Experiments on Electroluminescence*

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A summary of recent observations of the properties of ZnS:Cu:Pb and ZnS:Cu:Pb:Mn electroluminescent phosphors is reported. The experiments include studies of the optical and electrical response of these phosphors dispersed in "Lucite" to sudden changes in a constant applied field, as well as microscopic studies of the luminescence of individual particles. Both green and yellow phosphors were studied. The most important results observed primarily on green phosphors are the following: Slow changes are found to take place in a phosphor in any given constant electric field, but a steady state is finally approached. A sudden departure from this state produced by changing the applied field will in general produce very little light compared to that produced on returning promptly to the conditions under which the steady state was established. Further, the luminescence in alternating electric fields of individual grains is extremely inhomogeneous, being restricted to small "pinpoints" or "spots" very much smaller than the individual particles. The spots studied luminesced only once per cycle.

It is concluded that excitation of luminescent centers occurs primarily by ionization, with recombination and radiation occurring when subsequent electrical changes make this possible. Although excitation of luminescent centers to bound states followed by prompt radiation does occur, under the conditions of these experiments this process is of secondary importance in producing light in all the phosphors studied, and is quite negligible in the green phosphors. These and other results are discussed in connection with the several possible mechanisms by which electric fields may bring about the excitation of luminescent centers.

I. INTRODUCTION

THE experiments to be described below were undertaken in order to learn as much as possible concerning the mechanism whereby the energy of an oscillating electrical field applied to ZnS:Cu:Pb phosphor particles in an insulating matrix is converted into light. The phenomenon to be explained has been reported for other phosphors by Destriau[1] and described in a variety of papers by various investigators.[2-5] When an alternating field is applied to the phosphor-dielectric complex, the field having a frequency in the range typically from 60 to several thousand cps, and an amplitude ranging from a few thousand volts/cm to 100 kilovolts/cm, the phosphor is observed to give off light.

Piper and Williams[6] have studied the luminescence of single crystals of ZnS between metallic electrodes, while Boer and Kummel[7] have made similar observations on single crystals of CdS. In comparing the results obtained by these authors with ours, it should

be borne in mind that the presence or absence of metallic contacts may alter the relative magnitudes of currents and fields in the phosphors, and hence also the mechanism of light production.

Phosphors which electroluminesce generally can also be made to respond to ultraviolet or cathode ray excitation, but it is not established that this is a requirement for electroluminescence. ZnS containing 10^{-3} gram atoms Cu per mole and 10^{-5} gram atoms Pb per mole seems to be as effective as any other green-emitting electroluminescent phosphor mentioned in the literature.[8,9] The addition of 2×10^{-2} gram atoms Mn per mole to the green phosphor yields a yellow-emitting phosphor.[10] The observations to be described below are confined to such green and yellow phosphors. Details of the preparation of this type of electroluminescent phosphor have been reported elsewhere.[10]

It has already been demonstrated that the emission spectrum of an electroluminescent ZnS phosphor is composed of the same "bands" as are emitted during fluorescence.[11] The radiation process in both cases quite surely involves the excitation of the same kinds of luminescent centers, the primary difference between the two being the manner of supplying the energy needed for excitation. It has also been shown that the intensities of the emission bands depend on the concentration of the various activators[10] as well as on the frequency of the exciting alternating field.[11] The time-average intensity emitted in the green (5200A) band increases

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[4] S. Roberts, J. Opt. Soc. Am. 42, 850 (1952).

[5] S. Roberts, J. Opt. Soc. Am. 43, 590 (1953).

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[7] K. W. Boer and U. Kummel, Z. physik. Chem. 200, 193 (1952).

[8] H. C. Froelich, J. Electrochem. Soc. 100, 280 (1953).

[9] Zalm, Diemer, and Klasens, Philips Research Repts. 9, 81 (1954).

[10] Homer, Rulon, and Butler, J. Electrochem. Soc. 100, 566 (1953).

[11] J. F. Waymouth, J. Electrochem. Soc. 100, 81 (1953).

linearly with frequency up to several hundred cycles per second, and then saturates, becoming independent of frequency above 1000 cycles per second. The time-average intensity emitted in the blue band increases linearly with frequency at least to 2000 cycles per second.

In order to study more in detail the processes involved during excitation and radiation, we have studied the electrical and optical changes which take place in a multiparticle sample of phosphor in a dielectric when electric fields are applied or removed at a predetermined rate. The results of these observations are summarized in the next section. We have also undertaken extensive microscopic observations on individual grains. The primary result of these observations is that electroluminescence is confined to "spots" much smaller than the particles themselves, and that the spots studied emitted light only once, rather than twice per cycle, as is characteristic of lamps.[2,3] The results of these observations are summarized in Part III.

II. BALLISTIC OBSERVATIONS

The changes, optical and electrical, which occur in a multiparticle sample of phosphor in a dielectric when the electric field is changed have been studied using a ballistic galvanometer to measure the desired quantities.

In the study of the optical effects, the light emitted by the phosphor in a thin slab when a constant dc applied field was suddenly changed in some definite manner was measured by the deflection of a ballistic galvanometer connected to a phototube. The integrated light output (ILO) which followed any given electrical change could thus be measured. In particular, we wanted to determine whether the frequency dependence of the light output from lamps is determined by the time rate of change of the applied field. This was studied by varying the time constant of the circuit which produced the electric field applied to the phosphor.

In the second kind of experiment, closely related to the above, an attempt was made to find out something about the time rate of change of electric polarization under varying conditions, particularly to separate the
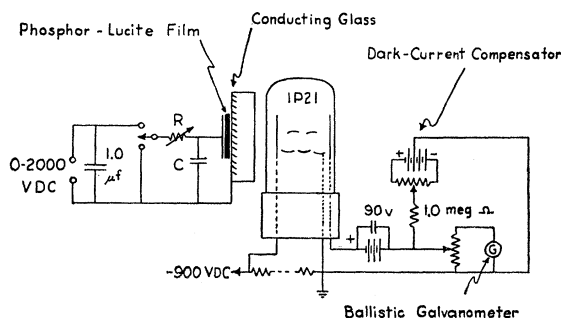

FIG. 1. Sketch illustrating apparatus used for the measurement of the integrated light output (ILO) from a phosphor-plastic sample upon application or removal of an electric field.
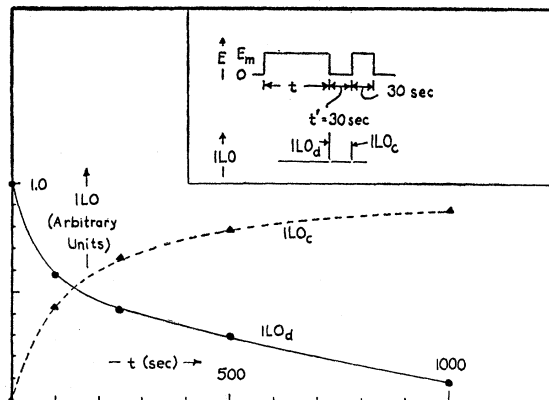

FIG. 2. Dependence of ILO_c and ILO_d on charging time t, in experiment diagramed schematically in inset. Phosphor was ZF 1081 AC, a green phosphor prepared by firing for one hour at 1580°F in a covered crucible ZnS containing several percent $ZnCl_2$, 0.002 gram atoms Pb per mole (added as $PbCO_3$), 0.001 gram atoms Cu per mole (added as CuO).

usual reversible polarization of a dielectric from more complex effects, possibly involving conduction currents, hysteresis, slow thermally induced changes, and so on.

The apparatus used in the optical ballistic measurements is shown in Fig. 1. The phosphor was imbedded in a Lucite film, 0.010 in. thick, which was aluminized on one side. A phosphor-bronze spring, making contact with the aluminized side, pressed the film against a piece of conducting glass, which formed the other electrode. A thin film of castor oil served to establish good dielectric contact between the phosphor-Lucite film and the conducting glass. The resistance R could be varied in steps of a factor of three from 1000 ohms to 30 megohms. Since the capacitance C was 0.05 μf, time constants from 50 microseconds to 1.5 seconds were available.

The light pulse emitted by the electroluminescent phosphor upon the change in electric field was allowed to fall upon the cathode of the 1P21 photomultiplier. The integral of the anode-current pulse from the photomultiplier was measured by means of the ballistic galvanometer.

The first observations with the green-emitting phosphor indicated that only erratic results could be obtained unless steps were taken to produce a standard condition of the sample to be investigated. Thus, the ILO resulting from the application of a field depended markedly on the time elapsed since the previous application of a field. A long waiting period, of the order of many hours, was needed to produce equilibrium. However, if the sample was left in zero field for a long time, overnight, for instance, then a reproducible condition was established. Upon the application of a field after the establishment of equilibrium in zero field, only a very small ILO was observed, if any. Then upon removal of the applied field within a matter of seconds after its application, a relatively very large light output was observed. This suggests that some sort of excitation

of the luminescent centers takes place when the equilibrium is disturbed by the application of the field; the emission of light occurs only upon return to initial conditions. Yellow-emitting phosphors, containing several percent of manganese in addition to copper and lead, display a larger light output than the green phosphors when the field is applied to the phosphor in zero field equilibrium. This light pulse has under some circumstances been observed as great as 25 percent of the light pulse on return to equilibrium in these phosphors.

It was soon found that the equilibrium condition could be established in a few seconds by the application of red-plus-infrared light with the sample condenser shorted out, instead of by waiting for hours. It has been established that the "erasure" of previous charging history and establishment of equilibrium is brought about by the photon energy of the light, and not simply through a heating of the sample. Photon energies between one and two volts are used for this purpose (that portion of the spectrum of a Sylvania 250-watt heat lamp that is transmitted through a water filter in series with a Corning 2412 red filter). The steady state which is produced by irradiation closely approximates that which is produced by allowing sufficient time to elapse for the cell to return to equilibrium of its own accord. It is doubtful that a true equilibrium state can be achieved at all, as more and more accurate measurements seem always to reveal small departures from a reproducible condition. We shall, however, refer to the steady state produced by infrared light as an equilibrium condition.

By using this technique of establishing equilibrium by the application of infrared light, it was found that once equilibrium of a green phosphor is established in any arbitrary field, a change from this equilibrium condition produces very little or no light, but a return to this equilibrium produces considerable light. Typical results of such experiments are shown in Figs. 2 and 3.

Figure 2 shows the results of the following experiment, which is diagrammed schematically in the inset.
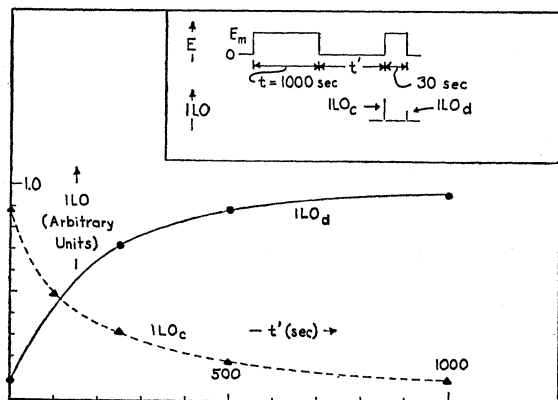

FIG. 3. Dependence of ILO_c and ILO_d of ZF 1081 AC (green) on discharging time t' in experiment diagramed schematically in inset.
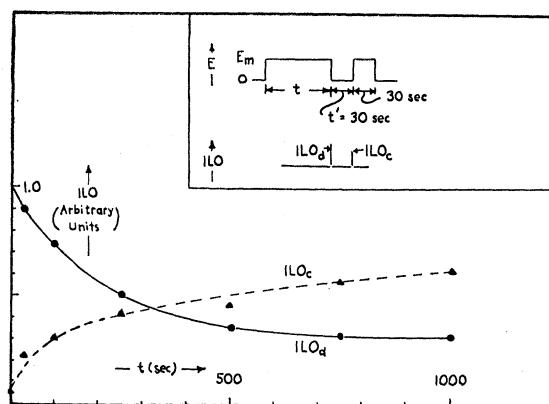

FIG. 4. Dependence of ILO_c and ILO_d on charging time t for ZF 774 AC, a yellow phosphor, prepared by firing for one hour at 1600°F in a covered crucible, ZnS containing several percent $ZnCl_2$, 0.002 gram atoms Pb per mole (added as $PbCO_3$), 0.001 gram atoms Cu per mole (added as CuO) and 0.015 gram atoms Mn per mole (added as $MnCO_3$).

With the sample in the discharged equilibrium condition, at $t=0$, a field E_m was applied to the sample for a length of time t seconds. At the conclusion of this period, the electric field was removed, and the integrated light output on discharging the sample condenser (ILO_d) was measured. Thirty seconds after the removal of the field, it was reapplied, and the integrated light output on charging the sample condenser (ILO_c) was measured. The thirty-second interval between discharging and charging was dictated by the requirement that the ballistic galvanometer return to zero after the measurement of ILO_d. The effect of the initial charging time t on ILO_c and ILO_d is shown in the figure. Note that ILO_c is zero for $t=0$, but increases toward a saturation value as t increases. ILO_d, initially high, approaches zero as t increases. One thousand seconds is insufficient time for equilibrium to be established.

Figure 3 shows the results of the inverse experiment, which is diagrammed schematically in the inset.

With the sample in the discharged equilibrium condition at $t=0$, a field E_m was applied for a period of 1000 seconds. As previously noted, this is insufficient time for the sample to reach equilibrium, but it permits the sample to reach a reproducible state. It was not realized at the time these experiments were performed that the sample could be gotten into equilibrium with any desired field in a few seconds simply by irradiating with red-plus-infrared light with the field applied. At the conclusion of this charging period, the field was removed for a time t'; at the conclusion of the time t', the field was reapplied, and ILO_c measured; after thirty seconds, the field was again removed and ILO_d measured. The dependence of ILO_c and ILO_d on the discharging time t' is shown in the figure. Note that ILO_c decreases toward zero, while ILO_d increases toward its zero field equilibrium value as t' increases.

Figure 4 shows the dependence of ILO_c and ILO_d of a yellow phosphor on charging time t. Note that the
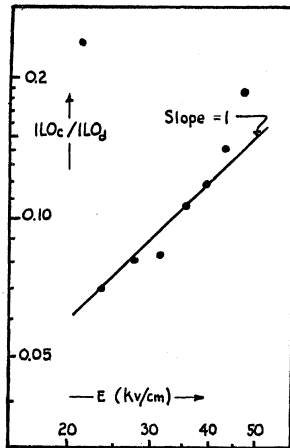
FIG. 5. Dependence of the ratio ILO_c/ILO_d on field strength E, for ZF 774 AC (yellow).

dependence is quite similar to that displayed by the green phosphor, except that ILO_c is not zero for $t=0$, and that ILO_d apparently does not approach zero as t increases. These data indicate that the same process occurring in the green phosphor takes place here, but that there is in addition a greater tendency for excitation of some luminescent centers to states which promptly radiate upon a first application of the field to a phosphor in equilibrium, in which there are supposedly no excited centers. This result suggests the existence of two processes which produce light, one involving excitation with prompt radiation, the other involving the retention of the excited center in this excited state for long times, of the order of hundreds of seconds. The existence of two processes is also suggested by Fig. 5 in which the ratio of ILO_c to ILO_d at $t=0$ is plotted for this same phosphor as a function of electric field. Note that this ratio varies approximately as E at low fields, and varies at a higher power of E at higher fields.

To study the electrical changes which take place in a multiparticle sample of phosphor when a constant dc field is applied or removed, the movable-plate condenser
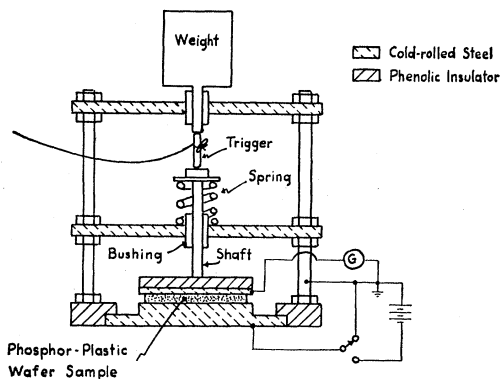

FIG. 6. Sketch illustrating construction of movable plate condenser employed for the measurement of frozen polarization.

illustrated in Fig. 6 was employed. The phosphors were impregnated in Lucite wafers 0.050 in. thick which were mounted in the condenser for measurement. The spring-loaded upper plate of the condenser, normally held in contact with the phosphor-Lucite wafer by the weight, could be rapidly elevated by pulling out the trigger.

It was found that if the sample condenser were charged for some minutes and then discharged, there still remained a "frozen" dipole moment per unit volume in the sample, which could be measured by quickly elevating the upper plate of the condenser and measuring the sizable charge which passed through the ballistic galvanometer. It was verified that this frozen polarization was a property of the phosphor and not of the binder by performing similar experiments on wafers containing no phosphor, wafers containing finely divided Cu powder, and on loose piles of phosphor. Only the latter displayed the frozen polarization.
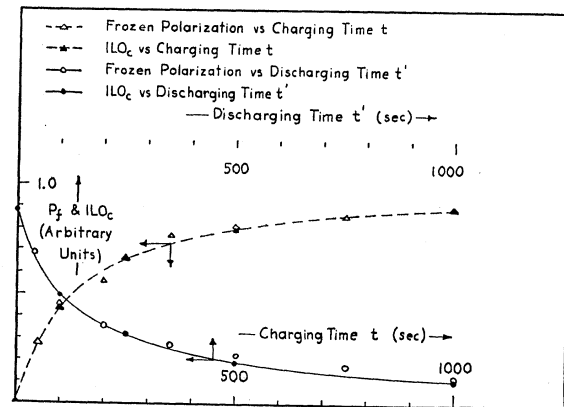

FIG. 7. Dependence of ILO_c and frozen polarization on charging time t (lower scale) and on discharging time t' (upper scale) ZF 1081 AC (green).

The behavior of frozen polarization with charging and discharging time is the same as that of ILO_c. It can be "erased" by irradiating the sample with red-plus-infrared light. In fact, for a given green phosphor, the same curves can be used to represent the behavior of both ILO_c and the frozen polarization. This is shown in Fig. 7. Figure 8 illustrates the variation of free, frozen, and total polarization with charging time. Note that the frozen polarization appears as an increase in total polarization, with "free" polarization remaining sensibly constant.

Concerning the mechanism of the development of frozen polarization, it seems reasonable to assume that electrical changes take place within a grain as long as sufficient electric field is present within the phosphor grains to produce the changes. The field finally approaches the value zero within the "working" part of the grain regardless of the magnitude of the applied field, provided the movable charge within the grains is

large enough. We specify "working" part of the grain, since there is ample evidence, to be discussed in the section immediately following, that the electroluminescent emission from grains of these phosphors is confined to a small fraction of the volume of the grain. The optical results are, therefore, explicable without assuming that the zero field condition is established in the entire grain.

The fact that the frozen polarization approaches a limiting value proportional to the field strength also indicates the validity of the above "zero-field" hypothesis. The only difference between the equilibrium condition with and without field is that in an externally applied field there is a certain frozen polarization which is absent if no constant field is present. We then conclude that luminescent centers are excited by the production of an applied field within the phosphor grains, and light is emitted when the region within the grains returns to its equilibrium condition.
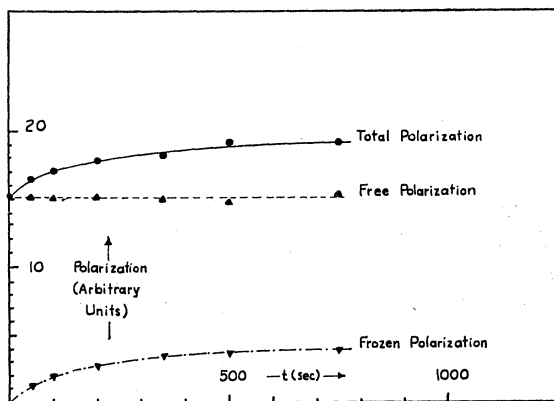

FIG. 8. Dependence of free, frozen, and total polarization on charging time t for ZF 1081 AC (green).

Having established the above points, we were in a position to return to one of the problems we had in mind in initiating these experiments, namely, to determine the effect of dE/dT on the light output in going from some initial field E_1 to some final field E_2. As we have said, in going from an equilibrium field, which in all probability is zero or small within a grain, to some final field E, the light output from a green-emitting phosphor is negligible under all conditions. On returning from the final field E to the equilibrium field, the light output depends on the time elapsed in the nonequilibrium condition, as has already been indicated, but is sensibly independent of the rate at which the return to equilibrium takes place in the entire range of time constants from 50 microseconds to 0.5 second, as shown in Fig. 9ᐧ The excitation which is brought about by the application of an electric field is also only slightly dependent on the rate of rise of the electric field, as shown in Fig. 10.
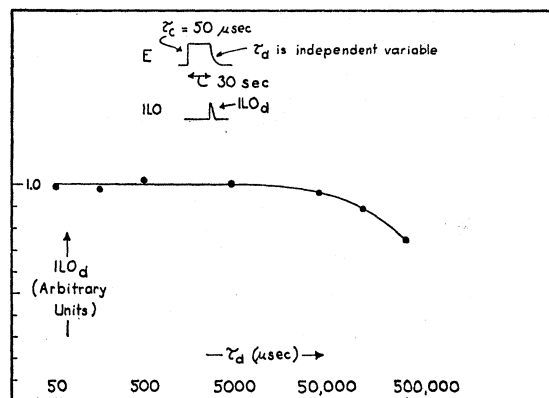

FIG. 9. Dependence of ILO_d on the time constant, τ_d, of remova of the electric field, for ZF 1081 AC (green).

It is thus established that the frequency dependence of the light emission from lamps is not due to the variation of dE/dT. The light "pulse" each half-cycle is at low frequencies independent of frequency, and the linear increase of light output with frequency results from the increase in the number of equal light pulses per second. At higher frequencies, other effects, involving either the duration of the voltage "pulse," or the interval between voltage "pulses," predominate and modify the magnitude of the light pulses emitted each half-cycle.

III. THE LUMINESCENCE OF INDIVIDUAL PARTICLES

While the measurements that have been described represent averages over large numbers of particles, the observations reported in this section consist of observations of the luminescence of single particles or small polycrystalline aggregates. The most fundamental observation to be made is that the luminescence of these particles is by no means uniform, but is confined almost exclusively to small, discrete, bright "spots."

Figure 11 shows a photograph of two large polycrystalline aggregates (about 50 microns in diameter),
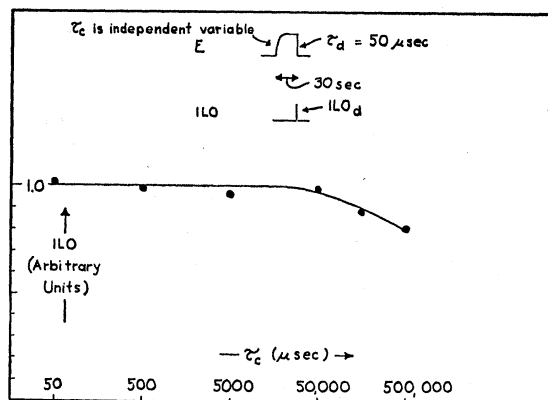

FIG. 10. Dependence of ILO_d on the time constant, τ_c, of application of the electric field, for ZF 1081 AC (green).
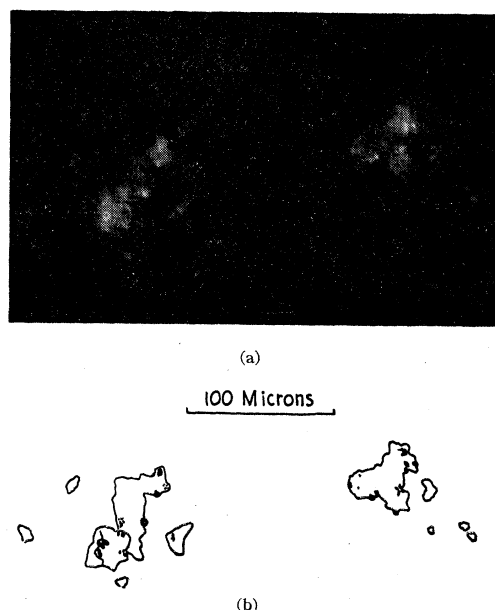
(a)

|100 Microns|

(b)

FIG. 11. (a) "Auto-micro-photograph" of two particles of electroluminescent phosphor taken by their own electroluminescence. (Photo by Herndon Associates, Inc., Ipswich, Massachusetts.) (b) Sketch showing approximate outlines of particles illustrated in (a), and approximate locations of "spots."

taken by their own electroluminescence. This photograph was obtained from a dilute dispersion of phosphor in Lucite between two sheets of 100-mesh gauze. The electric field strength was 100 kv/cm rms, and the viewing direction was approximately parallel to the field. The luminescence is far from uniform, and seems to be localized in certain bright pinpoints, which appear to be of the order of microns in size. If the particles are illuminated by 3600A ultraviolet light, no such nonuniformity is observed in their fluorescence. It is our firm belief that the striking properties of these spots, to be described in the following, make it unlikely that they are optical illusions due merely to the emergence of a volume luminescence at particular points owing to
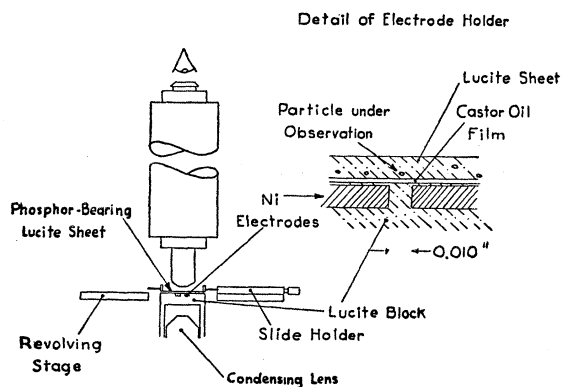

FIG. 12. Sketch of apparatus employed for microscopic observations of electroluminescing particles.

multiple internal reflection and focusing. The inhomogeneous electroluminescence shown here has also been observed by Roberts[5] in Zn(S·Se):Cu and by Zalm et al.[9] in ZnS:Cu.

The arrangement with which the photograph of Fig. 11 was taken suffers from the fact that the direction of viewing of the particle is parallel to the electric field. In general, if many spots are present in a particle, they are "in series" along the electric field vector. For this reason, it is usually desirable to have the direction of viewing at right angles to the direction of the electric field. In order to accomplish this, as well as to make it possible to study the influence of relative orientation of particle and electric field, we have used extensively the method of mounting shown in Fig. 12.

A thin sheet of Lucite containing a dilute dispersion of phosphor was fastened to the slide holder on the rotating stage of the microscope. A Lucite block containing two nickel electrodes was mounted on the condenser stage in such a way that the electric field between the electrodes was at right angles to the common axis of microscope and revolving stage, as shown in the diagram at the left. The sheet containing the phosphor was brought into close contact with the electrode block, and good dielectric contact between the two was assured by a thin film of castor oil, as shown in the enlarged sketch at the right of Fig. 12.

With this arrangement, the particle under observation was located in the "fringe" region of the electric field maintained between the two electrodes by an alternating potential difference. The field vector was at right angles to the direction of viewing, and the orientation of the particle relative to the field could be varied by rotating the revolving stage to which the Lucite sheet containing the phosphor was attached.

While only a small fraction of the observable spots can be classified, it has proved possible with this method of observation to identify at least two classes of spots, by their locations on the particles, and by their different dependence on the relative orientations of particle and field. Typical examples are shown in Fig. 13. The first class of spot is illustrated in Fig. 13 (a). It is to be found at the junction or interface between two apparently similar crystallites of an aggregate. It luminesces most brilliantly for the electric field approximately perpendicular to the interface. The second class of spot is illustrated in Fig. 13 (b). It is to be found at the tip of what appears to be a long needle-shaped crystallite, and luminesces most brilliantly when the field is approximately parallel to the axis of the crystallite.

In order to determine the effects of orientation of field, the voltage across the electrodes at which the spot seemed to the dark-adapted eye to extinguish was measured for each orientation. This is a quantity which is easily measured, and is related to brightness; the higher the extinction voltage, the lower the brightness

at a fixed voltage.[12] It is this extinction voltage which is plotted as a function of field angle for the two particles illustrated in Fig. 13. The difference in minimum extinction voltage for the two types which is shown in Fig. 13 is quite characteristic.

It has proved to be possible to photometer quantitatively the light emitted from the brightest of the junction spots. This was accomplished by means of the apparatus illustrated schematically in Fig. 14. The phosphor grains were mounted in the same manner as for the orientation experiments. The 45× objective formed an image of the spot, which could be considered to be a point source. Exactly in the image plane, a dia-

FIG. 14. Sketch illustrating adaptation of microscope for photometry of the luminous emission from "spots."

The average light output from a number of spots has been measured, using a galvanometer as an indicator. Photometry was performed almost exclusively on well-defined junction spots, as these were the brightest. The fluctuating light output has also been measured, using an oscilloscope as an indicator. Figure 15 shows a plot of the light emitted from the spot shown in the inset, as a function of the 60-cps alternating voltage across the electrodes. Note that there appears to be a threshold potential, above which the luminous emission increases linearly with voltage, over a considerable range. It is possible that departure from the linear relation is caused by light originating in other parts of the particle being scattered into the optical system.

For the purposes of comparison, a curve of light emission *versus* applied potential for a typical lamp is also reproduced in Fig. 15, with arbitrary scales. Note the considerably greater curvature, especially at low voltage. We feel this to be due to the fact that lamps are composed of large numbers of particles having a variety of luminescent thresholds and orientations.
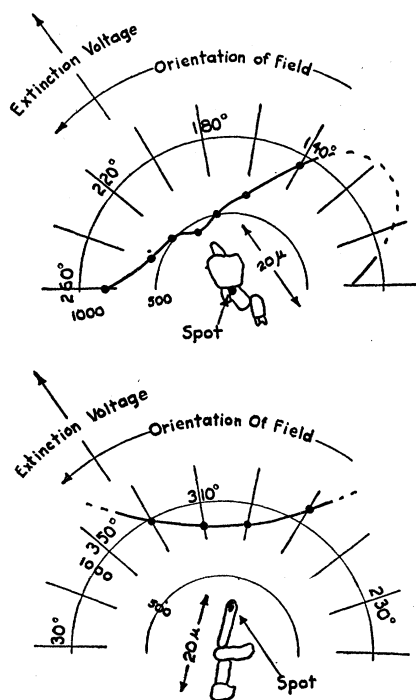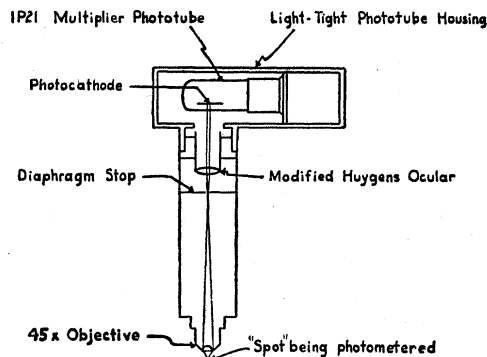

FIG. 13. (a) Sketch showing particle with "junction" type of spot, and showing variation in extinction voltage with orientation of field. Zero degree azimuth is arbitrary. (b) Sketch showing particle with "point" type of spot, and showing variation in extinction voltage with orientation of field. Zero degree azimuth is arbitrary.

phragm stop with a diameter of about 0.5 mm masked off the image of the rest of the particle. The light from the image of the spot was then focused on the cathode of a 1P21 photomultiplier by a Huygens ocular which had been modified by the removal of one lens. By suitable calculations, based on the assumption that the spot is a point source, and on the response of the photomultiplier when the point source spot was replaced by an area source of known brightness having the same emission spectrum, namely a green electroluminescent lamp, we could calibrate the system in absolute terms.

[12] These observations were made prior to the development of techniques for quantitative photometry described below. Subsequent observations verify the conclusions which are reached here.
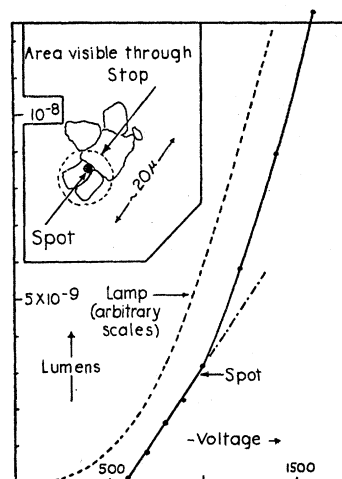

FIG. 15. Dependence of average luminous emission from spot illustrated in inset on ac voltage applied to electrodes (solid line). Variation of light output with voltage for a typical lamp is shown plotted with arbitrary scales (dashed line) for comparison.

Figure 16(a) shows a photomontage of the oscilloscope traces of potential applied to the electrodes, photomultiplier current due to spot luminescence, and photomultiplier dark current for a typical junction spot. This montage has been constructed with the assumption that the electroluminescent emission decayed to zero each cycle. Note that there is one "pulse" of light output each cycle; this is quite different from the behavior shown by lamps, as shown in Fig. 16(b). It is evident that inherent in the mechanism responsible for producing "spots" is some mechanism that is sensitive to the *polarity* of the applied field. The behavior of lamps can be understood by again recalling that they are composed of many spots, some of which are oriented to emit light during one-half of the cycle, others of which are oriented to emit light on the other half of the cycle. Hence, the light emitted by lamps pulsates at 120 cps, while the light emitted by spots pulsates at 60 cps.

It may be of interest to add that probably thousands of electroluminescing grains have been examined under the microscope leading to the qualitative observation that electroluminescence is inhomogeneous and particularly marked in small spots. Also the light output of hundreds of spots has been examined with an oscilloscope, leading to the conclusion that the appearance of

Potential applied to electrodes

Luminous emission from spot

Photomultiplier dark current

(a)

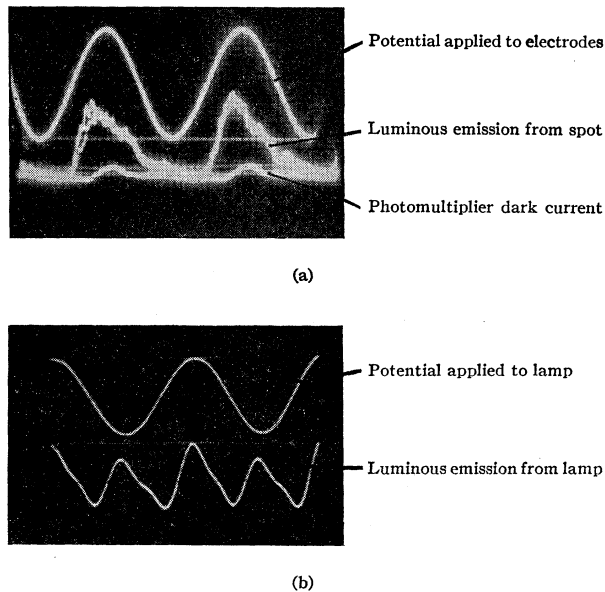Potential applied to lamp

Luminous emission from lamp

(b)

FIG. 16. (a) Photomontage of oscilloscope traces showing luminous emission from a typical junction spot, photomultiplier dark current, and potential applied to the electrodes, all as a function of time. (The variation in the dark current arises through the differentiation of the "sawtooth" hum wave of a few millivolts amplitude present in the dynode supply voltage by the RC circuit consisting of the cathode-to-anode capacitance of the photomultiplier and the anode load resistor.) (b) Photograph of oscilloscope traces showing luminous emission from a typical lamp, and potential applied to the lamp, as a function of time. The sensitivity used was sufficiently low that the variation in dark current with phase was negligible.

essentially only one major light pulse per cycle is not an exceptional phenomenon but the characteristic standard of behavior.

IV. DISCUSSION

We feel that the most important facts about electroluminescent phosphors to emerge in this investigation are the following.

(1) The luminous emission under alternating electric field excitation at fields of the magnitudes used is confined almost entirely to small, discrete "spots," of which at least the "junction" type appear to be "optically rectifying," in the sense that they emit light during only one half of a cycle.

(2) Under the conditions of these experiments, the most important light emission mechanism in all phosphors studied is a two-stage process, involving:

(a) excitation upon local application of an electric field.
(b) emission upon removal of the electric field.

(3) The total number of excited centers is nearly independent of the rate of rise of the electric field. This has been observed between rise times of 5×10^{-5} sec and 0.5 sec for the same total changes in field.

(4) There can be developed in these phosphors a frozen polarization whose dependence on previous electrical history is closely related to the light output obtained on application or removal of an electric field. This frozen polarization is presumably, therefore, localized at the luminescent spots.

The primary reason for the luminescence in "spots" may be the concentration of the electric field at those spots by the electrical inhomogeneity of the particle itself. As a specific example, consider a particle 20 microns long, bisected by a rectifying junction 1 micron thick, in an applied field of 10^5 volts per centimeter. For fields in the forward direction, the junction will behave as a conductor. There will be little or no electric field in it except that necessary to overcome the natural "bias" of the rectifying junction. For fields in the reverse direction, the junction will behave as an insulator; 200 volts will appear across the rectifying junction, giving a local field therein of 2×10^6 volts per centimeter. If the barrier were thinner, the local field would be correspondingly greater.

Such a barrier would have the required "optically rectifying" properties if we assume that the high fields present on the "reverse" half-cycle are responsible for excitation, either directly by a barrier penetration process, or indirectly by accelerating electrons which in turn produce excitation by collision. Among other workers in the field, the "collision" mechanism is almost unanimously believed to be responsible for the majority of the excitation. Curie[13] has endeavored to show theoretically how it might take place at the comparatively

[13] D. Curie, J. phys. radium 13, 317 (1952).

low average field strengths (2×10^4–10^5 volts/centimeter) at which the electroluminescence of powdered phosphors occurs. Burns[14] and Zalm[9] have also considered it; Piper and Williams[6] have based a detailed theory of the electroluminescence of single crystals upon it.

Barrier penetration, or direct field-ionization of luminescent centers has, on the other hand, been largely discounted. Piper and Williams[6] have proposed that electrons emitted from a negative metal electrode into the ZnS are responsible for the excitation of the "in phase" luminescence peak they observe in their single crystal experiments. However, they regard direct field-ionization of the luminescent centers in ZnS as being out of the question because the fields required, according to their calculations, are much higher than those required for ionization by electron impact.

It is interesting to note, in this connection, that McKay et al.,[15] have found evidence for ionization by electron impact in the increase in reverse current in "thick" germanium $p-n$ junctions at high back voltages, while McAfee et al.,[16] have found evidence for barrier penetration of the Zener type[17] in the increase of reverse current in "thin" germanium $p-n$ junctions at high back voltages, without ionization by electron impact. This apparent contradiction has been discussed by McKay,[15] who points out that, exactly as in gaseous discharges, the distance over which a high field is maintained is as important to the mechanism of ionization by electron impact as the existence of the high field itself.

At this stage we know that the electroluminescing junctions appear to be the result of a nonuniformity of the properties of the phosphor crystallites, but we have no exact knowledge of their thickness or of the charge distribution or luminescent center distribution within them. We hesitate, therefore, to make a choice of mechanism based on purely theoretical arguments as to which might occur at lower fields in a hypothetical crystal of uniform properties.

We may conclude at present, however, from the fact that the total number of excited centers in a given sample is independent of the rise time of the electric field over such a wide range, that if excitation by electron impact does occur, the primary electrons must be initially bound, either in "donor centers" or in luminescent centers themselves, in a region of very long relaxation time. These electrons must be liberated by the field when the field is already high enough to accelerate them to high energies. Otherwise, they will simply drift to the surface of the particle, neutralizing the field as fast as it is applied. A possible site for such a region is the rectifying barrier, postulated to explain the luminescence of spots, which in the "reverse" direction would be devoid of free charge.

Whatever the mechanism by which energy is transferred from the electric field to the luminescent centers, the most important process of excitation in the phosphors studied appears to be one in which electrons are removed from the luminescent centers. Emission occurs upon removal of the electric field when the electrons are allowed to return to the ionized centers, where they recombine with the emission of radiation. It is difficult to conceive of any excitation process other than actual ionization in which luminescent centers can be maintained in an excited state by an electric field for hundreds of seconds.

This may not be the only process of excitation. The result obtained with the yellow phosphors, in which light is emitted upon application of an electric field to a phosphor in equilibrium at zero field is compatible with the existence of another process. In this case, an electron in a luminescent center might be raised to an excited state which is bound, from which it promptly reverts to the ground state with the emission of radiation.

The mechanism of recombination of injected carriers, postulated by Lehovec et al.,[18] to account for the luminescence of silicon carbide crystals and described by Haynes et al.,[19] in germanium $p-n$ junctions, would seem not to be the dominant mechanism involved in light emission in the ZnS here studied since it would lead one to expect light emission upon application rather than removal of the field.

It is our opinion that one of the most important properties of an electroluminescent phosphor which is to be dispersed in an insulating medium and excited by alternating fields may be the high degree of electric inhomogeneity of the individual particles which we believe to be responsible for the "spots." It is this feature that might be responsible for the fact that effects normally associated with dielectric breakdown can be confined to such small regions that no macroscopic breakdown takes place.

[14] L. Burns, J. Electrochem. Soc. 100, 572 (1953).

[15] K. G. McKay and K. B. McAfee, Phys. Rev. 91, 1079 (1953).

[16] McAfee, Ryder, Shockley, and Sparks, Phys. Rev. 83, 650 (1951).

[17] C. Zener, Proc. Roy. Soc. (London) A145, 523 (1934).

[18] Lehovec, Accardo, and Jamgochian, Phys. Rev. 83, 603 (1951).

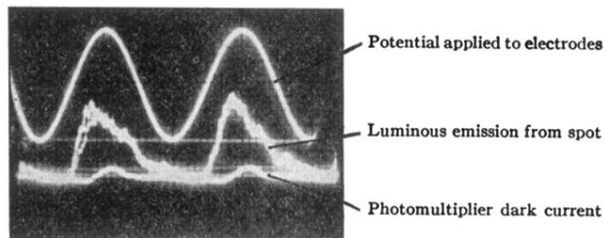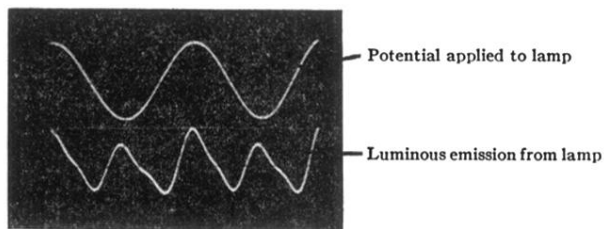[19] J. R. Haynes and H. B. Briggs, Phys. Rev. 86, 647 (1952).

(a)

100 Microns

(b)

FIG. 11. (a) "Auto-micro-photograph" of two particles of elec-
troluminescent phosphor taken by their own electroluminescence.
(Photo by Herndon Associates, Inc., Ipswich, Massachusetts.)
(b) Sketch showing approximate outlines of particles illustrated
in (a), and approximate locations of "spots."

Potential applied to electrodes

Luminous emission from spot

Photomultiplier dark current

(a)

Potential applied to lamp

Luminous emission from lamp

(b)

FIG. 16. (a) Photomontage of oscilloscope traces showing luminous emission from a typical junction spot, photomultiplier dark current, and potential applied to the electrodes, all as a function of time. (The variation in the dark current arises through the differentiation of the "sawtooth" hum wave of a few millivolts amplitude present in the dynode supply voltage by the RC circuit consisting of the cathode-to-anode capacitance of the photomultiplier and the anode load resistor.) (b) Photograph of oscilloscope traces showing luminous emission from a typical lamp, and potential applied to the lamp, as a function of time. The sensitivity used was sufficiently low that the variation in dark current with phase was negligible.