Edge Electroluminescence from ZnS Single Crystals

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(Received August 18, 1955)

IT has been generally believed that holes do not move appreciably in ZnS crystals and that they do not contribute to ZnS electroluminescence (EL). Several models have been proposed expressing the view that the significant EL is generated by the motion of electrons in an electric field of intensity near the dielectric breakdown strength.[1,2] The purpose of this letter is to present data indicating that both free electrons and holes may contribute to the EL from ZnS.

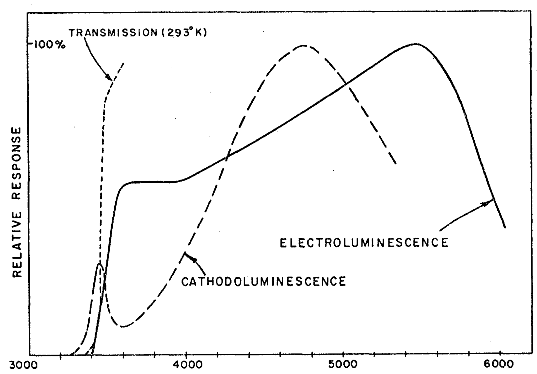

FIG. 1. Spectral emission curves for electroluminescence from ZnS single crystal and cathodoluminescence from ultrapure ZnS powder. The EL curve was recorded from 3000 to 6000 A with a resolution 100 A.

Figure 1 shows the ultraviolet and visible electroluminescence typical of several ZnS crystals measured. This dc electroluminescence was obtained with Ga electrodes placed on single crystals prepared by two separate groups: (1) crystals grown by W. W. Piper of the General Electric Company, and (2) crystals grown by E. L. Lind of these Laboratories. Impurities were not intentionally added to these crystals. The extent to which EL is observed in a crystal varies considerably with different crystals. With the above crystals, the electrodes were placed on opposite faces of the crystal, and separated somewhat more than the crystal thickness. The EL observed here is not confined to a particular electrode and there is reasonable evidence that it comes from the crystal between the electrodes. This is in agreement with the extended EL reported from ZnS by Frankl.[3] The fact that the EL is not confined to the electrodes but is observed in the bulk of the crystal is consistent with the view that electronic transitions, giving light emission, are occurring in the volume of the insulator.

The point to be emphasized in this letter is that electroluminescence is obtained in the region of the absorption edge in addition to the visible emission. The room temperature location of the ZnS absorption edge (3400 A $\approx$3.6 ev) is indicated by Van Doorn's[4] transmission curve for a flat plate of ZnS$\sim$0.2 mm thick, and by Shrader's cathodoluminescence[5] curve. The observation of edge emission is evidence for the recombination of free electrons and holes.

Similar observations have been reported[6] for CdS and it is not unreasonable to assume that similar mechanisms operate in both crystals. A model in which electrons and holes are injected, from opposite electrodes, into the insulator and subsequently recombine, directly to give edge emission, and through centers for the remaining emission, is consistent with these observations. This mechanism is to be contrasted with excitation by electrons in a high field at a cathode barrier, proposed by Piper and Williams[2] and with the stacked junctions proposed by Loebner[7] and Frankl.[3]

We want to thank Dr. Piper and Dr. Lind for the ZnS crystals and Dr. R. E. Shrader for permission to use his unpublished cathodoluminescence curve.

[1] D. Curie, J. phys. radium **13**, 317 (1952).
[2] W. W. Piper and F. E. Williams, Phys. Rev. **87**, 151 (1952); Brit. J. Appl. Phys. Supplement No. 4 (1955).
[3] D. R. Frankl, reported at Spring Meeting of The Electrochemical Society, Cincinnati, Ohio, May, 1955 (unpublished).
[4] C. Z. Van Doorn, Physica **20**, 1155 (1954).
[5] In this case ultrapure ZnS powder prepared without fluxing agents was used. This powder does not luminesce under uv excitation.
[6] R. W. Smith, Phys. Rev. **93**, 347 (1954); Phys. Rev. **98**, 1169(A) (1955).
[7] E. E. Loebner and H. Frund, Phys. Rev. **98**, 1545(A) (1955).

Thermoluminescence Measurements of Electroluminescent ZnS:Mn Films

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(Received August 22, 1955)

THERMOLUMINESCENCE measurements were made on films of chemically deposited ZnS:Mn formed by the vapor reaction method described by Studer, Cusano, and Young.[1] A number of films, in addition to being electroluminescent upon the application of an ac field, also emitted light when a dc field, approximately 3×10^5 volts/cm, was applied. A typical glow curve of a film which emitted light upon the application of an ac and dc field is shown in Fig. 1. These measurements were made between $-196°C$ and $+25°C$, and calculations of the three depths based on a formula of Randall and Wilkens[2] yielded the values of 0.37 ev, 0.41 ev, and 0.43 ev. The following points should be noted: (a) the formula of Randall and Wilkens is based on a glow curve containing only one peak and was used in the above calculations to give an approximate value of the trap depths, and (b) an exponential heating rate was used to obtain the curve of the figure since linear heating rates yielded values which deviated