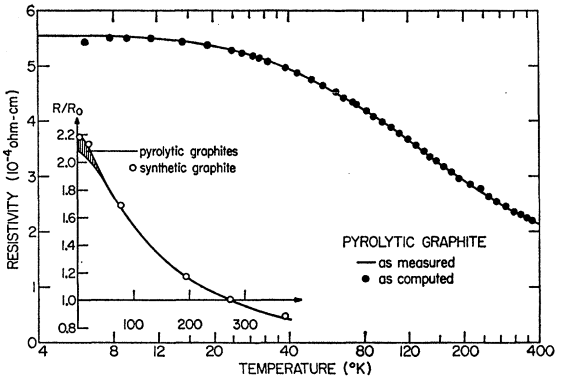

FIG. 3. Basal plane resistivity of a pyrolytic graphite specimen deposited at 2500°C. The filled circles are as given by Eq. (4) with parameters based on the indications of Figs. 1 and 2. The open circles illustrate how a synthetic specimen graphitized at 2600°C (reference 6) compares on a relative resistance scale with pyrolytic graphites deposited at $2300° < T_d < 2600°$C.

pyrolytic materials do namely coincide, although the conductivities differ by a factor of 3 or more, depending upon density and orientation. It may be pointed out that this substantiates Bowen's hypothesis[10]: In a conventional polycrystalline graphite the current carriers move perpendicularly to the c axes of the individual crystallites and are not exposed to multiple scattering effects in the areas of contact. Finally, a confrontation of Figs. 1 and 2 leads to the conclusion that large changes in the carrier mobility—that means crystallite size—do not induce noticeable carrier density variations. We believe that an interpretation of the polycrystalline graphite behavior in terms of near-ideal crystallites whose boundaries act in the manner of potential barriers is therefore justified.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to S. Cvikevich and O. Guentert for supplying adequate pyrolytic graphite specimens as well as most valuable indications on structural aspects of these materials.

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Thin-Film Elucidation of the Electroluminescence Process

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Very thin sulfide films emit light only on alternate half-cycles of the voltage sine wave, whereas the emission of thicker films and phosphor powders is quite symmetrical with polarity. This asymmetry of emission, together with clipping or dc bias of the applied voltage, is used to confirm unambiguously that the excitation and recombination steps in electroluminescence are separable and occur sequentially and under different field configurations, and that the recombination is field-driven.

INTRODUCTION

ELECTROLUMINESCENCE in zinc sulfide is a complex process which is not yet well understood. In this paper it is shown that the behavior of very thin zinc sulfide films confirms in a relatively unambiguous way long-standing ideas that the excitation and recombination steps in electroluminescence are (a) separable and occur sequentially and under different field configurations,[1,2] and (b) that the recombination is field-driven.[3–6]

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EXPERIMENTAL PROCEDURE

The electroluminescent films[7] used here are of zinc sulfide activated with copper and chlorine, and in some cases manganese in addition, made by a two-step evaporation-firing process on tin-oxide coated glass. Film thickness is about 1 μ. Aluminum was vaporized directly on the finished film to form the rear electrode, except in one case where an intermediate plastic (PVCA) film was interposed. The powder phosphor layers used for comparison are conventional sprayed dispersions of equivalent powder phosphors in PVCA.

An RCA-6217 photomultiplier and cathode follower with dc coupling was used for light detection; the signal from this circuit was introduced into a high-gain dc amplifier (y) of a Tektronix type 535 oscilloscope and the voltage applied to the phosphor was also used as the external (x) sweep. A careful check for extraneous

[7] W. A. Thornton, J. Appl. Phys. **30**, 123 (1959).

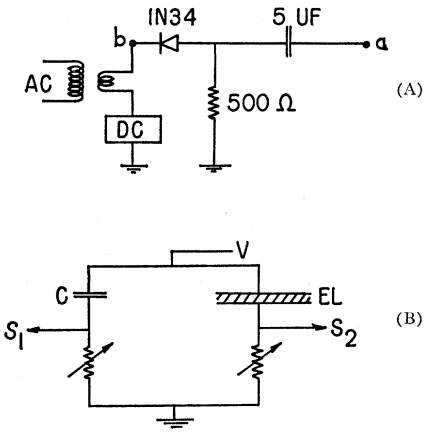

FIG. 1. Circuits used (A) for clipping the voltage sine wave and for adding dc bias, and (B) for subtracting out the capacitive component of the cell current.

phase shifts was made and no appreciable shifts were found. The applied voltage was introduced simultaneously into the x and y channels as one check, and the light signal was checked as follows. The intermittent Hg emission from a thyratron (884) oscillator was picked up by the photomultiplier; the oscillator was biased so as to pulse on only at the maximum of the sinusoidal voltage wave applied to the grid. The resulting light signal (y) was strictly in phase with the applied voltage on the (x) plates from 20 cps to 50 000 cps. Hence the phase relationships to be shown, as well as those in previous work,[3,8,9] are truly characteristic of the light emission from the phosphor.

Figure 1 shows the simple circuits used (A) for adding a dc bias to the ac voltage and for clipping the peaks of one polarity of the voltage sine wave, and (B) for subtracting out the capacitive component of the cell current. Only a Meissner capacitor with a 2-mil mica sheet as dielectric was found sufficiently linear to use as capacitor C in circuit 1B. Signals S_1 and S_2 were subtracted by introducing them into the inputs of the dc differential amplifier; these signals were always less than 10^{-3} of the applied voltage. The applied voltage served as the external (x) sweep as before. A Du Mont type 2620 mount and Polaroid camera were used to photograph the oscilloscope traces.

RESULTS

Some light output waveforms of a thin green-emitting film and a corresponding powder phosphor layer are shown in Fig. 2 for two voltages and two frequencies. (For an explanation of the shape of these waveforms, see reference 3.) The spot is the beam position at $L=0$, $V=0$. The instantaneous light emission increases upwards while the applied sinusoidal voltage lies to left and right such that the polarity in which the rear metal electrode of the cells is positive lies to the right in Figs. 2–5. The size of the waveform is normalized by means of gain adjustments in both coordinates. These waveforms show the two-peak doublet per half-cycle common to the emission of most electroluminescent phosphors.[3,10–13] The direction of the trace is such that the primary (larger) peak always precedes the associated secondary[13] (smaller) peak; for example, the lower trace along the baseline of Fig. 2(B) is moving from right to left but the lower trace of Fig. 2(C) (higher frequency) is moving from left to right. Since the x coordinate is linear in instantaneous applied voltage, rather than time, the integrated area under the peaks of Fig. 2 is not a measure of the total light emission.

A plastic (PVCA) coating several microns thick on the bare film, upon which the aluminum electrode is vaporized, does not change the character of the light-output waveform from the film.

Asymmetrical light waveforms similar to Fig. 2(A)–(D) were observed by Waymouth and Bitter[2] from a single emitting spot, and were also predicted[3,4] as the light emission expected from a small volume element of phosphor.

It is apparent from Fig. 2 that the thin film emits predominantly during the half-cycle when the metal electrode is positive, while with the powder layers and with thicker films (6–8 μ) the light emission is quite symmetrical. The question arises in the case of the thin films whether the negative polarity voltage swing serves a useful purpose. Therefore the voltage sine wave was clipped with the circuit of Fig. 1(A) (connection a). The resulting waveforms of voltage vs time are shown

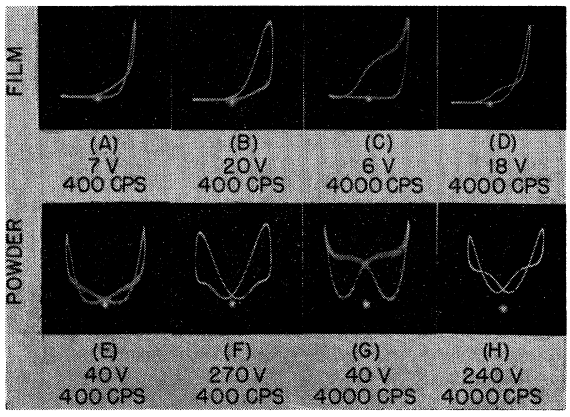

FIG. 2. Light emission-voltage waveforms for electroluminescent phosphor film and powder; the stationary spot is the beam position for $L=0$, $V=0$, with the voltage in the x direction and light in the y direction.

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[10] G. Destriau, Phil. Mag. **38**, 700, 774, 800, 885 (1947); Trans. Faraday Soc. **35**, 227 (1939).
[11] P. Zalm, G. Diemer, and H. A. Klasens, Philips Research Repts. **9**, 81 (1954).
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in Fig. 3(A), and the light-voltage waveforms in Figs. 3(B) and (C). Clipping of either polarity reduces light emission drastically.

An objection to the above experiment is that clipping reduces the applied voltage, and this in itself could cause the reduction in light emission. A dc bias, on the other hand, alters the magnitude of the voltage swing in each polarity while maintaining the rms value of the applied voltage; this was done with the circuit of Fig. 1(A) (connection *b*). The results were very similar to those of Figs. 3(B) and (C); they are shown in more detail, however, in Figs. 3(D)–(G) by displaying only the half-cycle, of positive polarity on the metal electrode, with time as the x coordinate and the trace running from right to left (because of the inverting mirror used in the camera mount). Either positive bias (which increases the positive voltage swing and decreases the negative) or negative bias reduces light emission drastically, as before. Positive bias, however, alters the phase of the light emission to earlier times as it is reduced, while negative bias does not affect the phase of the light emission.

The present experiments involved dc bias at a relatively low level where ac emission is quenched; at higher dc fields where appreciable dc electroluminescence occurs, the ac-dc enhancement effect begins to occur.

The current-voltage waveforms of film and powder layer are compared to corresponding light-voltage waveforms in Fig. 4. The current waveforms were obtained with the circuit of Fig. 1(B). Capacitive currents were taken to be eliminated when the net current flow at $V=0$ vanished as in Figs. 4(D)–(F). This is certainly approximately true, but there may be a residual current flow in either direction at $V=0$ which is indeterminate; in addition, it is possible that since electroluminescent layers are nonlinear capacitors[14] as regards rms voltage, they are also nonlinear as regards instantaneous voltage.

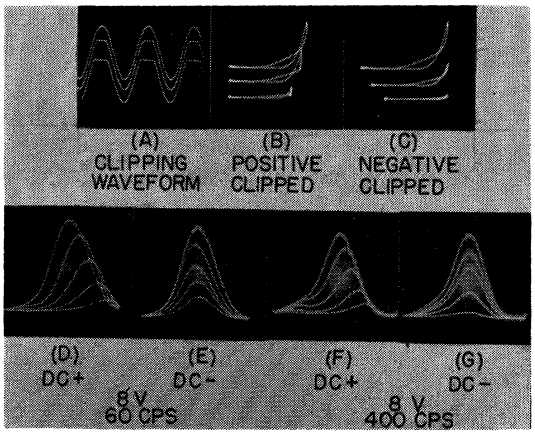

FIG. 3. (A) The voltage sine wave before and after clipping. (B) and (C) The effect on the light-voltage waveform of clipping of each polarity. (D)–(G) The decrease in light emission due to dc bias of each polarity, and the phase shift due to positive bias.

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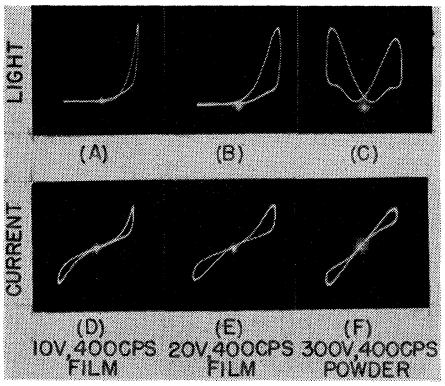

FIG. 4. A comparison of light-voltage waveforms (A)–(C) to current-voltage waveforms (D)–(F) for phosphor film and powder.

Hence the indicated currents of Figs. 4(D)–(F) may still contain a (nonlinear) capacitive component. Although there is strong polarity asymmetry in the light emission of films, the resistive currents are quite symmetrical. It is strikingly apparent also, in these and most other cases observed, that the shape of the current waveform in both films and powders is very similar to that of the light emission waveform. This implies that resistive current and light emission are strictly in phase, although not that current and light emission are proportional. Although not shown in Fig. 4, dc bias of either polarity results in an approximately exponential increase in current of that polarity; for example, positive dc bias in Fig. 4(D) increases the right-hand current trace upward in an exponential manner, and negative bias increases the left-hand trace downward in the same manner.

A similar film was deposited on nonconducting glass, and adjacent aluminum electrodes with a 1-mil gap were vaporized on the top surface of the film. Transverse excitation of the film by this means leads to the light waveforms of Fig. 5. These are symmetrical, as are those of the powder phosphor [see Fig. 2(E)], so the usual film asymmetry of light emission is related to "through" excitation and perhaps to the tin oxide electrode.

The light-output waveform of a single 15-μ particle[2] of green-emitting powder phosphor was measured for comparison with a green-emitting film. Although the particle was isolated from the electrodes and embedded in PVCA, the waveform was strongly but not completely asymmetrical, like that of the film.

Yellow-emitting ZnS:Cu,Mn,Cl films behave much as the blue- or green-emitting ZnS:Cu,Cl films.[7] How-

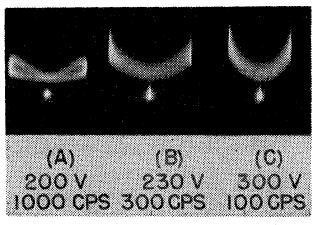

FIG. 5. Light-voltage waveforms due to transverse excitation of a film.

ever, the light-output waveform of films (and powders) containing manganese contains no secondary peak. Also, whereas the recombination in ZnS:Cu,Cl phosphors is accompanied by prompt emission within a few microseconds and probably much less, the recombination in phosphors containing manganese appears to be into a metastable state, since the emission is not complete even after 0.1 msec. In addition, dc emission is so strong in manganese-activated films[15] that the dc bias effects of Fig. 3 are largely masked. The current waveform of the yellow-emitting films is as shown in Fig. 4.

X-ray diffraction measurements on the films have shown that they are predominantly cubic with a small fraction of hexagonal structure; no unambiguous indication of orientation has yet been shown.

DISCUSSION

Light emission from these thin films occurs only on alternate half-cycles, when the metal electrode is positive (hereafter called "positive" polarity), rather than symmetrically with polarity as in the case of the powder phosphor (or thicker films). The thin film waveform is essentially identical, however, to half of the powder waveform (Fig. 2) so it must be concluded that, aside from the asymmetry of the films, the light-producing processes are the same. This nonsymmetrical behavior of the thin films can be used to confirm the long-standing idea that the excitation and recombination steps in electroluminescence are completely independent and separable in time.[1–6] The clipping experiments [Figs. 3(A)–(C)] suggest that a process necessary to light emission occurs during each half-cycle even though actual emission occurs only at positive polarity. The dc bias experiments [Figs. 3(D)–(G)] confirm this, and show further that increasing the voltage swing in the positive direction advances the light emission to an earlier point in the cycle, while increasing the voltage swing in the negative direction does not. These observations are interpreted as showing that the excitation process, whatever its nature, occurs during the negative half-cycle and the recombination process, accompanied by light emission, occurs during the positive half-cycle. Increasing positive bias has two effects: (a) The negative excitation swing, and therefore the total light emission during the following half-cycle, is progressively reduced; (b) the positive recombination swing is progressively increased, and therefore a given field strength driving the recombination (light emission) is reached earlier in the cycle; hence the light emission peaks earlier in the cycle and then decreases due to depletion of excited centers. Negative bias increases the excitation swing and the number of excited centers but reduces the recombination swing; since depletion never occurs, maximum emission will occur at the maximum of the recombination swing and so no phase shift is involved. The above sequence of events has long been thought to occur[1–6] but has not heretofore been demonstrated so unambiguously, nor has the field-driven nature[3–6] of the recombination been shown so clearly.

Since (a) transverse excitation (Fig. 5) with aluminum electrodes leads to symmetrical emission, (b) a thick plastic coating between the thin film and the metal electrode does not affect the light waveform, and (c) films several times thicker than those discussed here do not show the asymmetry in light emission, this asymmetry must be due to some influence of the tin oxide electrode which is not yet understood.

The light-output waveform from a thick film, even though in good contact with both electrodes, is essentially identical to that of sprayed phosphor layers (Fig. 2) in which the particles are for the most part electrically isolated, and to that of powder layers with no dielectric materials and particle-to-particle contact.[3] The implication is that in general neither electrodes nor embedding dielectric material play an important part in electroluminescence, with the single exception of the very thin films considered in this paper. Neither this observation nor the other experimental results serve to differentiate among the several possible excitation mechanisms of electroluminescence[10,16–21]; however, other evidence published elsewhere suggests minority carrier injection as most likely.[22]

Whatever its nature, the excitation step must depend upon current flow which in turn depends on applied voltage or electric field. The dc bias experiments show that current during excitation can increase rapidly at the same time light emission is decreasing due to insufficient recombination field. Therefore, light emission and applied voltage in electroluminescence need not be directly related. The same conclusion is suggested by the fact that excitation and recombination so definitely occur sequentially, with energy storage in between, and under different field configurations.

ACKNOWLEDGMENTS

I am indebted to G. Grasso for film preparation and to H. F. Ivey for helpful comment and encouragement.

[15] The dc emission of these films will be reported elsewhere.

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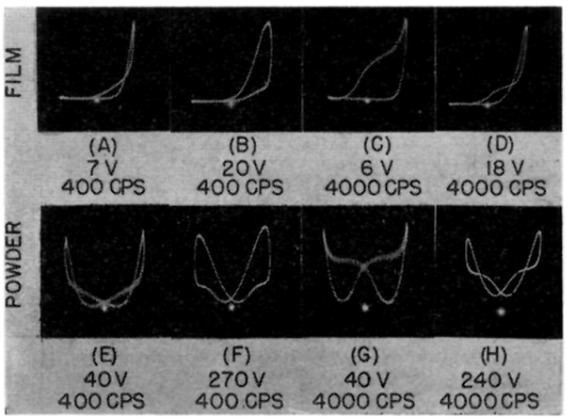

FIG. 2. Light emission-voltage waveforms for electroluminescent phosphor film and powder; the stationary spot is the beam position for $L=0$, $V=0$, with the voltage in the x direction and light in the y direction.

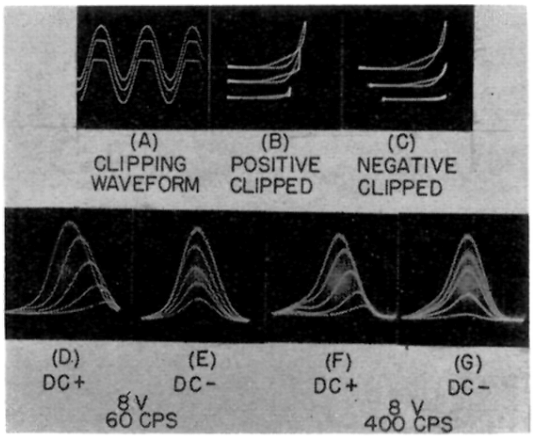

FIG. 3. (A) The voltage sine wave before and after clipping. (B) and (C) The effect on the light-voltage waveform of clipping of each polarity. (D)–(G) The decrease in light emission due to dc bias of each polarity, and the phase shift due to positive bias.

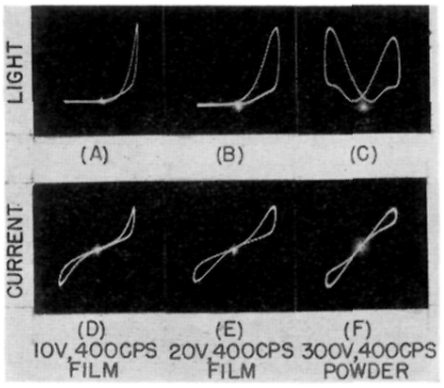

FIG. 4. A comparison of light-voltage waveforms (A)–(C) to current-voltage waveforms (D)–(F) for phosphor film and powder.

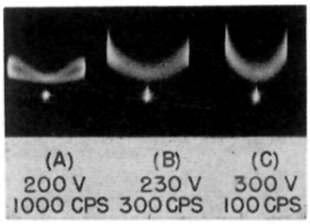

FIG. 5. Light-voltage waveforms due to transverse excitation of a film.