FIG. 1. Change in resistance $\Delta R$ in a graphite single crystal as a function of $H^{-1}$ at 4.22°K (solid line). $\delta$ is the difference between the experimental values and the dashed curve.

leads were soldered. Since an unknown amount of contact resistance is present in such a configuration, the change in resistance (rather than the usual ratio of change in resistance to zero field resistance) is reported. In Fig. 1, the change of resistance $\Delta R$ of the sample in a magnetic field $H$ is plotted as a function of $H^{-1}$. Since the probable error was estimated as less than the thickness
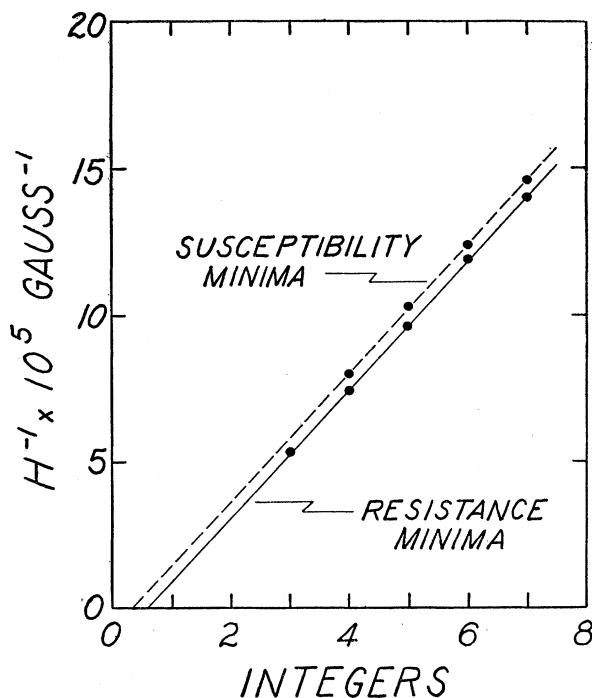


FIG. 2. Values of $H^{-1}$ for which magnetoresistance and susceptibility oscillations in graphite exhibit minima are plotted against integers. The susceptibility data are those of Shoenberg (reference 6).

of the plotted curve, the experimental points could not be indicated. Consequently, in order to illustrate the nature of the anomalies better, the differences $\delta$ (as read from a larger graph) between the experimental points and the dashed curve (which is accurately represented by $\Delta R \propto H^{0.811}$ between 12 and 25 kilogauss) are plotted on an expanded scale at the bottom of Fig. 1. Values of $H^{-1}$ for which $\delta$ exhibits minima are indicated by arrows in Fig. 1 and are plotted against integers in Fig. 2 (solid line). For comparison, Shoenberg's de Haas-van Alphen data[6] on graphite were extrapolated to the same orientation ($H$ parallel to the hexagonal axis), and values of $H^{-1}$ for which graphite exhibits susceptibility minima are also plotted on Fig. 2 (dashed line). Since these lines are parallel, a one-to-one correspondence in period $\beta/E_0 = 2.2 \times 10^{-5}$ gauss$^{-1}$ is indicated.[7] This point should be emphasized in view of the fact that the more complicated nature of the electronic constant energy surfaces for bismuth had made it impossible to state unambiguously from the experimental evidence alone whether the period of the magnetoresistance oscillations was one half that of the long-period susceptibility oscillations or was just equal to the period of the short-period susceptibility oscillations. (The one-to-one correspondence in period is further borne out by the zinc data.) Although the separation between the lines in Fig. 2 indicates a phase difference of approximately $\pi/2$ between the resistance variations along a binary axis and the susceptibility oscillations along the hexagonal axis in graphite, no great accuracy is claimed for this parameter since the susceptibility and resistance measurements were not carried out on the same crystal. Furthermore, the analysis is complicated somewhat by the fact that $\delta$ is not a simple monatonically modulated sinusoid (see Fig. 1). However, this is to be expected in view of the existence of a subordinate term in the susceptibility[6] having a period $\frac{3}{4}$ that of the dominant term.

More detailed investigations of the correlative effects are in progress and will be reported at a later date.

[1] P. B. Alers and R. T. Webber, Phys. Rev. 91, 1060 (1953).
[2] Ted G. Berlincourt, Phys. Rev. 91, 1277 (1953).
[3] N. M. Nachimovich, J. Phys. (U.S.S.R.) 6, 111 (1942).
[4] Jules A. Marcus, Phys. Rev. 76, 621 (1949).
[5] L. Mackinnon, Proc. Phys. Soc. (London) B62, 170 (1949).
[6] D. Shoenberg, Trans. Roy. Soc. (London) 245, 1 (1952).
[7] $\beta$ is a double effective Bohr magneton involving the effective mass, and $E_0$ is the chemical potential of the pertinent electrons.

## Electroluminescence in Thin Films of ZnS:Mn

R. E. HALSTED AND L. R. KOLLER
General Electric Research Laboratory, Schenectady, New York
(Received November 10, 1953)

TRANSPARENT films of sulfide phosphors of the order of 10 microns in thickness have been prepared by the vapor reaction method of Cusano and Studer.[1] Such films offer a crystalline form of these materials particularly suitable for study under high voltage gradients. Preliminary data on films of ZnS:Mn (approximately 0.5 percent Mn) reveal some interesting variations from previously reported electroluminescent behavior.

Samples were prepared in the form of condensers with one transparent conducting electrode on a glass substrate, a transparent phosphor dielectric, and a second electrode of evaporated metal. ZnS:Mn films so prepared respond with a Mn emission peaked at 5900A to either cathode-ray or electroluminescent excitation. They have a specific resistance in the dark of the order of $10^{13}$ ohm cm measured at an average gradient of $10^4$ volts/cm. Thermoluminescent measurements between $-196°$ and $+200°$C yield one "glow peak" corresponding to a 0.3-ev trap (frequency factor of $10^8$/sec assumed). This trap is observed also in ZnS films with no Mn.

Except for a transient flash on application and removal of dc fields, no dc luminescence is produced by fields below breakdown (approximately $5 \times 10^5$ volts/cm). Two light pulses per cycle are observed on application of an ac potential. As can be seen in Fig. 1, these light pulses are very closely in phase with the applied

voltage and are of unequal amplitude. The larger pulse occurs when the metal electrode is negative. The light output produced by a pulsed wave form, also given in Fig. 1, confirms that the light is associated with voltage changes in the film.

The average brightness of the films varies approximately as the seventh power of the applied voltage through 5 decades in brightness. A small difference is observed in this dependence for the alternate light pulses, but a strong power relationship gives a good approximation for each. The electroluminescent emission color of the samples is not altered by variations of either frequency or voltage of excitation. For a fixed voltage the average brightness increases with the frequency from 20 to approximately 5000 cps. The specific brightness *versus* frequency relationship is influenced by several factors: (1) The decay time constant of the electroluminescent Mn emission is 1.3 milliseconds. (2) Above approximately 2000 cps the resistance of the transparent conducting substrate competes with the dielectric impedance for the applied voltage. (3) The electroluminescent emission is temperature-dependent. The dependence of average brightness on temperature for three different frequencies of excitation is shown for one sample in Fig. 2. The position and sharpness of the maxima vary
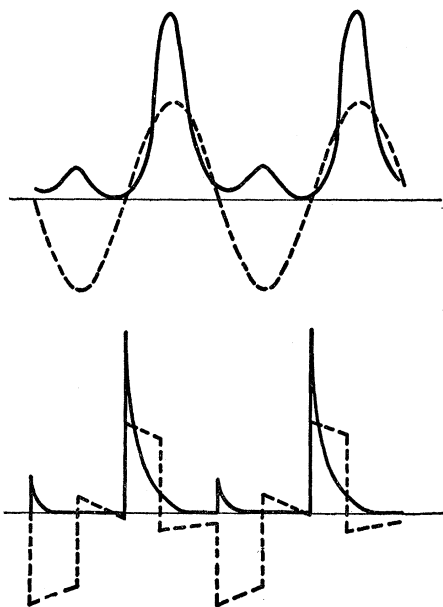


Fig. 1. Light output and voltage *versus* time for sinusoidal and pulsed excitation of ZnS:Mn films. Broken line indicates 60 cps voltage wave form.

appreciably for different samples and are dependent in a given sample on its history of exposure to temperatures of the order of 200°C. However, the general feature of a single, frequency-dependent maximum in brightness has always been observed in this temperature range.

No contradiction with the qualitative impact excitation mechanism proposed by Piper and Williams[2] and Curie[3] is apparent in the information noted above. The absence of dc luminescence can be correlated with the high resistivity of the ZnS:Mn. Variations in the phase relation between light pulses and applied sinusoidal voltages could be explained by variations in the donor level distribution. For example, the "in-phase" ac light production of ZnS:Mn might be the result of a reduction in the number of shallow donors postulated[2] in ZnS:Cu to produce the space charge for "out-of-phase" luminescence.

The voltage dependence of electroluminescent brightness in ZnS:Mn films is stronger than previously reported.[4-6] The near linearity of brightness *versus* frequency of excitation at low frequencies and room temperature is in agreement with previous
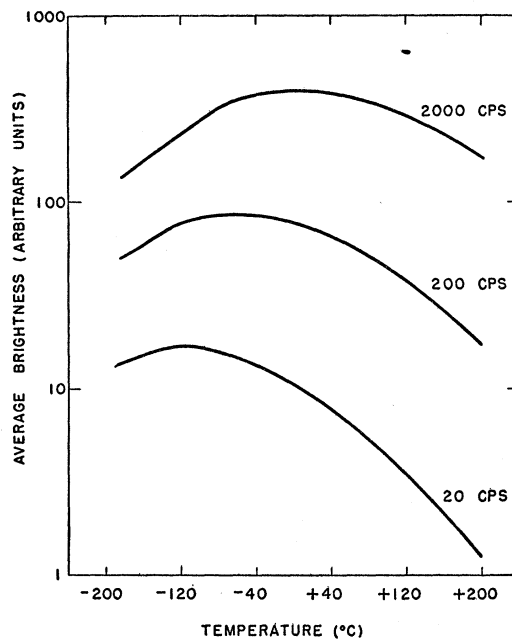


Fig. 2. Average brightness of electroluminescence of ZnS:Mn film *versus* temperature for three frequencies of excitation. Data for the three frequencies were taken on the same temperature run with the sample in vacuum.

results, in particular the demonstration by Waymouth that the integrated electroluminescent light output is independent of the rise time of a single voltage pulse.[7] The structure of thin film cells permits an examination of the temperature dependence of their electroluminescence over a somewhat greater range than has been reported for powder cells.[4,5] The single 0.3-ev electron trap contrasts with the multiplicity of traps reported from this type of experiment on powdered ZnS:Mn phosphors (e.g., Bube[8]) and encourages a hope that phenomena observed in these films will be amenable to interpretation.

It is anticipated that an extension of this work with films can contribute towards an understanding of a variety of phenomena in phosphors.

[1] D. A. Cusano and F. J. Studer, J. Opt. Soc. Am. 42, 878 (1952).
[2] W. W. Piper and F. E. Williams, Phys. Rev. 87, 151 (1952).
[3] D. Curie, J. phys. radium 13, 317 (1952).
[4] S. Roberts, J. Opt. Soc. Am. 42, 850 (1952).
[5] G. Destriau, Phil. Mag. 38, 700 (1947).
[6] Payne, Mager, and Jerome, Illum. Eng. 45, 688 (1950).
[7] J. F. Waymouth and F. Bitter, New York Meeting of the Electrochemical Society, April, 1953, Abstract 27 (unpublished).
[8] R. H. Bube, Phys. Rev. 90, 70 (1953).

## Low Temperature Diamagnetism of Electrons in a Cylinder

WILLIAM BAND
State College of Washington, Pullman, Washington
(Received November 30, 1953)

AS a result of some private correspondence with S. F. Ham at Harvard University and G. H. Wannier at Bell Telephone Laboratories, the writer is persuaded that the conclusions presented in a recent paper under the above title[1] are incorrect. The leading term in the result is in conflict with a general theorem[2] on the asymptotic number of eigenvalues corresponding to a volume of any shape. The source of the error appears to stem from the fact that terms to second order in the field should have been retained in the general expression for the wave functions, Eqs. (8) and (9), to yield a consistent theory of the susceptibility.