^{-3} radians. On the assumption that the electroluminescence occurs in a stream of free carriers which pass through a uniform potential gradient, a mobility of the order of $100 \text{ cm}^2/\text{volt-sec}$ is indicated.

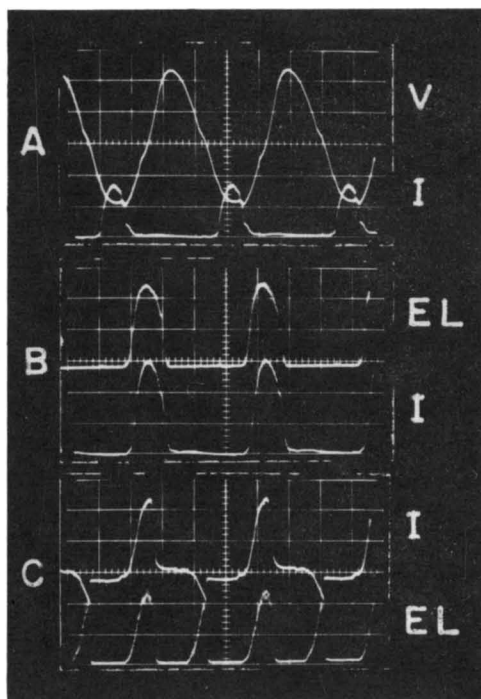


Fig. 6 - AC operation of an electroluminescent crystal. V is the 60 cps applied voltage. (B) the current I and corresponding electroluminescence EL obtained with 'forming' in one direction. (C) I and EL obtained with both electrodes 'formed'.

Interpretation

These experiments are interpreted in terms of two basic processes: (1) conductivity induced in the insulator by the injection of electrons and holes into the crystal

* There are beams which pass over the anode surface. A magnetic field produces very large deflections of these. However, since they appear in the region where the electric field is highly distorted, they are not considered in this argument.

from the contacts, and (2) electroluminescence produced by the radiative recombination of these carriers. The presence of both free electrons and free holes is inferred from the intrinsic recombination radiation. Since this edge emission, which is strongly absorbed, is seen through-out the volume of the crystal, it follows that there are free carriers recombining throughout and not in isolated regions from which the light can be scattered. The low field in the central part of the crystal precludes the internal generation of free carriers by impact ionization or similar mechanisms requiring a very high field. The free carriers, then, are injected into the insulator from the contacts and drift through the crystal with the electric field.

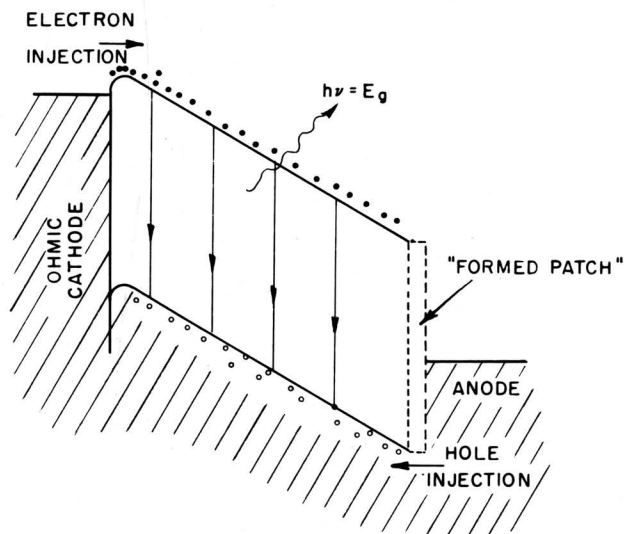


Fig. 7 - Model for CdS electroluminescence.

It has been shown previously that electrons are readily injected into CdS from In or Ga contacts.¹² The absence of a potential drop at the cathode is consistent with this. Holes on the other hand are injected from *formed* patches in a high field region at the tip of the anode. This is shown schematically in Fig. 7. The observation of electron-hole recombination radiation extending over 1 mm in the crystal corresponds to the range expected from carriers with life times of 10^{-6} sec and mobilities of $100 \text{ cm}^2/\text{volt-sec}$, drifting in a 1000 volt/cm field. Independent measurements⁹ on these crystals indicate a minority life time of approximately 10^{-6} sec and a majority life time of approximately 10^{-5} sec, assuming carrier mobilities of the order of $100 \text{ cm}^2/\text{volt-sec}$.

The efficiency of converting electrical energy into edge radiation is low due to the small probability of direct electron-hole recombination. The free-electron free-hole capture cross section in CdS is not known. It can be estimated, however, by scaling (using an expression derived by Rose¹³) from germanium, a material of known cross section. On this basis and assuming the

same absorption constants and the Van Roosbroeck and Shockley¹⁴ value of $S = 2.9 \times 10^{-21} \text{ cm}^2$ for Ge, a cross section of $3 \times 10^{-20} \text{ cm}^2$ is expected for CdS. This is to be compared with $3 \times 10^{-19} \text{ cm}^2$ computed from the measured efficiency of 5.6×10^{-8} . In this calculation the density of free-electrons and holes is assumed to be approximately equal.* The observed decay time of the radiation being less than $1 \mu\text{s}$ is consistent with the recombination life time expected from the measured efficiency.

* The direct recombination of free electrons and free holes is a bimolecular process and so the emission should be proportional to product of the electron (n) and hole (p) densities. Intensity is measured proportional to the current. This implies that the current in the crystal is proportional to np .

Electroluminescence has been reported in CdS also by Boer and Kummel³ and by Diemer⁴. In both cases activated crystals (photosensitive) were used. Boer and Kummel operated their crystals at liquid air temperature and obtained green and red emission. Diemer observed yellow spots at the tip of the anode and orange-red flames in the crystal. These workers ascribe the electroluminescence they observe to the action of a high electric field on electrons and do not consider hole injection. Although the crystals used here were considerably different from theirs, the I-V characteristics are nearly identical. The abrupt increase in current coincident with the appearance of the yellow patches at the anode is emphasized. It is believed that holes are injected into the crystal at this point.



Roland W. Smith

References

1. R.W. Smith, *Phys. Rev.*, **93**, 347 (1954); **98**, 1169 (1955).
2. D. Curie, *J. Phys. Radium*, **13**, 317 (1952); **14**, 510 (1953).
3. K. Boer, V. Kummel, and R. Rampe, *Z. Phys. Chem.*, **200**, 180 (1950).
4. G. Diemer, *Philips Res. Rep.*, **9**, 109 (1954).
5. W.W. Piper and F.E. Williams, *Brit. J. Appl. Phys. Supplement*, **4** (1955).
6. D.R. Frankl, *Phys. Rev.*, **100**, 1105 (1955).
7. R.H. Bube and S.M. Thomsen, *J. Chem. Phys.*, **23**, 15 (1955).
8. A. Rose, *Proc. I.R.E.*, **43**, 1850 (1955).
9. H.S. Sommers, R.E. Berry, and I. Sochard, *Phys. Rev.*, **101**, 987 (1956).
10. F.A. Kroger and H.J.G. Meyer, *Physica*, **20**, 1149 (1954); L.R. Furlong and C.F. Ravillious, *Phys. Rev.*, **98**, 954 (1955).
11. J.R. Haynes and W. Shockley, *Phys. Rev.*, **82**, 935 (1951).
12. R.W. Smith and A. Rose, *Phys. Rev.*, **97**, 1531 (1955).
13. A. Rose, *Proc. I.R.E.* **43**, 1856 (1955).
14. Van Roosbroeck and W. Shockley, *Phys. Rev.*, **94**, 1558 (1954).