

# Electron traps and dielectric changes in phosphorescent solids

BY G. F. J. GARLICK AND A. F. GIBSON

*Department of Physics, University of Birmingham*

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Some luminescent solids, such as zinc sulphide with a specific impurity, exhibit considerable increases in their dielectric constant and loss when excited in the presence of a small electric field by ultra-violet light or other suitable radiation. The effect is found to be confined to those phosphors which show photoconductivity associated with the luminescence process. The total change in dielectric constant of such phosphors may increase by as much as 75% of the normal value (about 8) for quite moderate intensities of excitation. The loss increase, expressed as the change in equivalent a.c. conductance, may change from less than  $10^{-8}$  to  $10^{-5}$  ohm $^{-1}$  during excitation.

Experimental investigations and theoretical considerations show that the dielectric changes occur when electron traps are filled by electrons. The relatively low binding energy of the trapped electron to its trap (from 0.1 to 0.7 eV in most zinc sulphide phosphors) permits large displacements of the electron from its mean position when an external field is applied. This gives rise to the increase in dielectric constant. Increase of dielectric loss of the phosphor is associated with the existence of a finite relaxation time of the filled electron traps which causes phase differences between the variation of the applied alternating field and the movement of the trapped electrons. This gives rise to energy absorption from the applied field by the filled traps. It is found from experiment that electrons moving in the conduction energy levels of the phosphor crystal make a negligible contribution to the dielectric effects when compared with the contribution from trapped electrons.

The dielectric changes are found to increase rapidly with temperature following an exponential variation. They are also dependent on the applied field frequency over the frequency range comparable in order to the reciprocal of the relaxation time of filled electron traps which is found to be of the order of  $10^7$  sec. $^{-1}$ . The relaxation time does not vary rapidly with the temperature. The dielectric changes show small variation with the wave-length of the exciting light between 0.35 and 0.41  $\mu$  for most zinc sulphide phosphors, but decrease rapidly as the wave-length decreases to 0.25  $\mu$ , due to a rapid rise in the absorption coefficient of the phosphors. The long wave-length limit for production of the dielectric changes corresponds to the wave-length limit for photoconductivity and for the filling of electron traps and is dependent upon the constitution and structure of the particular specimen.

The electron-trap theory of phosphorescence established by previous workers enables many of the dielectric effects to be correlated with the luminescence processes in phosphors. The studies confirm the results of previous workers and enable their observations on the dielectric changes to be given a theoretical interpretation.

## GENERAL INTRODUCTION

It has been known since the early work of Lenard & Saeland (1909) that some luminescent materials, such as zinc sulphide with an impurity activator, show an increase in dielectric constant in an applied electric field when excited to emit luminescence. The effect has been studied by other workers (Gudden & Pohl 1920; Herweg 1923; Wilde 1923; Schmidt 1923; Goos 1939; and others); the corresponding change in dielectric loss has been studied by Gisolf (1939). From the results of these investigations it was found that the effects were limited to those phosphors in which photoconductivity occurred in association with the luminescence process. The increase in dielectric constant was observed to be of the same order as the normal value (about 8) in the case of some zinc sulphide specimens, this increase being for quite normal intensities of excitation.

The present studies confirm the previous findings and provide in addition new experimental facts which enable a theoretical model to be established to explain the origin of the dielectric changes in phosphors. Previous workers in this laboratory have shown that the phosphorescence processes in photoconducting phosphors such as zinc sulphide and the alkaline earth sulphides depend on the storage action of thermally metastable centres in the phosphors known as electron traps. These traps capture electrons liberated from the luminescence centres of the phosphor by the excitation and retain them until thermal energy added to the traps by local lattice vibrations enables the electrons to escape and give rise to phosphorescence by recombining with luminescence centres. The mean time spent by an electron in a trap determines the time at which it gives rise to phosphorescence (Randall & Wilkins 1945). It has also been shown that this electron-trap mechanism can govern the phosphorescence characteristics at very small decay times of the order of 1 msec. (Garlick & Wilkins 1945). By the use of theoretical ideas formulated by these workers it has been possible to interpret the dielectric changes in phosphors in terms of the electron-trap processes and to relate the dielectric phenomena to the luminescence properties of phosphors. Phosphorescence which is governed by the action of electron traps is markedly dependent on the conditions of excitation and the phosphor temperature. A similar dependence is shown by the dielectric changes during fluorescence, phosphorescence and thermoluminescence of the material. From the correspondence between the luminescence and dielectric effects it is inferred that the dielectric changes arise from the behaviour of electrons during the time in which they are separated from the luminescence centres. This means that the dielectric changes may be due to the properties of electrons moving through the conduction band of the phosphor or to the effects of trapped electrons.

#### THEORETICAL INTRODUCTION

As the theoretical ideas developed in these studies include many of those established by previous workers (Randall & Wilkins 1945), a brief survey of the electron-trap theory of phosphorescence is given embodying portions relevant to the interpretation of the dielectric phenomena. In luminescent solids activated by the inclusion of a small amount of a specific impurity, the seat of the luminescence emission is in the impurity atoms or ions which are dispersed throughout the matrix lattice of the solid. The heat treatment of the phosphor in preparation effects this dispersal and also gives rise to potential defects in the periodic field of the crystal lattice (Mott & Gurney 1940). Some of these defects will be capable of trapping and storing electrons liberated from the luminescence centres by the exciting light. The exact nature of these trapping centres is not known, but there is some evidence that they are associated with the neighbourhood of the impurity centres; it is hoped to publish such facts shortly. The number of effective traps is estimated to be of the same order as the number of luminescence centres. Using the collective electron model for insulating solids now generally accepted, the luminescence mechanism

is described as follows: excitation of the phosphor frees electrons from the luminescence centres, and these electrons move through the conduction band of the crystal either returning to luminescence centres or being trapped in the electron traps. The energy states of the traps are assumed to lie just below the lowest states of the conduction band. In most phosphor specimens there are many trapping energy states of various depths below the conduction band.

The time spent by an electron in a trap will depend on the depth of the trap below the conduction band and on the temperature. If  $p$  is the probability per unit time that an electron will escape from a trap of depth  $E$  at a temperature  $T$  and  $t$  is the mean time spent in the trap then  $p$  and  $t$  are given by

$$p = 1/t = s \exp(-E/kT), \tag{1}$$

where  $s$  is a constant which may, however, vary slowly with temperature and  $k$  is Boltzmann's constant. The constant  $s$  has the dimensions of a frequency and is often considered as bearing a simple relation to the natural frequency of vibration of the filled electron trap. From phosphorescence and thermoluminescence experiments it is estimated to be of the order of  $10^{8\pm 1}$  sec.<sup>-1</sup> for zinc sulphide phosphors. It is associated later with the relaxation time of the filled electron traps as measured by dielectric experiments. A method of finding the number of electron traps at different depths below the conduction band has been developed by Randall & Wilkins which involves the measurement of the variation of thermoluminescence glow emission with temperature when a phosphor is warmed at a uniform rate in the dark after excitation at a low temperature so that nearly all traps are saturated with electrons. The luminescence emission intensity of the phosphor is proportional to the rate of escape of electrons from traps, which is proportional to the number of trapped electrons and their probability of escape  $p$ . Thus if there are  $n$  trapped electrons in traps of depth  $E$  the emission intensity  $I$  is given by

$$I = -dn/dt = pn = ns \exp(-E/kT). \tag{2}$$

This set of relations is based on the assumption that there is no retrapping of escaping electrons. For practical cases where there are many traps of different depths in the phosphor the equations must be integrated over all values of  $E$  and  $n$ . The number of electrons trapped will depend on the excitation conditions, the temperature and the form of the trap distribution with respect to depth. It can be shown from simple considerations of equilibrium conditions that for steady excitation at a fixed temperature the number of electrons in traps of depth  $E$  is given by

$$n = N_E / \{1 + s/A \exp(-E/kT)\}, \tag{3}$$

where  $N_E$  is the total number of traps of depth  $E$  and  $A$  is a constant proportional to the exciting light intensity. When there are many traps of different depths the total number of trapped electrons is given by the integral of  $n$  over all  $E$  values:

$$N = \int_0^{E_{\max.}} n dE = \int_0^{E_{\max.}} N_E / \{1 + s/A \exp(-E/kT)\} dE, \tag{4}$$

where  $N$  is the total number of trapped electrons. Thus by means of equations (2) and (3) the decay of phosphorescence with time may be determined for different excitation intensities.  $N_E$  for each trap depth can be found from the thermoluminescence experiment. Randall & Wilkins have given the derived phosphorescence decay equations for saturated conditions (that is  $n = N_E$ ), and for long decay times only for certain variations of  $N_E$  with  $E$ . One of these relations is relevant to the study of dielectric changes in phosphors during phosphorescence. It is that obtained for  $N_E$  varying exponentially with  $E$  between certain values of  $E$ . If, therefore,  $N_E \text{ const. exp}(-\alpha E)$ , where  $\alpha$  is a constant, then the intensity of phosphorescence at a decay time  $t$  is given by

$$I = \text{const.}/t^{\alpha kT+1}. \quad (5)$$

The constant  $\alpha$  can be obtained from the thermoluminescence experiment and can be compared with the value obtained from measurement of phosphorescence decay at a fixed temperature. Correlations between the two derivations of the constant have been given for several different phosphors by Randall & Wilkins (1945, p. 398).

#### THEORETICAL INTERPRETATION OF DIELECTRIC CHANGES IN PHOSPHORS

The observed increases in dielectric constant and dielectric loss of the phosphors studied are found to occur only when luminescence is accompanied by photoconduction processes. From this it is inferred that the effects are due to the action of electrons which have been freed from the luminescence centres by the excitation and are either moving in the conduction band or are captured in electron traps. Electrons moving in the conduction band are known to give rise to conduction processes in the phosphor in the presence of an applied field and might therefore contribute to the dielectric changes observed when the field is alternating. The motion of such electrons will give rise to an increase in dielectric loss and also to increase in dielectric constant if they are subject to suitable constraining forces so that they do not move in phase with the field. Dielectric changes might also occur when an electron is captured in a trap, since the binding energy associated with its captured state is usually small in phosphors (from 0.1 to 0.8 eV; see Randall & Wilkins 1945). Thus a trapped electron can be displaced from its mean trapped position by the action of an external applied field. This displacement might be referred to as the polarization of a filled electron trap. It would cause increase in the dielectric constant of the phosphor and also increase in dielectric loss if the displacement motion was not in phase with the applied field variation. Such a phase difference would arise if the natural vibration frequency of the filled trap system was of the same order as the applied field frequency.

Experimental evidence indicates that the dielectric changes are predominantly due to the displacements of trapped electrons. Some of the most significant experimental facts are given here in summarized form to emphasize the negligible effect of electrons in the conduction band on the dielectric properties of phosphors compared with the effect of filled electron traps.

(a) When the phosphor is excited at a fixed temperature to an equilibrium state the total fluorescence emission is found to increase linearly with the intensity of excitation. At normal intensities of excitation the fluorescence is mainly due to electrons which have not been captured by electron traps but which return directly to luminescence centres after excitation. Although the fluorescence emission shows this simple linear variation with intensity of excitation and therefore the increase in the number of electrons in the conduction band also varies regularly with excitation intensity, yet the dielectric changes show a saturation effect at quite low intensities. This is shown by the results given in figure 3. The same saturation effect occurs for the number of trapped electrons and for the phosphorescence after cessation of excitation. The relation between the dielectric changes and the excitation intensity is found to be identical with that for the variation of the number of trapped electrons with intensity of excitation.

(b) When a phosphor is excited at liquid-air temperature most of the electron traps are filled and will remain filled after excitation has ceased if the low temperature is maintained. After excitation ceases the phosphorescence decays rapidly to a negligible value, but the dielectric changes decay to a steady value which is still about 70–80 % of the value during excitation. Such a large residual change in dielectric constant or loss cannot be due to electrons present in the conduction band, as there is no phosphorescence emission due to their capture by luminescence centres. If after a considerable time the phosphor is irradiated with infra-red light, then a burst of luminescence occurs due to the release of electrons from traps. The dielectric changes decrease to zero with no initial enhancement such as would be expected if they were due to conduction band electrons. This behaviour has been observed by other workers (Goos 1939).

(c) From measurements of the frequency dependence of the dielectric changes, values of the relaxation times of the polarizable systems causing the dielectric changes are obtained and are of the order of  $10^{-7}$  sec. Such large values are not likely to be associated with electrons in the conduction band, but it is not difficult to associate them with filled electron traps as previous workers have given estimates of the values of the natural vibration frequencies of filled traps as being  $10^{8\pm 1}$  sec.<sup>-1</sup> (Randall & Wilkins 1945, p. 383). This frequency will be closely related to the reciprocal of the relaxation times of the filled traps.

From this and other experimental evidence described later it is concluded that the dielectric changes are due to the properties of trapped electrons and that electrons in the conduction band make no significant contribution. The increase in dielectric constant therefore involves the displacement of trapped electrons from their mean positions. An estimate of the magnitude of this displacement can be obtained from the number of filled traps and the percentage increase of the dielectric constant. The number of trapped electrons is certainly less than  $10^{18}$  per c.c. (Randall & Wilkins 1945, p. 404), and the dielectric constant can be more than 75 % of its normal value. Thus the electron displacement to effect such a change must be several lattice spacings of the phosphor in magnitude. In order to explain the corresponding

increase in dielectric loss the trapped electrons must be capable of absorbing small quanta of energy from the applied field which implies the existence of a number of energy states for the trapped electron which are sufficiently close together to allow the energy absorption. Such a configuration implies a large effective trap diameter. Large orbits associated with trapped electrons have been postulated by previous workers to explain some of the properties of semiconductors (Mott & Gurney 1940, p. 166). The magnitude of the trapped electron displacement will depend on the depth of the electron trap as will its capacity to absorb energy from the applied field. The dielectric changes would be expected to decrease with increase of trap depth together with a similar decrease in the relaxation time of the filled trap.

Since the binding conditions of the trapped electron are affected by the temperature (e.g. equation (1)), it would be expected that the dielectric changes would depend upon the temperature of the phosphor. It is found from the experimental data that the dielectric changes increase exponentially with the temperature above about 200° K., but below this point they do not vary rapidly with temperature. These facts might be used to predict the form of the potential-energy functions of trapped electrons, but considerable extra data are required for this purpose and the functions have not been estimated as yet. The above theoretical discussions show that if the dielectric changes in phosphors are due to filled electron traps then the magnitude of the effects will depend on the number of electrons trapped, the trap-depth distribution, the relaxation times of the filled traps, the applied field frequency and particularly the temperature of the phosphor. That is, the filled electron traps can be considered as polarizable and absorbing systems in the matrix phosphor material, and that they consist of a loosely bound electron which is readily displaced by applied fields and an ionic or atomic system of much greater mass or inertia to which the electron is bound.

#### EXPERIMENTAL METHOD

For measurements of dielectric changes or luminescence the phosphor is mounted in a very thin layer on a rhodium-plated copper surface forming part of a small German silver Dewar vessel. This apparatus has been used for previous work (Garlick & Wilkins 1945) and is particularly suited to the variation of the phosphor temperature over the wide range from 90 to 600° K. The temperature variation is effected by filling the inner tube of the Dewar vessel with liquid air or by the use of a small electric heater attached to the rear of the surface on which the phosphor is mounted. The phosphor, which is *in vacuo*, is excited through a quartz window in the outer structure of the Dewar vessel. For dielectric measurements the phosphor is covered by a thin glass slip with a graphite coating in grid form on its outer surface through which the exciting radiation can pass. The phosphor is thus enclosed in a condenser cell formed by the rhodium-plated surface and the graphite grid and forms part of the dielectric of the cell the rest being due to the glass of the cover-slip. Electrical connexion is made to the graphite and to the plated-copper surface, the latter being

maintained at earth potential. A thermocouple is attached to the front of the copper surface to measure the temperature of the phosphor in the cell. The source of exciting radiation in most of the experiments is a high-pressure mercury arc lamp of the Osira type used in conjunction with suitable filters for the wave-length desired. In most of the experiments a wave-length of  $0.365\mu$  has been used.

*Apparatus for the measurement of dielectric changes*

As the dielectric changes of the phosphor had to be measured while varying with time or temperature the conventional methods of determining dielectric constant or loss were not suitable and electrical circuits were devised which would measure, independently of each other, the dielectric constant or loss changes with time or temperature. A diagram of the electrical circuits of the measuring apparatus is given in figure 1. A conventional tuned anode-tuned grid radio-frequency oscillator

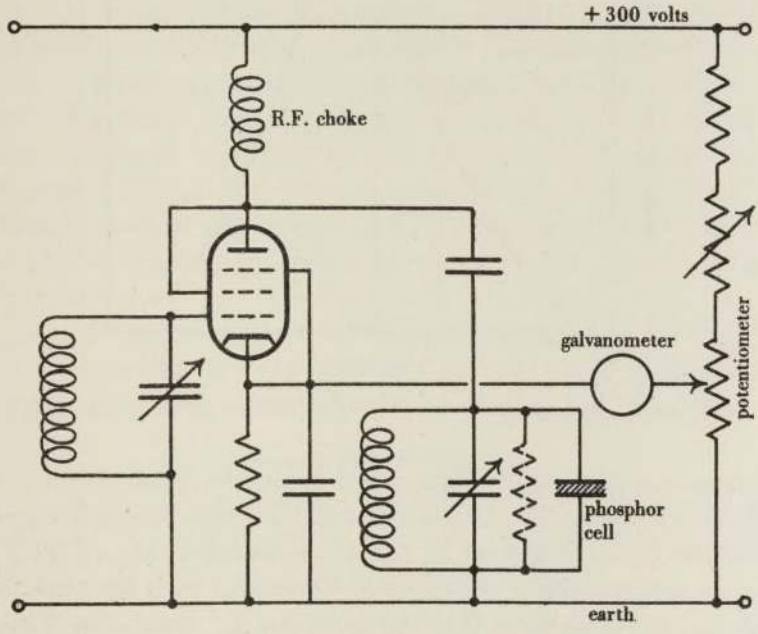


FIGURE 1. Circuit diagram of dielectric change-measuring apparatus.

is loosely coupled to the grid circuit of the valve shown in figure 1. This valve is a pentode (Mazda SP 41) working as a triode and as an anode bend detector; its normal grid bias provided by the cathode load is about  $-13\text{ V}$ . The anode circuit of the valve contains a tuned circuit in which the phosphor cell of the Dewar apparatus is connected in parallel with a variable condenser and suitable inductance. The anode voltage is supplied through a radio-frequency choke from stabilized power supplies which also feed the master oscillator. By means of stabilization and careful screening random fluctuations during measurement can be reduced to a very small minimum. The circuit operates as follows: A radio-frequency voltage due to the oscillator is

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established in the tuned grid circuit of the valve and results in the development of a radio-frequency voltage across the tuned anode circuit. When the grid and anode circuits are in tune a sharp resonance state occurs due to feed-back through the valve. The resonance curve of radio-frequency voltage across the tuned anode circuit for changes in capacity of the circuit is given schematically in figure 2. Changes in dielectric constant in the circuit cause a capacity change in the circuit, while changes in dielectric loss cause a flattening of the resonance curve. The voltage changes across the anode circuit due to dielectric changes are recorded by the galvanometer in the cathode circuit of the valve. A potentiometer system is provided to annul the normal cathode voltage existing when no changes occur.

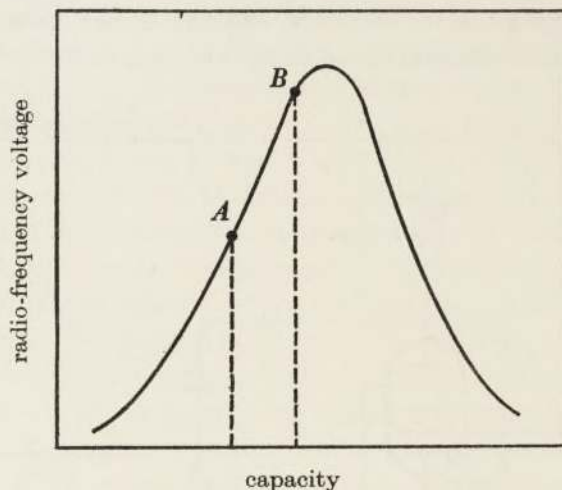


FIGURE 2. Resonance curve for tuned anode circuit of figure 1.

In order to measure capacity changes, which are due to dielectric constant changes, separately from the effects due to dielectric loss the anode circuit is tuned by means of its variable condenser to a point on the resonance curve shown by *A* in figure 2, and a relatively low resistance is connected in parallel with the phosphor cell. Its value is chosen to be much lower than the minimum a.c. resistance of the cell due to dielectric loss increase during luminescence. Although this procedure lowers the sensitivity of the system to capacity changes it is still sufficient for practical measurement and enables the effect of loss changes during capacity measurement to be reduced to a minimum as a contribution to the galvanometer deflexion. This contribution is found to be less than 1% in experiment. The linearity of the galvanometer response to capacity changes is tested by the use of standard condensers across the tuned anode circuit, the same condensers being used for calibration of the capacity changes in micro-microfarads. The phosphor cell has a capacity of about  $10\ \mu\mu\text{F}$ . in the dark; the apparatus can detect a change in capacity of  $0.01\ \mu\mu\text{F}$ .

For the measurement of dielectric loss changes the parallel resistance inserted for capacity change measurements is removed. The circuit is then tuned to a point *B*



shown in figure 2 near to the peak of the resonance curve. Under these conditions the change in voltage across the tuned circuit recorded by the galvanometer will be mainly due to the flattening of the resonance curve when loss changes occur. The contribution from changes in capacity is found to be less than 2% of the recorded change. The calibration of the galvanometer for loss measurements is effected by inserting standard non-inductive resistances across the tuned circuit. There is some departure from linearity between loss change and galvanometer response but this is included in calibration.

*Measurements of dielectric changes at different frequencies of the applied field*

The apparatus described above has been used mainly at a frequency of 3 Mcyc./sec. In addition, measurements of dielectric changes have been made at a lower frequency of 1 Mcyc./sec., using the same apparatus. In general, however, it is not possible to extend the use of the apparatus to all desired frequencies for complete measurement of the dielectric changes during fluorescence, phosphorescence and thermoluminescence. Measurements of the dielectric changes have been made for steady excitation of fluorescence at fixed temperatures over a frequency range from 100 kcyc./sec. to 10 Mcyc./sec. This range proves sufficient to include the anomalous frequency variation of the dielectric changes due to the particular values of relaxation times of the polarizable systems. For these measurements at different frequencies of the applied field the phosphor cell is connected to the circuit of a conventional 'Circuit magnification or  $Q$  meter', by means of which the dielectric constant and loss changes are recorded.

All changes in dielectric constant are denoted by  $\Delta\epsilon$  in the description of experimental results. Loss changes are measured as the change in equivalent parallel conductance  $\Delta\gamma$  of the cell in units of reciprocal ohms.

*Luminescence measurements*

For the determination of the luminescence characteristics and electron-trap distributions of the various phosphor specimens examined the methods described previously have been employed (Randall & Wilkins 1945).

EXPERIMENTAL RESULTS

Studies of the dielectric changes during luminescence in many different specimens of zinc sulphide and zinc-cadmium sulphides have been made. The results given here are for a few of these phosphors only but are typical of those obtained for all specimens. In all cases the dielectric characteristics of the phosphor cell in the dark, unexcited state are determined so that the changes due to the luminescence processes only can be deduced from the results. Such control experiments are made over the range of temperature from 90 to 600°K. For each specimen the fluorescence-temperature, the saturated phosphorescence-time and the thermoluminescence-temperature characteristics are measured in order to define the luminescence characteristics of each specimen. In all cases it is found that the dielectric constant

and loss of the unexcited phosphor show no marked temperature effects over the range investigated and no anomalous variation with the applied field frequency. Above 600° a temperature is reached at which loss changes due to semi-conduction processes in the phosphor occur.

Absolute measurements of the dielectric changes are difficult to obtain, as all the phosphors are in powder form and mounted in a very thin layer so that the accuracy of estimating cell dimensions and effective volume of the dielectric due to the phosphor is relatively low. Thin layers are essential to obtain complete and uniform excitation of the specimen thus avoiding anomalies due to non-uniform excitation (Goos 1939). Measurements made show that the normal dielectric constant of phosphors of the zinc sulphide type is about 8 and that for high excitation the value increases to about 14 for some of the specimens. Previous workers have claimed to have observed increases of the order of 100% of the normal value (Gudden & Pohl 1920). In view of the above difficulties the measurements of the dielectric changes, with the exception of those recorded in figure 3, have been made in arbitrary units. Relative accuracies of measurement are high, of the order of 1 or 2%. Dielectric loss changes can be measured in absolute units as previously stated, but the low values for the unexcited phosphor are inaccurate because of their small magnitude. The values are certainly less than  $10^{-8}$  ohm<sup>-1</sup>.

(1) *Variation of the dielectric changes with the intensity of excitation at fixed temperature*

When a phosphor is excited for a sufficiently long time at a fixed temperature, in this case room temperature, by a steady source of ultra-violet light it reaches a state of equilibrium when its emission intensity is constant and is proportional to the excitation intensity. There are accompanying changes in dielectric constant and loss, but these changes tend to saturate at quite small excitation intensities. A typical variation of the dielectric constant change with excitation intensity is given in figure 3 for a zinc sulphide phosphor activated by silver impurity. The ordinate of the figure is the change in dielectric constant  $\Delta\epsilon$  in absolute units, the scale being accurate to  $\pm 10\%$  in absolute value. The abscissa is the exciting light intensity in arbitrary units. Measurements such as those given in figure 3 have been made for all specimens over intensity ranges of more than 1000:1. From the experimental results of figure 3 it can be seen that saturation effects occur at low intensities and that the curve flattens out more as the intensity increases. It is found that at high intensities the dielectric changes  $\Delta\epsilon$  and  $\Delta\gamma$  vary linearly with the logarithm of the exciting light intensity  $I$ . From the experimental results a more complete empirical formula relating the dielectric changes and the excitation intensity has been derived. It is

$$\Delta\epsilon \text{ or } \Delta\gamma \text{ is proportional to } \log(Ib + 1), \quad (6)$$

where  $b$  is a constant which can be determined from the results at high intensities. It is obtained by plotting  $\Delta\epsilon$  or  $\Delta\gamma$  against  $\log I$  and producing the straight line for the high intensities when its intersection with the abscissa for  $\Delta\epsilon$  or  $\Delta\gamma$  equal to

zero is at  $-\log(b)$ . The product  $Ib$  in equation (6) is denoted by  $A'$ , this factor still being proportional to the excitation intensity. Experimental results are given in figures 4 and 5 to show the validity of the empirical relation for six typical phosphors. The ordinates of the figures 4 and 5 are the change in dielectric constant  $\Delta\epsilon$  and the change in dielectric loss  $\Delta\gamma$  respectively. The abscissa of each figure is the quantity  $\log(A' + 1)$ , the value of  $A'$  being determined for each phosphor as described above. It is found that the number of filled electron traps, as measured by the thermoluminescence experiment, varies with the excitation intensity according to the relation given by equation (6) and the value of  $A'$  obtained from the thermoluminescence measurements agrees with the values obtained for the variation of the dielectric changes with excitation intensity.

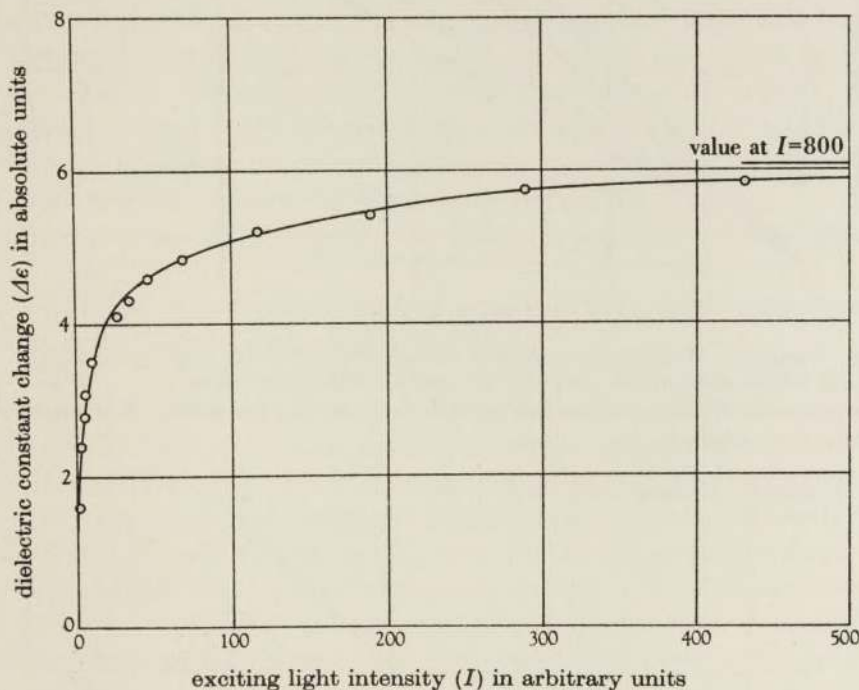


FIGURE 3. Variation of dielectric constant change with exciting light intensity for atypical phosphor (ZnS-Ag) at 291° K. (Absolute accuracy of ordinate units is  $\pm 10\%$ .)

The above experimental results indicate that the dielectric changes are proportional to the number of filled electron traps. Using the conceptions developed in the theoretical section above a derivation of equation (6) can be obtained. If the temperature, and the field frequency, remain fixed and the variation of the dielectric changes with trap depth is neglected, then the dielectric changes at any intensity will be proportional to the number of filled traps. This number will be given by equation (4). If  $N_E$  is constant or is varying slowly with  $E$  then the equation has the solution

$$N = N_E kT \log [(Ax_m + 1)/(A/s + 1)].$$

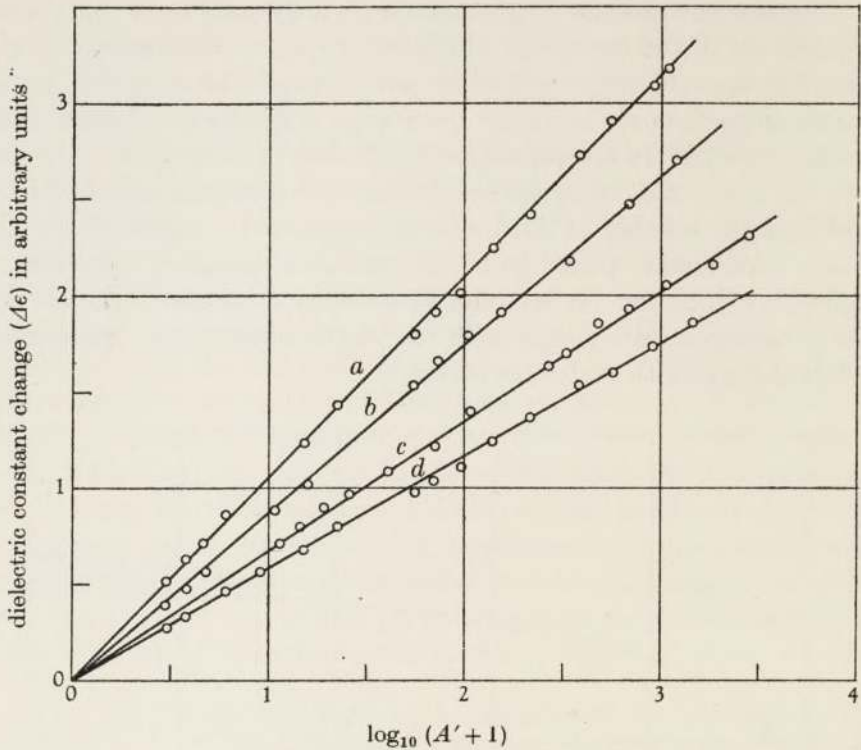


FIGURE 4. Variation of dielectric constant change with exciting light intensity for various phosphors at room temperature (291° K). (a) ZnS-CdS-Cu (short after-glow); (b) ZnS-Cu (long after-glow); (c) ZnS-Ag (short after-glow); (d) ZnS-Zn (short after-glow).  $A'$  = constant factor  $(b) \times$  exciting light intensity  $(I)$ .

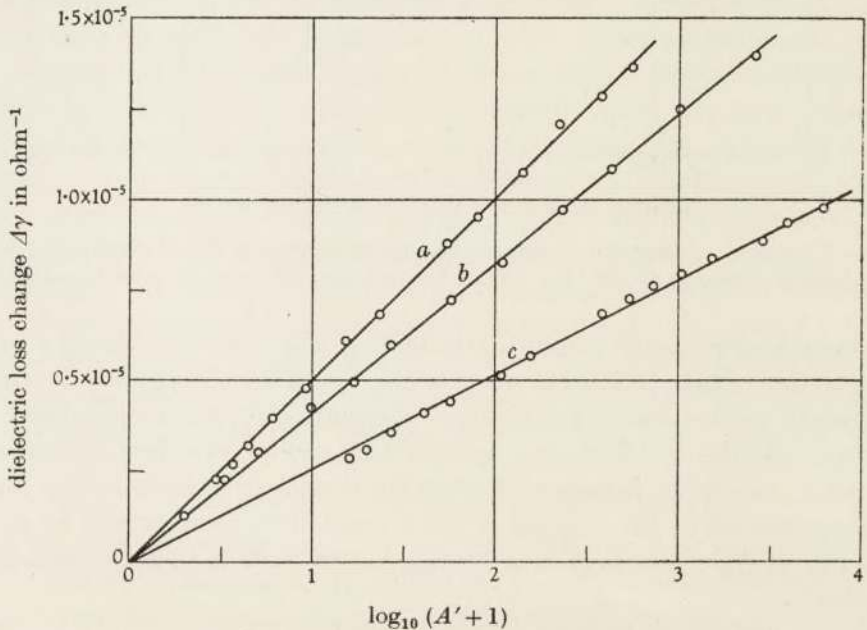


FIGURE 5. Variation of dielectric loss change with exciting light intensity for various phosphors at room temperature (291° K). (a) ZnS-Cu (long after-glow); (b) ZnS-Ag (short after-glow); (c) ZnS-CdS-Cu (long after-glow).  $A'$  = constant factor  $(b) \times$  exciting light intensity  $(I$  in arbitrary units).

where  $x_m = s^{-1} \exp(E_{\max.}/kT)$ . From experiment it is found that over the intensity range used  $A$  is much smaller than  $s$  so that the above expression becomes

$$N = N_E kT \log(A' + 1), \tag{7}$$

where  $A' = Ax_m$ . As the dielectric changes  $\Delta\epsilon$  and  $\Delta\gamma$  will be proportional to  $N$  this derivation is equivalent to the relation found empirically in equation (6). The agreement shows that the assumption that the variation of dielectric changes with the trap depth is slow is justified. The assumption that  $N_E$  is constant or varies but slowly with  $E$  is also justified if all traps are considered.

(2) *Decay of the dielectric changes with the decay of phosphorescence*

If the phosphor specimen is excited to an equilibrium state at room temperature and then the excitation is cut off the phosphorescence will decay in intensity with time. The intensity-time relation will be determined by the extent to which the traps are filled by the excitation. The dielectric changes also decay with time during phosphorescence. To determine the relation between the dielectric changes and the decay of phosphorescence the following experiments were carried out:

- (i) Measurement of the decay of phosphorescence with time.
- (ii) Measurement of the decay of the dielectric constant and loss changes with time.
- (iii) Measurement of the decrease in the number of trapped electrons with time by means of the thermoluminescence experiment.

Experimental results for two of the phosphors studied are given in figures 6 and 7. The co-ordinates are logarithmic, the abscissa of each figure being the decay time. The ordinates of each graph give the intensity of phosphorescence, the dielectric changes  $\Delta\epsilon$  and  $\Delta\gamma$  and the number of trapped electrons, all quantities being expressed in arbitrary units. From an inspection of the curves of these two figures it is evident that the slopes of the dielectric constant and loss change curves are about the same as the slopes of the curves giving the decay in the number of trapped electrons with time. However, these several slopes are different from that of each respective phosphorescence curve by about unity. The results show that the dielectric changes depend mainly upon the number of filled electron traps.

The difference in slope between the curves for the dielectric changes and number of trapped electrons and the curve for the decay of phosphorescence may be explained by reference to equation (5) above. The number of electrons in traps at a decay time  $t$  when the phosphorescence intensity is  $I$  will be given by

$$N = \int_t^\infty I dt.$$

The phosphorescence decay of the two phosphors in question follows the relation of equation (5) and therefore the integral becomes

$$N = \int_t^\infty (\text{const.}/t^{akT+1}) dt = \text{const.}/t^{akT}.$$

Thus the respective slopes should differ by unity when the decay processes are presented as in figures 6 and 7 on logarithmic co-ordinates. When considering the variation of the dielectric changes with excitation intensity it was assumed that  $N_E$  varied slowly with  $E$  or was constant, whereas in the present instance an exponential variation of  $N_E$  is assumed. In the interpretation of the results given in §(1) above it is justified to consider  $N$  as essentially constant, as all traps of all depths are involved; in the case of phosphorescence decay at long decay times only deep traps are involved, and their number may vary exponentially with  $E$  without invalidating the assumptions of §(1) for all traps.

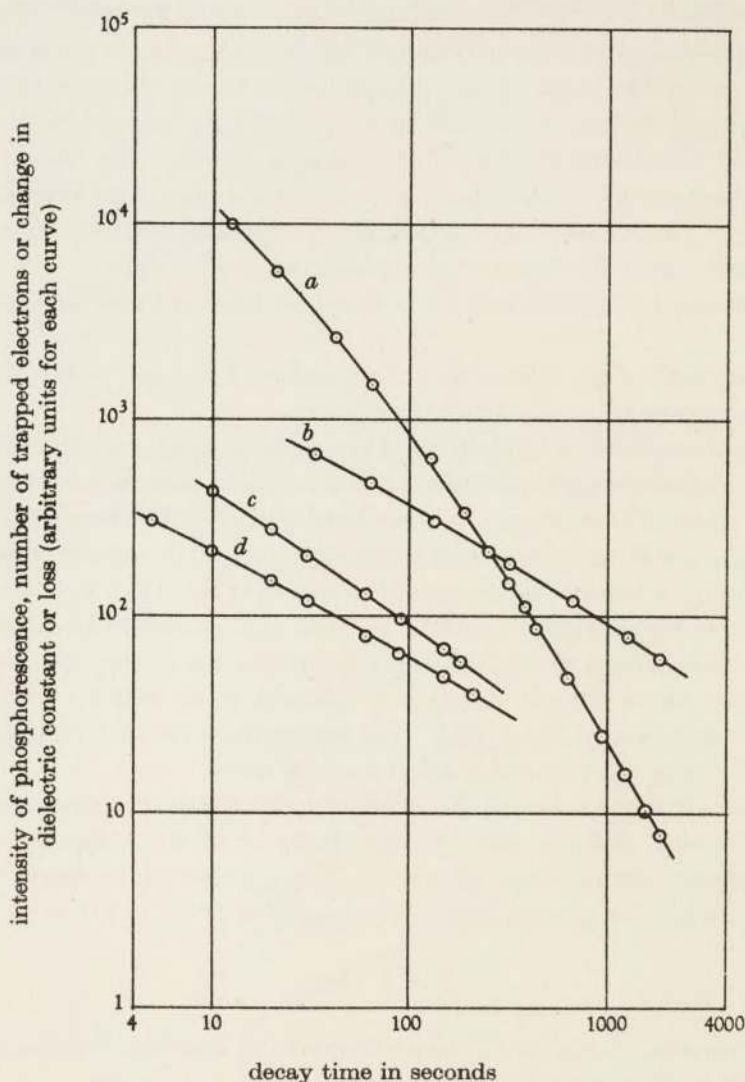


FIGURE 6. Decay of dielectric changes, phosphorescence and number of trapped electrons with time for ZnS-Cu phosphors at 291° K. (a) decay of phosphorescence; (b) decay of number of trapped electrons; (c) decay of dielectric loss change; (d) decay of dielectric constant change.

The approximate nature of the agreement between the slopes of the curves for the dielectric changes and those for the decay of the number of trapped electrons indicates that the effect of trap depth on the dielectric changes may not be negligible. The dielectric changes will decrease with the depth of the filled traps, and as the decay proceeds the electrons remain in the deeper traps so that the dielectric changes have a more rapid decay than that which would occur if there were no effect due to trap depth.

In addition to the measurement of phosphorescence decay and the corresponding decay of the dielectric changes some qualitative experiments have been made at

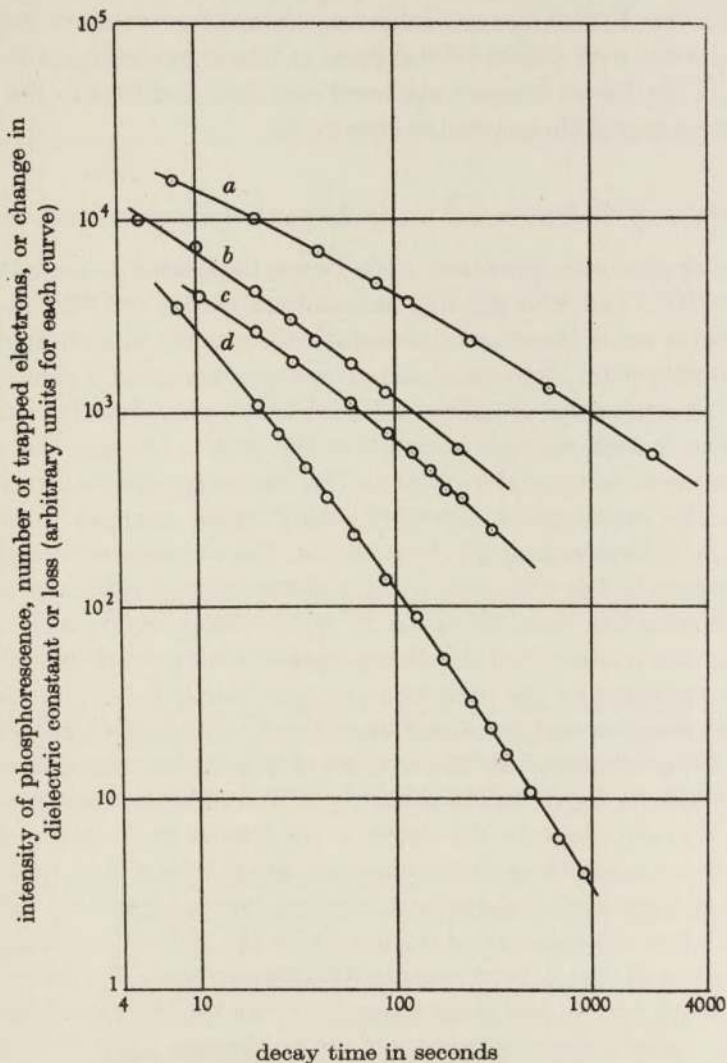


FIGURE 7. Decay of dielectric changes, phosphorescence and number of trapped electrons with time for a ZnS-CdS-Cu phosphor at 291° K. (a) Decay of number of trapped electrons; (b) decay of dielectric constant change; (c) decay of dielectric loss change; (d) decay of phosphorescence.

liquid-air temperature which have already been briefly described in the theoretical section above. They involve the release of trapped electrons by infra-red light. Similar experiments made at room temperature confirm earlier work (Goos 1939; and others). The irradiation of a phosphor during phosphorescence decay with infra-red light can cause a temporary enhancing of the phosphorescence with a subsequent decay which is more rapid than its normal progress. In some cases the initial enhancing does not occur but the decay becomes more rapid. The occurrence of one or both of these phenomena depends on the particular specimen used. However, in no case is any initial enhancing of the dielectric changes observed. The enhancing of phosphorescence may also be produced by a strong electric field which can release electrons from traps. In this case an earlier worker has shown that no initial increase in dielectric constant ever occurs (Herweg 1923). These experiments show that the dielectric effects are due to trapped electrons and that electrons in the conduction band contribute a negligible amount to the effects.

### (3) *Variation of the dielectric changes during thermoluminescence emission*

If the phosphor specimen, mounted in the Dewar apparatus, is cooled to liquid-air temperature, excited and then warmed at a uniform rate in the dark ( $2.5^\circ \text{K/sec.}$  in all experiments) it emits thermoluminescence which varies in a characteristic way with the temperature for each specimen. The variation gives a representation of the number of electron traps of different depths in the phosphor if excitation at the low temperature is high enough to saturate the traps. During the emission of thermoluminescence changes also occur in the dielectric constant and loss of the specimen. In the experiments described below these changes during thermoluminescence have been measured. In addition, the temperature variation of the conduction current in the phosphor when a static applied field is present during thermoluminescence has been measured as representing the number of electrons moving through the conduction band at any instant during the thermoluminescence emission. The variation of the dielectric changes during thermoluminescence together with the emission and the variation of the d.c. conduction current are given in figure 8 for a typical phosphor. The abscissa of this figure is the temperature. The ordinate represents for curve (a) the intensity of thermoluminescence, for curve (b) the change in dielectric loss  $\Delta\gamma$ , for curve (c) the change in dielectric constant  $\Delta\epsilon$ , for curve (d) the magnitude of the conduction current for a d.c. applied field. It can be seen that there is good agreement between curves (a) and (d) but that there is no simple relation between curves (b) and (c) for the dielectric changes and curve (a) for the variation of thermoluminescence with temperature. The dielectric changes do, however, reach zero at the same temperature as the thermoluminescence and the conduction current showing that there are no changes when the electron traps are all empty.

To interpret the curves (b) and (c) of figure 8 it is assumed that the dielectric changes depend on the number of filled traps, but in addition it is assumed that there



may be a variation of the dielectric changes with temperature. To ascertain the nature of the temperature variation the first assumption is used. At any temperature  $T_G$  during the thermoluminescence emission the area remaining under the curve (a) between  $T_G$  and the temperature at which emission ceases is proportional to the number of trapped electrons. In the absence of a temperature variation of the dielectric changes then the ordinate of either curve (b) or (c) at  $T_G$  would be proportional to this area on the above assumption. Thus the temperature function for the dielectric changes may be found by dividing the ordinate of curves (b) or (c) by

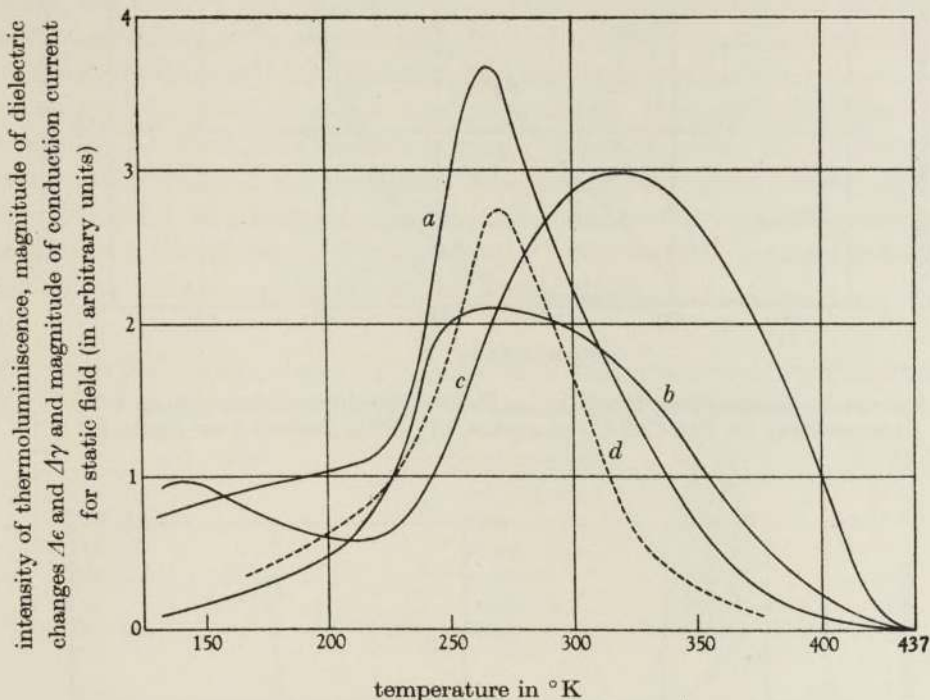


FIGURE 8. Variation of thermoluminescence emission and corresponding dielectric changes with temperature for ZnS-CdS-Cu phosphor after excitation at 90° K. (a) Thermoluminescence-temperature curve; (b) dielectric loss change-temperature curve; (c) dielectric constant-temperature curve; (d) current flowing in phosphor during thermoluminescence in static applied field.

the area left under the thermoluminescence curve. If this is carried out at all temperatures the intrinsic variation of the dielectric changes with temperature may be obtained. The temperature functions so derived are given for the dielectric constant and dielectric loss changes in figures 9 and 10 respectively. Figure 9 has temperature as the abscissa and the temperature function of the dielectric constant change as the ordinate, denoted by  $f_{\Delta\epsilon}(T)$ . The ordinate is given with linear and logarithmic scales corresponding to curves (b) and (a) respectively in order to show the form of the function. The abscissa of figure 10 is the inverse of the temperature and its ordinate the temperature function for the dielectric loss change on

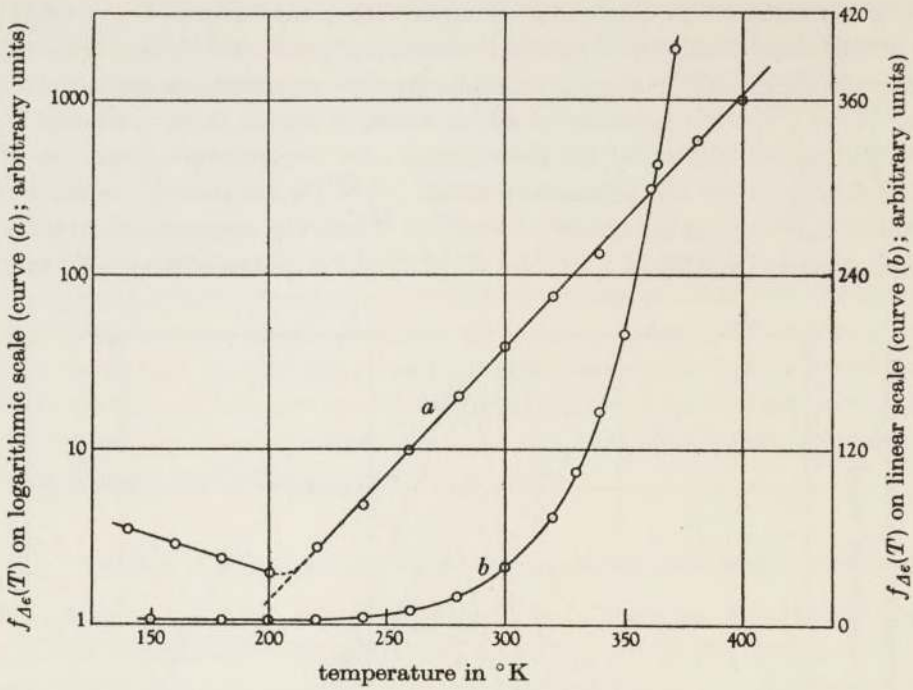


FIGURE 9. Temperature function  $f_{\Delta\epsilon}(T)$  for dielectric constant change with temperature for ZnS-CdS-Cu phosphor. ( $f_{\Delta\epsilon}(T)$  is derived from figure 8.)

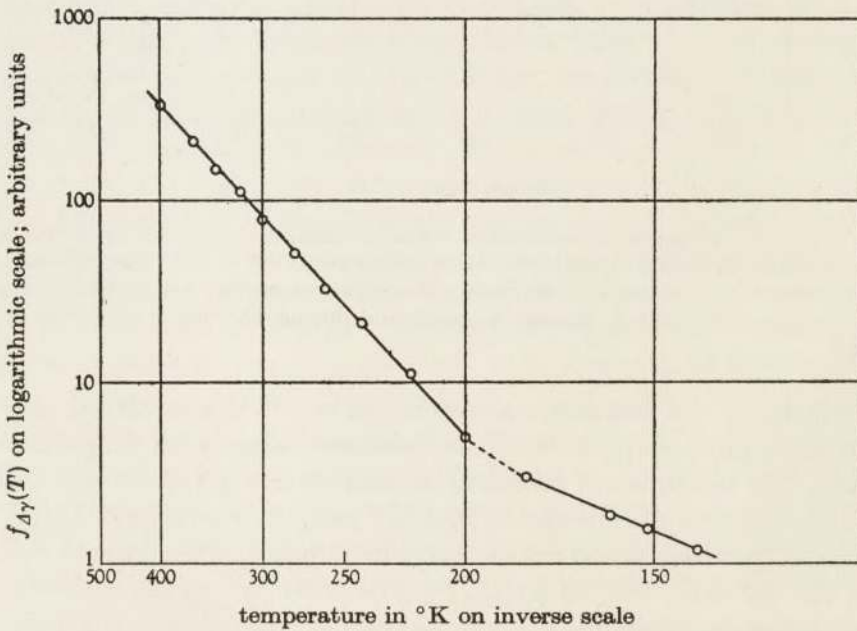


FIGURE 10. Temperature function  $f_{\Delta\gamma}(T)$  of dielectric loss change with temperature for ZnS-CdS-Cu phosphor. ( $f_{\Delta\gamma}(T)$  is derived from figure 8.)

a logarithmic scale, the function being denoted by  $f_{\Delta\gamma}(T)$ . From the curves of figures 9 and 10 the respective temperature functions are found to be

$$f_{\Delta\epsilon}(T) = \text{const. exp}(\alpha T), \quad \text{where } \alpha \text{ is a constant,}$$

$$f_{\Delta\gamma}(T) = \text{const. exp}(-\beta/T), \quad \text{where } \beta \text{ is a constant,}$$

these relations holding above 200° K. All phosphor specimens show a departure from these relations at temperatures below about 200° K, where the dielectric changes are approximately independent of temperature.

No theoretical explanation of these temperature variations of the dielectric changes has been found. Experimental values of the constants  $\alpha$  and  $\beta$  in the temperature functions for several phosphors with different luminescence characteristics are given in table 1. An inspection of the table shows that the values of  $\alpha$  and  $\beta$  show no marked change from specimen to specimen. It appears from these results that the temperature functions are intrinsic properties of the filled electron traps and do not depend on the particular phosphor to any great extent. Again, the different trap depths associated with long and short phosphorescence specimens have little effect on the constants. Variation of the field frequency appears to have little effect on the temperature functions over a wide range.

TABLE 1. VALUES OF THE CONSTANTS  $\alpha$  AND  $\beta$  FOR THE TEMPERATURE VARIATION OF THE DIELECTRIC CHANGES IN PHOSPHORS

phosphor	phosphorescence	$\alpha$ ( $^{\circ}\text{K}^{-1}$ )	$\beta$ ( $^{\circ}\text{K}$ )
ZnS-Zn	very short	0.018	810
ZnS-Ag	short	0.0165	960
ZnS-Cu	short	0.015	1000
ZnS (70 %)-CdS (30 %)-Cu	medium	0.0125	670
ZnS (95 %)-CdS (5 %)-Cu	medium	0.014	720
ZnS-Cu	long	0.010	840

(4) *Comparison of the dielectric changes during fluorescence and thermoluminescence of phosphors*

The ratio of the intensity of fluorescence at room temperature to the maximum intensity of thermoluminescence emission is usually of the order of 100 : 1 for most specimens. The corresponding ratio for the dielectric changes is of the order of unity. These experimental facts provide further evidence that the dielectric effects are due to trapped electrons and depend on their number, which is not very different during fluorescence or thermoluminescence. The high intensity of fluorescence is due to the return of excited electrons to luminescence centres without being captured by traps between excitation and return. Thus the two ratios would be expected to be of different orders.

Examination of the dielectric changes with temperature during fluorescence shows that their variation is slow. This can be explained as follows: The number of trapped electrons during fluorescence will decrease rapidly with temperature, as

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shown by equation (3), for a single trap depth. In addition to this decrease there is the rapid rise in the dielectric effects due to their intrinsic temperature functions described in the last section. The combination of the two different rapid variations with temperature can give rise to a resultant variation with temperature which is relatively slow.

(5) *Variation of the dielectric changes in phosphors  
with the frequency of the applied field*

Measurements of the behaviour of the dielectric changes in excited phosphors when the frequency of the applied electric field is varied have been made by the use of the circuit magnification meter as stated in an earlier section. It is found that the changes in the dielectric constant due to the filling of electron traps decrease as the frequency of the applied field increases while the changes in dielectric loss increase as the field frequency increases. These variations with field frequency are characteristic of polarizable systems which have finite relaxation times and which therefore show anomalous dispersion and absorption at field frequencies of the same order as the reciprocal of the relaxation times. A general theoretical treatment of such systems has been given by many workers, notably Debye (1929), and in the presentation of the experimental results for phosphors use has been made of the theoretical developments of Murphy & Morgan (1939). Their derivations are for systems in which there is a charged particle of negligible mass bound to some system of relatively high inertia and are found to be applicable to filled electron traps. The present treatment of the results separates the dielectric effects due to filled traps from those occurring in the unexcited phosphor. Control experiments on the unexcited specimens indicate no anomalous variation of the dielectric properties with frequency when all traps are empty. This would be expected as the relaxation times of the matrix ions or atoms of the phosphors are very small, of the order of  $10^{-12}$  sec.

(a) *Variation of the change in dielectric constant with field frequency.* From the derivations of Murphy & Morgan (1939), the dielectric constant change  $\Delta\epsilon$  at an angular frequency  $\omega$  of the applied field is related to its values at static and infinite frequencies  $\Delta\epsilon_0$  and  $\Delta\epsilon_\infty$  respectively, thus:

$$\Delta\epsilon = \Delta\epsilon_\infty + (\Delta\epsilon_0 - \Delta\epsilon_\infty)/(1 + \omega^2\tau^2),$$

where  $\tau$  is the relaxation time of the polarizable centre, in this case a filled trap. This equation may be rewritten thus:

$$\frac{\Delta\epsilon_0 - \Delta\epsilon}{\Delta\epsilon - \Delta\epsilon_\infty} = \omega^2\tau^2 = 4\pi^2f^2\tau^2, \quad (8)$$

where  $f$  is the field frequency in cyc./sec. In practice  $\Delta\epsilon_0$  and  $\Delta\epsilon_\infty$  can be obtained by extrapolation at the extreme ends of the frequency range used. Thus the left-hand side of equation (8) should be a linear function of the square of the applied field frequency. Results of experiment for a zinc sulphide-cadmium sulphide phos-

phor activated by copper are shown in figure 11, plotted to show the agreement with equation (8). The ordinate is the expression on the right-hand side of the equation as obtained from experiment, while the abscissa is the square of the field frequency. The results are given for two different temperatures, and it is evident that equation (8) is followed by the experimental results. The slopes of the two straight lines of figure 11 will give values for the relaxation times of the filled traps at the two temperatures. Values obtained in this way for several phosphors are given in column iii of table 2.

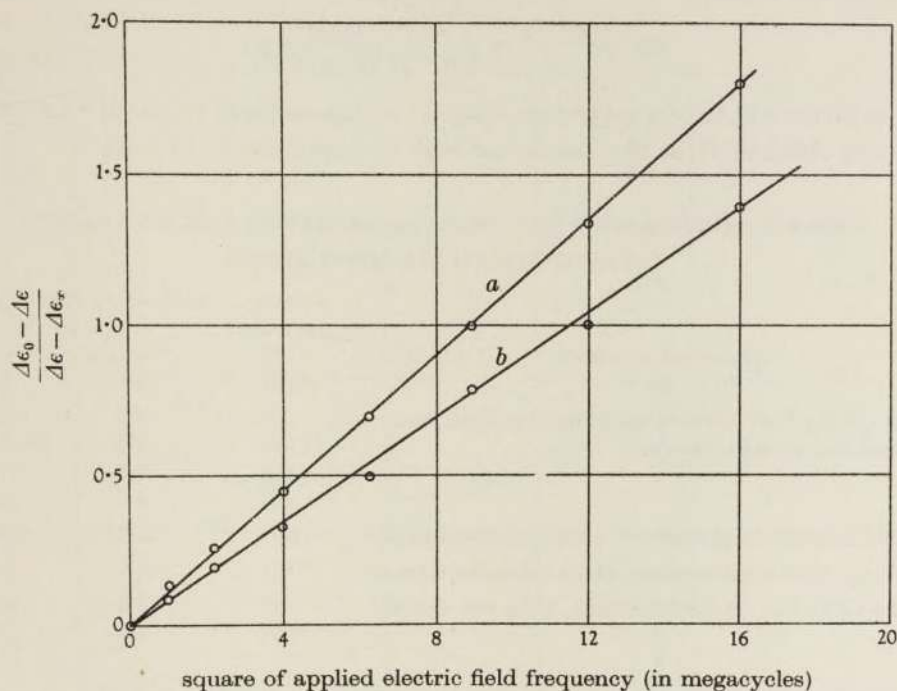


FIGURE 11. Variation of dielectric constant change with applied electric field frequency for ZnS-CdS-Cu phosphor at two different temperatures for constant excitation intensity. (a) Phosphor temperature 291°K; (b) phosphor temperature 361°K.  $\Delta\epsilon_0$  = dielectric constant change at zero field frequency.  $\Delta\epsilon_\infty$  = dielectric constant change at infinite field frequency.  $\Delta\epsilon$  = dielectric change at intermediate frequency.

(b) *Variation of the change in dielectric loss with field frequency.* From the derivations of Murphy & Morgan the change in dielectric loss, expressed as the change in equivalent parallel conductance  $\Delta\gamma$ , will vary with the applied field frequency according to the relation

$$\Delta\gamma = (\Delta\epsilon_0 - \Delta\epsilon_\infty)\omega^2\tau / 3.6\pi \times 10^{12}(1 + \omega^2\tau^2) \text{ ohm}^{-1},$$

which can be rewritten

$$\frac{\tau (\Delta\epsilon_0 - \Delta\epsilon_\infty)}{\Delta\gamma 3.6\pi \times 10^{12}} = \frac{1}{\omega^2} + \tau^2 = \frac{1}{4\pi^2 f^2} + \tau^2. \quad (9)$$

Thus the inverse of  $\Delta\gamma$  will vary linearly with the inverse square of the field frequency. Using this equation the experimental results for the same phosphor for which the results are given in figure 11, are presented to show its validity in figure 12. The ordinate is the inverse of the dielectric loss change  $\Delta\gamma$  and the abscissa is the inverse square of the applied field frequency. Values of the relaxation times for the filled traps cannot be obtained from these results as the absolute values of  $\Delta\epsilon_0$  and  $\Delta\epsilon_\infty$  are not known accurately. However, an independent derivation of the values of  $\tau$  can be obtained from the variation of the loss factor  $\Delta\epsilon''$  with field frequency which is given by the relation

$$\Delta\epsilon'' = \frac{4\pi\Delta\gamma}{\omega} = \frac{(\Delta\epsilon_0 - \Delta\epsilon_\infty)\omega\tau}{0.9 \times 10^{12}(1 + \omega^2\tau^2)}$$

This loss factor will have a maximum when  $\omega\tau = 1$ . A series of values of  $\tau$  for different phosphors obtained from the loss factor is given in column iv of table 2.

TABLE 2. EXPERIMENTALLY DERIVED VALUES OF THE RELAXATION TIMES OF FILLED ELECTRON TRAPS

phosphor specimen (i)	tem- perature °K (ii)	relaxation time $\tau$ in sec. ( $\times 10^{-8}$ )	
		(iii)	(iv)
ZnS (70 %)-CdS (30 %)-Cu, orange luminescence, medium phosphorescence	90	9.0	8.0
	291	5.3	7.8
	361	4.7	5.3
	457	4.3	4.0
ZnS-Cu, green luminescence, long phosphorescence	291	13.3	16.0
ZnS-Ag, blue luminescence, short phosphorescence	291	5.8	4.7
CdSe-CdTe-Cu, no luminescence, infra-red excited	90	13.4	15.0
	291	4.4	3.8

(c) *The significance of the relaxation time  $\tau$  and its variation with temperature.* Values of the relaxation time  $\tau$  for filled electron traps in different phosphor specimens have been given in table 2. Included in this table are values for a non-luminescent material which changes its dielectric constant and loss properties when irradiated with visible or infra-red light. The mechanism giving rise to its sensitivity to infra-red is essentially the same as that causing dielectric changes in phosphors, and the values of the relaxation times for this specimen are of the same order as those for phosphors. The values of the relaxation times for different phosphors do not show marked variation from one specimen to another. The results given in the table show that the relaxation time does not vary rapidly with temperature. It is found to be approximately proportional to the inverse of the temperature. The relaxation time of a filled trap is significant, as it should be closely related to the reciprocal of the constant  $s$  of equation (1) which is assumed to be a simple function of the natural frequency of vibration of the filled trap (Randall & Wilkins 1945, p. 372). The same workers have made determinations of the value of  $s$  for some phos-

phors, but the accuracy of their results is not high enough to make comparisons with similar derivations from the relaxation times of the filled traps determined from the dielectric experiments. In the above derivations of the relaxation times the theoretical relations used neglect the possibility of interaction between adjacent polarized centres. However, such interaction is not likely to affect the value of the relaxation time by a factor greater than two (Murphy & Morgan 1939; Williams 1934; and others). The assumption of non-interaction is probably justified, since the estimates of the concentration of traps in the phosphor matrix give about one trap per  $10^3$  or  $10^4$  lattice atoms.

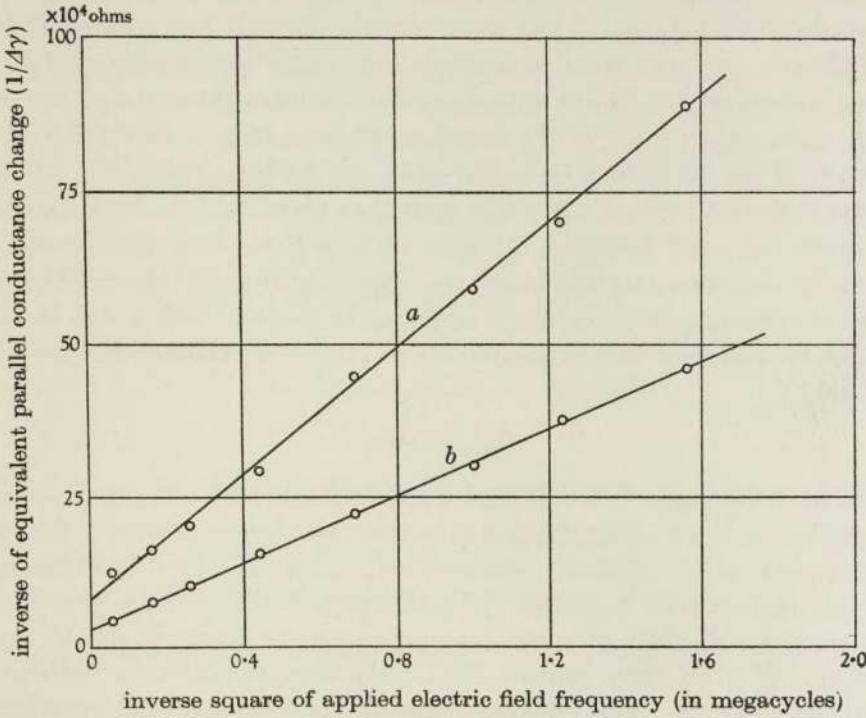


FIGURE 12. Variation of dielectric loss change with applied electric field frequency for ZnS-CdS-Cu phosphor at two different temperatures for constant excitation intensity. (a) Phosphor temperature 291°K; (b) phosphor temperature 361°K.

(6) *Variation of the dielectric changes in phosphors with the wave-length of the exciting radiation*

The effect of the variation of excitation wave-length on the dielectric effects in phosphors has been studied by earlier workers (Gudden & Pohl 1920; Gisolf 1939). The experimental results of these workers have been confirmed. It is found that there are no dielectric changes in phosphors unless the exciting radiation wave-length is sufficiently short to produce photoconductivity, that is, to free electrons from luminescence centres. Thus there are no dielectric effects in zinc sulphide-manganese activated phosphors when excited by radiation of  $0.43\mu$  wave-length. This

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is explained by the absence of filling of electron traps by such excitation (Garlick & Wilkins 1945). It has been shown by Gisolf (1939) that there is no change in the dielectric loss of such phosphors when the excitation wave-length is in the absorption region of the manganese impurity. In all zinc sulphide phosphors examined the dielectric changes showed the same behaviour when excited by light of wave-lengths between 0.35 and 0.41  $\mu$ , but they become very small when the wave-length is decreased to less than 0.33  $\mu$ . This decrease for short wave-lengths can be explained by the rapid rise in absorption coefficient of the phosphors below 0.35  $\mu$  (Gisolf, de Groot & Kröger 1941). This rise in absorption coefficient allows only a thin layer of the phosphor dielectric to be excited and the saturation of traps occurs at very low intensities of excitation. Thus the dielectric changes per unit volume of the whole dielectric are very small compared with those for excitation with longer wave-lengths, which give almost uniform excitation throughout the phosphor layer. The long wave-length limit of the dielectric phenomenon is dependent upon the constitution of the particular specimen as shown by the special case of the non-luminescent specimen whose relaxation times are given in table 2 for the dielectric effects due to infra-red radiation. In general, it is found that the increase in the percentage of cadmium sulphide in the zinc-cadmium sulphide phosphors shifts the limit for the dielectric phenomenon to longer wave-lengths. This is due to the shift of the wave-length limit for the production of photoconductivity and the filling of electron traps.

#### CONCLUSION

Studies of the changes in the dielectric constant and dielectric loss of phosphors during excitation by suitable radiation show that the changes are due to the polarization and absorption properties of electron traps which are filled by electrons. The trapped electron can be displaced by small applied electric fields due to its low binding energy compared with the binding energy of electrons bound to lattice atoms or ions or to impurity centres. This displacement constitutes polarization of the filled trap. The changes in dielectric constant and loss observed experimentally depend on the magnitude of the electron displacement and the phase relation of the displacement to the alternating applied field. Phase differences arise because of the finite relaxation times of filled electron traps which are of the order of  $10^{-7}$  sec. Thermoluminescence experiments and measurements of the corresponding dielectric changes show that the polarization and absorption of electron traps containing electrons vary rapidly with the temperature. It is found by experiment that electrons moving in the conduction energy levels of the phosphor crystals make negligible contributions to the dielectric effects compared with those due to filled electron traps. The spectral sensitivity of the dielectric changes has a maximum in the region of 0.35–0.41  $\mu$ . The long wave-length limit of the dielectric phenomenon is dependent upon the particular constitution of each specimen but is the same as that for the production of photoconductivity. These studies provide new and significant additions to the knowledge of the properties of electron traps in phosphors.



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The effect of temperature on the intensity of X-ray reflexion.

By E. A. OWEN AND R. W. WILLIAMS

*University College of North Wales, Bangor*

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The effect of temperature on the intensity of X-ray reflexion by gold, copper and aluminium has been studied by making microphotometric measurements on lines in X-ray structure spectra obtained with powder specimens in a Debye-Scherrer camera. A special method was employed to make cylindrical powder specimens, 0.8 mm. in diameter, which held together without adhesive and were free from a core of foreign material. The primary beam was standardized by means of a flat-plate X-ray camera, furnished with a plate of powdered gold which provided a spectrum whose lines could be accurately measured. The powder specimen under investigation was maintained *in vacuo* at temperatures ranging up to about 900° K, and its temperature estimated from lattice parameter measurements.

The observed fall in intensity of X-ray reflexion by gold and copper as the temperature is raised up to about 900° K can be accounted for if the characteristic temperature varies with temperature in accordance with the relation  $\Theta_T = \Theta_1[1 - \alpha\gamma(T - T_1)]$ , where  $\Theta_T$  and  $\Theta_1$  are the characteristic temperatures at temperatures  $T$  and  $T_1$ ,  $\alpha$  is the cubical coefficient of thermal expansion and  $\gamma$  is the Grüneisen constant. This relation is found to hold also for aluminium up to about 600° K. Beyond 600° K the fall of intensity exceeds that to be expected from the above relation, and it is suggested that another factor becomes prominent in the case of aluminium at the higher temperatures.

The characteristic temperatures of gold, copper and aluminium now found by X-ray measurement at different temperatures, agree with the values obtained at those temperatures by specific heat and electrical conductivity methods.