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

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With the aid of ac impedance measurements, the influence of strong ac and dc fields applied during the decay of photoconductivity of ZnS and ZnCdS phosphors is described. Rise and decay curves of photoconductivity with and without additional field application are presented which demonstrate that electric fields accelerate the de-excitation process. Ac fields are capable of removing all excited electrons from the pre-excited ZnS (*LG*) phosphor and dc fields show a similar but weaker effect. This de-excitation is attributed to the considerable reduction of retrapping of excited electrons when these phosphors decay under the action of electric fields.

A. INTRODUCTION

THE following effects of electric fields on phosphors are known:

1. Electroluminescence is produced by ac and dc fields.[1,2]

2. A transient decrease or increase of the fluorescent light emission is produced by the application or removal of ac and dc electric fields, depending upon the special phosphors used. Quenching phosphors show practically no increase. The integrated effect of the electric field consists often in a decrease of light emission, indicating an increase of the rate of radiationless recombinations to the ground state. Experiments in this laboratory and others have shown these effects very clearly.[3–9]

3. There is also an effect of an electric field on the photoconductivity. If the impedance of an excited phosphor is observed with ac fields, a definite decrease of capacitance occurs with increasing field strength which results from a decrease in photoconductivity (see Fig. 1).[10–12] Phosphor (*L*) was slightly light-stimulable by infrared light and (*K*) shows mainly a strong infrared quenching effect,[13] and a larger decrease in photoconductivity with increasing field strength. These measurements demonstrate a definite quenching effect by the electric field which is probably related to the quenching effect described under 2. Again this effect has to be considered as a transient effect since it occurred under application of an ac field.

4. A transient increase and decrease of light emission is also observed when an electric field is applied or removed during the phosphorescence.[4,8,14]

5. The observations by Pohl and collaborators[15] may be mentioned in which it was shown that the coloration produced by irradiation of alkali halides can be shifted through the crystal by electric fields. This effect is probably related to the observations described in this paper.

The observation under 3 indicates that an electric field may increase the number of recombinations of excited electrons with the ground state and those under 4 show that the electric field affects even the electrons stored after excitation. The following question arises: What processes occur when ac or dc fields are applied to a phosphor in which a certain number of excited electrons are still stored in traps from the preceding excitations; what is the extent and the rate with which these stored electrons are removed?

B. METHODS

The investigation of this question makes use of ac impedance measurements with ZnS and ZnCdS phos-

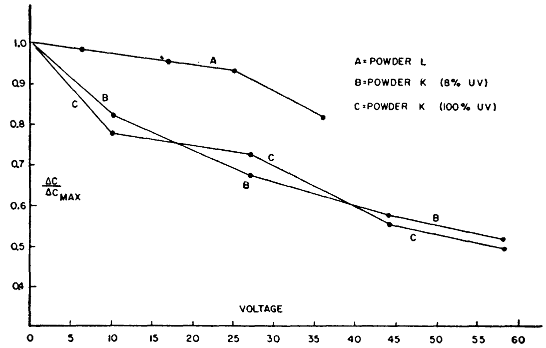

FIG. 1. Plot of the change in capacitance of two ZnCdS phosphors as the applied bridge voltage is increased while the phosphor is under ultraviolet excitation ($\lambda=0.366\mu$; $100\%=10$ μw/cm^2).

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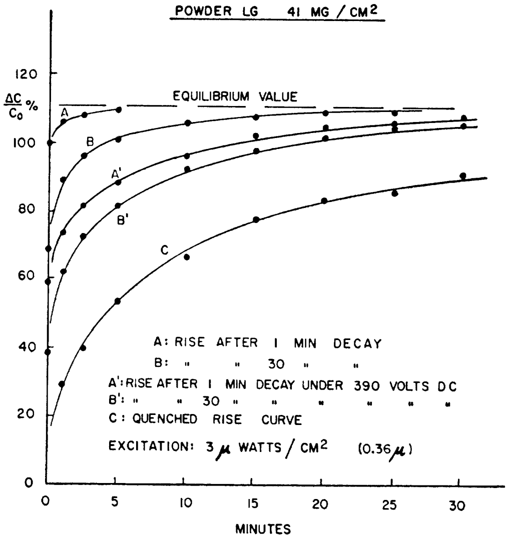

FIG. 2. Rise of capacitance in phosphor *LG* (ZnS, Pb, Cu, Fe, and Ni activators). Curves *A* and *B* were obtained by exciting the powder after a decay of 1 and 30 minutes respectively from previous excitation. Curves *A'* and *B'* were obtained under conditions similar to those for curves *A* and *B*, with 390 volts dc applied during the decay intervals. Curve *C* was obtained after de-excitation with infrared radiation ($\lambda > 0.72\mu$).

phors[16,17] excited with uv or fast electrons. In one method the finite rise of photoconductivity measured by $\Delta C/C_0$[18] (where ΔC is the change in capacity under illumination and C_0 is the capacity of the de-excited sample) is determined. Their deficiency areas[13,19] are a qualitative measure of the number of electrons stored in the sample. Rise curves taken after the previously excited sample had been kept in the dark for various periods of time, are all above the rise curve obtained after the sample had been thoroughly quenched (see curves *A*, *B*, and *C*, Fig. 2) and the areas between them are a qualitative measure for the number of electrons which have recombined during the indicated time interval. They do not, however, represent the number of stored electrons directly as the areas of the fluorescence rise curves do.

Further the ΔC values themselves are not proportional to n_c because of the grain structure of the sample.[16] One can, however, compute n_c roughly from the measured ΔC and thus determine n_t (number of trapped electrons) with the proposed theory.[20] A closer estimate of the number of trapped electrons can be obtained by determining ΔC as a function of the exciting intensity over a wide range of intensity (see Figs. 1 and 4 of a previous paper[16]). A certain exciting intensity and thus a certain emitted intensity can be assigned to each ΔC. In this way one can transform the ΔC curves into light emission curves. It is assumed hereby that the observed light emission corresponds to the ΔC values along the rise curve in the same way as for the equilibrium case. Then one can transform these ΔC curves into light emission curves which would give the number of trapped electrons directly. The curves obtained in this way coincide fairly well with the directly observed rise and decay curves of fluorescence (compare Figs. 4 and 6). Because of this correspondence it is mostly sufficient to consider the actual $\Delta C/C_0$ curves.

A second method of studying the effects of electric fields consists in observing the decay of photoconductivity ($\Delta C/C_0$) with and without applied field during the decay period. This method gives a more detailed knowledge of the effectiveness of the field but since the photoconductivity remaining in the powder is not a unique function of the number of the excited electrons left in the sample, this method does not determine this figure. The measurements were always performed in such a way as to measure the ac conductivity without additional field; only during the period preceding this measurement was the field applied. The fields used for measuring the ac conductivity were always negligibly small compared to those applied otherwise to the sample [1 volt (rms) at 1 kc for measuring purposes compared with 50 to 400 volts otherwise applied].

C. RISE CURVE MEASUREMENTS

From rise curves without and with an electric field (ac or dc) applied during the dark time interval τ, the following results were obtained. Curves *A* and *B* of Fig. 2 describe ΔC rise curves of phosphor *LG* [ZnS with Pb $\cdot$(0.040%), Fe (0.01%), and Cu (0.0031%) activators[13]] for two dark periods. The long extension

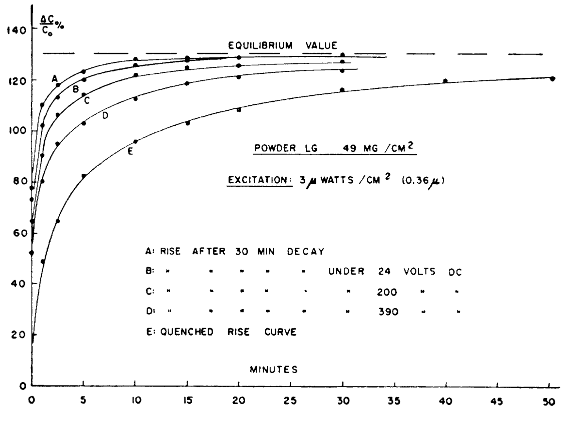

FIG. 3. Rise of capacitance in phosphor *LG*, showing that with increasing field strength applied during the decay process, the de-excitation of the sample progresses.

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

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

[18] Instead of $\Delta C/C_0$, the dissipation factor could as well be used to describe the change in photoconductivity.[16] It may be recalled that the changes in C and D under illumination in these photoconductors are due to the changes in photoconductivity.[10,16,17]

[19] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, New York, 1949), Chap. VII, p. 578.

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

of the quenched rise curve, *C*, below the equilibrium value indicates that it took several hours at this intensity of illumination to fill traps closely to equilibrium. Curves *A′* and *B′* of the same figure show the corresponding curves with a dc electric field of 390 volts applied during the same dark periods. Otherwise they were obtained under identical conditions as curves *A* and *B*. It is quite apparent that the primed curves all lie below the respective unprimed curves indicating that the field (field strength of about 15 000 volts/cm) has removed many excited electrons from the sample. The effect is by no means transient in its nature; curve *B′* is still far below *B*. Figures 3 and 4 describe the influence of the strength of the electric field on phosphor *LG*; they show the progressive de-excitation of the sample with increasing field strength. 390 volts dc removes the majority of the electrons trapped. The number of electrons per unit volume which remain stored after various field free dark periods was carefully measured with the fluorescence rise curve method. This total number is of the order of 10^{15} and of these about 30% persist for more than one week and nearly 50% more than 1 day.[13,21] Thus in 30 minutes the field has removed most of the trapped electrons which would otherwise persist far beyond one day. Ac fields with peak voltages V_p quench the sample slightly more strongly than a dc field of the same strength (see also Sec. D). With 400 volts (rms) and 60 cps, the phosphor *LG* was completely de-excited. It was even found that the dark capacity of the sample was smaller after the de-excitation by the field than after normal strong de-excitation by infrared irradiation.

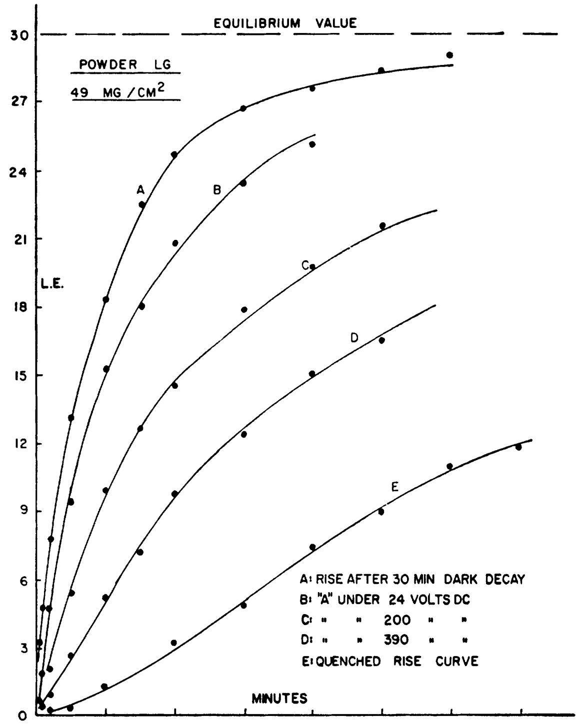

FIG. 4. Rise of capacitance in phosphor *LG* transformed into light emission curves. These curves were obtained by transforming the curves of Fig. 3 with the aid of a plot of ΔC *vs* exciting intensity for this phosphor.[17] The ordinate L.E. represents the calculated light emission in arbitrary units.

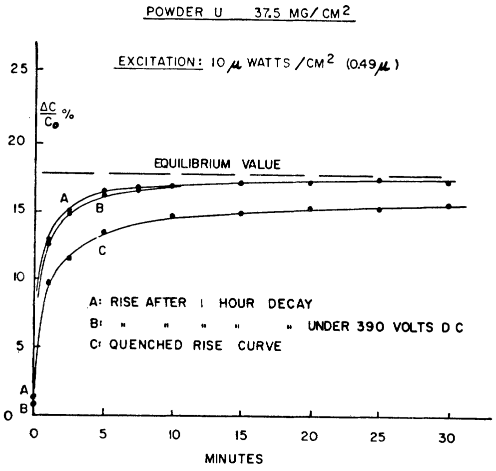

FIG. 5. Rise of capacitance in phosphor *U* (Zn 29.9%, Cd 42.6%, Ag, and Pb activators), showing that a potential of 390 volts dc has only a slight de-excitation effect when applied during a 1-hour decay interval. The conductivity of this phosphor decays very quickly after excitation.

Several other ZnCdS phosphors were tested in a similar way. The following results were obtained: (1) The field quenching effect is independent to a large extent of the Cd content and of the activator (Ag and Cu). (2) A dependence on additional activators was found in the sense that phosphors containing quenchers are less susceptible to field quenching. Figure 5 represents rise curves for ZnCdS phosphor *U* [Zn 29.9%, Cd 42.6% containing Ag (0.04%), and Pb (0.001%)][13] which has a very steep drop in photoconductivity after excitation. It is seen that the field has only a slight de-exciting effect which is much smaller than that observed with all the other phosphors investigated. (3) The quenching effect is always strongest at the onset of the field application. (4) With ac fields, practically all trapped electrons can be eliminated from the sample which otherwise would persist for weeks.

In those phosphors without Cd, the exciting light of 0.36 μ is absorbed only in the tail of the absorption curve and one may assume that the sample is rather uniformly excited. Nevertheless, one could suspect that some inhomogeneity exists and may have influenced the effects observed. To dispel such suspicion, a sample of substance M^{13} between a Nesa glass plate and an aluminum foil transparent to fast electrons was excited by a strong Sr^{90} source. In this case the field exercises a similar strong de-exciting influence which progresses with increasing duration of field application as in the case of ultraviolet excitation. Finally, rise curves,

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[21] M. Sidran (private communication).

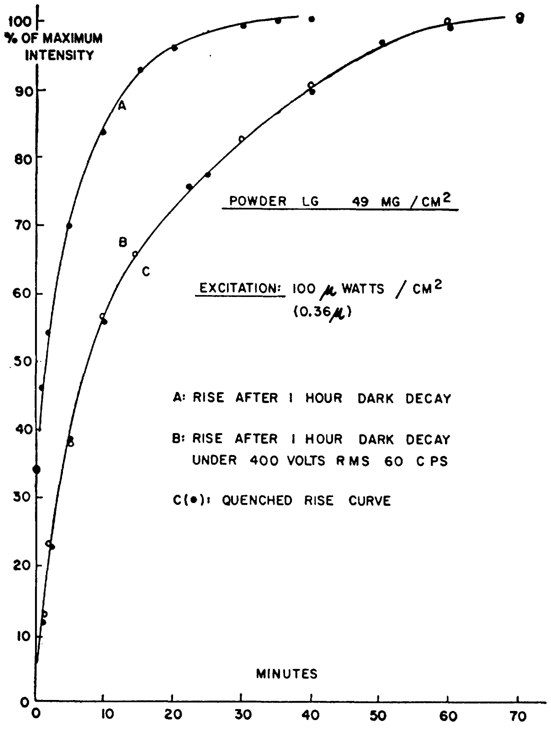

FIG. 6. Rise of fluorescence in phosphor *LG*, showing that a potential of 400 volts (rms) 60 cps applied during a 1-hour decay interval has completely de-excited the phosphor.

similar to those for ac photoconductivity, were taken by observing the fluorescent emission.[22] Figure 6 represents a rise of fluorescent emission obtained from phosphor *LG*. Curve *C* represents the rise taken after strong infrared de-excitation and curves *A* and *B* represent the rise curves obtained after a one-hour dark interval, first (*A*) when no electric field is applied during the decay and second (*B*) when a potential of 400 volts (rms) 60 cps is applied during the one-hour decay. The coincidence of curves *B* and *C* on this figure shows that the phosphor has been completely de-excited by the applied ac field in one hour and, consequently, that the field has removed almost all excited electrons from the phosphor.

D. DECAY MEASUREMENTS

In this section, decay of conductivity measurements with and without applied field are described. The curves of Fig. 7 were obtained by applying the electric field for a certain time and by measuring the conductivity immediately after the removal of the field. When the field was removed it was not reapplied again; rather the sample was re-excited and again allowed to decay under the influence of the applied field. The above procedure was repeated to obtain each point on the decay curve. These curves display the effect of field de-excitation more directly; they are completely in line with those obtained from the rise curve measurements. The following results can be gleaned from Figs. 7 to 9:

(1) Instantaneously with the application of the field a very strong decrease in conductivity sets in, similar to the initial drop caused by infrared irradiation. The drop is very steep for most of the powders.

(2) The decrease in conductivity due to the field continues, as can be seen from the decay curves. When the field is turned off, their slopes definitely diminish. This means that a dc field, even after a long time of application, still produces additional recombination of excited electrons. This is in agreement with the findings from the rise curve investigation.

(3) There is an important difference between field and infrared quenching. After infrared quenching, the conductivity curve first drops rather abruptly and thereafter flattens out. After field quenching, the respective curves become flatter immediately. The abrupt drop after infrared quenching is attributed to the fact that infrared has two different kinds of effects: one of decreasing the conductivity and one of stimulating it (perhaps by releasing positive holes). With the cessation of the infrared irradiation this additional conductivity is abruptly cut off, and this effect produces the sharp drop in conductivity. Since after field application no such drop is observable, it must be concluded that the field has only a quenching effect upon conductivity.

(4) The quenching effects of ac and dc fields are similar (see Figs. 8 and 9), but the conductivity is diminished somewhat more by an ac field than by a dc field which has the same strength as the peak of the ac field (see Fig. 9).

(5) The very sharp initial decrease in conductivity after field application is not due to the special state at the beginning of the decay curve. It occurs at any

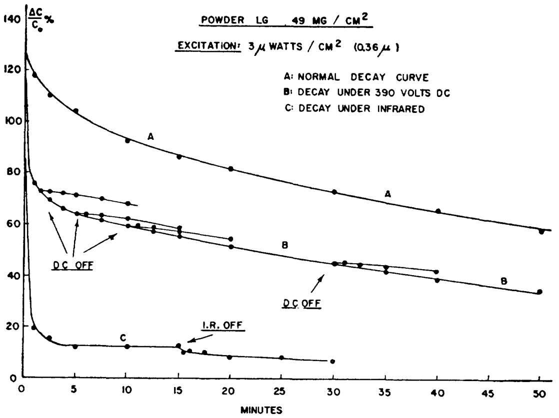

FIG. 7. Decay of capacitance from previous ultraviolet excitation ($\lambda=0.36\mu$, 3 μw/cm²) in phosphor *LG*. Curve *A* presents the natural decay, curve *B* the decay under 390 volts dc, and curves *C* the decay under infrared radiation ($\lambda>0.72\mu$). The conductivity is seen to drop when the infrared radiation is removed but no such drop is apparent when the applied voltage is removed during the decay.

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[22] E. Sucov (private communication).

point of the decay curve after field application (see Figs. 8 and 9).

(6) The sharp initial drop followed by a considerable slowing down of the decay of conductivity under field application is not due to a polarization effect inside the sample, since it occurs also with an ac field. Repeated application of a dc field does not increase the decay. If the field is applied for a time long enough to reach the flatter part of the decay curve, and is then removed and reapplied after various time intervals, no new steep drop in conductivity is obtained.

(7) If one compares two points of equal conductivity along the decay, one reached by natural decay without a field and one reached by application of a field, the effects of the field at these points of equal conductivity are quite different. The application of the field at the point on the natural decay produces a sharp drop, whereas at the point reached by application of the field the conductivity decays much less steeply under the influence of the field. Again this is also true for an ac field. This shows that the two states of equal conductivity reached by various ways, one by waiting without field and one (in a much shorter time) by application of a field, present difference internal trap occupations.

Similar experiments were performed to observe the decay of the phosphorescence.[22] Here the situation is more complicated because the field also produces an additional light emission besides de-exciting the sample. This additional light emission is easily observed with ac fields[4,5] but not with dc fields. Consequently, one cannot immediately see the quenching effect of fields from an ordinary phosphorescence curve. Experiments are now in progress which measure the ac photoconductivity while a strong dc field is applied to the sample during the decay-measuring process. This has been made possible by altering the bridge circuit so that dc fields could be applied to the terminals while measurements are made. These curves look very similar to those presented in this section.

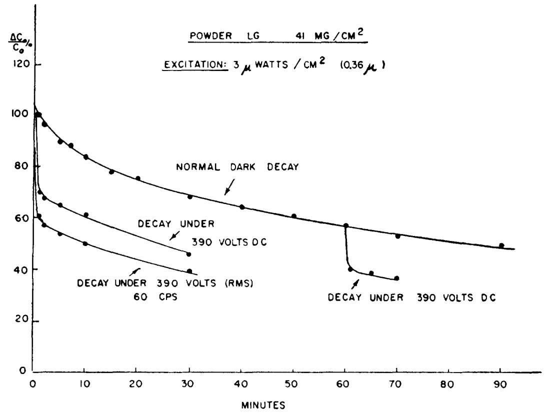

FIG. 8. Decay of capacitance in phosphor *LG*, comparing the action of an ac with a dc field applied at the onset of the decay and with a dc field applied 60 minutes after the onset of the decay.

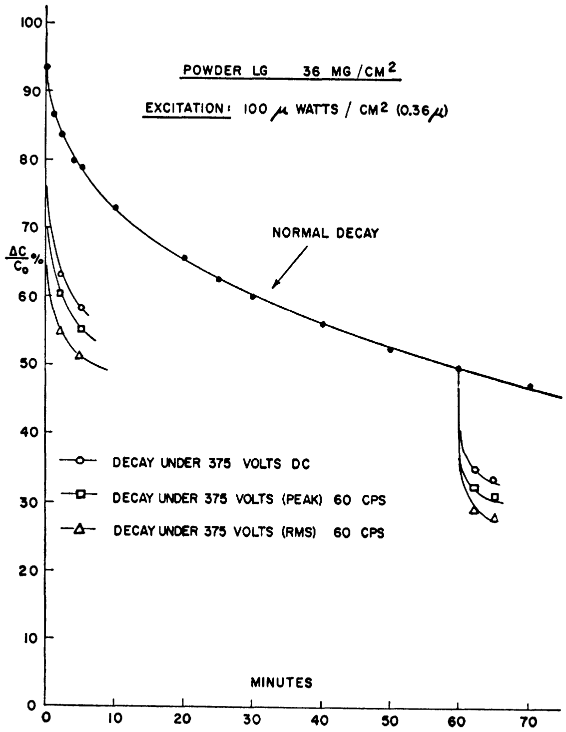

FIG. 9. Decay of capacitance in phosphor *LG*, comparing the action of a dc field with ac fields of rms and peak strengths equal to the dc field applied at the onset and 60 minutes after the onset of the decay.

E. THEORETICAL CONSIDERATION

The most striking results of these observations are: (1) the electric field eliminates even those electrons which otherwise remain excited in the sample for a very long time, (2) dc field de-excitation is comparable to that by ac field, and (3) materials with slowly decaying photoconductivity seem to be de-excited by electric fields readily whereas those with photoconductivity of short duration are less susceptible to field quenching.

The de-excitation by electric fields cannot be due to a field emission in which the electric field removes the electrons from the traps directly: (1) small electric fields already de-excite the sample and also decrease the conductivity (see Figs. 1, 3, and 4), and it is difficult to believe that 24 volts corresponding to 1000 volts per cm can produce a considerable field emission of electrons from traps; (2) the decrease in conductivity shows directly that there is no increase in free charges; (3) the curves of Fig. 7 do not drop when the electric field is turned off as they do in the case of infrared de-excitation. This means that the electric field does not introduce an additional increase in free carriers (as infrared does) which vanish when the field is turned off.

The following three mechanisms may be responsible for the field de-excitation:

(1) In a substance in which a considerable number of excited electrons are stored for many days and weeks,

these electrons are bound in trap levels which are situated less than one electron volt below the conductivity band and a similar situation prevails for the positive charges with respect to the valence band. Their longevity is wholly due to the predominance of retrapping over recombination.[23] More than 10^{14} trapped excited electrons per cubic centimeter persist for a very long time.[13] Nevertheless the electrons may be emitted from traps within a fraction of a second and then be retrapped. The probability of recombination decreases with diminishing number of electrons and positive charges.[21,24] Application of a field shifts the electrons towards the positive electrode; there a larger number of traps are filled and as a consequence, retrapping decreases in this region. In the rest of the sample, the electrons are released from traps and moved towards regions of higher trap occupation and thus of higher recombination probability. If the positive charge is also shifted, one must consider that the motion of the positive and negative charges may have different phase shifts with respect to the field. Thus maximum light emission under the application of an ac field will not coincide with the maximum of the applied field. This has actually been observed.[5,22] It is, however, difficult to understand how the field and particularly a dc field should de-excite the sample to a high degree according to this mechanism since the negative charges are amassed at the positive electrode and the positive charges near the negative electrode.

(2) Another important mechanism may be the actual ejection of electrons and holes from the powder into the electrodes. This mechanism which is similar to that observed by Pohl (see Part A5) could be responsible for the high degree of de-excitation also observed with dc field.

(3) A further possibility of de-excitation may exist when positive and negative charges are amassed at grain boundaries opposite each other. They may recombine when they are thrown across such a boundary.

It is difficult at this stage to decide which of these mechanisms is the most effective one. Two experiments have been performed which may shed some light on this question. First the powder was placed between two Mylar sheets, and the field was applied from outside so that the electrons could not be ejected from the sample into the electrodes. This experiment showed that de-excitation still occurs but to a smaller extent. This decrease in de-excitation can be completely understood from the fact that the field inside the sample is weaker with Mylar sheets than without such sheets. Thus this experiment indicates that ejection of electrons is certainly not the only process of de-excitation. At least at the beginning of field de-excitation, this ejection process is not important. It may be, however, that such an ejection process is responsible for the eventual complete de-excitation by fields.

That the field changes the trap distribution inside the sample can be concluded from the observation described under Part D7. Thus, the second experiment, shows that the point on the normal decay curve (see right side of Fig. 9) just before application of the field represents a different trap occupation than the point obtained when a potential of 375 volts (rms) 60 cps has been applied for about 7 minutes, although at both these points the sample has the same conductivity ($\Delta C/C_0=50\%$). Probably the former represents a trap occupation distribution where more but deeper traps are filled, as compared with the latter where a smaller number but more shallow traps are occupied. Consequently, at the point obtained after 60 minutes of normal decay, the total number of electrons available for quenching is larger than at the point of equal conductivity reached in a shorter time by application of a field.

Similar experiments in de-excitation of phosphors by electric fields have been performed by observing their internal polarization; they confirm the strong de-exciting effect of electric fields. This work will be published in the near future.[25] In the meantime, changes in the bridge circuit have also made it possible to apply strong dc and ac fields directly to the bridge terminals and thereby to measure the impedance change in the sample while strong fields are applied and while the phosphor is under excitation. These measurements will be reported on in the near future.

The authors wish to extend their gratitude and appreciation to Dr. Bernard Kramer for helpful and stimulating discussions relating to this investigation and valuable suggestions regarding the writing of this paper. Our thanks go also to Dr. Miriam Sidran for furnishing information on infrared stimulation and to Mr. Eugene Sucov who kindly supplied us with the fluorescence measurements.

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[23] The ratio of retrapping over recombination is determined by comparing the retrapping coefficient $\beta'\sim10^{-7}$ cm^3 sec^{-1} and the recombination coefficient $\beta^*\sim10^{-11}$ cm^3 sec^{-1}. These are the values which can be gleaned from experiments. Retrapping is given by $\beta' n_0$, where n_0 is the number of traps per unit volume, of the order of 10^{15} cm^{-3}. Recombination is given by $\beta^* n_t$, where n_t is the density of trapped electrons, of the order of 10^{14} to 10^{15} cm^{-3}.[20] This gives a ratio of retrapping over recombination of the order of 10^5.

[24] H. Kallmann, J. Phys. radium, Colloque de Luminescence, Paris, May, 1956.

[25] J. Freeman (private communication).