of ΔS and C has twofold significance. First, it indicates the essential correctness of all three of the experimental values. Second, it provides an additional example, in what may well become a new subclass of ferroelectrics, of the applicability of the equation $P^2=2C\Delta S$. In the light of the general agreement of this equation in previously studied ferroelectrics, it appears that a single free-energy function theory may be capable of explaining ferroelectricity in general.

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Influence of Alternating Electric Fields on the Light Emission of Some Phosphors

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The influence of an alternating electric field on the fluorescence and phosphorescence of various ZnS and ZnS:CdS phosphors was investigated. The light pulses and the average brightness of the luminescence were measured simultaneously. The wave pattern during fluorescence consists of two different pulses per cycle. The two pulses differ in their respective amplitudes, time dependence, and shape. The pulses corresponding to positive polarity of the illuminated electrode show a similar behavior for all phosphors. The second pulse differs for the various phosphors. Voltage dependence of the amplitudes and light sums per cycle were found to be different for the two pulses. These two pulses must be due to two different processes and suggest surface effects.

INTRODUCTION

THE effects of alternating electric field on the luminescence of powdered nonelectroluminescent phosphors have been investigated by a number of authors. As early as 1920, Gudden and Pohl[1] found that on application of electric fields some of their photoconducting phosphors emitted momentary light flashes. Destriau and his co-workers[2–5] have made extensive investigations of the various influences of the electric field on the luminescence of some types of ZnS phosphors. They have studied in particular the changes in the average brightness of luminescence as a function of the voltage and temperature both during excitation and phosphorescence.

Olson[6] has investigated the quenching of the phosphorescence caused by the ac field as a function of the frequency for one particular phosphor (ZnS:CdS:Cu). Matossi and Nudelman[7] have studied the quenching during excitation as a function of the frequency for another particular phosphor (ZnS:Cu). Matossi[8] has attempted to explain the effects observed during excitation by extending the theory of Randall and Wilkins[9] on luminescence in phosphors. By including assumptions that the electric field causes emptying of traps as well as draining off of electrons by field-induced nonradiative transitions, he seems to account for the momentary illumination, subsequent quenching, and superposition of a ripple of frequency twice that of the applied voltage. It will be shown in this paper that there are a number of important effects which make it doubtful whether this theory in its present form can be applied to the phosphors we have investigated.

There has recently been a considerable amount of experimental and theoretical work on electroluminescent phosphors.[10] It should be emphasized, however, that explanations which may be valid in cases of electroluminescence do not necessarily account for the various effects of electric fields during fluorescence and phosphorescence. The hope of practical applications of electroluminescence has induced many workers to concentrate mainly on this phase of research. An understanding of the influence of electric fields on the usual nonelectroluminescent phosphor is more general in nature and may shed light on electroluminescence as well.

This series of experiments was undertaken in the hope of finding unifying features in the wealth of experimental data on the influence of ac fields on powdered phosphors. This paper is concerned with phosphors of the type ZnS and ZnS:CdS with Cu and Ag activators. In a later publication, we intend to report results on the effects of ac fields on doubly activated infrared-stimulated phosphors.

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[2] G. Destriau, J. Chim. Phys. **34**, 117, 462 (1937).

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[4] G. Destriau and J. Mattler, J. Phys. radium **11**, 529 (1950); **13**, 205 (1952).

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[9] R. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 390 (1945).

[10] A discussion of work in electroluminescence will be found in Brit. J. Appl. Phys., Supplement No. 4 (1954).

We have studied the various effects of a 50-cps ac field during both excitation and phosphorescence on the same phosphor. These effects were investigated as a function of the phosphor composition. Particular attention was paid to the shape of the light pulse, the light sum per pulse, and the amplitude, as functions of the time after the beginning of the application of the field and of the applied potential difference.

As will be shown later, our results indicate that there are two light pulses per cycle during both excitation and phosphorescence, each with different characteristics. During excitation these two pulses have different decay times, different light sums, and sometimes different shapes. All these effects are a function of the applied voltage, the function being different for the two pulses. It is probable, therefore, that there must be at least two mechanisms responsible for the emission of these two pulses. No simple model so far proposed can explain all the observed phenomena.

EXPERIMENTAL METHOD

The purpose of the experiments was to measure the slow changes in the average light output as well as the periodic light ripple. The light output was, therefore, measured by two methods:

(1) The light pulses from the phosphor cell were measured by a 1P21 photomultiplier tube, operated from a stabilized power supply. Suitable absorbing filters could be placed in front of the photomultiplier tube. The output was brought to the *Y*-axis of a cathode-ray oscilloscope equipped with a dc amplifier. The time base was synchronized to the line voltage. The pattern on the scope was recorded by means of an oscillo-record camera. The film of the camera could be moved with various constant speeds in the *Y*-direction of the scope.

(2) The above method was particularly suitable for measuring the characteristics of the light pulses but was not convenient for recording the slow changes of average brightness. For the latter purpose the output of the photomultiplier was fed to a moving coil galvanometer. The deflections were registered on photographic paper attached to a drum which was rotated at constant speed by means of a timing motor.

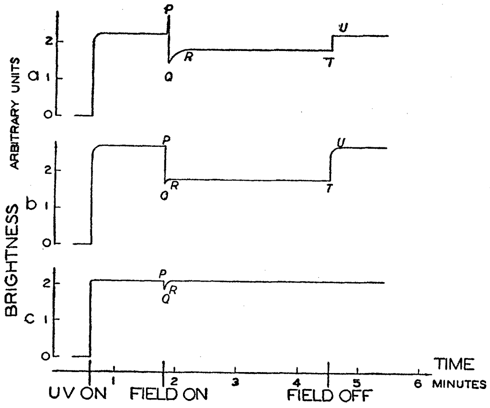

FIG. 1. Effect of the alternating electric field on the average brightness during excitation for the phosphors (a) ZnS:Cu (RCA *F*-2040), (b) ZnS:Ag (RCA *F*-2030), (c) 20ZnS:80CdS:Ag (RCA *F*-2038).

The phosphor cells were similar in construction to those reported by other observers.[3,10–12] The phosphors were embedded in thermal-setting polystyrene or in araldite. Conducting glass was prepared by the method of Gomer,[13] using microscope cover glasses in order to minimize ultraviolet absorption. Contact to the conducting glass was made by means of a thin aluminium foil and aluminium strips fastened to the foil at the edge of the glass.

Cells were constructed in which both electrodes were made of conducting glass, and others in which one electrode was of brass. In some cells the phosphor matrix made direct contact with the electrodes, in others thin mica sheets were placed between the matrix and the electrodes.

The phosphor was excited by ultraviolet light (mainly 3650 A) from a stabilized mercury vapor lamp operated from a dc supply. A camera shutter and suitable filters could be placed in front of this lamp. The exciting light was focused on the conducting glass. The emitted light, passing through this glass, fell on the photomultiplier cathode. Measurements were made only when the phosphor was fully excited (in general after two minutes of excitation).

A condenser of capacity 0.1 μf was connected across the phosphor cell in order to prevent possible voltage transients caused by switching the field on and off.

Phase measurements were made by means of the *Z* amplifier of the scope. A pulse-sharpening circuit was connected between the ac source and the *Z* amplifier. After making corrections for the phase difference caused by the pulse sharpener and amplifier, one could measure the phase difference between the maxima of the applied voltage and the maxima of the light pulses. Sufficient time was allowed between experiments for the decay of the phosphor.

EXPERIMENTAL RESULTS

The phosphors investigated were of the type (a) ZnS:Cu (RCA *F*-2040), (b) 80ZnS:20CdS:Cu (RCA *F*-2042), (c) ZnS:Ag (RCA *F*-2030), (d) 80ZnS:20CdS:Ag (RCA *F*-2032), (e) 20ZnS:80CdS:Ag (RCA *F*-2038). The various effects observed have been tested in dielectric cells made of polystyrene and araldite. The results are reproducible and those reported are an average of many cells. The following general conclusions can be inferred from the experimental results.

1. On application of an alternating electric field during *excitation*, the average brightness is increased

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[12] Payne, Mager, and Jerome, Illum. Eng. **45**, 688 (1950).

[13] R. Gomer, Rev. Sci. Instr. **24**, 992 (1953).

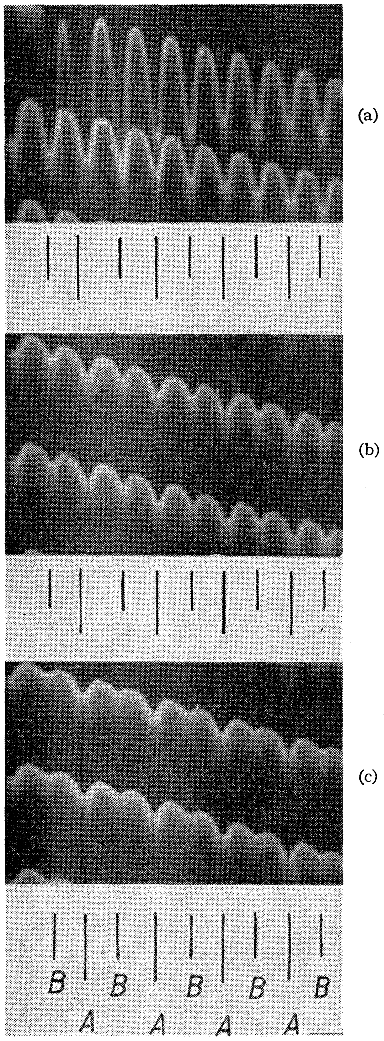

FIG. 2. Motion pictures of light pulses during excitation of ZnS:Cu for various times after application of the field. ($V=630$ volts.) (a) $n>0$, (b) $n>80$, (c) $n>1000$. (n in units of 1/50 sec.) The maxima of the pulses are directed downwards. Pulses A correspond to positive polarity of illuminated electrode.

initially for all phosphors investigated. This sharp increase [at P in Fig. 1(a)] lasts only a very short time, and is followed by a momentary dip [at Q in Fig. 1(a), (b), (c)]. In most phosphors, this increase lasts less than half a second and the galvanometer record does not show it [Fig. 1(b) or 1(c)]. Photographic records, however, indicate this rise. After this transitory period (time $P-Q$) the average brightness for most phosphors reaches a new equilibrium level ($R-T$), lower than the luminescent level before application of the field. The phosphor 20ZnS:80CdS:Ag is an exception and shows only a momentary dip and no stationary quenching [Fig. 1(c)].

An ac wave is superimposed on the average brightness level. The shape and amplitude of these light pulses change rapidly in the transitory period and have constant characteristics in the stationary state (time $R-T$). Figure 2 shows a typical photograph of the light pulses for ZnS:Cu phosphor during the transitory period [Fig. 2(a)] and stationary period [Fig. 2(c)].

2. The various phosphors show no clear-cut relationship between the height of the pulses and the amount of quenching in the stationary period. There is some indication that in phosphors which show large quenching the corresponding pulses are small, and conversely in those which show small quenching the amplitudes are large. For example, ZnS:Ag shows large quenching and very small pulses, while 20ZnS:80CdS:Ag shows no quenching (except momentarily) and larger ac pulses. But ZnS:Cu shows significant quenching and very large pulses.

3. In the transitory period, all phosphors show two pulses per cycle. In the stationary period ($R-T$ in Fig. 1) there are either one or two pulses per cycle, depending on the applied voltage. At very high voltages two pulses per cycle always appear. The behavior of the two pulses depends on the polarity of the illuminated electrode and not on the direction of observation. We distinguish between pulse A observed when the illuminated electrode is positive and pulse B when the illuminated electrode is negative.

4. The two observed pulses per cycle differ in the stationary state considerably in their characteristics: (a) The amplitude A and light sum per cycle S_A are not equal to B and S_B.[14] This is seen in Fig. 2 for the phosphor ZnS:Cu. (b) Their dependence on applied voltage is different (see Figs. 3 and 4). (c) The amplitude B always starts to appear at a higher threshold voltage than A. In some phosphors (as in 80ZnS:20CdS:Cu) the pulse B is missing for all voltages except extremely high voltages close to dielectric breakdown. (d) For low, medium, and in some cases even for high voltages, the A component is larger than the B component.

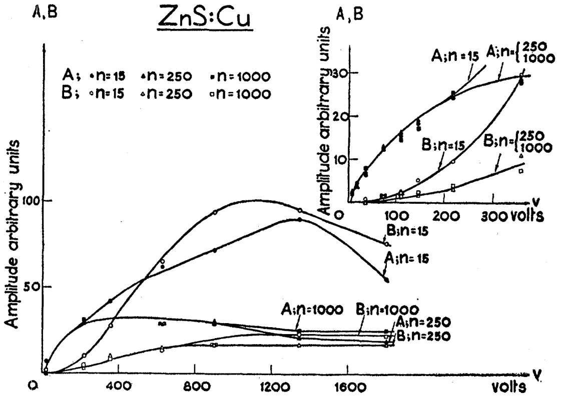

FIG. 3. Amplitudes of light pulses A and B during excitation as a function of the potential difference for ZnS:Cu (RCA F-2040). The insert is an enlarged portion of the same graphs for low potential differences.

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[14] The amplitude is measured by drawing a straight line connecting adjacent minima and measuring the vertical distance from the apex to this line. The light sum is similarly measured by integrating the area bounded by this line and the outline of the pulse.

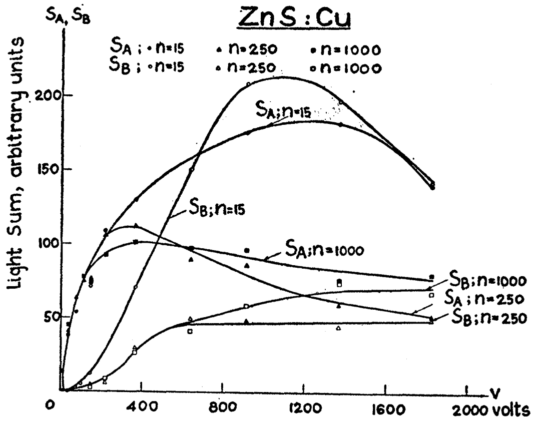

FIG. 4. Light sum per cycle, S_A and S_B during excitation as a function of the potential difference for ZnS:Cu (RCA *F*-2040).

5. In the stationary state the amplitude A and the light sum per cycle S_A show a similar dependence on the voltage for all phosphors. Figures 3 and 4 show the typical variations with voltage in the case of ZnS:Cu. The pulse A has a relatively low threshold voltage (differing for the various phosphors in magnitude), and rises with the voltage to a maximum and subsequently decreases. The amplitude B has a higher threshold voltage and rises slowly in an S-shaped curve to a saturation value. At very high voltages, the two components A and B are nearly equal (ZnS:Cu), and in some phosphors B may even be larger than A. At extremely high voltages, both A and B decrease with further increase of voltage.

6. The shape of the pulse A is a function of the voltage and of the time. With increase of voltage the pulse becomes more and more peaked and narrower at its base (broad minima and sharp maxima). In the copper activated phosphor, the shape of pulse B shows a similar behavior (see Figs. 2 and 5). The silver-activated phosphors behave differently. There the pulse B becomes broader and larger in shape as the voltage increases. Moreover, the B component shifts its phase from about 180° out of phase with respect to the preceding pulse A to a much smaller phase angle as the voltage is increased (see Fig. 6).

7. All phosphors show two pulses during the transitory period. These amplitudes change rapidly with time. The amplitudes A and B decay with different time constants. In some phosphors, the amplitude B may be initially larger than A and decay to a value smaller than A. Figure 7 shows the amplitudes A and B as a function of time (in units of 1/50 sec) both in the transitory and stationary state for ZnS:Cu.

8. On application of alternating electric fields during *phosphorescence*, the average brightness increases initially and is followed by some quenching. Two light pulses A and B are superimposed and are always present for all phosphors. The amplitudes A and B decay with nearly equal time constants which are much smaller than that of the normal phosphorescence. For some phosphors A is larger than B; for others (e.g., ZnS:Cu) B is larger [(see Fig. 7(b)]. There is a reversal in the relative magnitudes of A/B with time in some phosphors.

9. The results are qualitatively similar for cells made of various dielectrics and are independent of whether the phosphor matrix makes direct contact with the

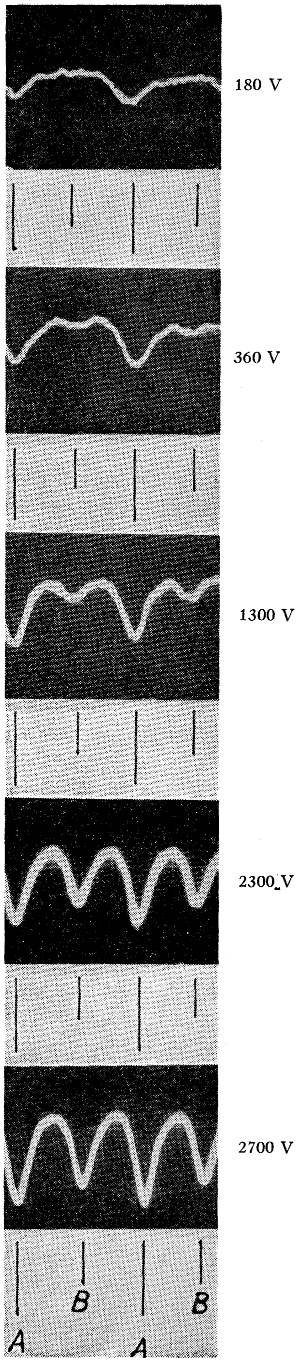

FIG. 5. Light pulses A and B during excitation as a function of the potential difference, in the steady state region. Note the changes in shape of the pulses A and B. ZnS:Cu (RCA *F*-2040). Maxima directed downwards.

electrodes or is separated by means of mica sheets from these electrodes. The effects are independent of whether the conducting glass or the metal electrode is grounded.[15]

10. If the electric field is applied before the excitation, it takes a few seconds until the amplitudes *A* and *B* are built up to their respective magnitudes.

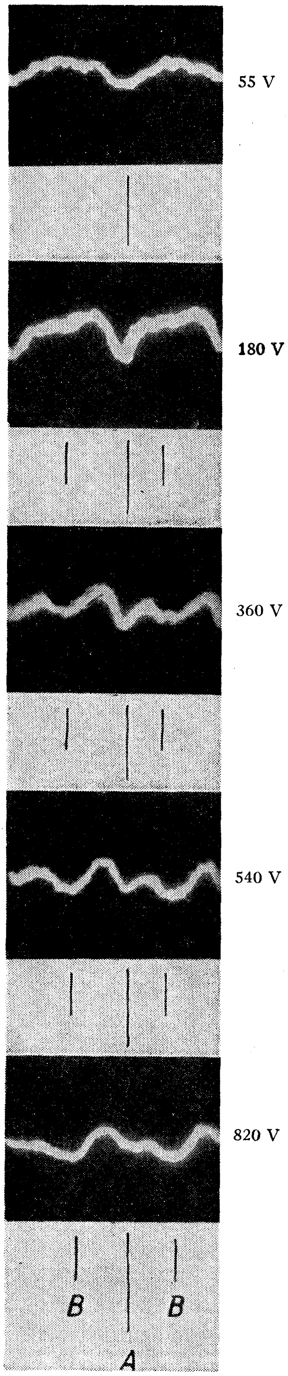

FIG. 6. Light pulses (*A* and *B*) during excitation as a function of the potential difference, in the steady state region, for 80ZnS: 20CdS:Ag (RCA *F*-2032). Maxima directed downwards.

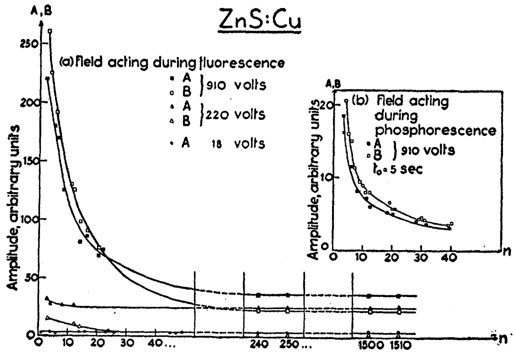

FIG. 7. Amplitudes of the light pulses *A* and *B* of ZnS:Cu (RCA *F*-2040) as a function of time when the field is acting (a) during excitation; (b) during phosphorescence. The field was applied at $t_0 = 5$ sec after cessation of the excitation.

DISCUSSION

Our results indicate that the two observed amplitudes *A* and *B* are due to two different effects, because the dependence of these pulses on voltage and on time is very different for all phosphors. The observation of the two effects is possible, because the exciting radiation is strongly absorbed in the phosphor. This was tested, for example, on a symmetrical phosphor cell (both sides having conducting glass electrodes) containing 80ZnS:20CdS:Cu, and it was found that less than 1% of the exciting radiation (3600 A) was transmitted. On the other hand, the transmission of light of wavelength 6000 A, corresponding to that of the emitted light of this phosphor, was about 25%. This indicates that in our experiments the polarity of the amplitudes *A* and *B* is to be defined by the polarity of the ultraviolet-illuminated electrode. The amplitude *A* corresponds to a positive polarity of this electrode. This was checked by changing the direction of the exciting illumination, the direction of the observation remaining the same. It was found that, in this case as well, *A* occurred when the illuminated electrode was positive. We can, therefore, conclude that the effects we observed occurred in the main near the illuminated electrode.

The amplitudes *A* and *B* differ not only in magnitude but also in character. The difference between the voltage thresholds of the two amplitudes could possibly be explained by absorption effects. However, the very different voltage dependence, and the fact that in some phosphors the ratio of the two amplitudes A/B changes from >1 to <1 with increase of voltage, precludes such an explanation. In a similar way, one cannot explain the differences in time dependence and phase and shape changes without the assumption of at least two different processes.

Pulse *A* shows very similar characteristics for all phosphors in its voltage dependence, differing only by scale factors from one phosphor to the next. Pulse *B*, however, has different characteristics for copper- and silver-activated phosphors, either case differing from

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[15] See A. Luyckx and A. S. Stockking, reference 10, paper 10.

those of pulse A. In the case of copper-activated phosphors the pulse shape of B is very similar to that of A and is about 180° out of phase with respect to A. The voltage and light sum per pulse curve is reminiscent of the voltage to current relationship of a space-charge-saturated diode. In the case of silver-activated phosphors, pulse A leads pulse B by about 90°. With increase of the voltage the pulse width gets broader and the amplitude larger (the width getting relatively wider than the corresponding increase of the amplitude). Pulse B is probably a function of the impurities in the phosphor.

There are similarities between the effects during the transitory period and those during phosphorescence. In both cases one observes rapid changes in the average brightness and always two amplitudes per cycle. For short persistent phosphors the transient effects during both phosphorescence and excitation are of short duration. Apparently this effect can be connected with emptying of traps. The subsequent quenching may also be related to changes in transition probabilities (or radiationless transitions) due to the influence of the electric field.

From the theory of Matossi[8] it follows that two pulses of equal amplitude per cycle should be observed. We found at some voltages only one pulse. Furthermore, as explained before, the different behavior of A and B proves that whenever there are two pulses per cycle, they are due to two different effects.

We think that the appearance of the two amplitudes suggests that surface effects are involved.

Experiments in electroluminescence have shown that there exist in general two pulses of light per cycle which are out of phase with voltage.[16–18] At certain voltages, two secondary light pulses are found about 90° out of phase with the main peaks.[16,19] For silver-activated phosphors, we found that the pulse B was about 90° out of phase with the pulse A, whereas for copper-activated phosphors B was about 180° out of phase. Zalm *et al.*[19] found no secondary light peaks for copper-activated phosphors. It is tempting to correlate the secondary peaks observed in electroluminescence with the pulses B observed during excitation. In this case, the nonobservance by Zalm *et al.* of the secondary peak in copper-activated phosphors in electroluminescence could possibly be explained by a masking of the secondary peak by the next main peak (because of about 180° phase shift). Apparently no such correlation can exist, however, between the main peaks in electroluminescence and the pulses A, as the former are emitted near the cathode[16] and the latter near the anode.

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[16] W. W. Piper and F. E. Williams, Phys. Rev. **87**, 191 (1952).

[17] J. F. Waymouth and F. Bitter, Phys. Rev. **95**, 941 (1954).

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Paramagnetic Resonance Absorption in Glass*†

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Paramagnetic resonance absorptions occurring with spectroscopic splitting factors of 4 and 6 were noted in all glass samples studied. These were apparently anisotropic g-values for a specific impurity and the peaks recorded are interpreted as being the result of a distribution of Stark fields over all directions in the glass. Resonances were also recorded having g-values near 2. Nearly all of these showed hyperfine structures characteristic of the known paramagnetic additions in the glasses. The absorption line observed for cupric ions in lattice modifying positions in a soda-lime-silica base glass has been quantitatively explained and the parameters compared favorably with those resulting for copper in the Tutton salts.

I. INTRODUCTION

CHANCE observations of paramagnetic resonance absorption in glass have led to a detailed study of such absorption in numerous glass samples of varying composition furnished by the Corning Glass Works, Corning, New York. The results have indicated possible applications of this technique to glass technology as well as in the study of the vitreous state.

It has long been known that if an atom has a partially filled electronic shell, there will exist a permanent electronic magnetic dipole moment. Hund's rules[1] and the Pauli exclusion principle allow one to predict the manner in which the electrons in the unfilled shell, with their intrinsic spins, will fill the available orbital angular momentum levels.

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† Submitted to the graduate board of Washington University, St. Louis, Missouri, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[1] F. Hund, *Linienspektren und periodisches System der Elemente* (Verlag Julius Springer, Berlin, 1927), p. 124.

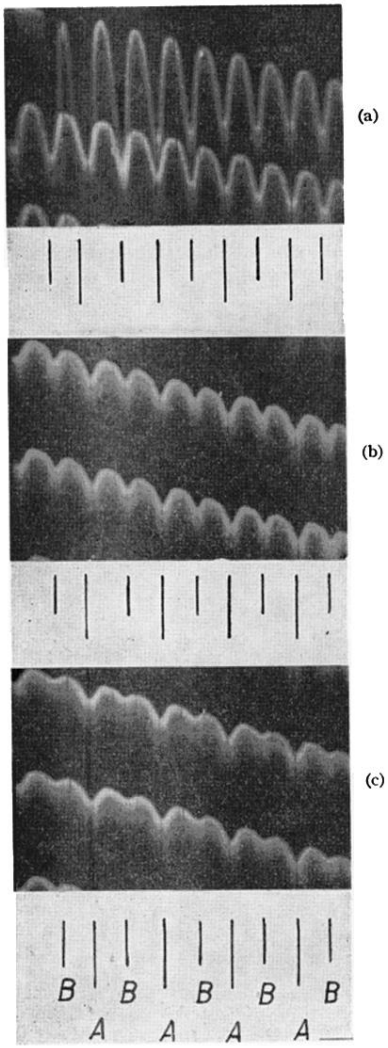

FIG. 2. Motion pictures of light pulses during excitation of ZnS:Cu for various times after application of the field. ($V=630$ volts.) (a) $n>0$, (b) $n>80$, (c) $n>1000$. (n in units of 1/50 sec.) The maxima of the pulses are directed downwards. Pulses A correspond to positive polarity of illuminated electrode.

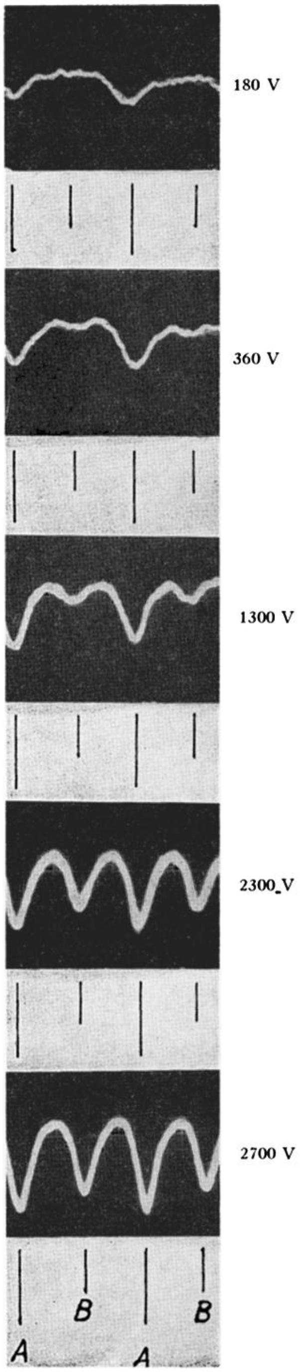

FIG. 5. Light pulses *A* and *B* during excitation as a function of the potential difference, in the steady state region. Note the changes in shape of the pulses *A* and *B*. ZnS:Cu (RCA *F*-2040). Maxima directed downwards.

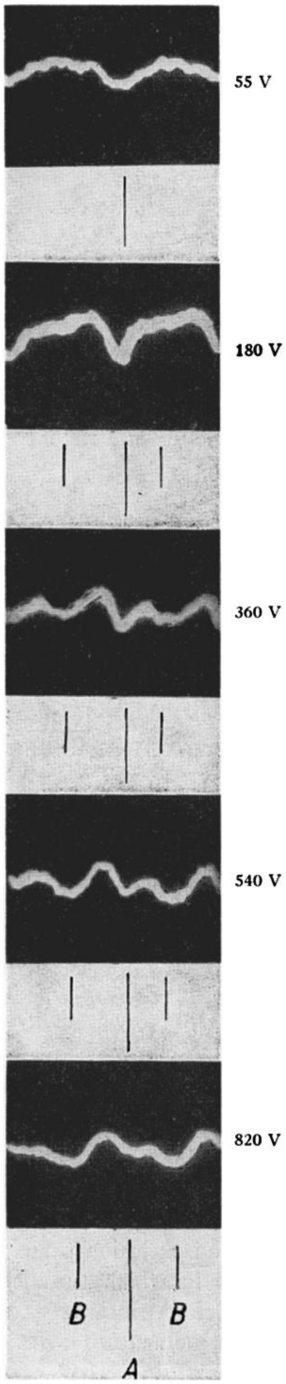

FIG. 6. Light pulses (*A* and *B*) during excitation as a function of the potential difference, in the steady state region, for 80ZnS: 20CdS:Ag (RCA *F*-2032). Maxima directed downwards.