

Electroluminescence at Low Voltages

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Electroluminescence occurs in activated ZnS thin films at 1.5 volts rms (peak voltage 2.2 volts) corresponding to electron energies less than the band gap (3.8 electron volts) and less than the mean energy (2.6 electron volts) of the photons emitted. The light emission decreases by 10^4 between 2.0 and 1.5 volts rms and shows no tendency toward a threshold, nor does its spectral character change at low voltage. This behavior suggests that electroluminescence does not depend upon collision ionization but perhaps on carrier injection or free electron temperature.

ELECTROLUMINESCENCE has been observed in ZnS at peak applied alternating voltages corresponding to electron energies less than the band gap (3.8 electron volts) of the phosphor crystal, and less than the equivalent mean energy (2.6 electron volts) of the photons emitted. This emission of photons more energetic than the applied voltage is an anomalous situation, and its observation has not apparently been reported previously. The spectral character of the low-voltage electroluminescence is not found to differ from that at more conventional voltages. For these experiments, thin ZnS phosphor films¹ made by a two-step evaporation-firing process, about one micron in thickness, and activated with copper and chlorine were used. These films were deposited on conducting glass and aluminum was vaporized directly on the finished film to form the rear electrode. Light emission was measured with an RCA-6217 photomultiplier,

either at room temperature or cooled to liquid-nitrogen temperature, at the lower levels and converted to foot-lamberts at higher levels with a Spectra Spot Brightness meter. The alternating voltage was measured with a Hewlett-Packard 400D VTVM calibrated against a standard cell with the use of a Tektronix 514AD ac-dc oscilloscope.

In Fig. 1 the low-voltage electroluminescence emission in foot-lamberts is plotted logarithmically against $V^{-1/2}$, where V is the rms value of the sinusoidal applied voltage. The voltage of the lowest plotted point corresponds to about 2.2 volts peak. While the curve deviates from a straight line (the light emission from most electroluminescent materials follows an $\exp[-(V_0/V)^2]$ relation, where V_0 is a constant) at higher voltages, the curve is straight through the lower four decades as if the emission follows the same relation at even lower voltages. It seemed worthwhile to examine the emission spectrum to as low light levels as possible.

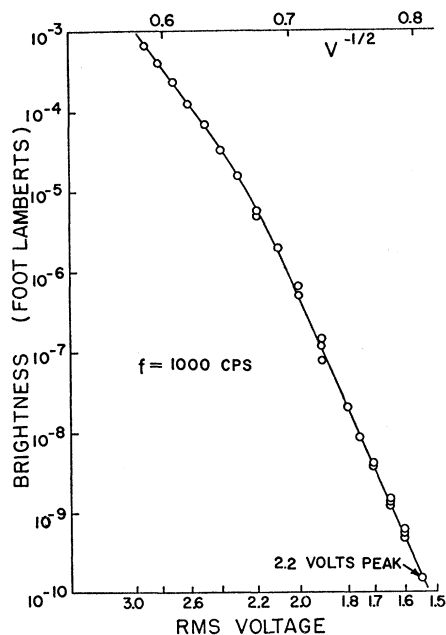


FIG. 1. The low-voltage dependence of electroluminescence emission from a thin film of ZnS : Cu, Cl. Frequency, 1000 cps.

¹ W. A. Thornton, J. Appl. Phys. **30**, 123 (1959).

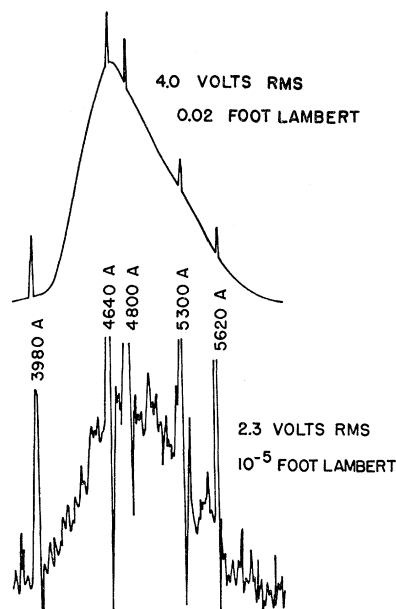


FIG. 2. The low-voltage spectra of electroluminescence emission from a thin film of ZnS : Cu, Cl. Frequency, 1000 cps. The markers occur at arbitrary standardizing wavelengths calibrated against the visible mercury lines.

The spectra of Fig. 2 show that it is essentially unchanged between 4.0 volts rms and 2.3 volts rms (3.5 decades) and filter measurements show no differences down to 1.8 volts rms, below which measurement becomes difficult. The frequency response, predicted² to be weak at very low voltage, was flat to ten percent from 10^2 cps to 10^4 cps when measured at 1.7 volts rms. Rapid temperature quenching occurred above room temperature; measured at 2.0 volts rms, emission dropped to fifty percent at 100°C and to five percent at 150°C.

Although Destriau, in his definitive 1947 paper,³ described electroluminescence below 30 volts rms, the idea of a threshold voltage appeared^{4,5} later in both experiment and theory. Destriau and Domergue⁶ argued against the existence of a threshold in electro-

luminescence by demonstrating no tendency toward extinction down to brightnesses of 10^{-8} foot-lamberts and nine volts (presumably rms). Powder phosphor layers with a trace of binder show appreciable ac electroluminescence at 3 or 4 volts rms⁷ and single layers of crystals of mean diameter 2-3 microns show ac electroluminescence at two volts rms. Even if space charge fields persist from cycle to cycle, conceivably but improbably leading to an effective potential drop of twice the peak applied voltage, the present results on thin films show that voltages about equivalent to the band-gap lead to measurable ac electroluminescence and show no tendency toward a threshold. This behavior suggests that electroluminescence does not depend upon collision excitation but perhaps on carrier injection or free electron temperature.

² W. A. Thornton, Phys. Rev. **102**, 38 (1956).

³ G. Destriau, Phil. Mag. **38**, 700 (1947).

⁴ W. W. Piper and F. E. Williams, Phys. Rev. **87**, 151 (1952); Brit. J. Appl. Phys. Suppl. No. 4, S39 (1955).

⁵ J. F. Waymouth and F. Bitter, Phys. Rev. **95**, 941 (1954).

⁶ G. Destriau and L. Domergue, *Proceedings of the International Colloquium on Semiconductors and Phosphors, Garmisch-Partenkirchen, 1958* (Interscience Publishers, Inc., New York, 1958).

ACKNOWLEDGMENTS

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⁷ W. A. Thornton, Phys. Rev. **113**, 1187 (1959).