

Low-Field Electroluminescence in Insulating Crystals of Cadmium Sulfide

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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 ~ 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.

I. 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 paper 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. We believe that our crystals are essentially uniform and that the only prominent barriers present are patches from which holes are injected at the anode. This hypothesis is in contrast with other published work²⁻⁶ 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.

II. CdS CRYSTALS

The crystals examined were grown by the vapor phase technique by Thomsen, Stripp, Busanovich, and 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, Cu), and (3) relatively conducting crystals with high photoconductivity (highly doped).

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 lifetime and a short hole lifetime.⁸ The insensitive crystals which display electroluminescence have a relatively shorter electron lifetime and a longer hole lifetime.⁹ Table I indicates a probable range of the values of the electron and hole lifetimes for crystals of these two classes.

III. EXPERIMENTS

A. 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 $V-I$ 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 (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. 3.¹⁰ There are no spots in the body of the crystal and appearance and the movement of the green

TABLE I. Probable values of electron and hole lifetimes in CdS.

CdS crystal	Lifetime (sec)	
	majority	minority
Photosensitive	$\lesssim 10^{-8}$	$\lesssim 10^{-11}$
Electroluminescent	$\sim 10^{-5}$	$\sim 10^{-6}$

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 Boer, Kummel, and Rampe, Z. physik. Chem. **200**, 180 (1950).

⁴ G. Diemer, Philips Research Repts. **9**, 109 (1954).

⁵ W. W. Piper and F. E. Williams, Brit. J. Appl. Phys. Suppl. **4**, S39 (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. Inst. Radio Engrs. **43**, 1850 (1955).

⁹ Sommers, Berry, and Sochard, Phys. Rev. **101**, 987 (1956).

¹⁰ The author is indebted to C. J. Busanovich for taking the original photographs.

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.

B. 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. Figure 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

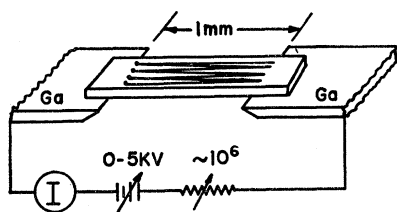


FIG. 1. Experimental arrangement used to study CdS electroluminescence.

that the green electroluminescence is intrinsic recombination radiation (edge emission).

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°K prominent photoluminescence bands have been reported around 5180 Å.¹¹ Apparently the same transition giving rise to the 5180 Å band is produced by both photons and by an electric field.

C. Potential Distribution

The potential distribution along the surface of the crystal was measured with a fine wire probe and a high impedance electrometer. Figure 5 is a plot of $V(x)$ along the top and bottom surface of the crystal under

¹¹ F. A. Kroger and H. J. G. Meyer, *Physica* **20**, 1149 (1954); L. R. Furlong and C. F. Ravilious, *Phys. Rev.* **98**, 954 (1955).

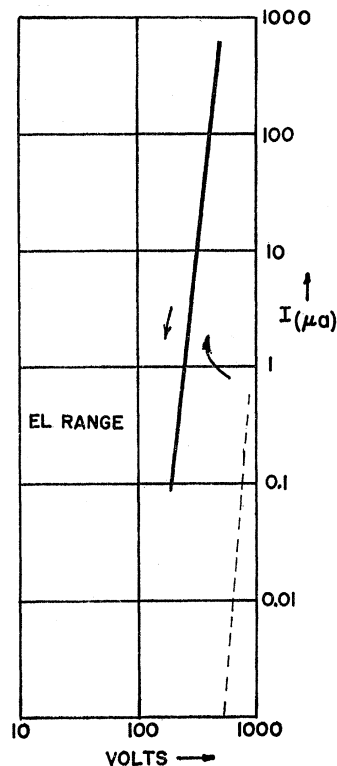


FIG. 2. $V-I$ characteristic of CdS in electroluminescent range.

conditions giving green electroluminescence extending between the electrodes. The important features are the following: (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.

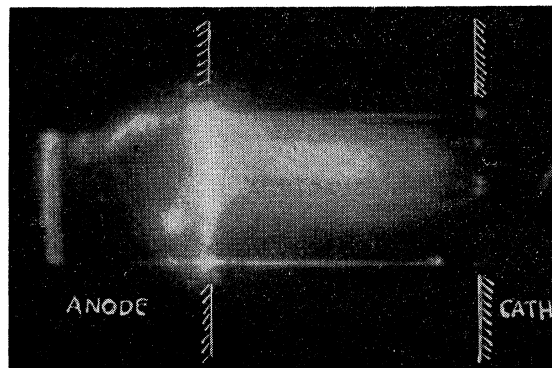


FIG. 3. Photograph of electroluminescence from CdS. The overexposed region at the tip of the anode is an array of yellow (EL) spots. The spots at the tip of the cathode are not usually observed.

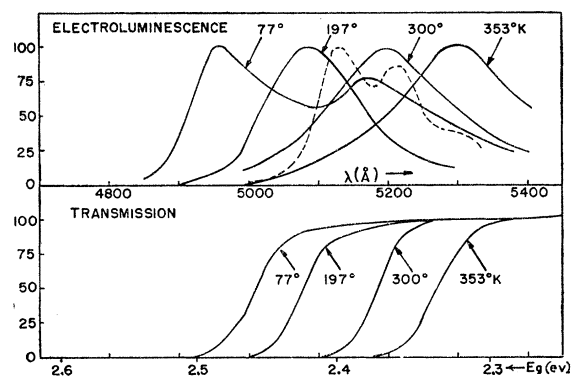


FIG. 4. Spectral distribution of electroluminescence and corresponding optical transmission of CdS at indicated ambient temperature. The dotted curve shows the uv-excited photoluminescence at liquid air temperature.

D. 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.

E. ac Behavior

The ac performance of the crystals is shown in Fig. 6. Consider a crystal with electrodes to which dc is first

applied until EL 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 dc 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 dc 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.

F. 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.¹² The displacement of the beam in traversing the crystal is given by the Hall

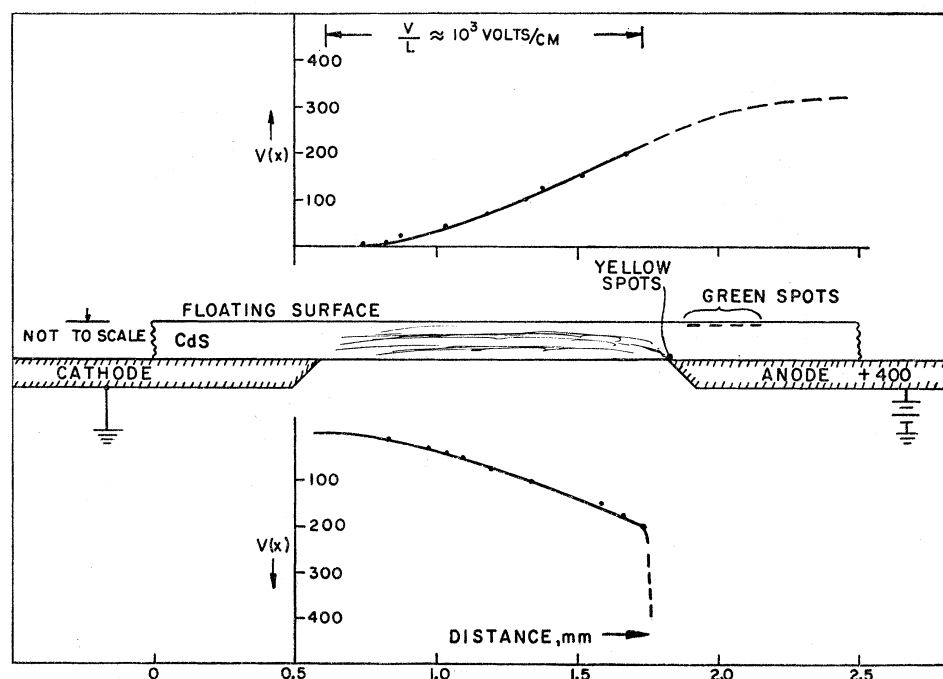


FIG. 5. The distribution of potential $V(x)$ along an electroluminescent crystal.

¹² J. R. Haynes and W. Shockley, Phys. Rev. 82, 935 (1951).

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.¹³ These beams are deflected in a properly oriented magnetic field. With 6000 oersteds applied, the angular displacement observed was $\sim 6 \times 10^{-3}$ radian. 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 cm²/volt-sec is indicated.

IV. 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 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 throughout 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

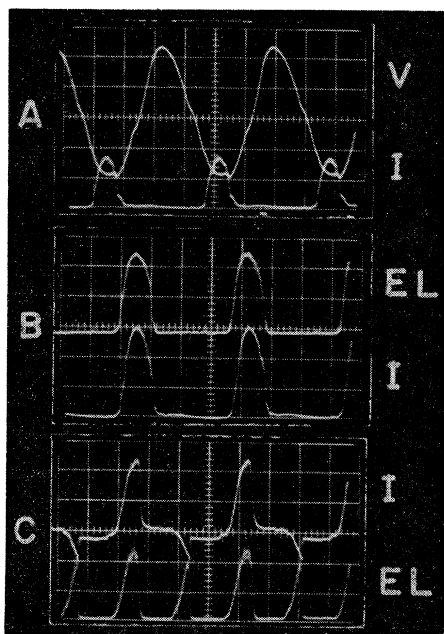


FIG. 6. Ac operation of an electroluminescent crystal. (A) V is the 60-cps applied voltage; (B) the current I and corresponding electroluminescence EL obtained with "forming" in one direction; (C) I and EL obtained with both electrodes "formed".

¹³ 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.

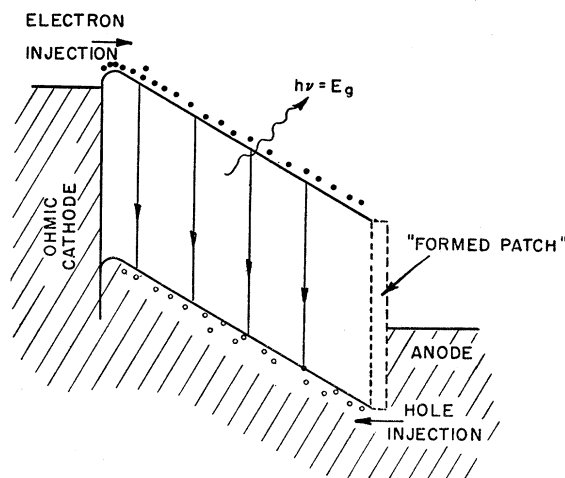


FIG. 7. Model for CdS electroluminescence.

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.

It has been shown previously that electrons are readily injected into CdS from In or Ga contacts.¹⁴ 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 lifetimes $\sim 10^{-6}$ sec and mobilities ~ 100 cm²/volt-sec, drifting in a 1000-volt/cm field. Independent measurements⁹ on these crystals indicate a minority lifetime $\sim 10^{-6}$ sec and a majority lifetime $\sim 10^{-5}$ sec, assuming carrier mobilities of the order of 100 cm²/volt-sec.

The efficiency of converting electrical energy into edge radiation is low owing 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 Rose¹⁵) from germanium, a material of known cross section. On this basis and assuming the same absorption constants and the van Roosbroeck and Shockley¹⁶ value of $S = 2.9 \times 10^{-21}$ cm² for Ge, a cross section of 3×10^{-20} cm² is expected for CdS. This is to be compared with 3×10^{-19} cm² 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.¹⁷ The

¹⁴ R. W. Smith and A. Rose, Phys. Rev. **97**, 1531 (1955).

¹⁵ A. Rose, Proc. Inst. Radio Engrs. **43**, 1856 (1955).

¹⁶ W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).

¹⁷ 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. We measure intensity proportional to the current. This implies that the current in the crystal is proportional to np .

observed decay time of the radiation being less than 1 μ sec is consistent with the recombination lifetime expected from the measured efficiency.

Electroluminescence has been reported in CdS also by Boer and Kummel³ and by Diemer.⁴ 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 our crystals are considerably different from theirs, the $I-V$ characteristics are nearly identical. We emphasize the abrupt increase in current coincident with the appearance of the yellow patches at the anode, at which point we believe holes are injected into the crystal.

V. ACKNOWLEDGMENT

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New Magnetic Anisotropy

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A new type of magnetic anisotropy has been discovered which is best described as an exchange anisotropy. This anisotropy is the result of an interaction between an antiferromagnetic material and a ferromagnetic material. The material that exhibits this exchange anisotropy is a compact of fine particles of cobalt with a cobaltous oxide shell. The effect occurs only below the Néel temperature of the antiferromagnetic material, which is essentially room temperature for the cobaltous oxide. An exchange torque is inferred to exist between the metal and oxide which has a maximum value at 77°K of ~ 2 dyne-cm/cm² of interface.

INTRODUCTION

A NEW discovery has been made in the field of magnetic materials that manifests itself in the form of a displaced hysteresis loop¹ as shown in Curve 1, Fig. 1. In addition, although from the same basic phenomena, the magnetic material has only one stable orientation in a magnetic field. In particular, it can be turned through 180° and it will still return to its original orientation.

The material that exhibits this property is a compact of fine particles of cobalt (100–1000 Å) that have a cobaltous oxide coating. The compact exhibits the normal behavior of a symmetrical hysteresis loop (Curve 2, Fig. 1) when cooled to 77°K in the absence of a field, but when cooled to 77°K in a strong magnetic field it exhibits the displaced hysteresis loop (Curve 1, Fig. 1).

Before this discovery, the known methods of increasing the coercive force of a material involved the strain, crystalline anisotropy, and shape anisotropy. We now have an additional mechanism involving an interaction between an antiferromagnetic material and a ferromagnetic material. Since the origin of this effect is postulated as being an interaction between the spins of the cobalt atoms in the metal and the cobalt ions in the antiferromagnetic cobaltous oxide, it might properly be termed an exchange anisotropy. It is shown by experi-

ment that this coupling results, for a specific case, in an exchange anisotropy constant of the same order of magnitude as the crystalline anisotropy of cobalt (5×10^6 ergs/cc).

TORQUE AND ENERGY FUNCTION

The new properties of this material are best described by comparison with well-known materials. Let us consider a small spherical single-domain particle of cobalt *without* an oxide coating as our classical material.

If the particle of pure cobalt is cooled to liquid nitrogen temperature in a strong magnetic field, say 20 000 oersteds, it will exhibit a normal symmetrical hysteresis loop of the type shown in Fig. 2(a). A torque curve taken on this material would be a $\sin 2\theta$ function as shown in Fig. 2(b). Hence,

$$T = -\partial E / \partial \theta = -K_1 \sin 2\theta,$$

$$E = \int K_1 \sin 2\theta d\theta = K_1 \sin^2 \theta + K_0.$$

Therefore the energy function would be as shown in Fig. 2(c), where it is apparent that energy minima occur at $\theta = 0$ and $\theta = 180^\circ$. That is, both directions along the c axis of the cobalt particle would be in stable equilibrium in an infinite field at $\theta = 0$ and $\theta = 180^\circ$.

Now let us consider the oxide-coated particle of cobalt that has a displaced loop of the type shown in

¹W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 5, 1413 (1956).

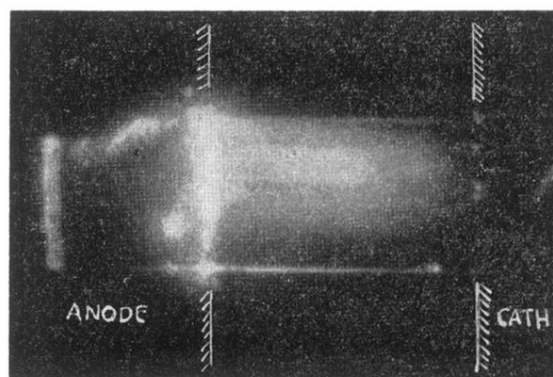


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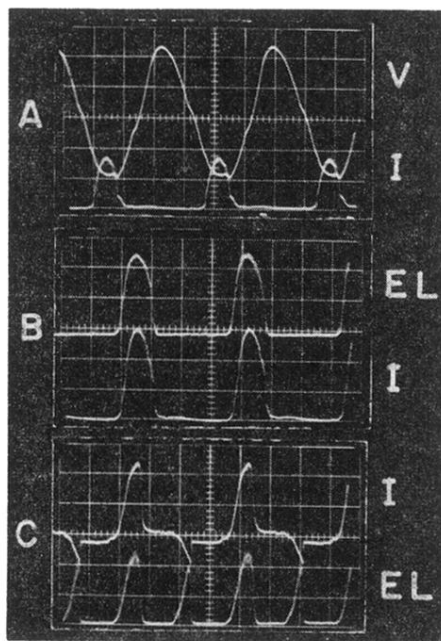


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