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De-Excitation of ZnS and ZnCdS Phosphors by Electric Fields*

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The change of impedance (photoconductivity) of certain ZnS and ZnCdS powder phosphor samples, brought about by external ac (60 cps) and dc fields (up to 15 000 volts/cm), applied both during and after excitation with ultraviolet light (3660 A), is described and compared with impedance changes due to irradiation with infrared light. Application of a dc field simultaneously with the exciting radiation results first in a sudden drop in both the capacitance ($\Delta C/C_0$) and the dissipation factor ($D=1/Q$) followed by a recovery to a new equilibrium level below the field-free case. Removal of the field is accompanied by another drop and a recovery to the original field-free values. The partial recovery is not seen during ac field application under the same conditions but the complete recovery also occurs upon field removal. Applied during the photoconductivity decay, both ac and dc fields accelerate the decay. The sudden drop and partial recovery under dc fields is also seen during the photoconductivity decay but to a lesser extent.

These phenomena are explained by a consideration of the distribution of conduction electrons created by the application of the field. The sudden capacitance drop seen under a dc field is attributed to a polarization effect. The free charge is swept close to the electrodes leaving the bulk of the phosphor sample nonconducting. The partial recovery is due to the buildup of the back field as well as to an increase in the conductivity of the bulk of the phosphor grains due to the creation of additional free charge by the exciting radiation and the emptying of traps into the conduction band. There is no partial recovery during ac field application because of the absence of the polarization field. The finite recovery time after field removal when the phosphor is under excitation as well as the acceleration of the photoconductivity decay due to the field application is attributed to a quenching action brought on by an increase in the recombination rate in those regions of the phosphor powder sample where conduction electrons have been piled up by the action of the applied field.

A. INTRODUCTION

IN a previous paper[1] the effects of strong ac and dc fields on the ac impedance (photoconductivity[2,3]) of certain ZnS and ZnCdS phosphors were described. These measurements consisted of two types: observations (1) of rise curves of capacitance $(\Delta C/C_0)^2$ following various dark intervals τ between the termination of previous excitation and the onset of subsequent excitation, during which ac and dc fields of various strengths were applied, and (2) of decay curves of capacitance before and after a strong ac or dc field had been applied. The experiments under (1) showed that the application of ac or dc fields during the decay interval τ caused the subsequent rise curves to be below those obtained after the same field-free interval τ for those phosphors which exhibited a slow natural decay of capacitance. Consequently, it was concluded that the applied fields are capable of accelerating the decay of excited electrons from traps which would, in the absence of applied fields, have remained occupied for a much longer time. The experiments under (2) showed that ac or dc fields applied to the same phosphors during the capacitance decay accelerated the decay, as might be expected in view of the rise-curve measurements. Furthermore, these measurements indicated that de-excitation by fields is brought about by a great reduction of retrapping under the action of an applied field and that electrons in shallow traps are more strongly influenced by this action than those in deeper ones.

The bridge circuit[4] used in the above experiments made it necessary to disconnect the phosphor samples from the bridge terminals when the external ac or dc fields were applied because the oscillator terminals were connected to the bridge arms through a transformer. Consequently, the actual impedance measurements were performed not while the fields were acting on the phosphor but either immediately before or after. This paper presents the results of an investigation in which the capacitance (photoconductivity) of the phosphors listed in Table I was determined under various conditions while the external de-exciting field was applied. These results compliment the previous ones in many respects and show that mainly the conduction electrons are directly acted upon by the external field.

B. METHOD AND APPARATUS

Figure 1(a) shows the bridge circuit adapted so that an additional dc field can be applied across the sample at the bridge terminals. A mica capacitor used as a dummy sample showed that this change in the bridge circuit did not affect the measured capacitance and dissipation-factor values although the sensitivity of the bridge was slightly reduced. For ac fields, the battery in Fig. 1(a) was replaced by a 60-cps generator. This circuit again left the measured capacitance and dissipation-

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[1] H. Kallmann and P. Mark, Phys. Rev. **105**, 1445 (1957).

[2] Kallmann, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953).

[3] C. F. Garlick, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19, p. 391.

[4] Kallmann, Kramer, and Perlmutter, Phys. Rev. **99**, 391 (1955).

TABLE I. Response of 12 ZnS and ZnCdS phosphors to ac and dc fields and infrared irradiation while under excitation.

1	2	3	4	4a	5	5a	6	6a	7	7a	8	8a	9	10	11	12	13
			Under 360 volts dc						Under 43 volts (rms) 60 cps		Under infrared[c]		Relative light emission intensities corresponding to $(\Delta C/C_0)$ % values of columns[d]				
Name	Areal density mg/cm²	$(\Delta C/C_0)$ % under ultraviolet	$(\Delta C/C_0)$ % dip when dc is applied	% difference from field-free case	$(\Delta C/C_0)$ % equilibrium under dc field	% difference from field-free case	$(\Delta C/C_0)$ % dip when dc is removed	% difference from field-free case	$(\Delta C/C_0)$ % equilibrium under ac field	% difference from field-free case	$(\Delta C/C_0)$ % equilibrium	% difference from field-free case	4	5	6	7	8
ZnS																	
1. *LG*[a]	36	98.0	82	16.5	90.8	7.4	81	17.3	78.4	20.0	73.7	24.8	0.14	0.56	0.13	0.13	0.04
2. *R*[a]	56	155.1	127	18.1	144.6	7.0	123	20.7	122.8	20.8	134.7	13.1	0.26	0.66	0.21	0.22	0.40
3. *M*[a]	41	89.1	65	26.9	78.3	12.1	61	31.7	69.4	22.1	71.5	19.8	...	...	...	...	...
4. *N*[a]	66	92.7	65	29.9	82.9	10.6	65	29.9	69.4	25.1	80.4	13.3	0.085	0.53	0.085	0.16	0.42
5. *D*[a]	60	80.1	52	35.0	71.6	10.6	53	33.9	46.7	41.7	73.1	0.8	0.062	0.58	0.072	0.034	0.66
6. RCA[a] (2040)	18	148.1	111	25.1	139.1	6.1	111	25.1	118.5	20.0	143.4	3.2	0.03	0.50	0.03	0.06	0.68
ZnCdS																	
1. *L*[a]	49	157.9	107	32.2	129.5	18.0	101	36.0	117.4	25.7	149.9	5.1	0.046	0.20	0.03	0.085	0.70
2. *O*[a]	44	93.9	30	68.1	80.1	14.7	25	73.5	24.0	74.4	82.5	12.1	0.013	0.66	0.007	0.0064	0.72
3. *K*[b]	50	46.9	29	38.2	39.3	16.2	28	40.4	...	...	...	...	...	...	...	...	...
4. *U*[b]	37	14.7	...	...	14.3	2.8	...	...	...	...	...	...	...	...	...	...	...
5. RCA[a] (2033)	11	28.2	21	21.6	26.6	5.6	16	43.4	13.7	16.0	22.4	20.6	0.60	0.90	0.27	0.21	0.65
6. *P*[a]	32	63.3	31	51.1	48.9	22.8	29	54.2	26.5	58	52.1	17.7	0.05	0.44	0.035	0.021	0.52

[a] Excitation radiation: 100 μw/cm² (3660 A). [b] Excitation radiation: 10 μw/cm² (4900 A). [c] Wavelength >0.72 μ; intensity 1 milliwatt/cm².
[d] These data are obtained by the method previously described (reference 1) using $\Delta C/C_0$ *vs* incident intensity curves obtained from these phosphors similar to those illustrated in Fig. 4 of reference 2.

factor values unchanged but also reduced the bridge sensitivity somewhat. The powder phosphor samples were prepared as before[4,5] but with the following minor changes [see Fig. 1(b)]. Instead of using an aluminum foil as the second electrode, another Nesa glass plate[6] was used for purposes of better reproducibility. This sandwich was tightly pressed together with a clamp and sealed around the edges with an epoxy resin while still under pressure. The areal densities of these samples varied between 20 and 60 milligrams/cm². The rest of the equipment remained unchanged.

The following measurements were performed: (1) the effect of the application and removal of ac and dc fields (up to about 15 000 volts/cm) on the photoconductivity while the phosphor is under excitation, (2) the influence of the application and removal of such fields during the photoconductivity decays, and (3) a comparison of voltage de-excitation (quenching) with quenching of the capacitance due to irradiation with infrared light.[7] The areal densities of the phosphors investigated are presented in column 2 on Table I; their compositions have been previously published.[8] Ultraviolet radiation of 0.3660-micron wavelength and 100-microwatts/cm² intensity was used to excite the samples and infrared radiation of wavelength greater than 0.72 micron (through a Corning 7-56 filter) and 1 milliwatt/cm² intensity was employed to obtain the infrared stimulation and quenching data. The bridge oscillator voltage and frequency were 1 volt (rms) and 1 kc/sec, respectively. The estimated percent error (bridge sensitivity) in the measured values of $(\Delta C/C_0)$ % was 0.2% using the original bridge circuit, 0.8% using the altered circuit with the dc source, and 2.0% using the ac source.

C. EXPERIMENTAL RESULTS

1. Dc and Ac Fields Applied During Ultraviolet Excitation

Application of a dc field of about 15 000 volts/cm to the phosphor sample while it is under excitation by ultraviolet light yields the following results common, to a greater or lesser degree, to all the phosphors examined. The behavior of a typical sample, phosphor *M* (predominantly copper-activated ZnS phosphor; long phosphorescence and capacitance decay)[8] is shown in Fig. 2. The sample is first excited with ultraviolet light until an equilibrium value of $\Delta C/C_0$ is attained (point *A*). A dc field of 360 volts (~15 000 volts/cm) is then applied which causes an instantaneous sharp drop in the $\Delta C/C_0$ value

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[5] H. Kallmann and B. Kramer, Phys. Rev. **87**, 91 (1952).

[6] Obtained from the Pittsburgh Plate Glass Company.

[7] See reference 4 for a thorough discussion of the infrared light quenching and stimulation effects observed with these phosphors.

[8] H. Kallmann and G. M. Spruch, Phys. Rev. **103**, 94 (1956). The compositions of the phosphors discussed in the text which do not appear in this reference are: (a) RCA(1), ZnS, copper-activated; (b) RCA(2), ZnCdS (Zn 70%, Cd 30%), silver-activated; (c) *P*, ZnCdS (Zn 47%, Cd 23%), silver- (0.02%) and iron- (0.001%) activated.

to point B followed by a subsequent slow rise (curve δ) to a new equilibrium value of $\Delta C/C_0$ (point C) definitely lower than that obtained in the field-free case. Consequently, there is a net decrease of capacitance when the phosphor is subjected to a strong dc field while under excitation by ultraviolet light. After equilibrium has been reached at point C, the field is removed and the battery in Fig. 1 (a) is replaced by a shunt. There appears a second sharp dip in $\Delta C/C_0$ to the point D in Fig. 2 which is of about equal magnitude (in this case) as that observed when the field is first applied (point B). This is followed by a slow recovery to the original field-free equilibrium value of $\Delta C/C_0$ (beyond point E) after a rather long period of time (about 90 minutes). This behavior is unchanged when the polarity of the applied field is reversed. Columns 3, 4, 5, and 6 of Table I list the $\Delta C/C_0$ values corresponding to points A, B, C, and D of curve δ on Fig. 2 for all the phosphors investigated (points B and D are only approximate since the capacitance decrease occurs very rapidly). Curve γ of Fig. 2 shows the data obtained from a similar experiment but with the applied field reduced to 110 volts dc. It is noteworthy that the difference between curves δ and γ (the dips as well as the equilibrium values) is not large in spite of the fact that in the latter case, the applied field is less by a factor greater than 3.

Upon the application of an ac field to the sample, the situation is quite different. As can be seen from curve β of Fig. 2, there is no slow recovery after the initial sharp reduction in the value of $\Delta C/C_0$ upon field application. Such recovery only occurs after the field is turned off. Further, the equilibrium value of $\Delta C/C_0$ of this phosphor reached for an applied voltage of volts (rms) 60 cps (curve β) is below that reached for 360 volts dc (curve δ). (Values for the other powders are listed in Table I.) This equilibrium value under the ac field is even below the deepest point of the equivalent dc curve (curve γ). Comparing curves α and β, one sees that a difference of a factor of 2 in the ac field strength causes a larger reduction in $\Delta C/C_0$ than a difference of a factor of 3 in the strength of the dc field indicating that the response is more sensitive to a variation of the ac voltage. The $\Delta C/C_0$ values using 43 volts (rms) 60 cps (curve α of Fig. 2) obtained from the other phosphors are listed under column 7 of Table I.

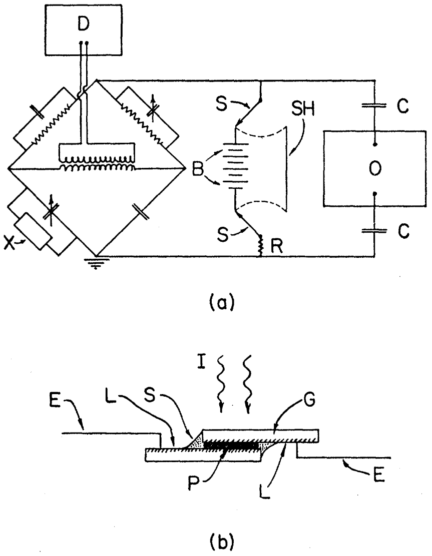

FIG. 1. (a) Schematic diagram of the General Radio 716-C Bridge (Schering type) adapted so as to make possible the application of an external dc field to the bridge terminals. D, detector; S, switch; B, battery (up to 380 volts); O, external oscillator; C, 0.5-μf capacitors; SH, shunt; R, 5×10^4-ohm resistor; X, unknown (phosphor sample). (b) Side view cross section of a powder phosphor sample. The Nesa glass plates are 1 in.$\times 1\frac{1}{2}$ in. with about 100-ohms resistance along the face diagonal. E, electrode; L-conductive layer; S, epoxy resin seal; G, Nesa glass plate; I, incident radiation; P, phosphor.

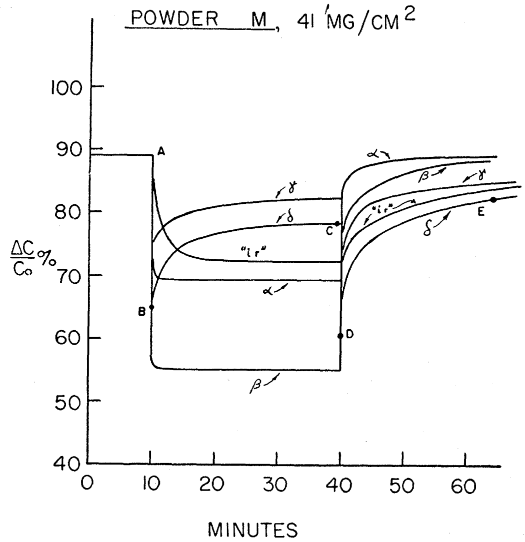

FIG. 2. Change of capacitance in phosphor M under ac fields (α, 43 volts (rms) 60 cps; β, 110 volts (rms) 60 cps), dc fields (γ, 110 volts; δ, 360 volts) and infrared light ("ir") applied simultaneously with the ultraviolet exciting radiation showing a partial capacitance recovery after the initial drop under dc fields, no recovery under ac fields and infrared light, and a finite recovery time after both fields and infrared light are switched off.

The behavior of these phosphors under a dc field differs completely from that under an ac field even after the removal of the fields. In both cases a recovery to the initial field-free value occurs but the ac recovery curves lie above the respective dc curves although during field application, the situation is reversed. The main difference is that the dip after removal of the dc field does not appear upon removal of the ac field. This fundamental difference will be explained below.

As comparison with the quenching action of the field, the response of $\Delta C/C_0$ of phosphor M to infrared irradiation, applied simultaneously with the ultraviolet exciting radiation, is indicated by the curve marked "ir" on Fig. 2 and, for the other phosphors, under column 8 on Table I. There is no similarity between the infrared and the dc field quenching curves, but there is some likeness to the ac quenching curves.

The capacitance drops rather quickly upon infrared light application and reaches a final equilibrium value. There occurs no partial recovery while the infrared light is on and after switching it off a slow recovery ensues without any new dips. But the drop in $\Delta C/C_0$ is not so sharp under infrared light as under the ac field and the recovery is much slower in the former case. Although the equilibrium value under infrared light is about that obtained under 43 volts ac, the recovery curve from the former lies below that of the latter. This is certainly due to a much greater emptying of traps by the infrared light than by the ac field (see the discussion below).

Similar experiments were repeated with phosphor *M* using an ultraviolet exciting intensity of only 3% of that used to obtain the curves of Fig. 2. Under these conditions, the ac curves corresponding to α and β of Fig. 2 are still separated by about $\Delta C/C_0=15\%$ (the equilibrium values of $\Delta C/C_0$ are 27% and 41% under 43 and 110 (rms) volts, respectively) while the dc curves corresponding to γ and δ are now much closer together (equilibrium $\Delta C/C_0$ values are 44% and 45% for 110 and 360 volts dc, respectively). In both cases, the general level of $\Delta C/C_0$ is reduced to $\Delta C/C_0=54\%$ because of the reduced exciting radiation intensity. This again points out the greater sensitivity of the capacitance to variations in the ac field over the dc field. In addition, the recovery times (after field removal) are all slower at reduced exciting radiation intensity.

Since the $\Delta C/C_0$ values are not direct measures of the conductivity,[1] the relative emitted light intensities,[1] corresponding to the $\Delta C/C_0$ values of columns 4, 5, 6, 7, and 8 of Table I, are listed in columns 9 through 13. These values are a more direct measure of the conductivity of the samples than the $\Delta C/C_0$ values. When comparing the dc with the ac values, one must consider that the dc field (360 volts) used to obtain the data of Table I is six times larger than the peak value of the ac field (60 volts). Thus, the fact that the absolute values of the dips produced by the dc field application and removal appear to be close to the ac values is accidental. Both types of fields induce a reduction of the conductivity to about 10% of the field-free value. If the dc changes could be measured fast enough, the dc dips would certainly be deeper and probably equal to the ac values for corresponding field strengths. All the ZnCdS phosphors investigated so far display the described effects independent of their Cd content and their activator content (Ag, Cu, Pb, etc.,) (see previously published compositions of the phosphors[8]). The magnitudes of the effects vary noticeably from substance to substance by a factor of about 20, if one considers the intensity values of column 12 as representative, but it is interesting how close some substances are in their values (e.g., *LG*, *R*, and *M*). The most sensitive phosphor is 0 with a drop in conductivity to almost $\frac{1}{2}\%$ of its original field-free value. There is a marked correlation between the dc dips of the various substances and their ac equilibrium values, but the correlation between dc dips and the dc equilib-

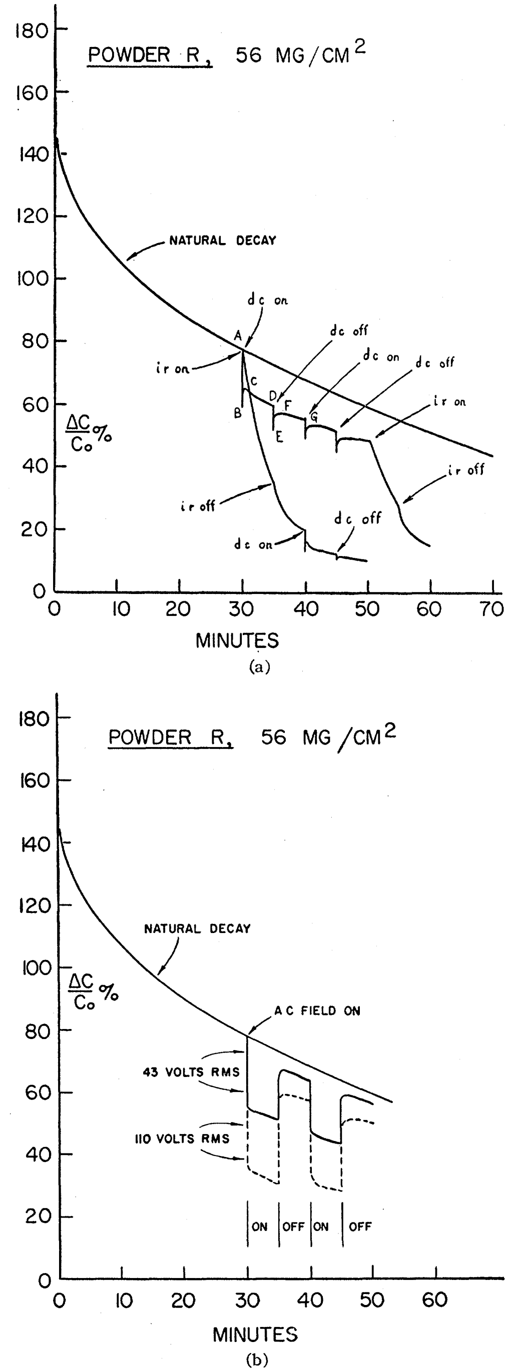

FIG. 3. (a) Decay of capacitance in phosphor *R*, comparing the action of a 360-volt dc field and of infrared light applied 30 minutes after the onset of the decay with the natural decay. Quenching due to infrared light is still in evidence after field application and vice versa. (b) Decay of capacitance in phosphor *R*, comparing the action of ac fields (43 and 110 volts (rms) 60 cps) applied 30 minutes after the onset of the decay with the natural decay.

rium values is much weaker. There is no correlation between the infrared and the field values. The quenching of phosphor *LG* by infrared light is particularly strong as a consequence of the fact that this phosphor is light stimulable under infrared light irradiation. The magnitudes of the field effects depend not only on the composition but certainly also on the areal density and the grain size of the powder. The thicknesses of most of the samples are comparable; the exceptions are the two RCA phosphor samples which are about three times thinner than the rest. Consequently, most of the substances are subject to the same field strengths. No attempt will be made at this point to correlate these effects with the chemical compositions of the phosphors, rather correlations with the other physical properties will be set forth in the discussion below.

To summarize, the following are the main observed effects when electric fields are applied to these phosphors simultaneously with the exciting ultraviolet radiation. (1) Application of infrared light, ac and dc fields have the net effect of reducing the equilibrium capacitance. (2) The temporal behavior of the capacitance under an ac field differs completely from the dc case both during and after field application. (3) Sharp dips of about equal magnitude occur immediately after application and removal of the dc field which are absent under ac fields. (4) The $\Delta C/C_0$ equilibrium values for ac fields are much lower than those for dc fields (compare curves β and γ of Fig. 2) even if the dc field is stronger by a factor of 8 than the rms value of the ac field (compare curves α and δ of Fig. 2 and columns 5 and 7 of Table I). (5) The $\Delta C/C_0$ equilibrium values are more sensitive to changes in the ac field strengths than to those in the dc field strength. (6) The recovery times of $\Delta C/C_0$ after field removal are shorter for ac than for dc fields even though the starting values of $\Delta C/C_0$ are higher for the latter case than for the former. (7) The infrared curves have some similarity to the ac curves, but in spite of the higher $\Delta C/C_0$ equilibrium value of the former, they have the longer recovery times. (8) Quenching by infrared light is basically different from field quenching as evidenced by a comparison of columns 8 and 13 with those for field quenching. There is no correlation between these columns. That this difference is fundamental will become more evident from a consideration of the results obtained from experiments carried out during the capacitance decay of these samples (see next section).

2. Dc and Ac Fields Applied During Decay from Previous Ultraviolet Excitation

The measurements presented in this section are obtained as follows. The phosphor is first excited by ultraviolet light until an equilibrium value of $\Delta C/C_0$ is reached. Then the exciting radiation is removed and ac or dc fields are applied simultaneously with the measuring voltage at some point along the natural capacitance decay. Figures 3(a) and (b), and Figs. 4(a)

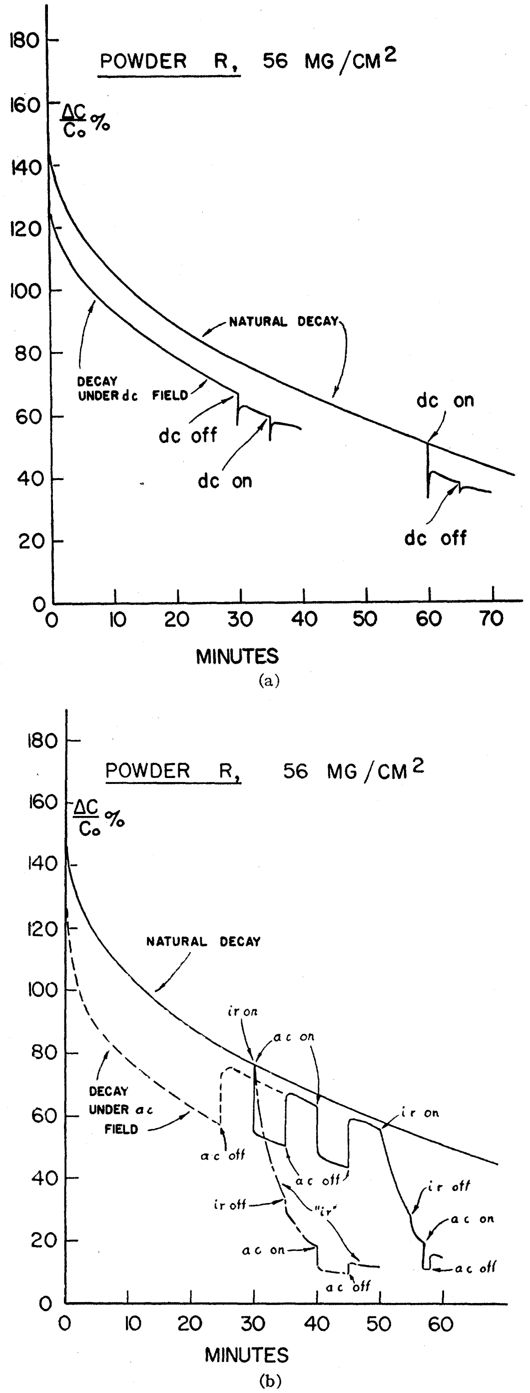

FIG. 4 (a) Decay of capacitance in phosphor R, comparing the action of a 360-volt dc field applied at the onset of the decay with the natural decay. The curve commencing at $t=60$ minutes, when compared with the decay curve under field application, indicates that it is only the first application of the field which results in a net capacitance quenching. (b). Decay of capacitance in phosphor R, comparing the natural decay with the decay under 43 volts (rms) 60 cps applied both at the onset and 30 minutes after the onset of the decay, showing that the net quenching is about the same for the latter two cases. Quenching due to infrared light is still in evidence after field application and vice versa.

and (b) present, respectively, the results of the application of dc and ac fields, the first two for the case when the field is switched on thirty minutes after the onset of the decay and the latter two when the field is applied at the beginning of the decay. The influence of fields upon the decay of capacitance is very similar to that during simultaneous excitation, as Figs. 3(a) and (b) show for the case of phosphor *R* (copper-activated ZnS phosphor; long phosphorescence and capacitance decay; strong light and capacitance stimulation under infrared light). This phosphor is quite typical of all the substances investigated. Dc field application thirty minutes after the beginning of the decay [Fig. 3(a)] produces a sharp dip in $\Delta C/C_0$ followed by a considerable recovery to a value which is below the natural decay value at that specified time. Removal of the field produces another dip followed again by a subsequent recovery. Ac field application [Fig. 3(b)] produces only a reduction of $\Delta C/C_0$ without any recovery and after removal of the field, $\Delta C/C_0$ rises rather quickly to a value which is below the normal decay value. Successive field applications produce equivalent effects but to a smaller degree. This means that the $\Delta C/C_0$ reduction becomes smaller the further one goes along the decay curve. After the first field application and removal, the $\Delta C/C_0$ values are considerably reduced but a subsequent field application and removal produces only a slight further drop as seen from Fig. 3(b) [100 volts (rms)]. After the second field removal, the $\Delta C/C_0$ values are certainly not a continuation of the curves after the first removal but are below these values. This further reduction is, however, much less than that after the first application and removal.

Another typical effect is that described by Fig. 4(a). If the field is applied immediately or very soon after termination of the excitation, the dc induced drop is not followed by an immediate recovery. The rather steep capacitance decay at the beginning of the decay curve apparently masks the recovery. If the measurements plotted in Fig. 4(a) could have been made in shorter time intervals, such a recovery would have been noticed. But the still rather fast decay of $\Delta C/C_0$ after the first instant overshadows the recovery. Figures 4(a) and 4(b) show that the decay of $\Delta C/C_0$ is equally fast under both ac and dc fields and further that the application of the field at a point along the natural decay has about the same net effect after removal as field application at the beginning of the decay. It would appear, then, that the duration of the field application has no effect on the final $\Delta C/C_0$ value. This is not so. The curves of Fig. 4(b) were obtained under only 43 volts (rms) so that the total field effects are small. With larger field strengths, the net reduction of $\Delta C/C_0$ increases with the time of field application. Figure 5 compares the effects of ac and dc fields. The curves show that after field removal, the net effects of the ac and dc fields are very similar although one must keep in mind that the peak value of the ac field which produces roughly the same net effect as the dc field is only about two-fifths as strong. During field application, however, the difference between the two cases becomes very evident.

Figures 3(a) and 4(b) also present infrared light quenching curves.[7] They show that infrared light when applied at a point along the natural $\Delta C/C_0$ decay produces a less steep decrease in $\Delta C/C_0$ than the field, but the quenching is much more thorough in the long run. The quenching action continues with time and eventually the net reduction of capacitance brought about by infrared is greater than that due to fields and becomes more so the longer the infrared light remains on. Upon switching off the infrared light there is a further reduction of $\Delta C/C_0$ without a subsequent recovery, quite different from the behavior after field application. Applying the field after infrared light irradiation causes the appearance of the normal field effect. This is true for both ac and dc fields. It appears as though the fields, applied after irradiation by infrared light, have a relatively strong quenching effect upon the capacitance since the $\Delta C/C_0$ values after field removal are definitely below those before field application. This is not so. After field removal [see curve "i.r." on Fig. 4(b)], the $\Delta C/C_0$ values are almost a continuation of the $\Delta C/C_0$ decay before field application. The capacitance is reduced only in the interval during which the field is acting on the sample. Should the infrared light be applied after field quenching, Figs. 3(a) and 4(b) show

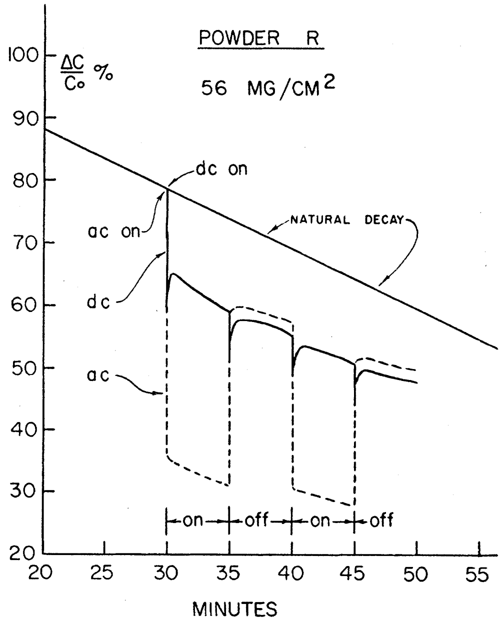

FIG. 5. Decay of capacitance in phosphor *R* illustrating the difference between the action of an ac field [110 volts (rms) 60 cps] and a dc field (360 volts). The two cases differ completely during field application but are comparable when the fields are switched off even though the dc field is approximately three times stronger than the rms value of the ac field.

that a quenching due to the infrared light is very much apparent after both dc and ac field application.

Figure 6 presents the behavior of phosphor L [copper-activated ZnCdS (Zn, 56%; Cd, 13%), slow phosphorescence[8] and capacitance decay], emphasizing the difference between quenching due to fields and infrared light. One sees that the initial reduction in $\Delta C/C_0$ under the dc field is huge and still continues after the first measured point. The infrared curve is much flatter in the beginning but eventually drops way below the field decay curve. The small peak appearing when the infrared light is turned on and the drop noticed when it is turned off indicate that phosphor L is capacitance stimulable by infrared light.

The effect of ac and dc fields along the capacitance decay of these phosphors can be summarized as follows: (1) The effect of dc and ac fields along the decay of capacitance are analogous to those observed under simultaneous excitation and field application. (2) If dc fields are applied soon after termination of the excitation radiation, the recovery after field application is apparently masked by the still rapid decay of capacitance. (3) The largest effect of instantaneous and of net reduction of $\Delta C/C_0$ is observed after the first field application. (4) Further field application or prolonged application increases the net reduction of $\Delta C/C_0$ only slightly. (5) The field and infrared light effects are completely different from each other. Infrared light causes a slower onset of $\Delta C/C_0$ reduction than do the fields but the reduction continues with prolonged infrared light irradiation and after a long enough time, the net reduction due to infrared light is much larger than the net reduction of $\Delta C/C_0$ due to the fields. (6) Field application after infrared light irradiation shows the same effect as before infrared irradiation, but the net reduction is very small. The reverse is also true; that is, irradiation by infrared light after field application also causes the same effect as before field application. The two effects seem to be independent.

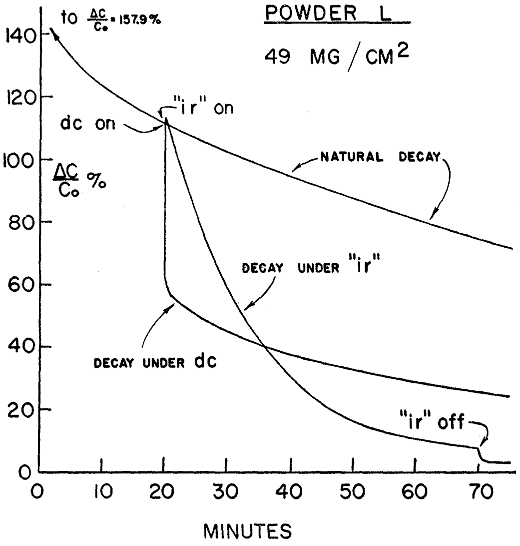

FIG. 6. Decay of capacitance in Phosphor L comparing the long time effects of a 360-volt dc field and infrared light. The decay under the dc field sets in more quickly than the decay under infrared light but the latter is stronger as time progresses.

D. DISCUSSION OF THE FIELD EFFECTS

The effects of strong electric fields on the photoconductivity of these phosphors which have been presented in Sec. C are essentially due to four processes: (1) The turning on of an external field sweeps the conduction electrons out of the bulk of the material thereby making the interior less conducting. This results in a decrease in the capacitance ($\Delta C/C_0$). This sweeping effect which consists of an actual removal of charge from the sample as well as piling up of charge near the electrodes[9] is responsible for the primary drop of capacitance under a dc field and to the reduction of capacitance under an ac field. (2) The electrons and also the positive charges which accumulate near the surface reduce the field strength in the interior of the whole layer or of the single powder grains. (3) There is a replenishment of interior electrons due to the exciting radiation and to the emptying of traps when the radiation is simultaneously applied during the decay due to the latter process only. Processes (2) and (3) together are responsible for the recovery observed under dc fields immediately after their application. Process (2) is also responsible for the second capacitance dip observed after the removal of the dc field since now the internal polarization acts as an applied field. This second dip is a direct indication of the buildup of a polarization field of strength similar to the applied field. (4) There is another effect which results in a net decrease of trapped electrons during field application as evidenced by rise curves following field application during dark decay[1] as well as the slow rise of capacitance observed during excitation when the ac field is switched off. This means that the fields cause an increase of the transition rate to the ground state (see below). These four processes are now discussed in greater detail.

A sweeping-out of electrons can only occur when there is not enough replenishment from the electrodes. Since one knows that for dc field applications strong polarization occurs in these samples due to an incomplete current flow from the electrodes,[9] the sweeping out of electrons is to be expected. The capacitance recovery during dc field application (i.e., while the field is still on) can be due to two causes. Either there is a replenishment from the electrodes which, however, sets in only slowly or this type of replenishment is negligible and the recovery is due to processes (2) and (3) above. As a consequence of this, the draining-off of electrons from the interior decreases [process(2)] and the density of free electrons and therefore the capacitance increases

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[9] These charges give rise to the polarization effects discussed in H. Kallmann and B. Rosenberg, Phys. Rev. **97**, 1596 (1955).

again [process (3)] but not to the original field-free value. Rather the ultimate capacitance recovery is to a somewhat smaller value because the field in the interior is not completely annulled. The recovery time is determined by two factors: (a) the buildup time of the polarization field and (b) the time required to replenish the electrons (conduction and trapped) removed by the dc field since the drop in conduction electrons is also accompanied by a drop in the number of trapped electrons, with which they are in fast exchange due to retrapping. Both effects (a) and (b) are probably of importance.

Consider effect (b): Since the equilibrium free-electron density, while the dc field is on, is reduced to about half of its original value (see column 10 of Table I) the number of trapped electrons is also considerably reduced. Since the ratio n_t/n_c (n_t=density trapped electrons, n_c=density of conduction electrons) is always much greater than unity,[5] the number of electrons removed from traps is, of course, much larger than the number of electrons removed from the conductivity band. For this case (traps not saturated), about half of the trapped electrons would be removed, which would mean about 10^{14} electrons per cm^3,[3,5] or, for these samples, about 10^{12} electrons. Of course, these electrons are not all found in the polarization layer which never contains more than 10^{11} electrons per cm^2 in a very thin layer close to the electrodes, as known from polarization measurements.[9] Rather, they have been used up in the increased number of recombinations brought about by the field [see process (4)]. That capacitance recovery is not observed under ac fields is due to the fact that no appreciable polarization field is built up during one-half of the cycle of the ac field (1/120 sec).

The recovery during dc field application is partially due to the buildup of a polarization field [effect (a)] and is evidenced by the dip which appears following the removal of the dc field. In the moment the external field is turned off, only the polarization field remains and now the replenished electrons in the interior again see a strong field, this time in the opposite direction, which again sweeps these electrons out of the interior. Since the capacitance dips after application and removal of the field are of the same order of magnitude, one is tempted to conclude that the remaining polarization field is of the same order of manitude as the original field and that it cancels out the original field to a considerable extent while the latter remains on.

The finite recovery time observed after the removal of the dc field could also be due to the time necessary for the decay of the polarization field as well as the time necessary for replenishment of the removed electrons. Certainly, in this case, the latter is the predominating factor because (1) a long recovery time is observed even after an ac field had been applied and switched off during which no appreciable polarization field can persist and (2) the recovery time after dc field removal is much longer than that after application. One may ask what happens to those electrons which were replenished during field application. These have to a large extent disappeared because of the increased recombinations during the presence of the field. The considerably reduced number of trapped electrons in the equilibrium state under field application must be replenished after field removal and this takes time as is known from the normal rise curves.[1] The number of additional electrons stored within the polarization layer is certainly much smaller than the number missing in the interior. The electrons which come from the polarization layers certainly contribute to the recovery, but they are too few to accomplish complete recovery. The first very fast increase after the capacitance dip following field removal may be due to just these electrons.

In the case of field application simultaneously with the exciting radiation, this radiation is the main source of electron replenishment. Consider next the measurement taken during the capacitance decay after excitation. In this case, the replenished electrons are drawn from the electrons in traps, which evaporate into the conduction band and supply the electrons missing after field removal. After field removal, the $\Delta C/C_0$ values are always below the values observed before field applications even when one takes the natural decay during the time of field application into account. This means that there is always an additional loss of electrons produced by the field. This additional loss becomes rather small the further one goes down along the decay curve.

What, now, is the source of this field quenching [process (4)]? Several explanations have already been suggested in the previous paper.[1] Certainly the most obvious explanation is that connected with the filling of traps. Assuming that the positive charges move only slightly, the accumulation of electrons in the negative layers certainly brings the trap occupation closer to trap saturation in that region. Consequently there is no longer a proportionality between n_c and n_t since one can no longer neglect n_t against n_0 (the density of traps) in the relation $n_c=\gamma[n_t/(n_0-n_t)]$, where γ is temperature-dependent. If new electrons from the interior (from the conductivity band as well as traps) are brought into the polarization layer where the trapped electron density is closer to trap saturation, the total number of electrons which are in the conductivity band is increased and therefore an increased recombination rate results. This process explains why the quenching process at the first field application during the capacitance decay is always the largest and why the quenching is strongly reduced as the decay progresses. The greater the number of electrons which have recombined, the farther one is removed from saturation of traps and hence the smaller the quenching must be since the quenching action here described is based on the fact that n_c is not proportional to n_t.

The fact that an actual de-excitation process occurs under the influence of fields is corroborated by the rise-curve measurements schematically illustrated by Fig. 7. Two rise curves (curves *A* and *B*) are taken from a particular value of $\Delta C/C_0$ (given as $X\%$ of Fig. 7). Curve *B* is obtained by allowing the sample to undergo a natural capacitance decay until the value $\Delta C/C_0=X\%$ is obtained and then switching on the exciting radiation. Curve *A* is obtained by first allowing the phosphor to decay under the action of a field (dc or ac applied either at the onset of the decay as illustrated or at some other point along the natural decay). After a given time interval t_0 the field is switched off and the decay is allowed to proceed until the value $\Delta C/C_0=X\%$ is reached, in a shorter time than before. The rise curve is then obtained by re-exciting the sample. These rise curves differ from those already presented[1] in that the former commence at equal $\Delta C/C_0$ values whereas the latter commence after equal decay-time intervals. Since $\Delta C/C_0$ is assumed to be a function of n_c, two points (*A* and *B*) whose $\Delta C/C_0$ values are equal correspond to two states with the same n_c and n_t because of the above relation between these two quantities which is fixed for a given temperature. Consequently, one would expect the two rise curves, one starting at *A* and the other at *B*, to coincide. This does not turn out to be the case. Of these two rise curves, *A* is the slower which means that at point *A*, the phosphor is in a state in which fewer traps are occupied than at point *B* even though the capacitance values of the two points are the same.

There are two reasons for this discrepancy. First, after field application, the powder is no longer homogeneously excited as can be seen from the accompanying dissipation-factor value. For a sample which is consistently excited in the same way, there is a fixed and unique relation between the capacitance and the dissipation factor.[10] Assuming that the exciting intensity is greater than that required to obtain the maximum dissipation factor,[11] a reduction in the capacitance, due either to a reduction of the exciting intensity or the addition of infrared light (not considering stimulation), is always accompanied by an increase in the dissipation factor, provided, of course, that at the end of the experiment the capacitance corresponds to a dissipation factor still on the high intensity side of the maximum. If stimulation occurs, the momentary increase of capacitance is accompanied by a momentary decrease in the dissipation factor. If the exciting intensity is less than that required to obtain the maximum dissipation factor, the capacitance and dissipation factor value would vary together; both decrease when quenching occurs and momentarily increase when stimulation is present. Now, this relation between the capacitance and the dissipation factor is disrupted by the application of a field as can be concluded from the fact that the dissipation factor accompanying *A* (not illustrated) of Fig. 7 is lower than that corresponding to point *B* and that the dissipation factor always decreases along with the capacitance both at the instant of field application and removal while the phosphor is under excitation regardless of whether or not the exciting intensity is strong enough to pass the dissipation-factor maximum. This disruption is due to the fact that the charge distribution throughout the sample is altered by the application of a field. The second explanation for the discrepancy between rise curves *A* and *B* of Fig. 7 is that the above mentioned relation between $\Delta C/C_0$ and *D* is disturbed by the action of the field and is restored only slowly when the field is removed. Besides this quenching process, the two others mentioned in the previous paper,[1] namely, recombinations at electrodes and recombinations across grain boundaries, probably occur because the method of measurement previously used proved that fields de-excite the samples completely. This should, according to the trap mechanism described above, take place very slowly.

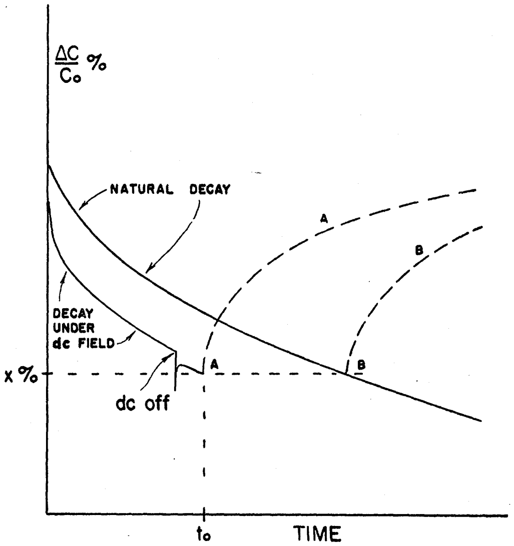

FIG. 7. Schematic plot of $(\Delta C/C_0)$ % *vs* time illustrating the method adopted to obtain rise curves from equal $\Delta C/C_0$ values reached in different ways; point *A* under field application and point *B* by means of a natural decay. It is found that curve *B* rises faster than curve *A*, indicating that point *A* corresponds to a trap occupation distribution in which there are fewer filled traps than the trap occupation distribution given by point *B*.

In addition, it may be useful to remark upon the variation of these effects among the various substances examined. Table I is not presented with the idea of establishing any exact relationship between these effects and the chemical compositions of the phosphors; rather, it is here to emphasize that these effects are common to all ZnS and ZnCsS phosphors investigated and that they are qualitatively independent of the cadmium, and of activator content and powder grain size.

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[10] See Fig. 14 and the accompanying discussion of reference 4.

[11] See Figs. 1 and 4 of reference 2. In these figures, *Q* stands for the reciprocal of the dissipation.