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LUMINESCENT MATERIALS

BY

G. F. J. GARLICK

UNIVERSITY OF BIRMINGHAM

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PREFACE

THERE has been a rapid growth of interest in luminescence and its associated phenomena during the last few years but very few attempts have been made to present a coordinated account of even a portion of the subject. In writing the present book one of the chief objects has been to remedy this deficiency with respect to luminescence in solids. Attention is therefore confined to the solid state, though some account of fluorescence in solution is given in Chapter VIII. It was thought necessary to include a chapter which would discuss investigations of luminescence in organic systems, in particular the quenching and polarization of fluorescence and the transfer and storage of energy in organic crystals, such as some of the aromatic hydrocarbons. The main body of the text has, however, been devoted to those aspects of luminescence in inorganic solids which have been popular since the first systematic studies at the end of the nineteenth century. These include phosphorescence, thermoluminescence, the electrical behaviour of phosphors, and the effects of infra-red radiation in releasing stored energy. Many of these effects have been brought to the fore by commercial interest in luminescent materials but there is a growing realization that future elucidation of the fundamental processes involved will necessitate investigation of solids of simple constitution having no immediate practical value. Happily, this position has been realized by many industrial research laboratories and it is hoped that the present text will be of value to those having to readjust their attitude to luminescence research.

Much of the development of a quantitative interpretation of phosphorescence, thermoluminescence, and related phenomena in solids has been due to the work of J. T. Randall and his associates in this laboratory. My own approach to the subject has naturally been coloured by this background which still has a valuable influence on our present research. It may now be said that luminescence constitutes one of the most fertile fields

of investigation for those interested in solid-state physics. It is my hope that this contribution to the existing literature of the subject will further stimulate the rigorous approach now being made to its phenomena.

In conclusion, I wish to thank all those who have given me valuable help in the preparation of this book; in particular I wish to thank Professor N. F. Mott, F.R.S., for his editorial and personal interest, Dr. E. J. Bowen, F.R.S., for his advice on some aspects of Chapter VIII, and Mr. D. E. Mason and Mr. C. Bull for their help in reading the manuscript and proofs.

G. F. J. G.

PHYSICS DEPT.,
UNIVERSITY OF BIRMINGHAM,
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CHAPTER I

GENERAL INTRODUCTION

1. The concepts of luminescence

LUMINESCENCE is a general term which includes the many phenomena involving the absorption of energy by a substance and its re-emission as visible or near visible radiation. The term was first defined as such by Wiedemann [1] in 1889. Luminescence is, however, to be distinguished from thermal radiation since the phenomenon does not follow Kirchhoff's law for absorption and emission [2]. The energy transmitted to the material and giving rise to luminescence may be that of ultra-violet light, X-rays, cathode rays, or other corpuscular radiation or it may be due to chemical action. If luminescence is produced by absorption of electromagnetic radiation, then it is called *photoluminescence*. Other prefixes are usually self-explanatory; for example, *cathodoluminescence* produced by electron bombardment, *triboluminescence* due to mechanical strain and fracture, *chemiluminescence* due to chemical reaction. In this book our main concern will be with photoluminescence and its associated phenomena.

When luminescent materials are excited by radiation or cathode rays, emission occurs during the excitation and, in the case of some solids, for considerable periods after the excitation has ceased. The emission during excitation is generally referred to as *fluorescence*, while that which persists after excitation has ceased is known as *phosphorescence* or *afterglow*. The definition of these terms has been the subject of much controversy in the past. They are defined above in a simple manner which appears to be the most convenient for describing types of emission, both of which can arise from the same physical processes. No discussion of the merits of such definitions will be given here; some of the opinions on the matter have already been published [3]. In order to provide a line of demarcation the limit for fluorescence is here fixed at 10^{-8} sec. after excitation has ceased, this being of the order of the relaxation time of an

isolated gaseous ion. Phosphorescence of duration greater than a microsecond has never been observed in the normal liquid state but longer persistence can occur in very viscous media [4, 5]. Phosphorescence of long duration is usually confined to crystalline solids of inorganic constitution whose luminescence is due to *activation* by traces of a specific impurity. Such solids require special preparation, the inclusion of the impurity being effected by heat treatment. A well-known example is zinc sulphide activated by copper which shows a green afterglow lasting for an hour or so. Such solids are called *phosphors*: this term is often loosely applied to all materials which are synthesized by heat treatment and become luminescent. In general, solids which show phosphorescence of long duration also show emission when warmed after excitation. This phenomenon is known as *thermoluminescence*. Thermoluminescence may be exhibited by other phosphors with afterglow of shorter duration if they are excited at a sufficiently low temperature and then allowed to warm up in the dark. The phenomenon is well known in some natural minerals [6]. It has been used in recent researches (see Chap. II) to investigate the nature of the processes by which energy is stored in phosphors [7].

Most substances, both liquids and solids, are not luminescent to any noticeable degree for normal physical conditions of excitation. Materials described here as luminescent are substances whose luminescence emission is easily observed. Such materials are not, as a rule, highly coloured when viewed in normal daylight or by the light of a tungsten lamp; they have thus no strong absorption bands in the visible spectral region, and in particular, in the region of their own emission spectra.

One of the most important aims of a theory of luminescence is to understand the various ways in which absorbed energy can be dissipated in a substance; another is the determination of the conditions necessary for such energy to be re-emitted as luminescence. In the case of photoluminescence only a few ways are known in which a substance can get rid of its absorbed energy:

(*a*) All the energy may be used up in increasing the thermal motion of the atoms of the substance.

(*b*) Some of the energy may be used in photochemical reactions.

(*c*) Absorption of energy may result in the emission of photoelectrons.

(*d*) Absorption may give rise to luminescence emission.

In most cases some of the incident energy is lost to the emission by thermal dissipation before emission occurs.

In general, non-luminescent substances must convert the absorbed energy into heat. In luminescent materials there is often a photochemical reaction due to the energy absorption (see Chap. VIII).

2. The general conditions for luminescence

The emission of luminescence by a substance will depend on the effectiveness with which the absorbed energy can be protected from loss in other ways, particularly by thermal dissipation. Unless the energy is absorbed and re-emitted at the same place in the material, there must also be an efficient means by which energy can be transported, without serious loss, from its place of absorption to the systems in which emission occurs. The latter systems are given the term *luminescence centres*. In such centres the electron transitions responsible for the luminescence emission can take place with a minimum of disturbance from the surroundings. Any such disturbance will increase the probability of a non-radiative dissipation of energy, that is, *quenching* of the emission is more likely to occur. A theoretical model which shows the conditions for luminescence emission and for quenching has been proposed by Seitz [8] and by von Hippel [9]. The model is applicable to all luminescent materials, although the nature of the emitting centres in these may be widely different. Weiss [10] has considered its application to organic substances. The treatment adopted is to plot graphically the potential energies of the normal and excited states of the luminescence centre against some configurational coordinate of the centre (x). Such a potential energy diagram is shown in

Figs. 1 and 2. Fig. 1 is for an emitting centre and will be considered first. The curves for both the normal and excited states of the centre possess minima. Thus, in both cases the system will take up a stable energy position. At all temperatures above absolute zero the presence of thermal vibrations will cause displacements from the minimum potential energy

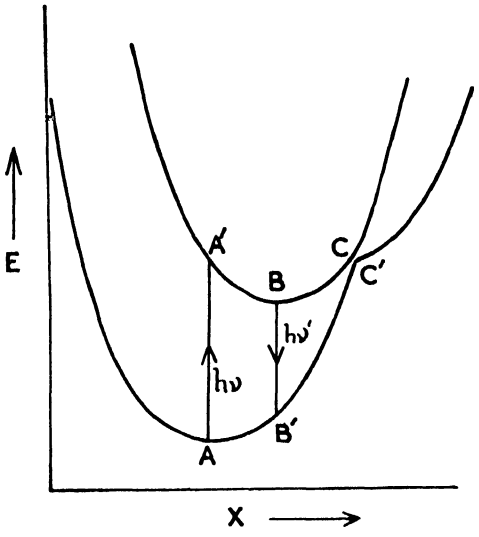

FIG. 1.

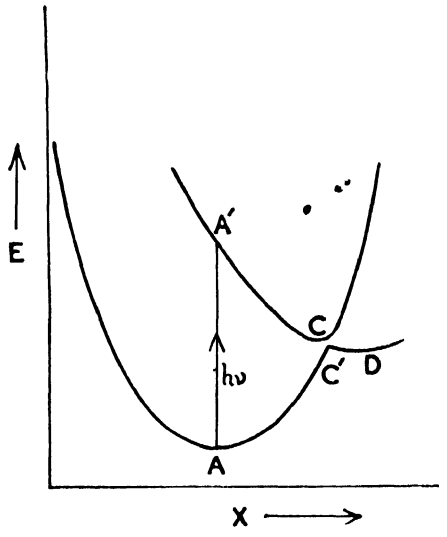

FIG. 2.

FIG. 1. Energy-configuration conditions for luminescence in an atomic centre after energy absorption. AA', absorption act; BB', luminescence transition; CC', radiationless transition.

FIG. 2. Energy-configuration conditions for radiationless dissipation of absorbed energy in an atomic centre. AA', absorption act; CC', radiationless transition; D, metastable state.

positions of the order of kT in magnitude. In general, the minima A and B will not have the same coordinate x because of the different interaction of the centre with its surroundings in each state. Seitz [11] has considered this interaction effect in detail for the thallium-activated alkali halide phosphors (see § 2*a*, Chap. III).

In order to apply this model to the explanation of luminescence emission, an important rule known as the Franck–Condon principle is introduced. This states that electronic transitions involved in absorption or emission take place in a very short time-interval compared with that required for the atoms or ions of the centre to move appreciably. Thus, all such

transitions are represented by vertical lines in Figs. 1 and 2. Direct absorption of energy in the centre will give rise to the transition AA' (quantum $h\nu$ absorbed) of Fig. 1. After this transition the system will not be in a state of minimum potential energy and so will move into the stable configuration B. The excess energy is dissipated thermally to the surrounding material. The time spent in this excited state depends upon the probability of the optical transition BB' which gives rise to the luminescence emission ($h\nu'$). When this transition occurs the centre is once more in its ground state and returns to the stable state A from B' with further non-radiative loss of energy. From this model it is evident that the emitted quantum is never greater than the absorbed quantum; the model thus provides an explanation of the classical Stokes's law.

We now consider the case when absorption of energy is not followed by luminescence emission, so that complete thermal dissipation of the energy occurs. The potential energy curves of Fig. 2 have been suggested to explain this case. Absorption of radiation leads to the transition AA' and the centre then adjusts itself to reach a stable configuration (D). This configuration D will be at or beyond the intersection of the two curves. Actual intersection or crossing of the curves for the normal and excited states respectively does not occur unless the states are non-combining. Thus, in moving to the position D there is a high probability that the centre may make a transition to the ground state by emission of a very small quantum of radiation at the position CC'. This complete cycle of excitation and energy loss (AA'–CC'–$C'A$) involves almost complete thermal dissipation of the absorbed energy. If the minimum D is reached (when its position is beyond C), then the lifetime of the centre in the excited state will be prolonged and its return to the ground state will be strongly dependent upon temperature. Evidence of these metastable states in non-luminescent solids is difficult to obtain. However, they occur in some types of luminescence centre as described in the next few chapters; they are responsible for the phosphorescence of the thallium-activated alkali halides [11].

Reverting to the model for luminescence centres, it is possible to use this to show the way in which the luminescence efficiency of the centre varies with the temperature. The efficiency of a centre may be defined in different ways, namely as *quantum efficiency* or *quantum yield* or as an *overall energy conversion efficiency*. The quantum efficiency is the ratio of the number of emitted quanta to the number of absorbed quanta; the conversion efficiency is the ratio of the total energy emitted to the total absorbed. In the following derivation the distinction is not very important. At all temperatures above absolute zero the centre will not be in its minimum potential energy state but will deviate from it by energy of the order of kT. Thus, when in the excited state, there is a finite probability that the system will reach the ground state by the path $BCC'A$. If the point C is at an energy E above B, then this probability is given by $b\exp(-E/kT)$, where b is a constant, k is Boltzmann's constant, and T is the absolute temperature. If the probability of the optical transition BB' is p, then the luminescence efficiency η will be given by

$$\eta = \frac{p}{\{p+b\exp(-E/kT)\}} = \frac{1}{\{1+c\exp(-E/kT)\}}, \qquad (1.1)$$

where c is given by b/p. The graphical form of this relation between luminescence efficiency and temperature is given in Fig. 3 for two different values of c, E remaining constant. The curve C is that measured experimentally for manganese luminescence centres in zinc sulphide when the excitation is confined to the centres. This efficiency will be referred to as the *intrinsic* efficiency to distinguish it from the luminescence efficiency for phosphors which show photoconductivity, and in which the movement and loss of electrons in the matrix lattice also affects the probability of non-radiative return to the ground states of the centres. The intrinsic efficiency, in contrast to the latter efficiency, is independent of the excitation intensity. The above expression for its variation with temperature was first derived by Mott and Gurney [12].

The qualitative agreement of equation 1.1 with experiment

has been shown by Randall [13]; many substances which are not luminescent at room temperature become so when the temperature is lowered. It has also been shown in a qualitative manner that the absorption and emission spectra become broader as the temperature is raised.

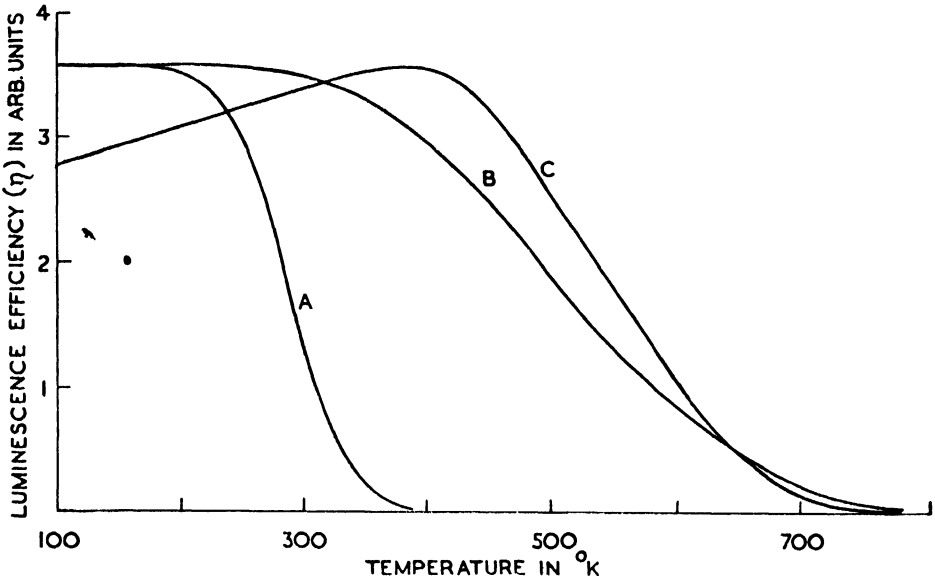

FIG. 3. Variation of luminescence efficiency (η) with temperature (T). *A*, theoretical curve from eqn. 1.1, $c = 10^7$; $E = 0{\cdot}4$ eV. *B*, theoretical curve from eqn. 1.1, $c = 10^4$; $E = 0{\cdot}4$ eV. *C*, experimental curve for centre process in ZnS—Mn phosphor (4,358 A) radiation.

3. The structure of luminescence centres in some materials

The conditions necessary for the emission of luminescence from a substance may be demonstrated by some experimental examples of luminescence centres in solids. In most inorganic phosphors the centres are usually formed by the small amounts of specific impurities present. Only a few solids can be said to be luminescent in the pure state: in many of them an excess of one constituent of their crystal lattice, for example, excess zinc in zinc sulphide, is necessary as an activating system for luminescence. Randall [13] has given a list of solids which show luminescence in the pure state, that is, the emission is not diminished by repeated purification. This is given in Table I of Chapter III. These solids include the manganese

halides, uranyl salts, platinocyanides, and salts of some rare earths.

With the exception of the iodide, the manganese halides luminesce when in the dehydrated form and the emission is due to the doubly ionized manganese ions of the lattice. Manganese is one of the most important activating impurities in many different synthesized, inorganic phosphors, notably zinc sulphide and zinc silicate phosphors. Absorption measurements on the manganese halides have been made by Gielessen [14], and Randall [15] has studied their emission spectra. The latter are shown in Fig. 4 By comparison of the frequencies of the absorption and emission spectra of the manganese ion; Randall has assumed that the configuration responsible for luminescence transitions in these ions is that denoted by $3d^3$—$4s^2$. From more extensive considerations Kröger [16] assumes that the configuration d^5 of the outer electrons represents the ground state of the manganese centres. In order to appreciate the arguments of Kröger, it must be pointed out that the emission spectra of the manganese halides consist of a broad band which is characteristic of transitions disturbed by the thermal motion of the environment. On the other hand, the emission spectra of the luminescence of rare-earth salts consist of sharp lines, characteristic of transitions within well-shielded electron shells of these ions. The emission spectrum of ruby consists of two sharp lines due to transitions within the chromium ions forming the impurity in the aluminium oxide crystal: this phosphor has been studied in some detail by Thosar [17] in recent years; earlier studies were due to Deutschbein [18]. Manganese contains an incomplete electron shell as in the case of the rare earths, but in the latter case this shell is well protected by the outer shells. Chromium, which is similar to manganese in this respect, gives sharper emission characteristics in ruby because it occupies a highly symmetrical position in the crystal by replacing aluminium. The energy states of the ion are also split by the action of the aluminium oxide lattice field (Stark effect). Reverting to the case of manganese ions, Kröger points out that for the Mn^{++} ion the d-shell is associated with the outer orbits

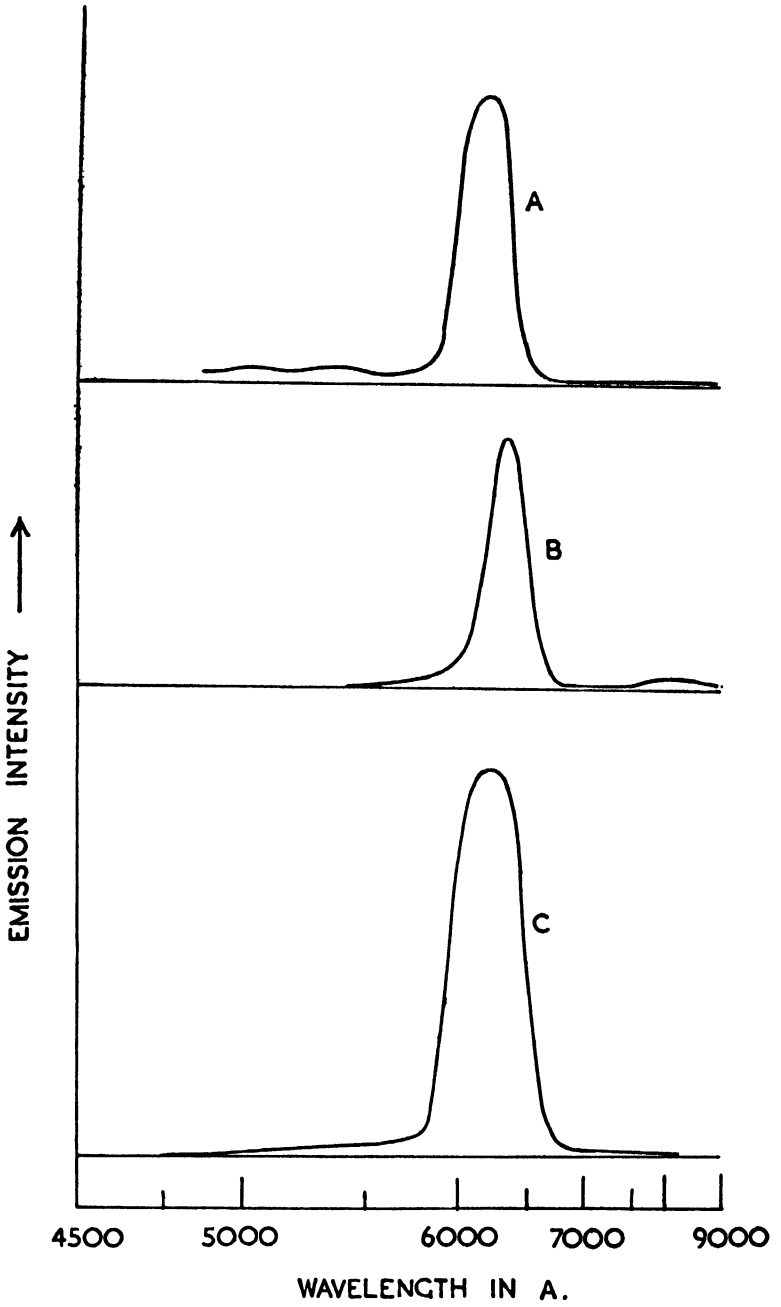

FIG. 4. Luminescence emission spectra of manganese halides at 90° K. (3,650 A excitation) (Randall). *A*, manganous fluoride; *B*, anhydrous manganous bromide; *C*, anhydrous manganous chloride.

and is effective in absorption and emission. Both the sharp-line absorption and the broad-band emission are due to transitions between states with the same principal quantum number.

The existence of inner, incomplete electron shells in an ion is very favourable to luminescence transitions. It has been shown by Peierls [19] that if absorption is confined to the incomplete shell, the shielding by outer shells will be very effective and the vibrational loss of the absorbed energy will be very small. This explains in a qualitative way the discrete nature of the luminescence spectra of the rare-earth salts when

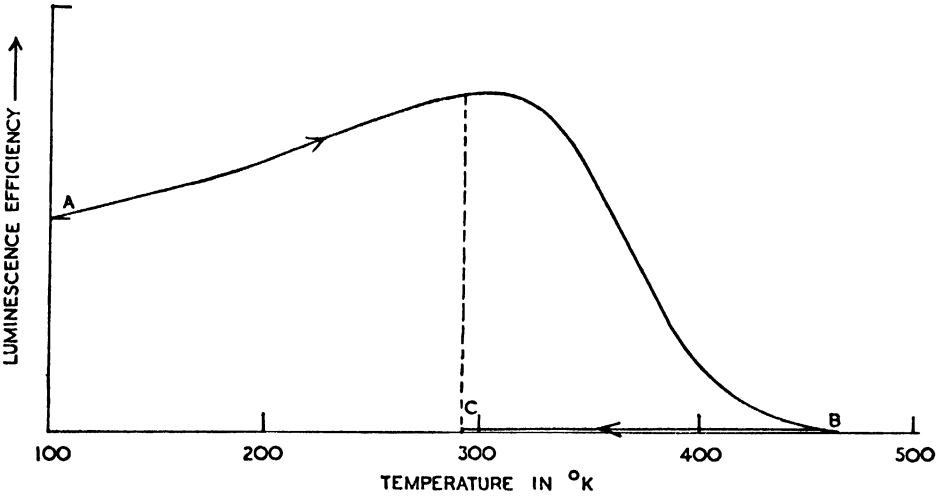

FIG. 5. Decrease in luminescence efficiency due to dehydration by warming of ammonium uranyl phosphate (3,650 A excitation). *AB*, warming curve. *BC*, cooling curve after dehydration.

compared with the band spectra of manganese halides. Thus, the surrounding lattice will have an effect on the emission band of manganese-activated phosphors; for example, the luminescence of manganese in zinc sulphide is orange but in normal zinc silicate it is green.

In luminescent uranyl salts and the platinocyanides the luminescence centres are not due to single atoms or ions but to larger systems, namely coordination groups. These groups provide the necessary shielding for the transition levels [13]. The platinocyanides are fluorescent both in the solid state and in solution, the platinum coordination group being the luminescence centre. The UO_2 coordination group forms the centre in the uranyl salts, the shielding of the group being due to water molecules [13]. This is shown to be so by the very large drop in luminescence efficiency when water is removed by dehydration.

Fig. 5 shows how the efficiency falls with increase in temperature, water being removed by the warming process. The efficiency does not return to its former value on cooling, as expected if it followed the form of equation 1.1; its original value is only reached when water is again added. Fig. 6 shows the complex emission spectrum of a uranyl salt. It has a vibrational structure characteristic of a molecular system.

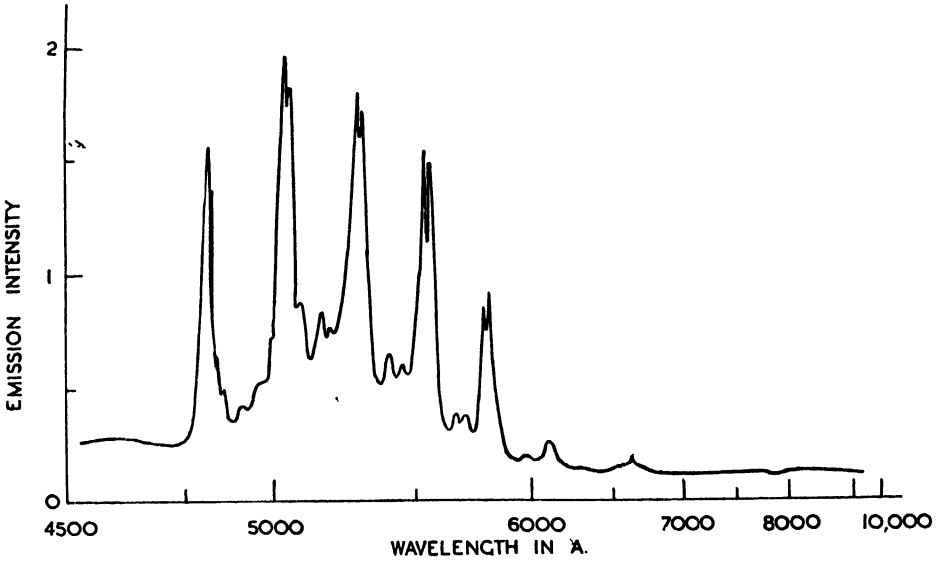

FIG. 6. Luminescence spectrum of uranyl nitrate (3,650 A excitation) (Randall).

From the few examples cited above it is evident that when the luminescence process is confined to the emission centres it is capable of relatively precise theoretical treatment. However, in most luminescent solids the centres are by no means well defined. This is shown by the broad structureless character of the emission spectra of zinc sulphide phosphors when activated by copper, silver, and even manganese. These are given in Fig. 7. With the exception of manganese, these activators have no incomplete, shielded electron shells favourable to luminescence, and so the centre must be formed by a suitable arrangement of the impurity ion and the surrounding lattice ions. As we shall show later, phosphors with such centres are usually quite different in their behaviour from those activated by rare earths or other well-defined impurity centres. The

emission spectra of zinc sulphide phosphors are often several hundreds of angstrom units in width. The emission is markedly dependent upon the surrounding lattice and on the presence of very small traces of deleterious impurities which suppress it. For example, a few parts in a million of nickel present will greatly diminish the luminescence of zinc sulphide. In these

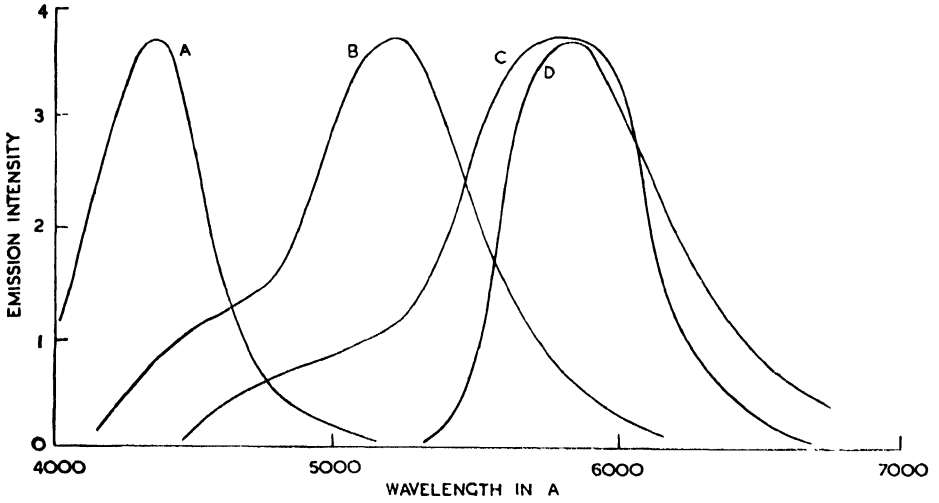

FIG. 7. Luminescence spectra of some conventional zinc sulphide phosphors with different activating impurities. *A*, ZnS—Ag; *B*, ZnS—Cu; *C*, ZnS—CdS—Cu; *D*, ZnS—Mn.

phosphors the fluorescence and phosphorescence processes are very dependent on the activating impurities and on the matrix material.

4. The scope of the text

The preceding sections have given a general introduction to luminescence in solids by considering the essential conditions for its occurrence. The chapters which follow deal in some detail with specific aspects of the phenomenon which have received most attention in recent studies. The account given is not intended to include all published work; it attempts rather to stress the more important theoretical and experimental investigations of fundamental processes. The chief phenomena of interest in phosphors of inorganic type have been the phosphorescence emission and the related thermoluminescence and electrical changes. The emission due to electron excitation has received much attention because it has a practical importance in the

development of phosphors for cathode-ray tubes used in television receivers. In the organic field interest has been centred in the relation of luminescence to molecular structure and to photochemical action; both the liquid and solid states have been studied in this respect.

In the remaining sections of this chapter we consider the historical development of luminescence studies; in particular we consider the theoretical advances with respect to phosphorescence.

5. The historical development of luminescence research

A more detailed idea of the state of the subject before 1937 can be obtained from the references given at the end of the chapter. In brief, the systematic study of luminescence began with the work of Becquerel [20] in the nineteenth century. He distinguished two types of decay process for phosphorescence; the simplest type is that in which the intensity of the emission decays exponentially with time after excitation has ceased. The kinetics of the decay are similar to those of a monomolecular chemical reaction. The other type of decay is that in which the emission intensity decreases as a hyperbolic function of the decay time. Its kinetics were assumed to be similar to those of a bimolecular chemical process. In the early part of this century Lenard and his school recorded additional observations of associated phenomena such as photoconductivity and dielectric changes during luminescence [21]. However, the studies of the Lenard school do not lend themselves to detailed interpretation or to repetition, and theoretical models of adequate form were not available until the late thirties. Some noteworthy studies of photoconductivity in zinc sulphide phosphors were made by Gudden and Pohl in the early nineteen-twenties [22]. An extensive classification of luminescent materials was made by Nichols, Howes, and Wilbur in the United States of America at about the same time [23].

6. Early theories of phosphorescence

The exponential decay of phosphorescence with time which is found in some phosphors can be explained in terms of the

intrinsic luminescence centre processes. The duration of a centre in the excited state depends upon the transition probability p. If at any time t, n centres are excited, then the phosphorescence intensity (I_t) at that time will be given by the equations

$$I_t = -dn/dt = pn, \tag{1.2}$$

since it is proportional to the rate at which centres return to normal states and therefore to the number excited and to their probability of return. Solution of the above equation gives

$$I_t = I_0 \exp(-pt), \tag{1.3}$$

where I_0 is the emission intensity at the beginning of the decay. The general characteristics of this type of decay may be summarized as follows [24]:

(*a*) The phosphorescence intensity decreases exponentially with time.

(*b*) The rate of the decay depends only upon the transition probability p.

(*c*) The decay rate is independent of the temperature of the phosphor and of the excitation conditions, that is the intensity and duration of excitation.

For some luminescence centres the transition probability may be quite low. This is because, in a shielded centre, transitions which are normally forbidden may occur. Values of p as low as 0·3 sec.$^{-1}$ have been measured for europium ions in strontium silicate (see Chap. III, § 2*c*). Typical phosphorescence decays of this simple type are shown in Fig. 8; the logarithmic ordinate is used to indicate the form of the decay. The electron transitions having these low probabilities must take place in systems of quadripole or multipole character since a simple dipole system has values for p of the order of 10^8 sec.$^{-1}$ (see Chap. VIII, § 4).

The observation of long afterglow in zinc sulphide and alkaline earth sulphide phosphors which decay hyperbolically with time did not receive a satisfactory theoretical interpretation by early workers. Since in most cases the luminescence was accompanied by photoconductivity, it was assumed that the

electrons normally confined to the emission centres were released from them during excitation. Thus the phosphorescence of these solids was considered to be due to the relatively slow rate of recombination of the freed electrons with centres. If n centres are excited, then there will also be n free electrons. If

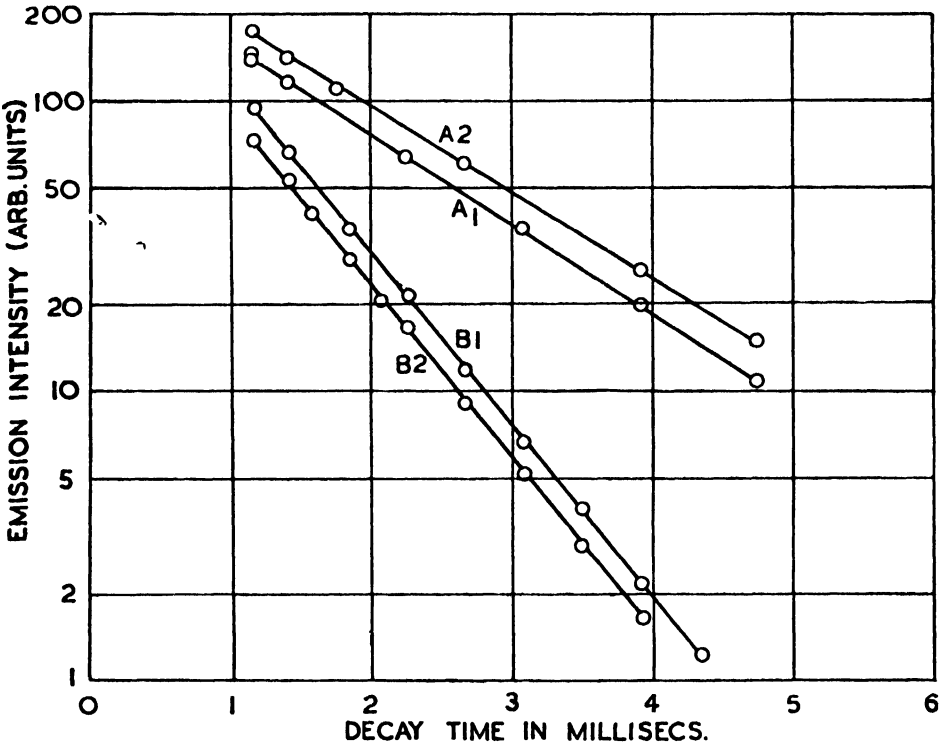

FIG. 8. Phosphorescence decay of exponential form due to optical transitions within luminescence centres of uranyl salts. (Curves 1 are for ten times exciting intensity of curves 2.) *A*, ammonium uranyl phosphate; *B*, uranyl nitrate. (Randall and Wilkins.)

β is the probability of recombination, then the decay equations for this process will be as follows:

$$I_t = -dn/dt = \beta n^2, \tag{1.4}$$

which on solution give

$$I_t = I_0/\{1+(I_0\beta)^{\frac{1}{2}}t\}^2, \tag{1.5}$$

where I_0, the initial intensity of emission, is given by βn_0^2; n_0 is the number of centres initially excited. The constant β will be given by the product of the capture cross-section of the empty luminescence centre and the mean velocity of a freed

electron in the matrix crystal. Since this velocity is proportional to the square root of the temperature, we should expect the phosphorescence decay to depend on the temperature in a regular way. Such a decay process is generally referred to as bimolecular, and its characteristics may be summarized thus [24]:

(*a*) The phosphorescence decreases hyperbolically with time and at large decay times is proportional to the inverse square of the decay time.

(*b*) The form of the decay depends only on the initial value of the intensity I_0 and is independent of the excitation conditions if I_0 remains the same.

(*c*) The rapidity of the decay increases steadily with temperature.

It is true to say that there are no phosphors with such phosphorescence characteristics. There are also some theoretical weaknesses in the assumptions made for the derivation of this bimolecular decay law. In order to explain the long duration of decay, the value of the capture cross-section of centres would have to be very small and electrons would thus have to remain in the free state in the phosphor for long times. Further, from experiment it is found that the power of the denominator of equation 1.5 is not usually equal to 2 but is generally less than 2. The decay is also found to vary in an irregular manner with the temperature and is not independent of the conditions of excitation. A critical discussion of the bimolecular decay hypothesis has been given by Garlick and Wilkins [24].

Among other attempts to explain long afterglow in phosphors of the zinc sulphide type there is an empirical treatment due to Hopkinson and Jesty [25] which includes the following equation for the phosphorescence decay:

$$I_t = \frac{I_0}{\{1+(I_0/a)^{1/b}t\}^b}, \tag{1.6}$$

where a and b are constants. A few phosphors show such a decay characteristic at room temperature. For those given as examples the value of b is about 1·5. This empirical equation

is the solution of the following equations, which should be compared with equations 1.4 above:

$$I = -dn/dt = An^c, \tag{1.7}$$

where $A = a^{1/(1-b)}$ and $c = b/(b-1)$. For b equal to 1·5, c would be 3, and so the kinetics of the process appear to be more complex than those of a bimolecular reaction.

An interpretation of long afterglow in phosphors, which has since proved to be satisfactory, was made by Johnson [26] in terms of the modern wave-mechanical concept of crystalline solids. This qualitative theory emphasizes that the electrons freed from luminescence centres must be captured in metastable energy states in the crystal and that phosphorescence of long duration is due to the slow release of these electrons and their subsequent recombination with empty centres. Since then the theory has been developed to give quantitative agreement with experiment [7], as will be shown in the next few chapters.

7. References to general literature on luminescence

We conclude this chapter with a list of general works which describe the earlier studies of luminescence and its associated phenomena. The publication of Pringsheim and Vogel [2] has already been referred to.

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PRINGSHEIM, P. *Fluorescenz u. Phosphorescenz* (Berlin, 1928).
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CHAPTER II

MECHANISMS OF LUMINESCENCE IN CRYSTALLINE PHOSPHORS

We may distinguish three main stages of the luminescence process in crystalline solids:

(*a*) The initial act of absorption.
(*b*) The transport and storage of the absorbed energy.
(*c*) The release of the stored energy and the emission of luminescent radiation.

We have seen in Chapter I that all these stages may occur within the luminescence centres; in this case the mechanisms are more easily understood. However, in the general case, the luminescence process appears to involve motion of electrons in the matrix crystal between absorption and emission. Only a few phosphors are known in which the storage of energy takes place within well-defined emission centres; an example is thallium-activated potassium chloride, to be discussed in Chapter III. The luminescence characteristics of most impurity-activated phosphors depend as much on the matrix crystal as on the impurity. Such materials often show photoconductivity during the luminescence process, that is, electrons or other charge carriers are moving through the crystal. The theoretical model adopted to explain the characteristics of photoconducting phosphors was first put forward by Johnson [1] for zinc sulphide and zinc silicate phosphors. His treatment is based on the 'collective electron' theory for crystalline solids first developed by Bloch [2]. A brief discussion of this model provides an introduction to its development and modification in more recent studies.

1. The collective electron model of a crystalline insulator

The theory originally developed by Bloch has been adequately explained by various authors [3, 4, 5, 6]. It is sometimes known as the band or zone theory of solids. In an isolated atom the energy states for electrons consist of discrete levels separated

by regions of forbidden energies. The allowed states are defined by Schrödinger's equation. However, when atoms or ions are arranged in an orderly way, and in close proximity to each other to form a crystal, their levels are disturbed by

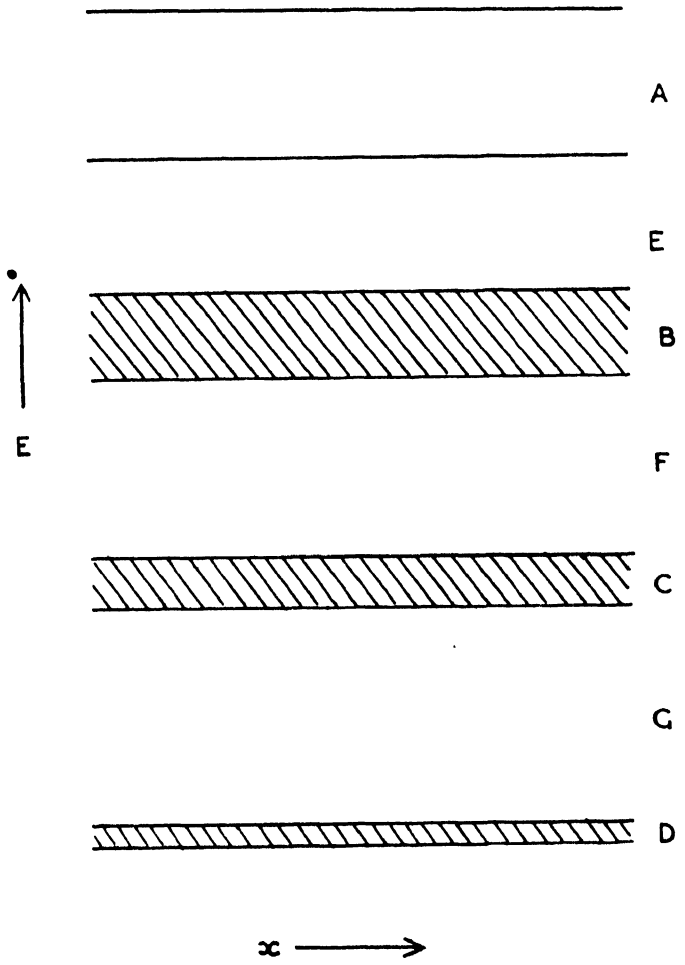


FIG. 9. Electron energy-band system for a perfect crystalline insulator. *A*, *B*, *C*, *D*, bands of permitted energy-levels; *A*, empty permitted band; *B*, *C*, *D*, occupied permitted levels; *E*, *F*, *G*, forbidden energy-bands.

mutual interaction. As a result, the discrete states of isolated atoms are now broadened into bands of allowed energy separated by bands of forbidden energy; these bands have a structure which may bear no resemblance to the arrangement of the original atomic levels. The energy-band system for an insulator is shown schematically in Fig. 9. The bands extend

throughout the crystal lattice so that electrons in them can move through the crystal without needing any activation energy to do so. In an insulator the allowed bands for electrons are either completely occupied by electrons or completely empty. When a field is applied to the crystal no current will flow, although electrons are free to move. This is because for every electron moving in one direction there will be another moving in the opposite direction to it. In order to contribute to a current in the crystal, electrons must be raised from a full band into a higher empty band. In an insulator the lowest empty band is usually several electron volts above the highest occupied band and so this process is not possible for normal field strengths. However, electrons may be raised into the unoccupied band by absorption by the crystal of radiation of suitable frequency. In phenomena such as photoconduction, luminescence, and the photographic process in silver halides, electrons make transitions between the highest filled band and the empty band immediately above it, which is known as the conduction band. The separation between the bands determines the maximum wave-length of the radiation which can be absorbed to effect these processes. The electrons which occupy the highest filled band are the valence electrons of the crystal atoms; in the alkali halides these electrons are those of the halide ions only. Electrons belonging to inner atomic levels can only take part in luminescence if they are first raised into the unoccupied band by the absorption of high-energy quanta, such as X-rays, or high-velocity particles.

In general the crystal lattice is not in the perfect state for which the model of Fig. 9 is true. Its periodicity is destroyed or disturbed by the presence of lattice defects, traces of impurities, or by lattice atoms in interstitial positions [6]. These non-periodic systems give rise to additional and usually discrete energy-levels for electrons, which may lie in the forbidden region between the highest filled band and the next unoccupied band. Because of their position they are of great importance in the luminescence process. Such levels are assumed to be provided by the activating impurity of a crystalline phosphor,

as shown in Fig. 10. They are shown as discrete levels in the figure and represent the normal and excited states of the impurity luminescence centre. Other lattice disturbances may provide extra levels for electrons lying just below the bottom of the conduction band. If these levels are normally unoccupied,

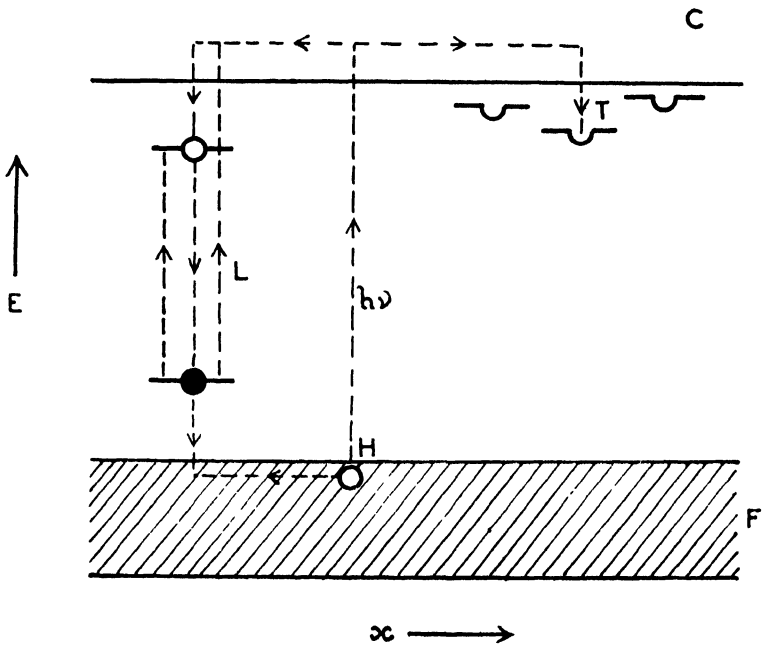


FIG. 10. Energy-level scheme for an impurity-activated crystalline phosphor. *C*, conduction band; *F*, filled band; *H*, positive hole; *L*, luminescence centre; *T*, electron traps.

then they can capture electrons which are moving through the conduction band. Because of this ability to capture electrons they are known as electron traps. A well-known example of a solid with such electron traps is that of an alkali halide crystal containing colour centres (*F* centres). These centres are electron traps formed by the lattice points from which negative ions are missing: the colour centre is formed when one of these defects captures an electron from the conduction band [6].

Having provided a short account of the general band theory for crystalline insulators, we may now consider its application to the explanation of luminescence processes in phosphors.

2. Absorption processes in crystalline phosphors

We consider the excitation of a phosphor by radiation lying in the ultra-violet or visible regions of the spectrum; excitation by cathode rays is considered in Chapter VII. As in the case of isolated atoms, the radiation is absorbed only if the resulting transitions for electrons are permitted. If the quantum energy is sufficiently large, then it may be absorbed by an atom in the crystal lattice. In this case an electron will be raised into the conduction band from the highest filled band as represented by the transition $h\nu$ of Fig. 10. The excited electron will now be free to move through the crystal under the influence of an applied electric field and so will contribute to conduction. The absorption bands due to such transitions of electrons are known as the fundamental absorption bands of the phosphor matrix. In most simple ionic solids they are situated in the ultra-violet or near visible regions of the spectrum. They occur at wavelengths below 2,000 A for the alkali halides. An electron which is removed from the filled band by absorption of radiation will leave behind a vacancy. This will behave as a positive hole and will be capable of moving through the lattice in an applied field. Such movement of positive holes can sometimes be detected in crystals since it affects the sign of the Hall coefficient.

Radiation which is not of sufficient energy to be absorbed by the matrix may be absorbed by the impurity centres. The resulting electron transition may then be either into an excited state of the centre or into the conduction levels. We thus expect to find additional absorption bands in phosphors due to the impurity activator: these bands will lie to the long wavelength side of the fundamental absorption bands. Absorption in them will give rise to photoconductivity if electrons are thereby freed from centres but the positive hole vacancies will not be free to move, except when electrons are raised into them from the filled band below. This is thought to happen in some phosphors and is discussed further in Chapter IV. In addition to absorption in the lattice leading to photoconduction and absorption in the impurity centres, a further possible process

must be mentioned. In alkali halide crystals absorption occurs for radiation lying to the long wave-length side of the fundamental absorption but no photoconduction is produced, although absorption is in the matrix [7]. It has been assumed that such absorption creates excited electrons which are still bound to their positive holes. The system thus formed by an electron and a positive hole moving in one another's field can move through the crystal but it will have no net charge. It has been called an *exciton* by Frenkel [8]. Its existence in phosphors has not been demonstrated by experiment, but some workers have assumed that it plays a part in the luminescence process.

We may now summarize the absorption processes possible in a crystalline phosphor activated by impurity:

(*a*) Absorption bands will exist which are characteristic of the phosphor matrix.

(*b*) Other absorption bands will be present which are dependent both on the matrix and on the activating impurity.

(*c*) Absorption bands may occur at longer wave-lengths than those of the first two systems and will be due to electron transitions confined to the impurity centres.

(*d*) Lattice defects and minor disturbances of the lattice may give rise to absorption at long wave-lengths when they are occupied by electrons.

The validity of the above theoretical model can be shown by a few examples taken from well-known classes of crystalline phosphors.

i. *Absorption characteristics of manganese-activated zinc sulphide phosphors*

Fig. 11 is a schematic diagram of the absorption spectrum of manganese-activated zinc sulphide (manganese content 2 per cent.). It is due to Kröger [9]. The limit of the fundamental absorption is at about 3,400 A [10]. To the long wave-length side of this limit a structureless tail extends, which is believed to correspond to the process of section (*b*) above; in this region

absorption gives rise to photoconductivity, as would be expected. This hypothesis is also supported by phosphorescence measurements [11]. Beyond 4,000 A a series of absorption bands occurs which is characteristic of the manganese ions

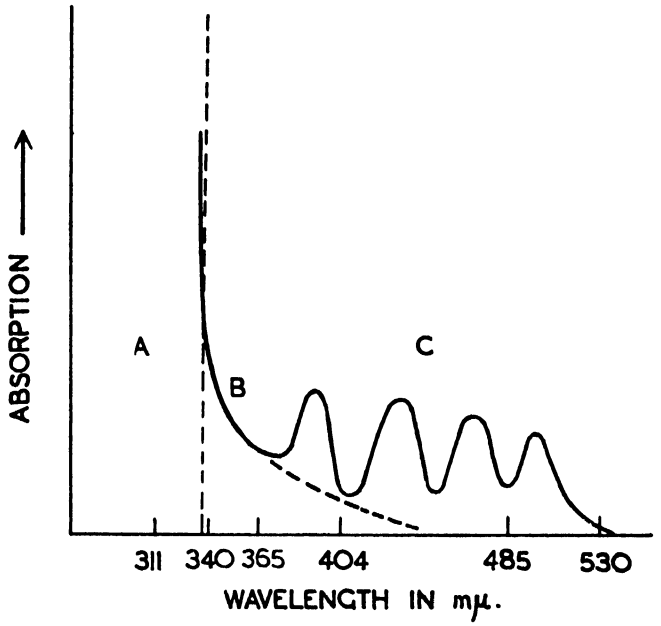


FIG. 11. Absorption spectrum of a ZnS—Mn (2 per cent.) phosphor. (Kröger.) (Wave-lengths are those of mercury lines.) *A*, absorption due to ZnS lattice; *B*, absorption due to ZnS—MnS; *C*, absorption due to manganese ion Mn^{2+} levels.

alone; no photoconductivity is observed for absorption in these bands, which suggests they correspond to those of section (*c*) above.

ii. *Absorption characteristics of copper-activated zinc sulphide*

Fig. 12 gives Gisolf's [10] measurements for copper-activated zinc sulphide. The impurity concentration is only about 0·01 per cent. At short wave-lengths the fundamental absorption occurs with a pronounced tail at its long wave-length limit which is dependent on the impurity and on the matrix. However, there is no evidence of a process of type (*c*) in this phosphor. This would be expected as the copper ion does not, in itself, possess suitable characteristics for luminescence. This indicates that the luminescence centre is formed by the copper ion and

the surrounding lattice ions. Further discussion of this type of centre is given in later chapters.

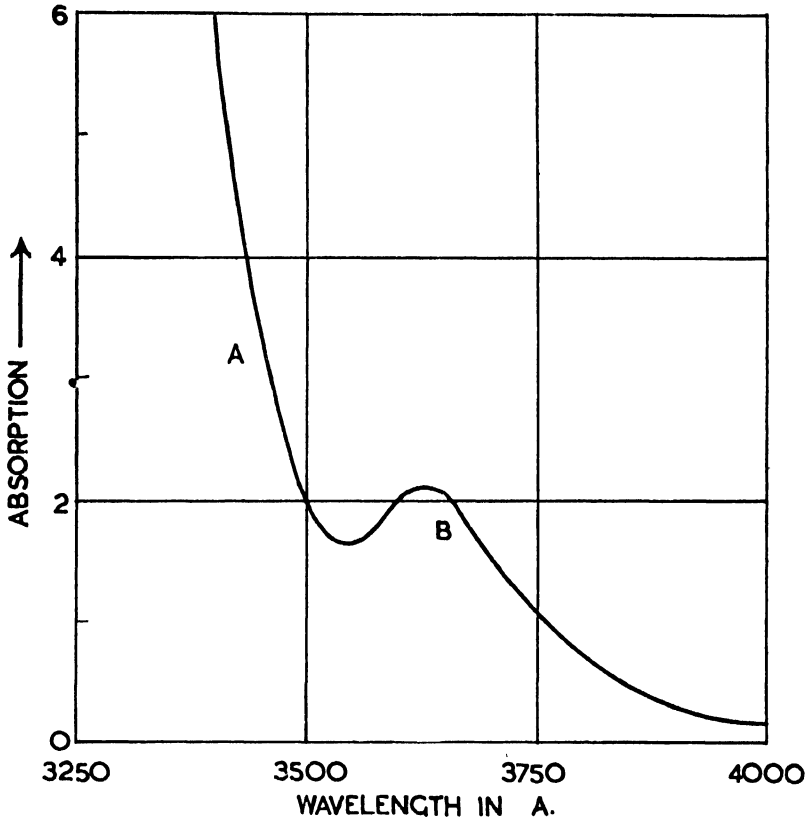


FIG. 12. Absorption characteristics of a ZnS—Cu phosphor. (Gisolf.) *A*, absorption due to ZnS lattice; *B*, absorption due to Cu centres.

iii. *The absorption of zinc-cadmium sulphide phosphors*

The energy separation between the filled band and the conduction band of a crystal will be altered by a change in the lattice dimensions. This occurs when the zinc sulphide phosphor is modified by the introduction of cadmium sulphide which forms mixed crystals with it. The addition of cadmium sulphide causes the separation between the bands to decrease and therefore causes the fundamental absorption limit to move to longer wave-lengths. Fig. 13 gives Gisolf's measurements of the absorption-edge shift with increase in cadmium content. The increase in wave-length of the absorption edge varies linearly with the cadmium content. The emission colour for self-activated, and for copper- and silver-activated phosphors,

changes in a similar manner since the emission centres are dependent for their formation on the matrix.

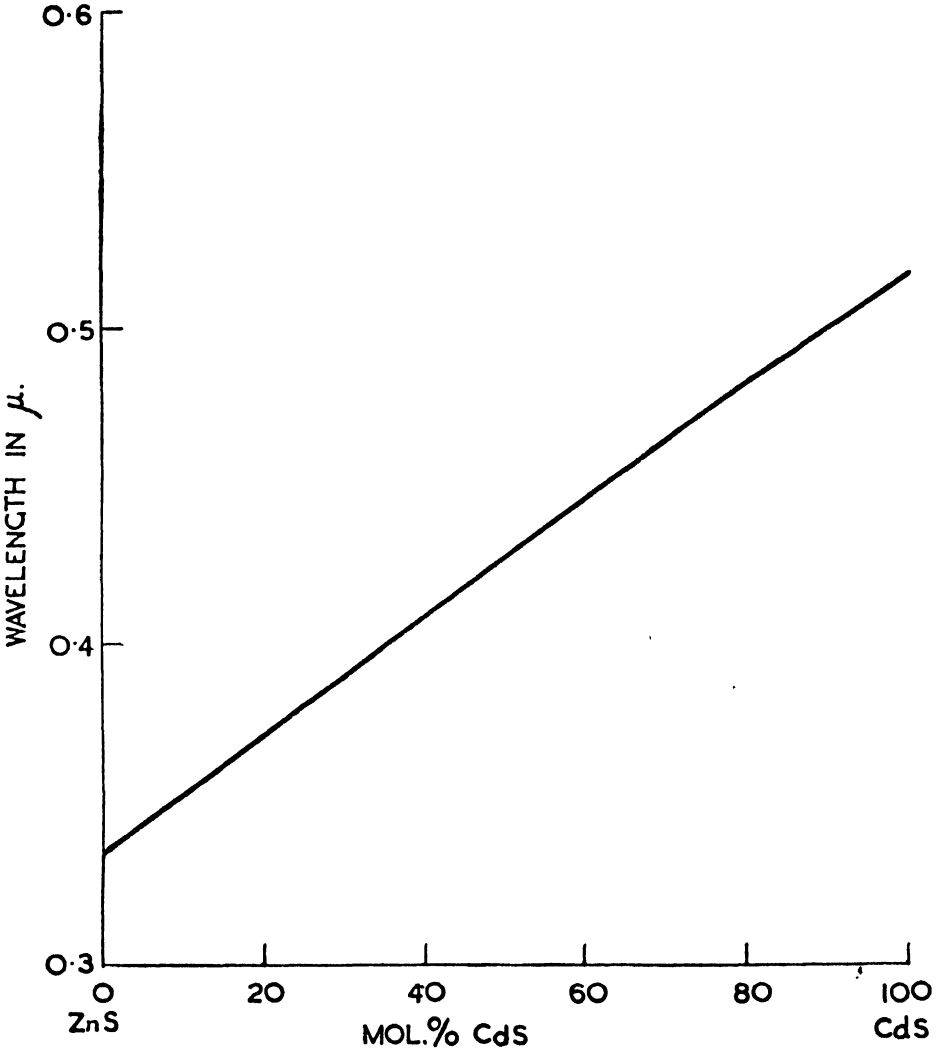


FIG. 13. Shift of absorption edge with per cent. CdS in the mixed crystal system ZnS—CdS. (Gisolf.)

iv. *Absorption characteristics of manganese-activated zinc silicate phosphors*

The absorption edge of zinc silicate crystals is situated below 2,250 A, but addition of manganese impurity causes it to move to longer wave-lengths. In addition the characteristic bands due to the manganese itself appear. The shift in the absorption edge is to be expected since the manganese replaces zinc in the

lattice and a mixed zinc-manganese silicate crystal is formed. Fig. 14 shows the absorption spectra of zinc silicate phosphors with different manganese contents, as measured by Kröger [12].

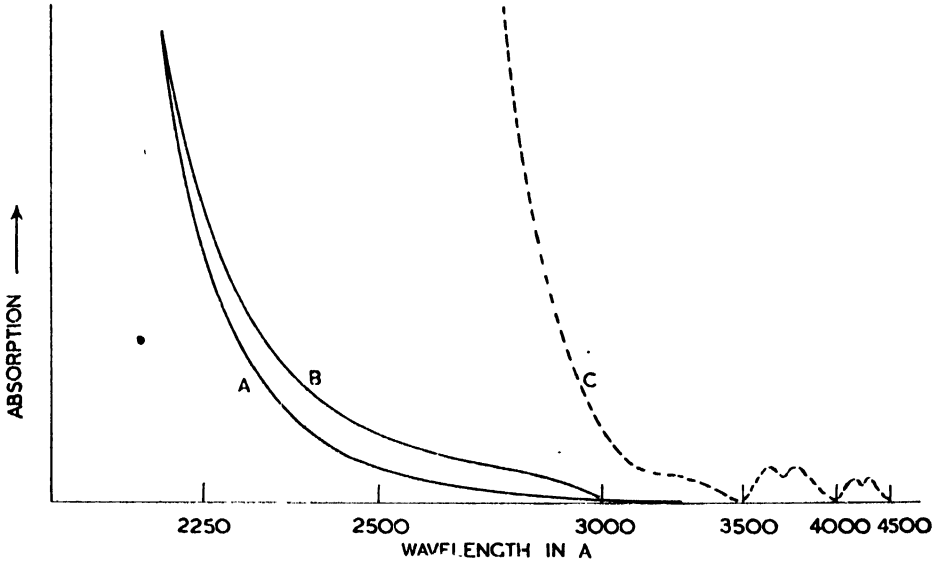


FIG. 14. Absorption spectra of Zn_2SiO_4—Mn phosphors. (Kröger.)
A, Zn_2SiO_4 no Mn; *B*, Zn_2SiO_4—Mn_2SiO_4 (1 per cent.); *C*, Zn_2SiO_4—Mn_2SiO_4 (5–20 per cent.).

These examples of the absorption spectra of different types of phosphor serve to illustrate the general agreement of the above theory with experiment.

3. The storage of energy and its re-emission in phosphors

We consider now the later stages of the luminescence process following the absorption act. The simplest case is that for phosphors in which the whole process is confined to the luminescence centres and is discussed first.

(*a*) *Energy storage and emission within luminescence centres*

We have seen in Chapter I that any delay in emission of absorbed energy, due to the forbidden nature of the optical transitions involved, will give rise to phosphorescence. The latter decays exponentially with time and is not dependent on temperature to any marked extent. Such emission does not persist for more than a few seconds, even in the most extreme cases known. However, in such phosphors as thallium-activated potassium chloride the afterglow continues for several minutes

after excitation finishes. The decay is exponential in form and its rate varies exponentially with temperature. The phosphor shows no photoconductivity but it exhibits thermoluminescence when warmed. Such phosphorescence and thermoluminescence processes are characteristic of metastable states for the electrons

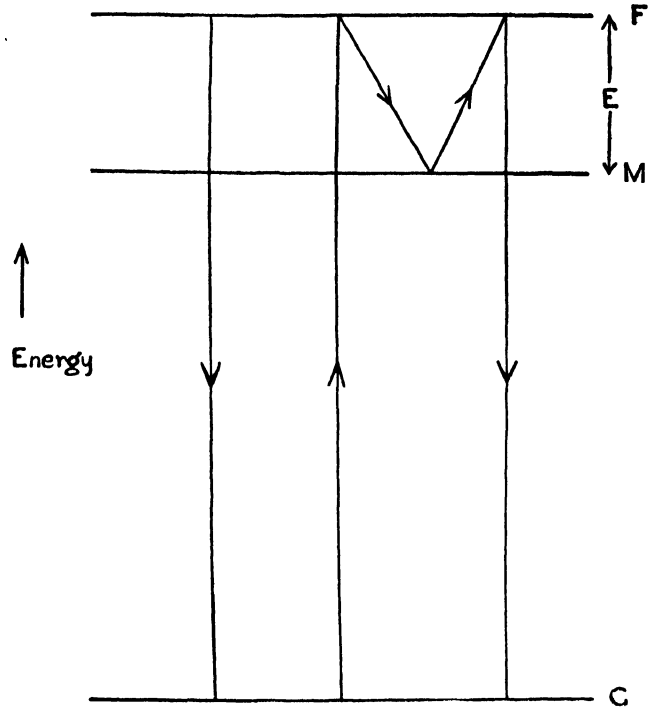


FIG. 15. Energy states for fluorescence and phosphorescence in a luminescence centre. G, ground state; F, excited state; M, metastable state or electron trap.

within luminescence centres. The action of these states can be shown by means of the simple energy diagram given in Fig. 15. This diagram was originally proposed by Jablonski [13] to explain similar processes in organic molecules. Absorption of exciting radiation by a luminescence centre raises an electron into the excited state F. It may then either return directly to the ground state G with emission of luminescence or it may fall into the metastable state M lying just below F. In the latter case a rearrangement of the atoms of the centre takes place and the transition M–G is usually forbidden. Thus electrons in metastable states can only return to the ground states if they are first raised into the excited states by receiving sufficient

thermal energy or by the absorption of long wave-length radiation. For the case of thermal excitation the probability of the transition M–F per unit time is given by

$$p = s \exp(-E/kT), \tag{2.1}$$

where s is a constant having the dimensions of frequency, E is the energy separation between the levels M and F, k is Boltzmann's constant, and T is the absolute temperature. If the transition probability for F–G is high compared with p above, then the phosphorescence emission depends on the rate at which electrons escape from metastable states and will be given by the following equations, n being the number of electrons in M states at any instant:

$$I = -dn/dt = ns \exp(-E/kT). \tag{2.2}$$

The solution of these equations for a fixed temperature gives

$$I = n_0 s \exp(-E/kT)\exp\{-st \exp(-E/kT)\}, \tag{2.3}$$

which is the form of the decay of phosphorescence with time, n_0 being the number of electrons in M states at the beginning of decay. It agrees with that found experimentally for thallium-activated potassium chloride by Bünger and Flechsig [14]. They have given the values of the constants s and E for this phosphor as $2{\cdot}9 \times 10^9$ sec.$^{-1}$ and 0·67 eV. respectively.

The variation of thermoluminescence with temperature has been investigated, both theoretically and experimentally, by Randall and Wilkins [15]. If the phosphor is excited at a low temperature and then warmed at a uniform rate in the dark, then equations 2.2 may be solved for these conditions. From these equations we have

$$-dn/n = s \exp(-E/kT)\, dt. \tag{2.4}$$

If the warming rate is β degrees/sec., we may write $dT = \beta\, dt$ and then integrate equation 2.4 to give

$$\log \frac{n}{n_0} = -\int_0^T \frac{s}{\beta} \exp(-E/kT)\, dT \tag{2.5}$$

and

$$n = n_0 \exp\left\{-\int_0^T \frac{s}{\beta} \exp(-E/kT)\, dT\right\}. \tag{2.6}$$

The variation of the emission with temperature is then given by the equation

$$I = n_0 s \exp(-E/kT) \exp\left\{ - \int_0^T \frac{s}{\beta} \exp(-E/kT)\, dT \right\}. \quad (2.7)$$

The graphical form of equation 2.7 is given in Fig. 16 for various values of the constants s and E, the warming rate being

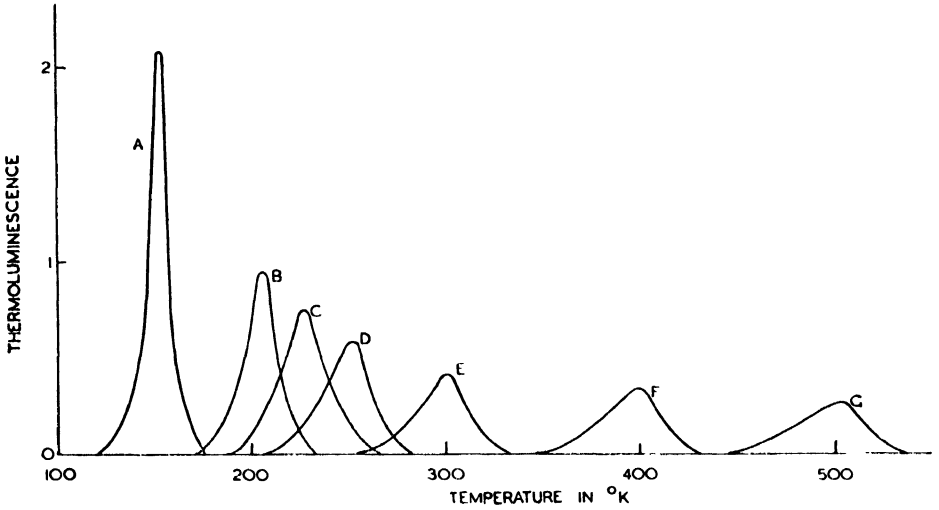


FIG. 16. Theoretical thermoluminescence curves for phosphors with single trap depths: retrapping neglected. A, $E = 0{\cdot}3$ eV., $s = 10^9$ sec.$^{-1}$; B, $E = 0{\cdot}4$ eV., $s = 10^9$ sec.$^{-1}$; C, $E = 0{\cdot}4$ eV., $s = 10^8$ sec.$^{-1}$; D, $E = 0{\cdot}4$ eV., $s = 10^7$ sec.$^{-1}$; E, $E = 0{\cdot}6$ eV., $s = 10^9$ sec.$^{-1}$; F, $E = 0{\cdot}8$ eV., $s = 10^9$ sec.$^{-1}$; G, $E = 1{\cdot}0$ eV., $s = 10^9$ sec.$^{-1}$

2·5 degrees/sec. in all cases. Fig. 17 shows the experimental curves for a specimen of thallium-activated potassium chloride together with the theoretical curve obtained by the use of the above values of s and E obtained by Bünger and Flechsig. These curves are due to Randall and Wilkins, and for the same rate of warming as used in experiment the theoretical curve shows good agreement with the experimental curve.

The characteristics of thermoluminescence due to the metastable states in luminescence centres have been enumerated in a summarized form by Garlick and Gibson [16] as follows:

i. As shown by Fig. 16, for fixed values of n_0, s, and β in equation 2.7, the temperature at which maximum emission occurs is approximately proportional to the activation energy E.

ii. For fixed values of n_0 and E, the emission maximum moves to higher temperatures as β increases or as s decreases.

iii. The area under each curve of Fig. 16 is proportional to n_0, the number of electrons initially in M states. However, the

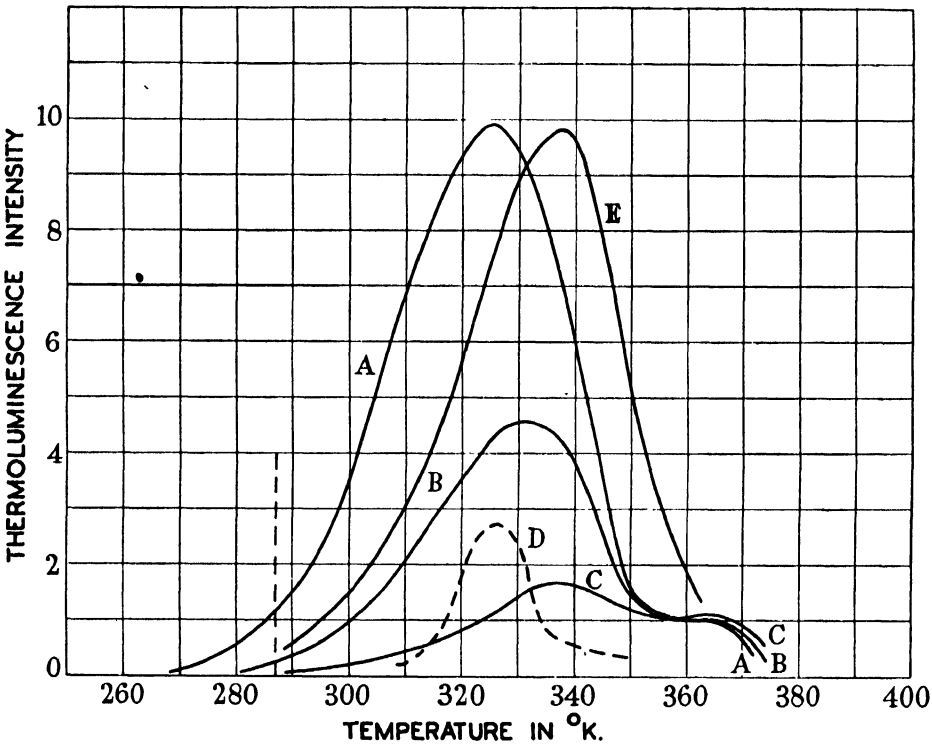


FIG. 17. Thermoluminescence curves for a thallium-activated potassium chloride phosphor after various times of decay at room temperature. (Randall and Wilkins.) A, after 10 sec.; B, after 7 min.; C, after 33 min.; D, probable distribution of trap depths about the mean value; E, theoretical curve from eq. 2.4 for $s = 2{\cdot}9 \times 10^9$ sec.$^{-1}$; $E = 0{\cdot}7$ eV.

shape of the curve for given s, E, and β values is independent of n_0. This applies also to the temperature at which emission is a maximum.

iv. At low temperatures the beginning of the curves follows the simple relation

$$I = n_0 s \exp(-E/kT). \tag{2.8}$$

Randall and Wilkins have found that the above theory can be extended to explain the phosphorescence and thermoluminescence characteristics of photoconducting phosphors such as

the zinc sulphide and zinc silicate phosphors. This involves the consideration of the conditions when there are metastable states of different E values in the same specimen. We consider the further theoretical development in the next section.

(*b*) *Phosphorescence and thermoluminescence in photoconducting phosphors*

In photoconducting phosphors excitation can free electrons from lattice atoms and from luminescence centres. They can then move through the crystal and either recombine with empty centres and lattice atoms or be captured in electron traps. As described earlier in the chapter, the latter can be due to lattice defects and irregularities and give rise to energy states below the conduction levels of the crystal (see Fig. 10). The electron traps will govern the phosphorescence and thermoluminescence processes in such phosphors in a similar way to the metastable levels within the luminescence centres in other non-photoconducting phosphors. However, the mechanism is not quite the same for photoconducting phosphors, since the final recombination of the escaping electrons with luminescence centres is a bimolecular process. It also involves the possibility that an electron escaping from a trap may be retrapped before reaching an empty centre. Randall and Wilkins found that in zinc sulphide and alkaline earth sulphide phosphors the luminescence process could be explained by the simple assumptions of the above section (*a*) rather than by the bimolecular process just described. They have also shown that although an empty luminescence centre and an empty electron trap have similar cross-sections for electron capture, yet retrapping is a negligible process during luminescence. We discuss first their development of the simple theory which neglects retrapping.

If a photoconducting phosphor contains only traps of one depth, then its phosphorescence and thermoluminescence will be described by the equations of section (*a*) above. The reasons for this are the following: if at any instant n electrons are in traps there will be n empty luminescence centres; we do not think it likely that in the unexcited state a phosphor con-

tains empty luminescence centres [17]. The number of electrons escaping from traps is usually much smaller than the number of empty centres, and so phosphorescence and thermoluminescence will be determined by the rate at which electrons escape from traps. This means that, in the absence of any retrapping process, the decay of phosphorescence or the emission of thermoluminescence will be given by solutions of equations 2.2. In most zinc sulphide and alkaline earth sulphide phosphors the electron traps are distributed in depth and so phosphorescence decay is due to a sum of the exponential terms for each trap depth. The form of the decay laws for certain types of trap distribution has been given by Randall and Wilkins [15] as follows:

i. For a single depth of trap equation 2.3 holds. If there are, however, $N_E\,dE$ traps of depth between E and $E+dE$, then the phosphorescence decay for saturated conditions is given by

$$I_t = \int_0^\infty N_E s \exp(-E/kT)\exp\{-st\exp(-E/kT)\}\,dE, \quad (2.9)$$

giving by integration, for a uniform trap distribution (N_E = constant),

$$I_t = \frac{N_E kT\{1-\exp(-st)\}}{t}. \quad (2.10)$$

Since after the first few microseconds for $s = 10^8$ sec.$^{-1}$ the exponential term is negligible, the equation reduces to

$$I_t = (N_E kT)/t, \quad (2.11)$$

that is, the phosphorescence follows a simple inverse function of the decay time.

ii. If the electron-trap distribution is exponential in form, that is, $N_E = A\exp(-\alpha E)$, as is found for many phosphors, the phosphorescence is given by

$$I_t = \int_0^\infty A\exp(-\alpha E).s\exp(-E/kT)\exp\{-st\exp(-E/kT)\}\,dE, \quad (2.12)$$

and when solved for very large values of st (i.e. $t > 1$ μsec) gives the decay law

$$I_t = \frac{\text{constant}}{t^{(\alpha kT+1)}}. \qquad (2.13)$$

Details of this integration are given by Randall and Wilkins. In experimental studies values of α can be calculated from the shape of the curve for the variation of thermoluminescence with temperature, as shown in Chapter IV. We give below values for the index $(\alpha kT+1)$ derived from thermoluminescence curves and from phosphorescence decay measurements as calculated by Randall and Wilkins. Table I contains these values for various zinc sulphide and zinc cadmium sulphide phosphors. The agreement between the differently derived values gives support to the above theory, that is, to the assumption that the process is effectively monomolecular in character.

TABLE I

Comparison of Values of the Decay Law Index $(\alpha kT+1)$ *derived from Measurements of Phosphorescence and Thermoluminescence*

Phosphor	*Index derived from phosphorescence decay*	*Index derived from thermoluminescence curves*
ZnS—Cu	1·5	1·57
ZnS—Cu	1·38	1·31
ZnS—Cu	1·5	1·51
ZnS—Cu—Ag	1·32	1·30
ZnS—CdS—Cu	1·65	1·57
ZnS—Cu	2·0	2·0

iii. Equation 2.11 shows that the product t is a constant and is proportional to N_E, where N_E will now be the number of traps in which the mean lifetime of an electron is t. Randall and Wilkins find that this equation holds for conditions under which N_E varies slowly: the variation of N_E with E gives the trap distribution. Thus since from equation 2.1 E is proportional to log t, the curve given by plotting $I_t \times t$ against log t will have the same form as the trap distribution and hence as the thermoluminescence curve. This simple relation between the phosphorescence and the thermoluminescence characteristics has

been found to give good correlation between these two phenomena as measured experimentally, and Fig. 18 gives trap-distribution curves obtained by Wilkins for an alkaline earth sulphide phosphor [18].

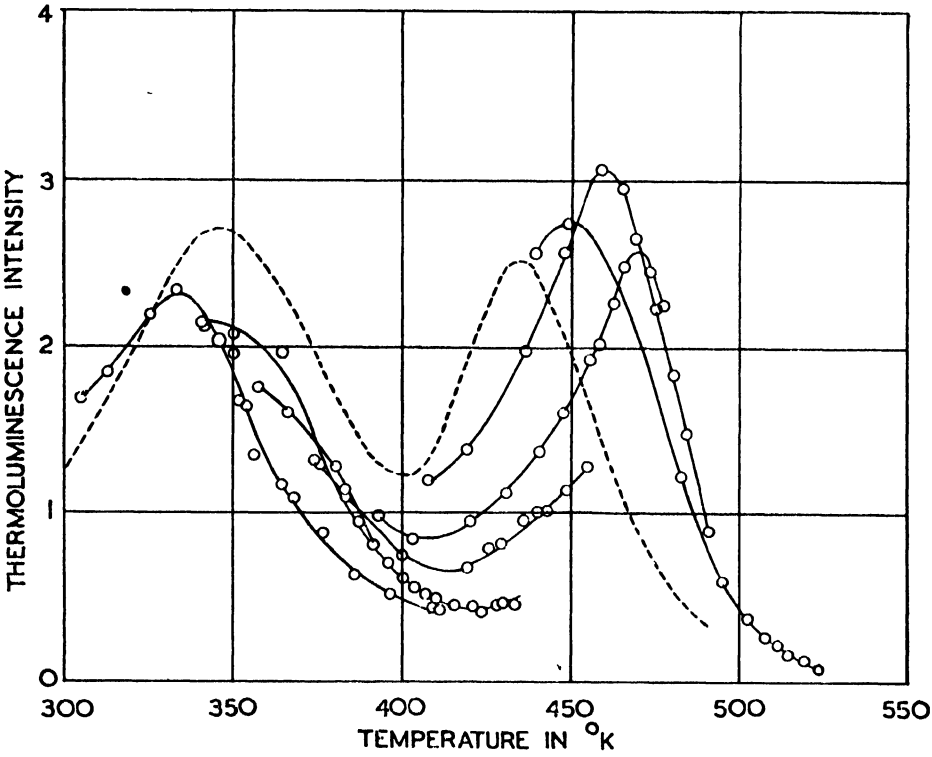


FIG. 18. Correlation between phosphorescence and thermoluminescence due to electron traps for a strontium sulphide phosphor. (Wilkins.) ⊙ Points derived from phosphorescence decay at different temperatures. – – – – Thermoluminescence curve derived experimentally.

Although experimental evidence for many types of photoconducting phosphors shows that the retrapping of electrons during luminescence is negligible, it is necessary to consider its effect on the above theoretical derivations.

(c) *The effect of retrapping of electrons upon phosphorescence and thermoluminescence*

We first discuss the conditions for which the retrapping of electrons is most likely to occur. It is evident that retrapping will be most likely when the number of empty electron traps is large compared with the number of luminescence centres. This

will occur at the beginning of excitation of a phosphor which has been previously heated in the dark or exposed to long wavelength light in order to empty the traps. Similar conditions will obtain at high temperatures, provided that the luminescence efficiency is still sufficient to allow observations, since at such

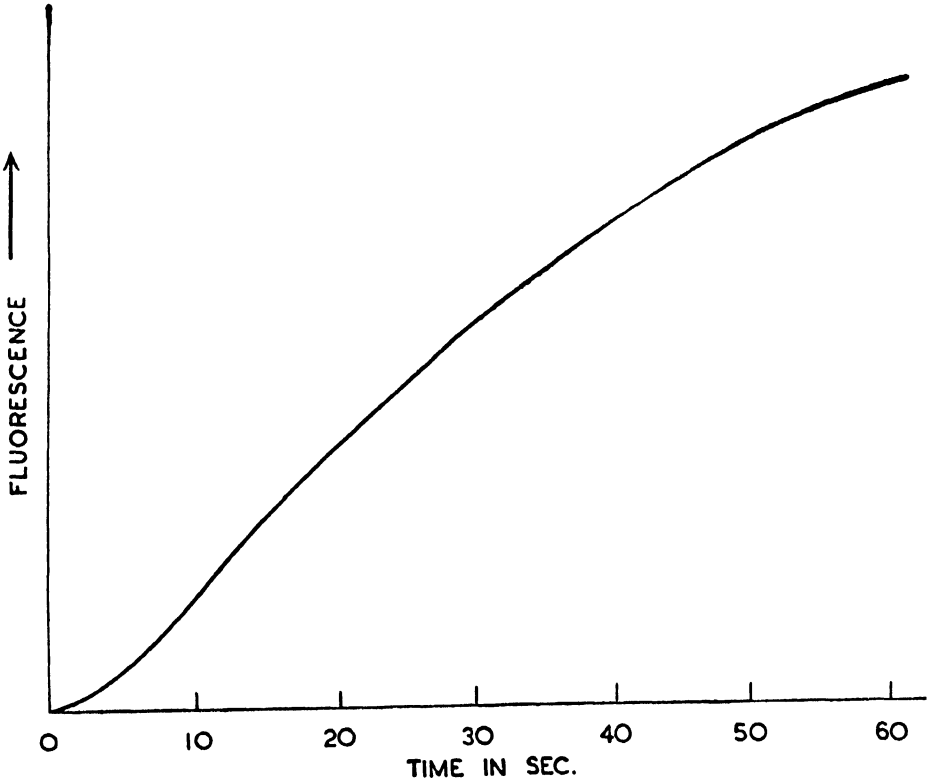


FIG. 19. Slow rise of fluorescence with time for a ZnS—Cu phosphor at room temperature and for very weak excitation.

temperatures all traps are effectively shallow and cannot retain electrons. The presence of retrapping is then indicated by an inflexion in the curve which shows the initial growth of fluorescence with time. Fig. 19 shows such a curve for a copper-activated zinc sulphide phosphor excited at room temperature after previous *deactivation* by heating. This curve is of interest not only because of the inflexion at its beginning but because it begins without a sudden rise due to an intrinsic excitation of luminescence centres. This means that an excited electron must first be trapped before it returns to the centre and gives rise to emission, and also that no empty luminescence centres are

present in the unexcited phosphor. Examples of inflexions in fluorescence-time curves for phosphors at elevated temperatures have been given by Garlick and Wilkins [11].

We now consider the effect of the retrapping of electrons on the phosphorescence and thermoluminescence emission equations for a phosphor with one depth of trap. For simplicity we assume that the probability of electron capture in an empty trap is the same as that for recombination of an electron with an empty luminescence centre; this assumption is justified by estimates due to Randall and Wilkins [15]. Thus if there are N electron traps of which n are filled and there are normally no empty luminescence centres in the unexcited phosphor, then there will be n empty centres and $N-n$ empty traps. The probability of electrons in the conduction band being captured by empty luminescence centres is thus given by

$$p = n/[(N-n)+n] = n/N,$$

and the equations for luminescence are therefore

$$I = -\frac{dn}{dt} = \frac{n^2}{N} s \exp(-E/kT), \tag{2.14}$$

which give on solution

$$I = \frac{n_0^2 s \exp(-E/kT)}{N[1+(n_0/N)st \exp(-E/kT)]^2}. \tag{2.15}$$

Comparing this equation with equation 2.3, which will apply to a photoconducting phosphor if retrapping is negligible, we see that retrapping causes a marked change in the decay characteristics of a phosphor. A more general treatment leading to a similar hyperbolic form for phosphorescence decay when retrapping is present has been given by Klasens and Wise [19].

From equations 2.14 we may also derive the variation of thermoluminescence with temperature for a uniform rate of warming after excitation at low temperatures. Using the previous notation, the following equation is obtained:

$$I = \frac{n_0^2 s \exp(-E/kT)}{N\left[1+\frac{n_0}{N}\int_0^T \frac{s}{\beta}\exp(-E/kT)\,dT\right]^2} \tag{2.16}$$

which may be compared with equation 2.7. The graphical form of equation 2.16 for different values of n_0 and E, other constants remaining fixed, is shown by the curves of Fig. 20. By comparison with Fig. 16 it will be seen that for saturation of the traps and for given values of the constants β, s, and E, the temperature at which maximum emission occurs is about the same. However, when retrapping is present the half-width of the peak

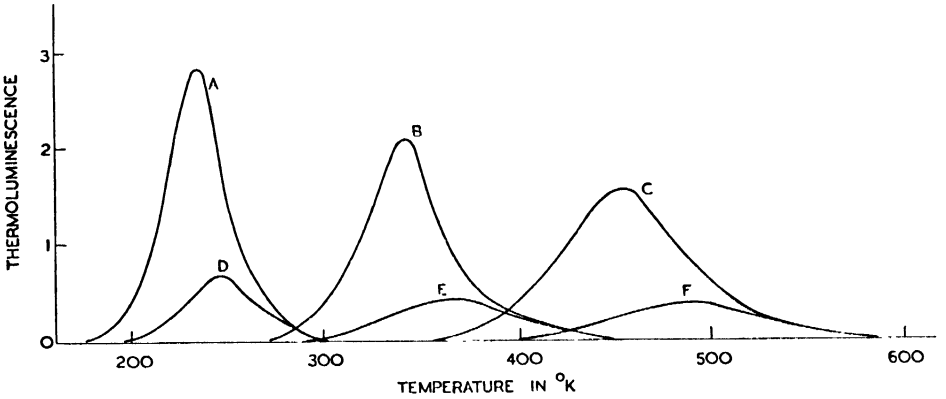


FIG. 20. Theoretical thermoluminescence curves for phosphors with single trap depths assuming retrapping (eq. 2.11): $s = 10^8$ sec.$^{-1}$: n_0 is number of electrons in the N available traps. A, $E = 0{\cdot}4$ eV.: $n_0 = N$; B, $E = 0{\cdot}6$ eV.: $n_0 = N$; C, $E = 0{\cdot}8$ eV.: $n_0 = N$; D, $E = 0{\cdot}4$ eV.: $n_0 = \frac{1}{4}N$; E, $E = 0{\cdot}6$ eV.: $n_0 = \frac{1}{4}N$; F, $E = 0{\cdot}4$ eV.: $n_0 = \frac{1}{4}N$.

of the curve for the same E value is much larger. Other characteristics, to be compared with those already enumerated for the case when retrapping is absent, are summarized as follows:

i. For fixed values of n_0, s, and β, the temperature of maximum emission is approximately proportional to the trap-depth E.

ii. For fixed values of n_0 and E, the temperature of maximum emission increases with increase in β or with a decrease in s.

iii. The area under each curve is proportional to the number of electrons initially trapped (i.e. n_0); the shape of the curve and the position of its maximum is dependent on n_0 (cf. characteristic iii for equation 2.7).

iv. At the beginning of thermoluminescence the form of the emission temperature curve is given by:

$$I = n_0^2 s \exp(-E/kT), \tag{2.17}$$

which differs in the power of n_0 from equation 2.8.

It will be evident from the above that the presence of retrapping will have a marked effect upon phosphorescence and thermoluminescence in photoconducting phosphors. In order to make experiments to distinguish between the cases treated above, phosphors must be selected which have traps of only one depth or at the most a very narrow distribution of trap depths. A few such specimens have been studied and the experimental results are described in Chapter IV. Because of the complexity of the treatment it has not been found possible to extend the theory which includes retrapping of electrons in the luminescence process to phosphors having a wide distribution of trap depths. The chief difficulty, as shown by the general equations of Herman and Meyer [20], is that electrons escaping from traps of one depth can be retrapped in traps of other depths.

(*d*) *The effect of the excitation conditions upon phosphorescence and thermoluminescence* [16, 21]

The form of phosphorescence decay or variation of thermoluminescence with temperature depends not only on the electron-trap distribution for a particular phosphor but also on the degree of saturation of the traps when excitation is removed. In most of the experiments of Randall and Wilkins steps are taken to obtain saturation conditions. However, the study of phosphors when the traps are not saturated provides additional evidence to determine the extent of retrapping and we shall consider some simple non-saturation conditions. If the phosphor is excited by a constant incident radiation at a fixed temperature its emission reaches a steady value. We may then derive the number of electron traps filled under such equilibrium conditions, first for the case in which no retrapping occurs and then for the case in which it is present.

i. *The non-saturated filling of electron traps when retrapping is absent.* If the phosphor specimen has only traps of one depth E

and there is a total number N of these traps, then for constant excitation by radiation of intensity J a number n_0 will be filled at any instant. Excitation is assumed to excite aJ electrons

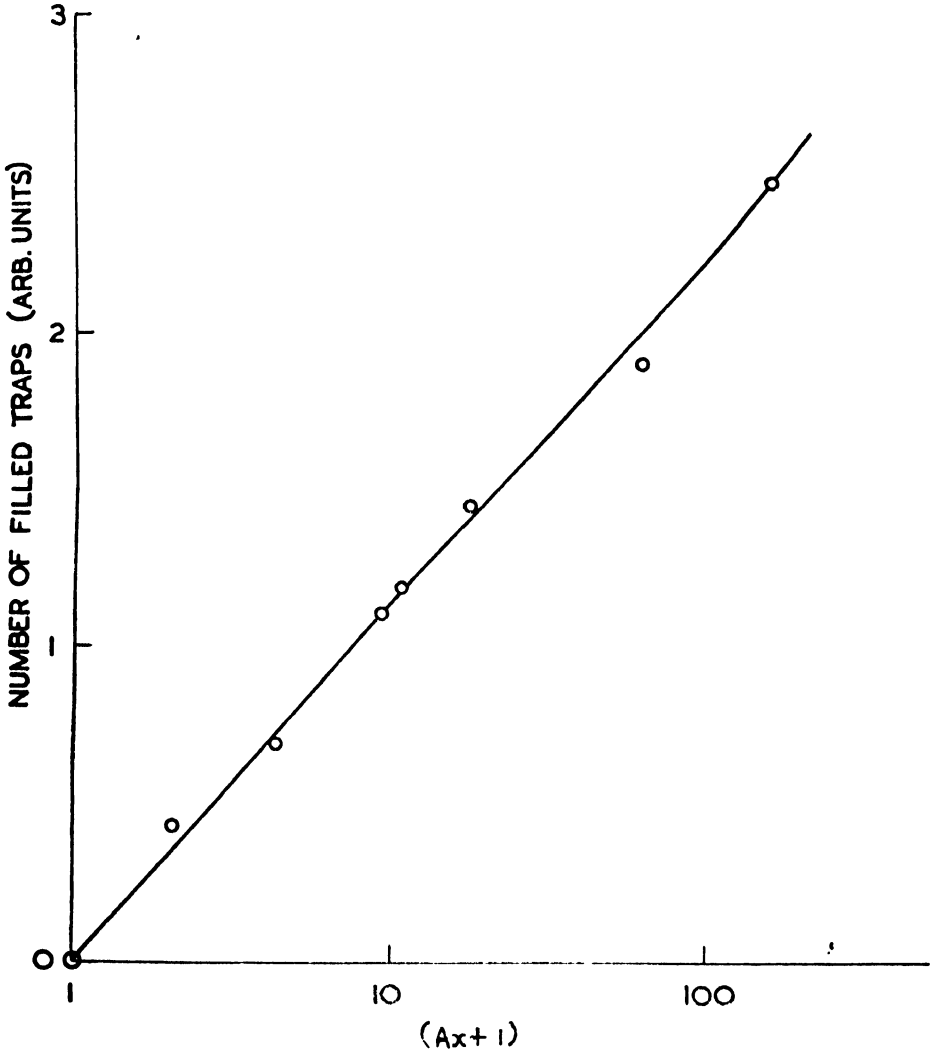


FIG. 21. Variation in the number of filled traps with excitation intensity for a ZnS—Cu phosphor at room temperature (eq. 2.16). Excitation intensity is proportional to A of abscissa.

per second, where a is a constant. For a monomolecular process such as occurs in many phosphors the number of electrons entering traps will be the same as the number leaving traps, and is given by

$$\frac{dn}{dt} = 0 = abJ(N-n_0)-n_0 s \exp(-E/kT), \qquad (2.18)$$

where b is the probability of capture of an electron by an empty trap; $N-n_0$ gives the number of empty traps available. Rearrangement of this equation gives

$$n_0 = \frac{N}{\{1+(s/abJ)\exp(-E/kT)\}}, \tag{2.19}$$

or

$$\left(\frac{N}{n_0}-1\right) = \frac{s\exp(-E/kT)}{ab}\frac{1}{J}. \tag{2.20}$$

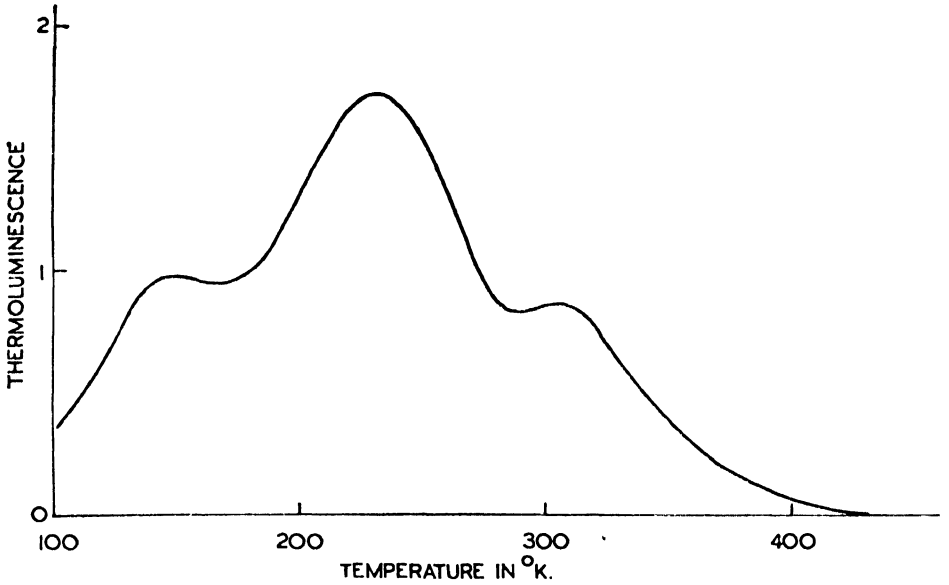


FIG. 22. Thermoluminescence curve for the phosphor of Fig. 21.

In experimental tests of this relation the values of N and n_0 are given by the areas under appropriate thermoluminescence curves. For complex trap distributions the equation 2.19 must be integrated over all values of N and E. If N is almost constant or varies only slowly with E, then such integration is straightforward and gives

$$n_t = NkT\log\left[\frac{Ax_m+1}{A/s+1}\right], \tag{2.21}$$

where n_t is the total number of electron traps filled, $A = abJ$ and $x_m = (1/s)\exp(E_{\max}/kT)$. For most experimental conditions A is much smaller than s and the equation is simplified to give

$$n_t = \text{constant}\times\log(A'+1), \tag{2.22}$$

where $A' = Ax_m$ and is still proportional to the excitation

intensity. At high intensities A' is much larger than unity, which causes a further simplification of equation 2.22. In experimental studies the form of the high-intensity variation of n_t with J is used to determine the constant A'. Fig. 21 gives this variation for a long afterglow zinc sulphide phosphor and shows how the relation of 2.22 is obeyed over a wide range of excitation intensities. Fig. 22 shows the saturated thermoluminescence curve for this phosphor.

ii. *The non-saturated filling of traps when retrapping is present.* When excitation of the phosphor causes electrons to leave the luminescence centres and pass through the conduction band before becoming trapped, then we have to consider the conditions for equilibrium of the electrons in the conduction band as well as those of trapped electrons. By using the above notation and assuming the retrapping conditions of section (*c*) above, we may derive equations which give the equilibrium states for the electrons in traps and in conduction levels. If m_0 is the equilibrium number of conduction electrons, these equations are as follows:

$$\frac{dm_0}{dt} = 0 = aJ - m_0 b(m_0+n_0) - m_0 b(N-n_0) + \\ + n_0 s \exp(-E/kT) \quad (2.23)$$

$$\frac{dn_0}{dt} = 0 = m_0 b(N-n_0) - n_0 s \exp(-E/kT), \quad (2.24)$$

where (m_0+n_0) is the number of empty luminescence centres.

The solution of these equations to give the variation of n_0 with the excitation intensity J is simplified for high intensities (i.e. for $n_0 \ll m_0$) and becomes:

$$n_0 = N \Big/ \left[1 + \frac{s \exp(-E/kT)}{b\sqrt{(aJ/\beta)}}\right]. \quad (2.25)$$

At lower intensities, when the electron traps are not near saturation conditions and when n_0 and m_0 may be of comparable magnitudes, a similar relation holds. These relations are different from those of equations 2.19 and 2.20, and thus indicate a further method of testing the validity of one or the other by experiment. When more than one depth of trap is present in a

phosphor it is not possible to derive expressions corresponding to those of equations 2.21 and 2.22 because of the complexity of the general equations for equilibrium.

4. Limitations of the theoretical model for a crystalline phosphor

There is no doubt that the application of the energy-band theory of crystals to the case of phosphors has been successful in providing a sound basis for the interpretation of the mechanisms of luminescence in solids. We shall show this in later chapters, but in addition we shall indicate the chief weaknesses of the model in its present form. From the above development of quantitative expressions for phosphorescence, thermoluminescence, and the equilibrium filling of electron traps we see that in order to establish the correct theoretical model, experiments must be carried out to determine the extent to which electrons are retrapped and pass through the conduction band of the phosphor crystal during the luminescence process. It is also necessary to prepare phosphors of the same class in different ways so that the effect of the preparation on the luminescence can be used to determine the nature of emission centres and electron traps. We would emphasize here that the establishment of a theoretical model for luminescence in a particular class of phosphors, such as zinc sulphide, demands exhaustive experiments on very many specimens prepared in different ways under carefully controlled conditions. It is only in this way that correct conclusions may be drawn since it is so easy to produce, but difficult to reproduce, 'freak' phosphors having characteristics favourable to interpretation by a particular theoretical model.

CHAPTER III

CLASSES OF LUMINESCENT MATERIALS

It is impossible to provide here an adequate survey of all classes of luminescent materials. For this reason it is our intention to discuss a few types of solid which are of some practical interest and which have been studied in recent years. The chapter is also confined to inorganic substances, organic materials being considered in Chapter VIII. The greater part of the chapter is devoted to those materials of high luminescence efficiency whose luminescence is due to the presence of small concentrations of specific impurities. However, there is some interest in solids which show luminescence in the pure state although their practical use is restricted. These solids are considered in the first section below, after which we discuss the classes of impurity-activated phosphors.

1. Luminescence in pure solids

The definition of the *pure state* with respect to luminescent materials is rather more specific than is generally implied in the chemical use of the term. If repeated purification of the material leads to no reduction in the luminescence emission, and spectroscopic analysis shows that there are no traces of foreign elements present, then the product is probably luminescent in the pure state. However, there are some materials which can be made to luminesce in their pure state by heating, e.g. zinc oxide and many tungstates and molybdates. In such cases heat treatment usually creates a stoichiometric excess of one or other constituent of the solid, the excess ions or atoms probably occupying interstitial positions in the crystal lattice. These materials may be thought of as impurity-activated since their luminescence characteristics are more akin to those of phosphors containing a specific impurity than to those of *pure* solids. They are usually known as *self-activated* phosphors. Randall [1] has discussed the occurrence of luminescence in pure solids and has given a list of materials which show this

inclusive of tungstates and molybdates: this is given in Table I below. We shall regard tungstate and molybdate phosphors as self-activated impurity phosphors in a later section.

TABLE I

Some Compounds luminescent in the Pure State

Manganous halides [2]	Tungstates of magnesium, calcium, and zinc
Samarium sulphate [3]	Various molybdates
Gadolinium sulphate	Uranyl salts
Various platinocyanides	

As a general rule, in the above phosphors the luminescence emission occurs in specific atoms or atomic groups in the solid. For example, the study of manganese halides and manganese-activated impurity phosphors has led to the assumption that the emission takes place in the divalent manganese ions: in the uranyl salts the emission takes place in the UO_2 coordination group [1]. In rare earths the emission occurs in the inner incomplete electron shells of the ions. By comparison of the luminescence efficiency of pure solids and of impurity-activated solids we find them to be of the same order. It is therefore unlikely that all the manganese ions in the manganous halides or all the uranyl groups of the uranyl salts are effective as luminescence centres. It may be that only ions or groups in the neighbourhood of defects in the lattice are capable of emission.

In this discussion of pure solids which show luminescence we must include a brief survey of the luminescence characteristics of diamond. In the earlier literature little mention is made of the luminescence of diamond. It was thought to be due to impurities [4], but the studies made by Raman and his school [5] show that luminescence is characteristic of very pure diamonds. We shall summarize their experimental results on diamond and show their relation to other physical properties in the following sections.

Luminescence and the structure of diamond

Diamond has a cubic structure of the zinc-blende type which may be represented as two interpenetrating face-centred cubic lattices. Raman postulates that there are four symmetry forms for diamond, two tetrahedral and two octahedral. His

hypothesis is very much open to question; but there is no doubt that two distinct types of diamond are found to occur, as shown by the experiments of Robertson, Fox, and Martin [6]. These have been designated type I and type II diamonds. Diamonds of type I are much more common than those of type II and when free from faults show an intense blue luminescence. Type II diamonds are stated to be non-luminescent, but there appear to be exceptions, in which case the emission is green-yellow. Diamonds of type I may show little or no birefringence, but those of type II show marked birefringence and have visible striations associated with regions of strain. Imperfect specimens, which may be mixtures of type I and type II diamond, show both blue and yellow luminescence, but the emissions vary in the expected way with the structure of the particular part of the specimen. The blue-emitting diamonds of type I have an intense green-yellow phosphorescence at room temperature, but on warming after excitation their thermoluminescence is blue with a faint green-yellow component.

The absorption characteristics of diamond

Diamonds of type I which show blue luminescence are opaque to radiations of wave-length less than 3,000 A, but non-luminescent specimens of type II are transparent to 2,500 A. Diamonds of intermediate type which have blue and green-yellow emission also have intermediate absorption characteristics. The blue luminescence of diamonds is due chiefly to a sharp emission line at 4,152 A which has a corresponding absorption line at the same wave-length. The green-yellow emission has a principal line at 5,032 A with a corresponding absorption line at the same wave-length. Other fainter emission lines occur near these wave-lengths, and some of them are due to combination of the principal line frequencies with those of the lattice vibrations. These lines lie to the long wave-length side of the principal lines.

Luminescence and X-ray reflections from diamond

The luminescence of type I diamonds often increases in intensity as the degree of homogeneity decreases. There is a

corresponding increase in the intensity of X-ray reflections from such specimens.

The origin of the luminescence in diamond

It is difficult to visualize the nature of the luminescence centres in a pure diamond crystal. It is likely that they are formed by the constituent carbon atoms. However, only a relatively small number of atoms are likely to form emission centres, perhaps only those near to lattice imperfections similar to F centres each of which involves only one vacant lattice site. It has been observed that although absorption occurs at 4,152 and 5,032 A, the dispersion of diamond in these spectral regions is not noticeably affected. This may be due either to the forbidden nature of the absorption and emission transitions or to the relatively small number of centres in which transitions of this type are possible. However, no experimental studies of the phosphorescence characteristics of these transitions appear to have been made. A comparison of the transitions $^3P_1$—$^1S_0$ and $^3P_2$—$^1S_0$ in the carbon atom with the transitions giving the doublet at 4,152 A in diamond suggests a possible explanation of the origin of luminescence. In the carbon atom there is also an intermediate state $^1D_2$, and by analogy there should be an emission line in diamond, but no absorption, at 7,849 A. This is confirmed by experiment since an emission line at 7,930 A has been observed which has no corresponding absorption at the same wave-length. The above forbidden transitions in carbon atoms may be allowed when the atom is adjacent to a defect which destroys the local lattice symmetry.

Future studies of the luminescence of diamond

We find that no quantitative measurements of phosphorescence or thermoluminescence in diamond appear to have been made. Such measurements would provide valuable information about the nature of the emission centres and the metastable states for electrons in the crystal. Since good luminescent diamonds are of type I and show very little photoconductivity, it is probable that luminescence processes are of monomolecular type. Studies of the stimulation of phosphorescence by radiation of

wave-length greater than 4,200 A should furnish valuable data on the optical activation energies for electrons in metastable states which could be compared with that obtained from thermoluminescence experiments.

2. The luminescence characteristics of impurity-activated phosphors

Most of the solids with which we are concerned in this section are of crystalline structure, but there are some which show luminescence in the vitreous state. A previous attempt at a classification and description of impurity-activated materials has been made by Birus [7]. We shall consider the following main classes of solid which have been studied in recent researches:

(*a*) The alkali halides activated by heavy metals.

(*b*) Sulphide phosphors, comprising two groups:

i. Zinc and cadmium sulphides activated by copper, silver, and manganese and by excess metal of the crystal lattice. ii. Alkaline earth sulphides, particularly those of calcium and strontium activated by bismuth, some other metals, and rare earths.

(*c*) Silicate phosphors inclusive of zinc, beryllium, cadmium, calcium, magnesium, strontium, barium, and manganese silicates.

(*d*) Oxide phosphors, particularly self-activated zinc oxide and chromium-activated aluminium oxide (ruby).

(*e*) Tungstate and molybdate phosphors.

(*f*) Vitreous phosphors.

(*a*) Alkali halide phosphors activated by heavy metals

Pure alkali halides show relatively feeble luminescence when excited by very short wave-length ultra-violet radiation, cathode rays, or X-rays. Some attention has been given to their characteristics in the past [8]. A recent study of their phosphorescence after X-ray excitation has been made by Katz [9] and by Bose [10]. The latter has related the decay characteris-

tics to the electron trap-depth distributions in the crystals. However, the greatest interest has been centred in the alkali halide phosphors activated by heavy-metal inclusions and having good luminescence efficiencies. For example, potassium chloride when activated by one per cent. or so of thallium can be excited by ultra-violet light to give an intense ultra-violet and blue emission with long duration of phosphorescence. Such phosphors were first systematically investigated by Hilsch [11], Hilsch and Pohl [12], and by Smakula [13]. They found that addition of small amounts of heavy metals to the alkali halides gave rise to new absorption bands lying to the long wave-length side of the alkali halide lattice absorption. In order to understand the absorption properties of these phosphors we shall consider in detail the case of thallium-activated potassium chloride which is a typical phosphor. Although most of the significant experimental data on this phosphor were available by 1932, it was not until 1938 that an adequate theoretical model was proposed by Seitz [14]. Further data have since been added by the measurement of thermoluminescence characteristics of this phosphor by Randall and Wilkins [15]. We discuss first the absorption characteristics.

The absorption characteristics of alkali halide phosphors. Hilsch and Pohl [12] have measured the absorption of the pure and impurity-activated alkali halides in the ultra-violet. Their measurements have been extended to shorter wave-lengths by the work of Schneider and O'Bryan [16]. The bands observed by Hilsch and Pohl in pure halides were ascribed by them to the transition of electrons from halogen ions to adjacent metal ions. A satisfactory treatment of the position of the bands was given by von Hippel [17] and his work has been adequately discussed by Mott and Gurney [18]. When thallium is added in small concentration to the alkali halide melt and then crystals are grown by the Kyropoulos method [19], the new absorption bands due to the heavy metal appear. Their positions are very similar for most of the alkali halides. Seitz has given a general schematic diagram of these bands as shown in Fig. 23. They consist of a band A in the long wave-length ultra-violet region and two over-

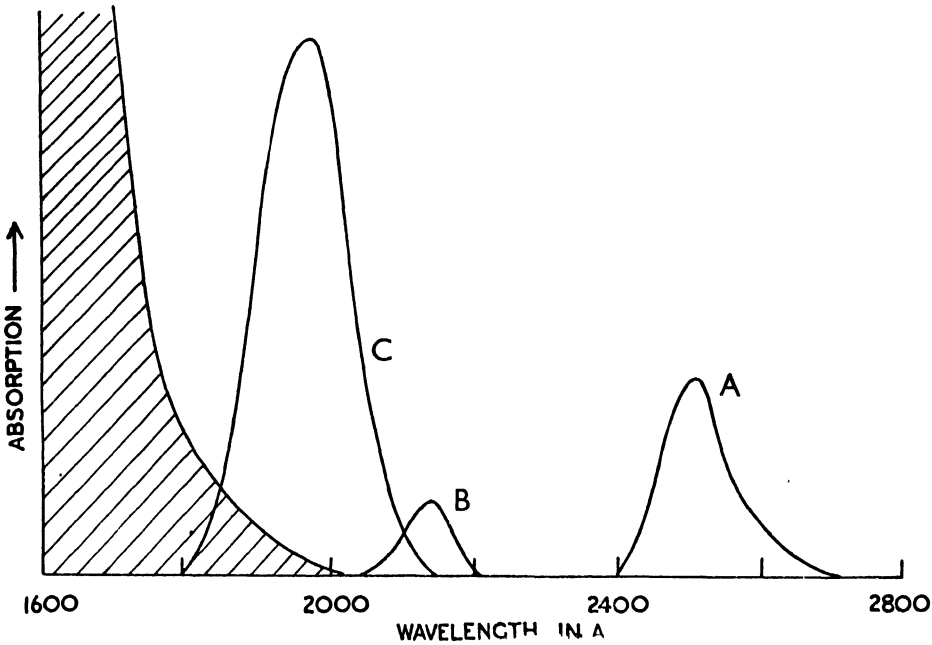


FIG. 23. Schematic absorption spectrum for thallium-activated alkali halide phosphors. (Seitz.)

lapping bands B and C at shorter wave-lengths. The following table gives their positions for various alkali halides:

TABLE II

Absorption Bands in the Alkali Halides due to Thallium and Position of the First Fundamental Lattice Peak. (Band positions in eV.)

Alkali halide	*Lattice peak*	*Peak A*	*Peak B*	*Peak C*
NaCl	7·82	4·87	5·8	6·2
KCl	7·6	4·92	5·9	6·3
RbCl	7·39	4·98	5·94	6·4
CsCl	7·63	4·90	5·9	6·3
NaBr	6·49	4·63	..	5·72
KBr	6·58	4·73	..	5·88
RbBr	6·43	4·77	..	5·82
CsBr	6·61	4·69	..	5·76
NaI	5·38	4·22	..	5·28
KI	5·63	4·3	..	5·23
RbI	5·55	4·32	..	5·15

The position of the bands A, B, and C will be seen to vary only slightly among the alkali halides, the maximum shift being 1·0 eV., whereas the fundamental lattice absorption may change

by as much as 2·1 eV. The fixed position of the bands A, B, and C and the absence of photoconductivity during such absorption [20] indicate that the absorption process is confined to the thallium centres. It has been found that the absorption bands of thallous ions in solution are very similar to those tabulated above if alkali halide ions are also present [21]. This is shown by the following table:

TABLE III

Absorption of Alkali Halides containing Thallium and other Ions in the Solid State and in Solution

Composition	*Crystal absorption*	*Solution absorption*
NaCl+TlCl	210 mμ	216 mμ
KCl+CuCl	267 mμ	272 mμ
KCl+$PbCl_2$	273 mμ, 196 mμ	272 mμ, 195 mμ
KCl+TlCl	247 mμ, 196 mμ	242 mμ

The emission spectra of the luminescence of the solutions has been found to agree with that of the crystal phosphor by Pringsheim and Vogels [22]. Thallous salts also show absorption in the same region as the thallium-activated alkali halides. From the above data Seitz has concluded that thallous ions replace the alkali metal ions of the crystal lattice. X-ray analysis due to Stasiw and Saur [23] supports this hypothesis since the change in lattice spacing due to the addition of 9 per cent. of thallium is only 0·008 per cent., half of that to be expected from the Wegard additivity law for mixed crystals.

When a thallous ion replaces a metal ion in the crystal the thallium energy-levels will be modified. Similar modification will occur in solution when the thallous ions form associations with halide ions present. Seitz [14] has attempted an interpretation of this modified energy-level scheme. In the unexcited state the interaction of the thallous ion with the lattice consists of electrostatic attraction and homopolar repulsion. In the first excited state the excited electron is shared by adjacent metal ions and the charge distribution is not the same as for the excited thallous ion in the free state. In this state the electrostatic attraction remains the same as in the normal state but the

homopolar interaction possesses an attractive minimum. This causes the energy levels of the excited state to be depressed relative to those of the free ion. The two main absorption bands C and A may be correlated with transitions from the ground state of the ion to the excited states shown by L and N respectively in Fig. 25. If the cubic symmetry of the crystal around the thallous ion is perfect, then other transitions are forbidden, but a local lack of symmetry may cause one or more of them to be present in absorption. Seitz assumes the absorption band B to be due to such a transition, this being suggested by its temperature dependence [24, 25].

Pringsheim [26] has prepared thallium-activated potassium chloride with similar absorption characteristics to the above crystals by co-crystallization from saturated solutions of the salts. He has observed absorption bands at 2,475 A and 2,610 A. He assumes that the absorbing centres are complexes formed by thallium and halide ions, although it is difficult to see how his treatment improves upon that of Seitz.

Emission characteristics of the phosphors. The luminescence emission of alkali halides activated by thallium consists of broad bands situated in the near ultra-violet and visible regions. All the bands are excited with the same relative intensities whether absorption takes place in the short wave-length bands B and C or in the band A. If the concentration of thallium is below 0·0015 mol per cent., then no long afterglow is observed. At higher concentrations absorption in the bands B and C causes phosphorescence with the same emission spectrum as the fluorescence. The afterglow characteristics were first measured by Bünger and Flechsig [27] for single crystal specimens. Bünger [28] found that the quantum efficiency of the luminescence process in the temperature range 50–150° C. was approximately unity. More recent work by Randall and Wilkins [15] has provided data on the thermoluminescence of these phosphors, and we consider this together with the phosphorescence measurements below.

The phosphorescence and thermoluminescence of the phosphors. The phosphorescence excited by absorption in the bands B and

C accounts for some 5 per cent. of the energy absorbed initially. Bünger and Flechsig found that the decay with time for some specimens was of exponential form, the decay rate increasing exponentially with temperature. Their results may be stated by the following decay equation with the notation already used in Chapter II:

$$I = I_0 \exp(-\alpha t), \tag{3.1}$$

where $\alpha = s \exp(-E/kT)$, s is a constant equal to $2{\cdot}9 \times 10^9$ sec.$^{-1}$, and E another constant (0·67 eV.). We are familiar with

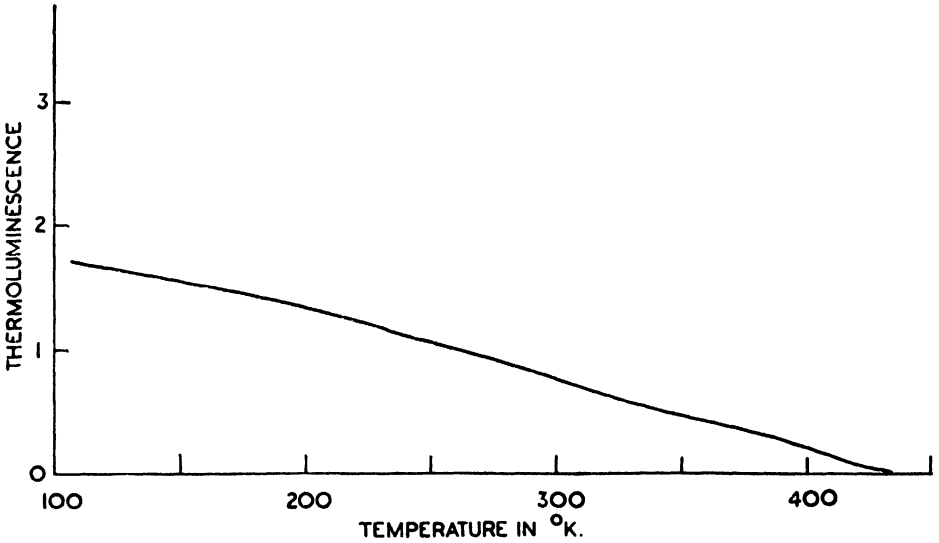


FIG. 24. Thermoluminescence curve for a KCl—Tl phosphor prepared from saturated aqueous solution.

this type of decay from the theoretical discussion of Chapter II. It is characteristic of a phosphor which has one depth of electron trap and which shows no photoconductivity. In this case the electron trap is a metastable state of the emission centre. The thermoluminescence also favours this assumption. The curve of thermoluminescence variation with temperature obtained for a typical phosphor specimen by Randall and Wilkins is shown in Fig. 17 of Chapter II. It is found that in general there is a narrow distribution of metastable levels in such phosphors. Such a distribution can account for the hyperbolic decays observed by Antonow Romanowsky [29] which result from a summation of exponential processes due to individual metastable states and not, as he suggests, to a bimolecular process.

In the case of the Pringsheim [26] types of these phosphors the distribution may be very broad, as shown by the thermoluminescence curve of Fig. 24 for a typical specimen.

Randall and Wilkins have observed an additional effect of some interest in their phosphor specimen. The peak in the thermoluminescence curve corresponding to the metastable level of activation energy 0·67 eV. occurs at 340° K. This peak is found to be much greater in intensity if excitation is carried out at a temperature not far below 340° K (e.g. 300° K) rather than at 90° K. This is attributed to the trapping of many of the excited electrons at 90° K in shallow levels. They are then released at low temperatures and return to ground states, being thus unavailable for emission at 340° K. At room temperature the shallow states cannot retain electrons and so most of the excited electrons are trapped in the deeper levels and contribute to the emission at 340° K.

The nature of the phosphorescence centres. In considering the nature of the phosphorescence centres in these phosphors we may summarize the following significant facts:

i. There is hardly any phosphorescence for small concentrations of thallium.

ii. The ratio of the phosphorescence light output to the absorption is roughly proportional to the activator concentration. Since the absorption itself is proportional to the activator concentration, the light output of phosphorescence is a function of the square of the thallium concentration.

Seitz assumes, therefore, that phosphorescence is peculiar to pairs of adjacent thallium ions in the alkali halide lattice. Such pairing would be rare at low activator contents. The energy-level scheme proposed by Seitz to explain the identity of fluorescence and phosphorescence spectra and the occurrence of metastable states is shown in Fig. 25. This is the simplified figure due to Mott and Gurney [18]. The metastable state with activation energy of 0·67 eV. is a configuration of the ground state and is indicated by M in the figure. After excitation of

electrons into the states L, N, and S, emission of fluorescence occurs by return transitions to the ground state. However, some of the excited centres will assume metastable configurations M. In this case return to the ground state must involve the thermal activation of the centres and emission of phosphorescence or

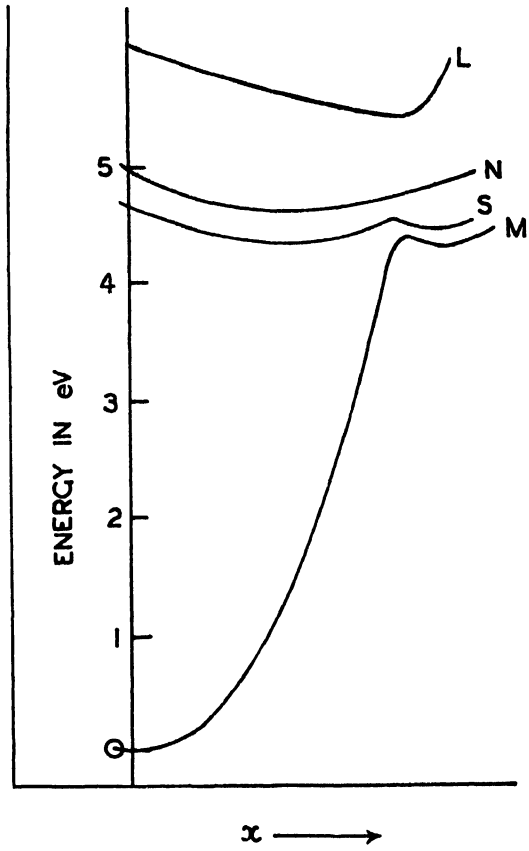


FIG. 25. Energy-configurational diagram for emission centres in KCl—Tl phosphors. (Seitz.)

thermoluminescence by the same transitions as in fluorescence. Long wave-length light can stimulate emission during phosphorescence provided that it is of wave-length shorter than that corresponding to about 0·67 eV. energy. The return to the normal state from the metastable state by the non-radiative transition over the barrier between the minima M and O is unlikely. This is because the centre will have a very small probability of reaching the saddle-point in a multidimensional configuration.

The above detailed treatment which we have given for the alkali halide phosphors containing thallium or other heavy metals has been made possible because of the relative simplicity of the optical measurements. They are facilitated by the availability of the phosphors in the form of large single crystals. As we shall see in the remainder of the chapter, the interpretation of luminescence in other systems is much less definite because the phosphors are only available in most cases as powders.

(*b*) Impurity-activated sulphide phosphors

i. *Zinc and cadmium sulphide phosphors*

The group of phosphors comprising zinc and cadmium sulphides activated by specific metallic impurities is of considerable practical importance. For this reason it has received the greatest attention of workers in the luminescence field. Perhaps the most distinctive phosphor of this class is the green luminescent, long-afterglow zinc sulphide activated by copper. Other impurities effective as luminescence activators include silver and manganese. An excess of the metallic lattice constituent of either zinc or cadmium sulphide can also function as an activator. It is generally assumed, except in the case of manganese impurity, that the activator occupies an interstitial position in the crystal lattice. We shall discuss three systems in this class of phosphors, namely, zinc sulphide, mixed zinc and cadmium sulphides, and the ternary system formed by the mixtures of zinc, cadmium, and manganese sulphides. The systems have the notation ZnS, ZnS—CdS, and ZnS—CdS—MnS respectively; the activator is denoted by an appended symbol, for example, ZnS—Cu or ZnS—CdS—Ag.

Zinc and cadmium sulphides can have two different crystalline forms, namely, a zinc blende or diamond-type cubic structure (sphalerite) or a hexagonal structure (wurtzite); both types can occur in the same crystal, their proportions depending on the preparation conditions. In zinc sulphide the hexagonal form is stable above the transition temperature of about 1,020° C. as found by Allen and Crenshaw [30]. However, the hexagonal

form can occur at lower preparation temperatures, and Seitz [31] has suggested that the lowest temperature for its formation is about 450° C. The transition point for cadmium sulphide has not been published, but it is known that the hexagonal form is the stable one at high temperatures. Zinc and cadmium sulphide form a mixed crystal system when they are fired together at a suitable temperature. Except for those specimens with high zinc sulphide content, the structure of the mixed crystals is of the wurtzite form. This is also found to be so in the case of the mixed crystal system ZnS—CdS—MnS as observed by Kröger [32].

Conditions for the preparation of luminescent zinc and cadmium sulphides. It is found that synthesis of the basic constituents of a zinc sulphide phosphor at a high temperature does not produce a luminescent specimen. Rothschild [33] reports that the product obtained by heating together zinc and sulphur is non-luminescent, but that an efficient phosphor is produced if a small amount of sodium chloride is added and the specimen reheated. His extensive experiments show that in the precipitation of zinc sulphide, which is the usual way of obtaining the basic material for firing, halogen ions are always included although the precipitate is well washed. It would appear that halogen ions are essential to the production of a good phosphor. Fluorine ions constitute an exception to this rule and will suppress luminescence if present. The precise action of the halogen ions is not known, but some hypotheses might be mentioned. Schlegel [34] suggests that these ions cause a partial dissociation of the sulphide lattice in the region of the activating impurity, this being essential for the formation of the emission centre. A. F. Gibson, of the author's laboratory, has noted that the crystal structures of cuprous chloride, bromide, and iodide, but not fluoride, are the same and each copper ion is surrounded tetrahedrally by four halogen ions. Thus if the complex centre in which emission takes place contains halogen ions as well as the activator impurity, it is probable that they form such a tetrahedral structure as the basic nucleus of the centre. Seitz [31] has suggested that only the hexagonal form of zinc sulphide

is luminescent, but Riehl [35] affirms that both cubic and hexagonal forms are luminescent. Randall [36] has stated that he believes the cubic form to be luminescent from his experiments. We shall see in this and later chapters that the emission centre in zinc sulphide phosphors is of complex structure. As a result the arguments of the above workers cannot be tested until more is known of the detailed structure of these centres. Such information cannot be obtained by X-ray analysis because of the small concentration of the centres in normal phosphor specimens.

Self-activated zinc and cadmium sulphide phosphors. It has been known for a long time that pure precipitated zinc sulphide (which may contain traces of halide ions) becomes luminescent when heated without deliberate inclusion of an impurity activator to a sufficiently high temperature. A. F. Wells *et alia* [37], working in the author's laboratory in the war period 1940–4, have shown that this temperature can be as low as 500° C. For firing temperatures below 1,000° C. the luminescence is a light blue in colour according to Schleede [38], who also found that a mixed blende-wurtzite lattice seemed essential for the production of luminescent specimens. The emission spectrum of a 'pure' zinc sulphide phosphor is like curve *A* of Fig. 7. The activation is supposed to be due to an excess of zinc ions in interstitial positions of the crystal lattice. The phosphorescence of these self-activated phosphors is very short-lived, but is due to the action of shallow trapping states. These are shown by the thermoluminescence curve of a typical phosphor in Fig. 26. Cadmium sulphide also becomes luminescent when heated without deliberate addition of impurity, but the emission is in the infra-red region of the spectrum and only the tail of the spectrum is visible. Addition of cadmium sulphide to zinc sulphide before heating causes a shift of the fundamental absorption edge of the pure zinc sulphide to longer wave-length, as shown by Fig. 13. The emission also shifts towards the red as the cadmium sulphide content increases [39].

Kröger [32] has found that at low temperatures excitation in the fundamental absorption band of zinc sulphide or cadmium

sulphide produces an emission which lies to the short wave-length side of the normal emission, being adjacent to the absorption edge. This emission, measured at liquid-air temperature for each phosphor, is shown in Fig. 27. The maximum of the emission is in the long wave-length ultra-violet region

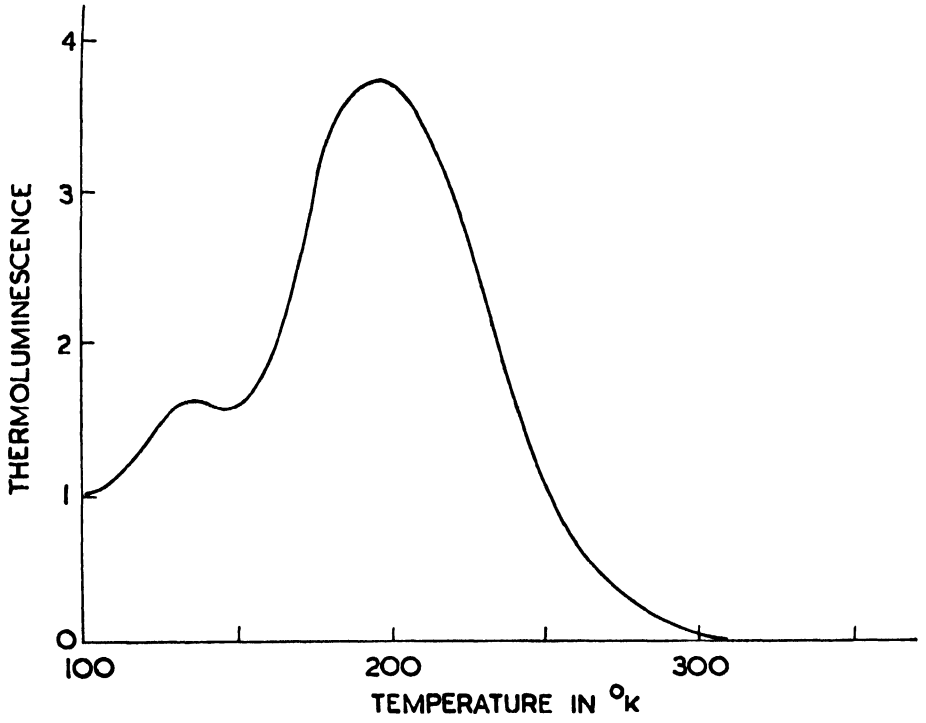


FIG. 26. Thermoluminescence curve of a typical self-activated zinc sulphide phosphor (wurtzite structure).

for zinc sulphide and in the green region for cadmium sulphide. For mixed crystals of zinc and cadmium sulphide its position is intermediate and depends on the proportions of the two sulphides present. Kröger attributes this emission to electronic transitions of the crystal coupled with vibrational levels of the ground states of the emission centres. This is likely since the spectra of Fig. 27 show a vibrational structure. This evidence shows that the luminescence centres are not simply impurity ions but these ions together with surrounding ions of the crystal lattice and of halogens or other elements present in trace amounts. Further discussion of such complex centres is given in later chapters.

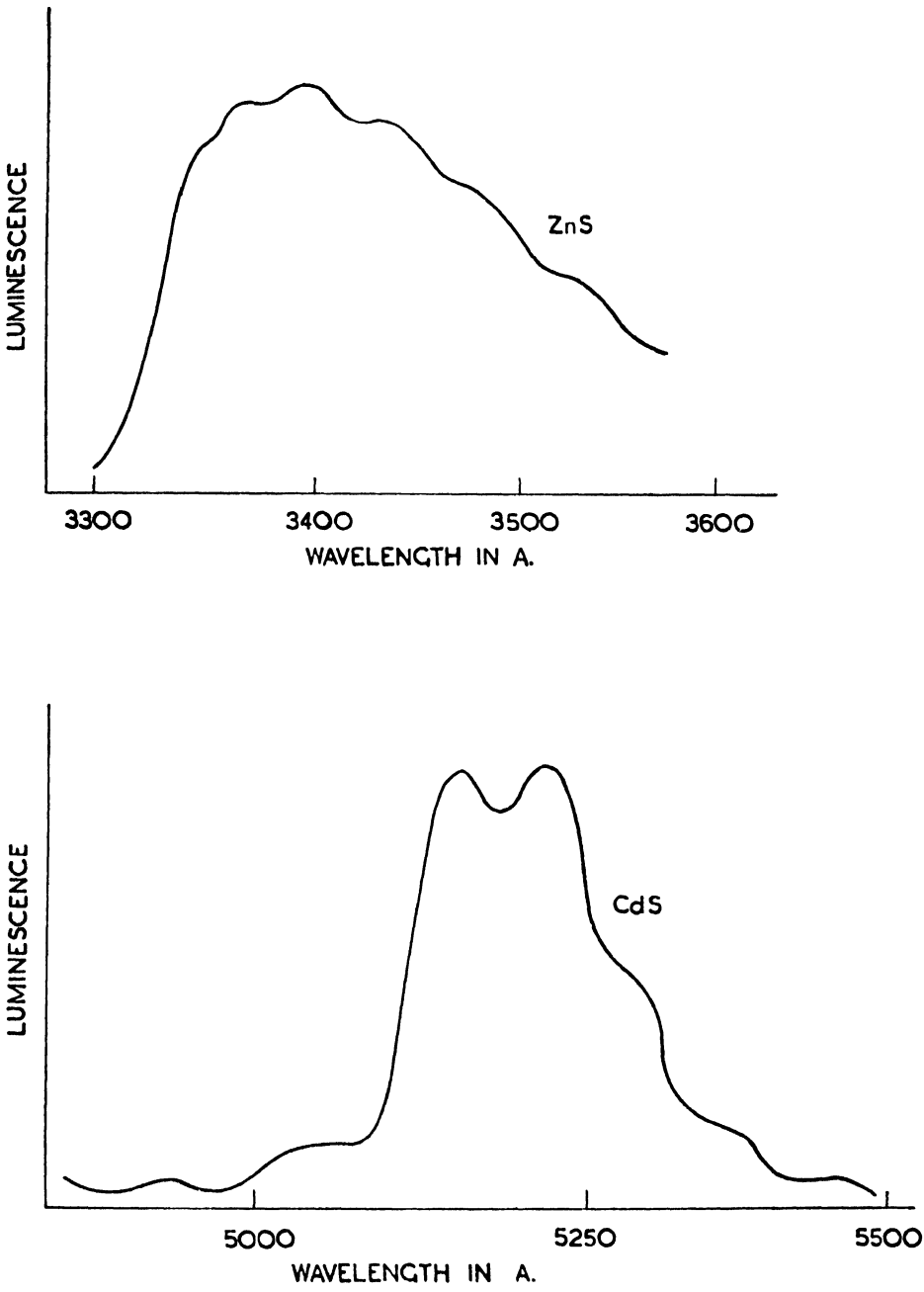


FIG. 27. 'Edge emission' luminescence spectra of self-activated zinc and cadmium sulphide phosphors at 90° K. (Kröger.)

Impurity-activated zinc and cadmium sulphide phosphors. In addition to self-activation, zinc and cadmium sulphide systems may be activated by impurity ions such as copper, silver, and

manganese included in small concentrations in the unfired materials. The luminescence efficiencies attainable with such impurities are much higher than those for self-activation. There is some recent evidence that large ions, like lead, can function as luminescence activators in zinc sulphide [40], although earlier experiments due to Riehl [41] seemed to indicate that the large diameter of such ions as lead and bismuth, both effective in alkaline earth sulphides, prohibited their entry into the interstices of the zinc sulphide lattice. The action of lead is discussed later in a consideration of the infra-red sensitivity of phosphors of this type (Chap. VI). Copper and silver (and also gold) behave in a similar way to zinc with respect to their functions as activators, but manganese falls into a separate category since its sulphide forms mixed crystals with zinc and cadmium sulphides in the ternary system ZnS—CdS—MnS; the manganese content can be as high as 2 per cent., whereas in the case of the other activators a concentration greater than 0·1 per cent. causes a large decrease in luminescence efficiency. Our first consideration of these systems will be that of the silver- and copper-activated zinc sulphide or zinc-cadmium sulphide phosphors.

Silver-activated zinc sulphide phosphors. The addition of silver to zinc sulphide in small concentration (0·01 per cent.) causes an emission consisting spectrally of a single band with a maximum at about 4,450 A as shown by the curve of Fig. 7 of Chapter I. The maximum is slightly variable with the conditions of preparation, such as the temperature of firing and the concentration of silver. Rothschild observes the variation to be a shift to shorter wave-lengths as the temperature increases or the silver content increases. Addition of cadmium sulphide causes a shift of the emission to longer wave-lengths for both silver- and copper-activated zinc-cadmium sulphides. The phosphorescence of zinc sulphide activated by silver is not marked as there are few electron traps of appreciable depth in the phosphor. A typical thermoluminescence curve for such a phosphor is given in Fig. 28, the electron traps being of about the same depth as in the 'pure' zinc sulphide (Fig. 26).

Copper-activated zinc sulphide. The addition of copper to zinc sulphide and subsequent firing give rise to a new and intense emission band in the green region of the spectrum with a maximum at about 5,300 A. The introduction of copper tends to suppress the blue emission of the 'pure' zinc sulphide even at

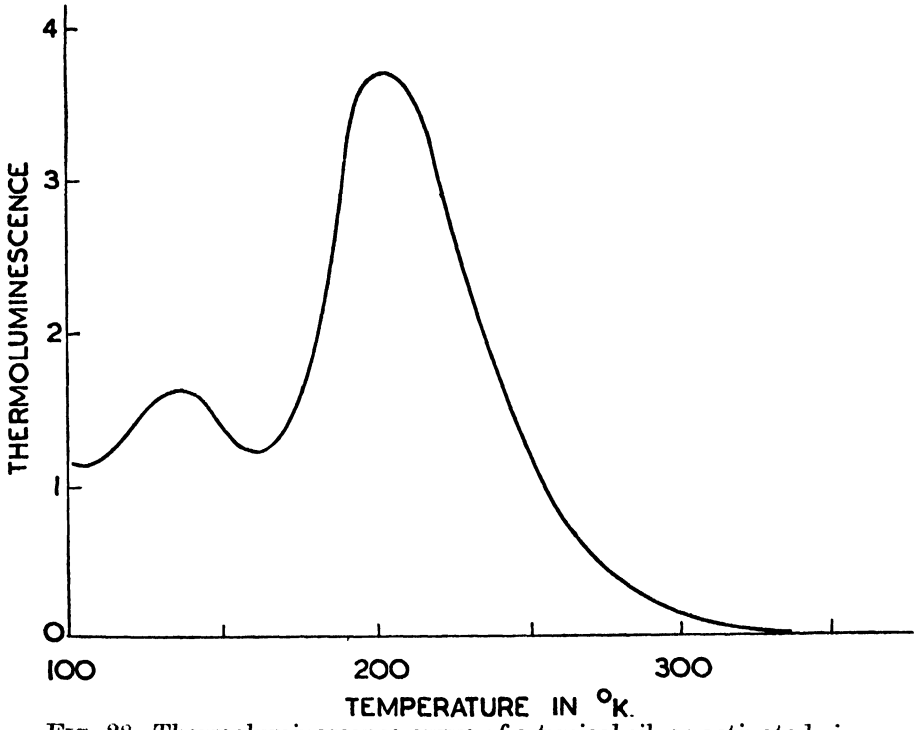


FIG. 28. Thermoluminescence curve of a typical silver-activated zinc sulphide phosphor (wurtzite structure).

concentrations of copper as low as 0·006 per cent. (Rothschild [33]). Considerable interest centres in the copper-activated zinc sulphides since the impurity also gives rise to a long-lived phosphorescence by the formation of relatively deep electron traps. The optimum conditions for this phosphorescence include the necessity of a wurtzite lattice. This is demonstrated by the thermoluminescence curves of Fig. 29 for two specimens of zinc sulphide each containing 0·01 per cent. copper and both fired at the same temperature, but one having a blende structure and the other a wurtzite structure, due to flux inclusions. The absence of the large number of deep electron-traps in the blende specimen is obvious. Similar differences between 'pure' zinc sulphides of different structures with respect to their

thermoluminescence curves are found. The phosphorescence of copper-activated zinc sulphides is markedly dependent on the preparation conditions and on traces of impurity. The entry of nickel into the phosphors is discussed in Chapter IV with respect to its 'killing' action on the phosphorescence

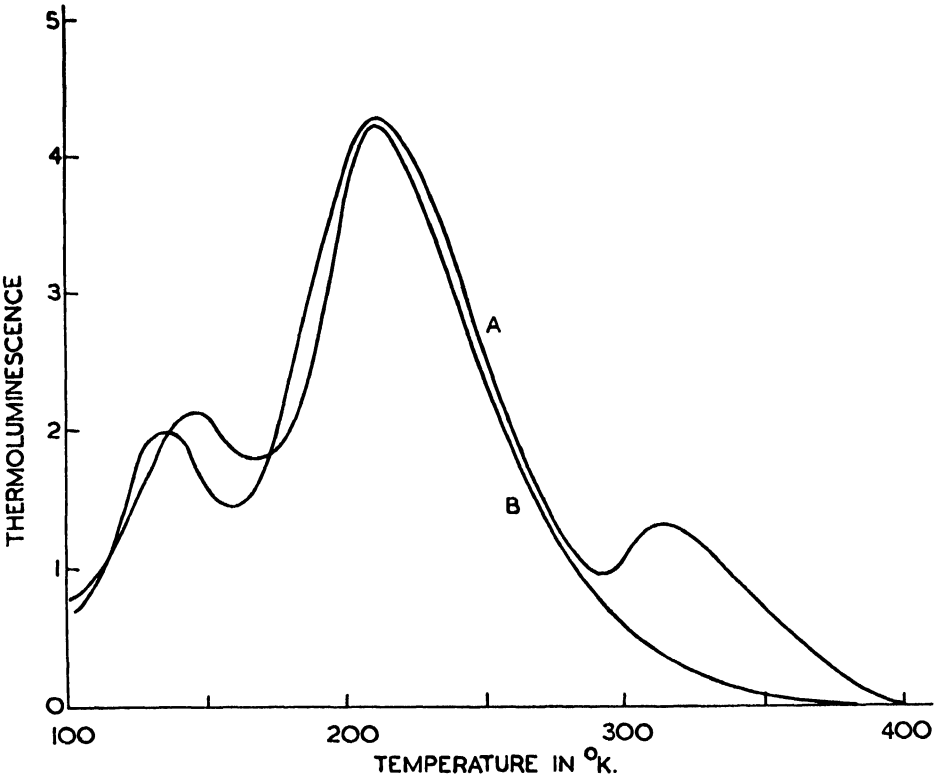


FIG. 29. Effect of lattice structure on the electron-trap distributions of ZnS—Cu phosphors made at 980° C. *A*, wurtzite lattice; *B*, blende lattice.

of zinc sulphides. The experiments of Riehl [41] show that copper can enter the zinc sulphide lattice at temperatures as low as 330° C. A. F. Wells *et alia*, working in the author's laboratory, have studied in addition the effect of preparation conditions on the electron-trap distributions in these phosphors [37]. Their values for the minimum firing temperature for copper activation show fair agreement. The chief results obtained by Wells *et alia* in their studies are summarized below:

(*a*) Phosphors made in one firing process at low temperatures only possess shallow traps and consequently their

room-temperature phosphorescence is very small and rapid. The effects of firing at different temperatures are represented by the thermoluminescence curves of Fig. 30.

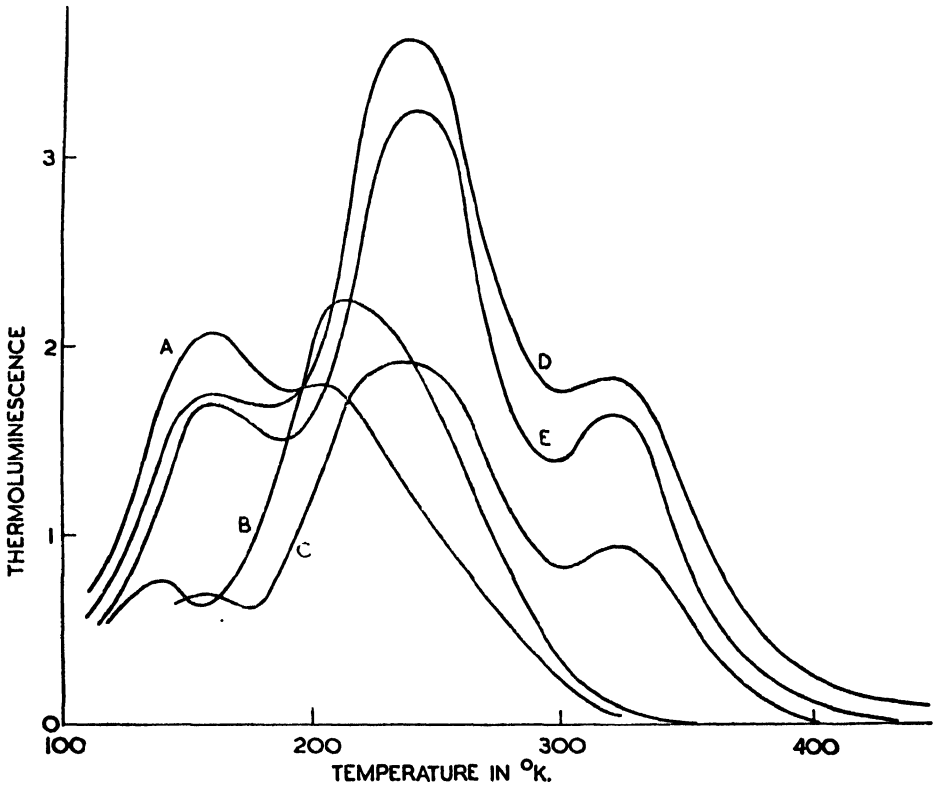


FIG. 30. Development of deep electron traps in ZnS—Cu phosphors with increase in firing temperature as shown by thermoluminescence curves. (Garlick, Wells, and Wilkins.) *A*, ZnS—Cu: 980° C.: all blende. *B*, ZnS—Cu: 1,000° C.: trace of wurtzite. *C*, ZnS—Cu: 1,028° C.: mostly wurtzite. *D*, ZnS—Cu: 1,180° C.: all wurtzite. *E*, ZnS—Cu: 1,480° C.: all wurtzite.

(*b*) Firing temperatures above 800° C. are necessary to produce phosphors with traps of appreciable depth and thus phosphorescence of observable duration.

(*c*) The long afterglow specimens have almost completely hexagonal structures and the corresponding electron traps of greater depth are indicated by the broad thermoluminescence peak at 320° K. in Fig. 30.

(*d*) The long afterglow phosphors may be produced in two stages, showing that the copper activation and the lattice

formation are independent processes. Curve *A* of Fig. 31 is the thermoluminescence-temperature curve of a 'pure' zinc sulphide made at 1,100° C. and having a wurtzite lattice. The electron traps shown by this curve are shallow and the emission is blue and characteristic of the self-activated phosphor. If

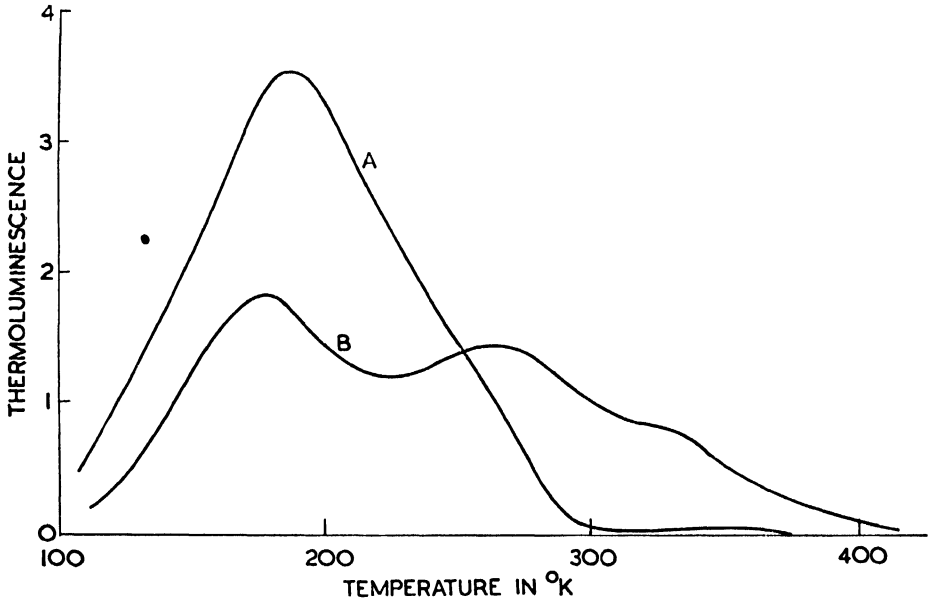


FIG. 31. Production of deep electron traps in a ZnS—Zn phosphor, made at 1,050° C. by addition of copper impurity at 425° C. (Garlick, Wells, and Wilkins.) *A*, thermoluminescence curve of ZnS—Zn (1,050° C.). *B*, thermoluminescence curve of ZnS—Zn—Cu prepared from *A* at 425° C.

this phosphor is reheated, with inclusion of 0·01 per cent. by weight of copper, to a temperature of only 400° C., then deep electron traps are produced, as shown by the curve *B* of Fig. 31. The emission due to these electron traps is green and characteristic of the copper impurity. The thermoluminescence curve is similar to those for copper-activated phosphors made in one process at 1,100° C. The low-temperature thermoluminescence peak of the curve *B* still gives blue emission. The inference from this experiment is that the deep electron traps are situated in the region of the copper centres but that they require the existence of a well-formed crystal lattice in order to be produced by the activator inclusion.

(*e*) *The action of fluxes.* Above the transition temperature for the blende-wurtzite forms the addition of flux, usually a salt of an alkali or alkaline earth metal (concentration 5–10 per cent. by weight), does not have any marked effect on the phosphorescence and thermoluminescence but only seems to aid in lattice formation. However, below 1,020° C. the flux has a marked effect on these characteristics, its action being to alter the blende-wurtzite proportions. It usually suppresses wurtzite formation, the explanation probably being that wurtzite is formed by a sublimation process and that the flux coats the grains, thus inhibiting the process and promoting the growth of the cubic lattice. A similar effect results from the presence of excess sulphur during preparation.

A considerable study has been made by Rothschild of copper-activated zinc sulphide [33]. His studies show that, for high copper contents (0·02 per cent.) and suitable preparation conditions, the green band due to copper becomes less intense and there is a growth of a blue band with a peak at 4,450 A and having short phosphorescence. He ascribes the blue band to monovalent copper ions and the normal green band to divalent copper ions. Seitz [31] has suggested that prolonged heating at high temperature, or with high copper concentrations, will lead to a replacement of lattice zinc by copper from interstitial positions. Thus, although the entry of copper into the lattice at low concentrations will suppress the self-activated blue emission, since this decreases the probability of occurrence of interstitial zinc, yet a replacement process will remove the copper and allow once more the luminescence from interstitial zinc. This may provide an alternative explanation of Rothschild's results.

The green emission of copper-activated zinc sulphide is shifted towards the red when cadmium sulphide is added, and simultaneously there is a change in the phosphorescence characteristics. The series of thermoluminescence curves in Fig. 32 shows how the electron-trap distributions change with the cadmium sulphide content. As this becomes large there is evidence of deep trap formation, as shown by the peak at 400° K.

in the last curve. These figures are not corrected for the change in the recording photocell sensitivity with emission wavelength and so the number of deep traps in phosphors of high cadmium content may be very large (cf. Chap. V, Fig. 68).

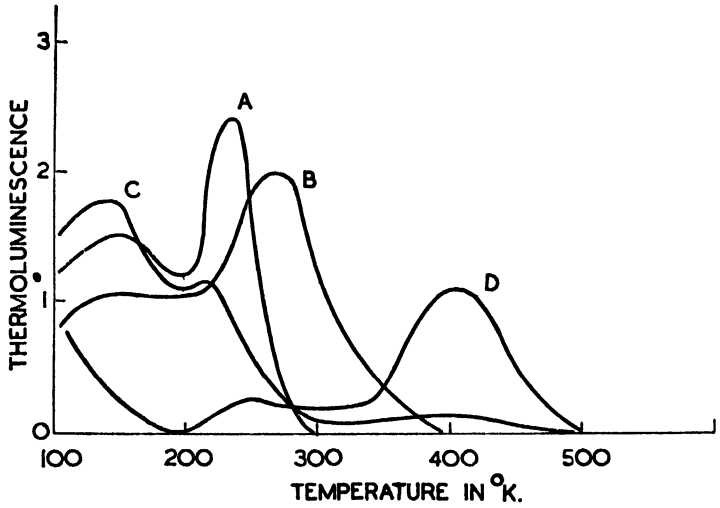


FIG. 32. Thermoluminescence curves of ZnS—CdS phosphors made at 1,100° C. (Garlick, Wells, and Wilkins.) *A*, ZnS (85 per cent.) CdS (15 per cent.) no copper. *B*, ZnS (85 per cent.) CdS (15 per cent.) Cu (0·01 per cent.). *C*, ZnS (55 per cent.) CdS (45 per cent.) Cu (0·01 per cent.). *D*, ZnS (45 per cent.) CdS (55 per cent.) Cu (0·01 per cent.).

General discussion of zinc and zinc-cadmium sulphide phosphors activated by silver and manganese. Although it is probable that the luminescence centres are formed by interstitial copper and silver (and zinc) in zinc sulphide, yet the ions of these metals in themselves possess no characteristic structures which would favour the occurrence of luminescence. The emission spectra for zinc, copper, and silver are very broad bands and are very dependent for position on the lattice parameters, as shown by the effect of cadmium sulphide inclusions. The centres are not effective unless the phosphor contains halide ions (with the exception of fluorine). Thus it must be assumed that the centres are not single interstitial ions but include the nearest, and possibly other, neighbouring ions of the lattice. In addition, it is likely that in the blende and wurtzite structures there will be preferred interstitial positions, since the structures have sites of symmetry with respect to the lattice ions, which would be

potential traps for impurity ions. This infers that in both the lattice forms the copper or silver ion will be tetrahedrally surrounded by sulphur ions. The idea of a complex luminescence centre of this type is given support by Kröger's measurements of the edge emission (Fig. 27) and its fine structure for 'pure' zinc sulphide. A discussion given for silver halides by Huggins [42] suggests a similar explanation of the structure of latent image sites and is perhaps relevant to the above discussion.

The system ZnS—CdS—MnS. The bulk of the information obtained in recent years for manganese-activated zinc and zinc-cadmium sulphide phosphors is due to the exhaustive studies of Kröger [43, 44]. Introduction of manganese sulphide into the system ZnS—CdS results in emission characteristic of the manganese ions present in the divalent state and the behaviour of these phosphors is essentially different from that of copper, silver, or self-activated phosphors. Solid solutions of ZnS—CdS—MnS occur up to 50 mol. per cent. MnS, all having the wurtzite structure except those with high ZnS content. The characteristics of the chief types of phosphor in this ternary system are as follows:

(1). ZnS—MnS *phosphors.* The emission spectrum of a ZnS—MnS (2 per cent.) phosphor is shown in Fig. 7 of Chapter I. The emission band, which is single, is narrower than those for copper, silver, and zinc and has a maximum at 5,850 A which is little influenced in position by the lattice. The luminescence efficiency becomes low if a manganese content greater than 5 per cent. is present (room-temperature observation). The blue emission of the 'pure' sulphide is suppressed as the manganese content increases but is still present for 0·01 per cent. Mn. The change in the absorption characteristics of zinc sulphide with the introduction of manganese sulphide has already been demonstrated by Fig. 11 of Chapter II. The fundamental absorption edge of zinc sulphide is shifted from 3,350 A towards the limit of 3,660 A which is the fundamental absorption edge of manganese sulphide. In addition absorption

bands occur at longer wave-lengths which are characteristic of the manganese ions themselves. The different types of phosphorescence decay due to absorption of exciting radiation lying in the different absorption regions have been investigated by

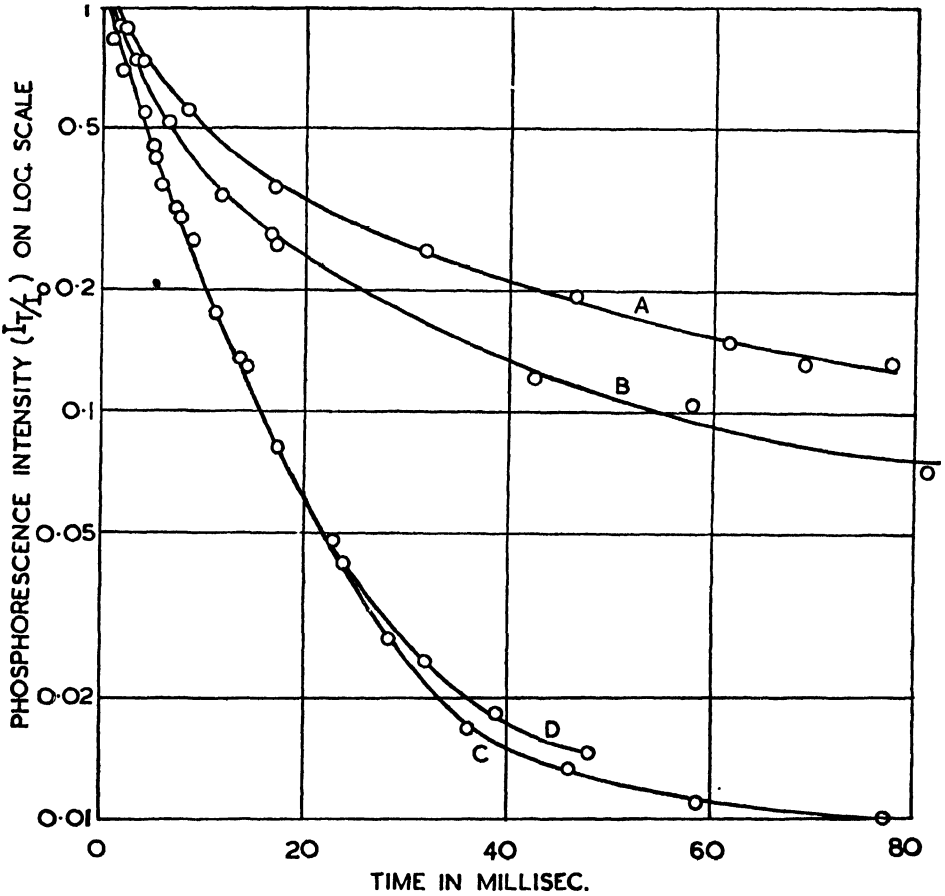


FIG. 33. Phosphorescence decay curves for ZnS—Mn (2 per cent.) for various excitation conditions at room temperature. (Garlick and Wilkins.) *A*, excited by 3,650 A: intensity = 1. *B*, excited by 3,650 A: intensity = 9. *C*, excited by 4,358 A: intensity = 9. *D*, excited by 4,358 A: intensity = 1.

Garlick and Wilkins [45]. Their results are summarized by Fig. 33, which shows that absorption in the characteristic bands of the manganese ions gives rise to exponential decay, due to optical transitions within the luminescence centres; the action of electron trapping is of a small order. Excitation by shorter wave-length radiation frees electrons which are then trapped and a longer duration phosphorescence, due to the trapping

mechanism, results. The thermoluminescence curve due to these traps for the phosphor containing 2 per cent. Mn is given in Fig. 34 showing that the traps are all relatively shallow.

Wells has shown that the formation of good phosphors of this class only occurs for firing temperatures of 800° C. or above.

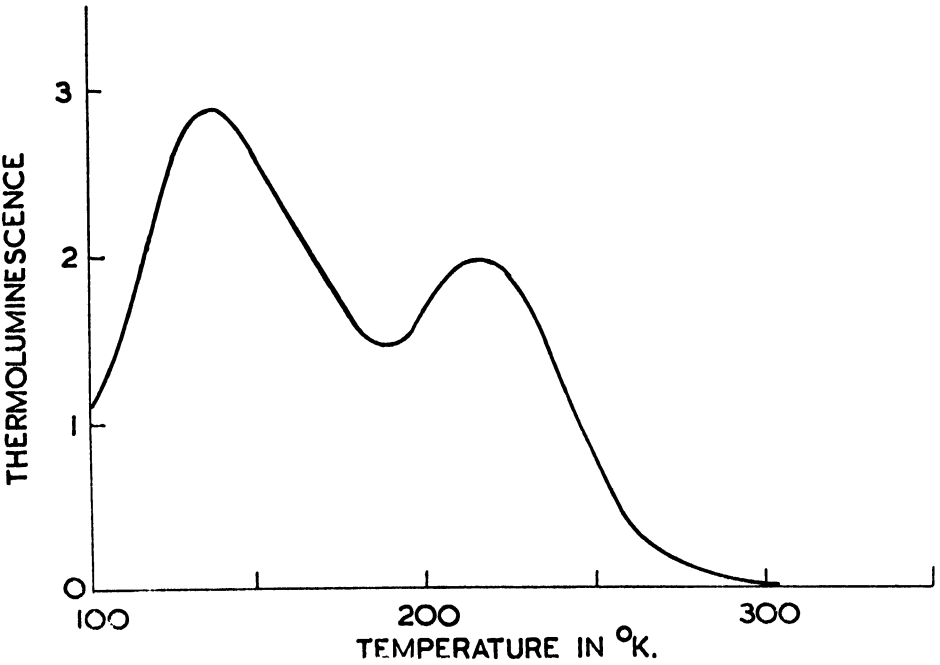


FIG. 34. Thermoluminescence curve of ZnS—Mn (2 per cent.) of Fig. 33.

However, Kröger has prepared ZnS—MnS phosphors, by co-precipitation from aqueous solution, that show the characteristic manganese emission without further heating above 400° C.; the efficiency of these phosphors is low, increasing markedly with the temperature of firing.

(2). *The system* ZnS—CdS—MnS. The following observations are taken from studies due to Kröger [46]. The system CdS—MnS gives phosphors which have a red emission, and increase in the MnS content causes the emission to move to shorter wavelengths; a similar behaviour is shown by the ternary system ZnS—CdS—MnS. However, with high CdS content the self-activated emission of ZnS—CdS occurs, even for relatively high MnS content. The transition is smooth with change in the

lattice and is distinct from the characteristic emission for manganese which remains independent of the lattice composition, although this emission is only visible for systems with small manganese content (5 per cent.) and for CdS content less than 20 per cent.

General discussion of manganese-activated phosphors of the above systems. This class of zinc or zinc-cadmium sulphide phosphors is different in nature from the silver-, copper-, and zinc-activated systems since the luminescence centres are almost certainly due to the manganese ions alone, although the emission band at 5,850 A is quite broad and suggestive of some effect of the surrounding lattice on the ionic transition levels. The manganese is built into the matrix lattice and is in the divalent form. Further evidence, showing the differences between manganese-activated and other impurity-activated zinc sulphide phosphors, is provided in later chapters.

ii. *Impurity-activated alkaline-earth sulphide phosphors*

The impurity-activated sulphides of calcium, strontium, and barium were investigated in a thorough way by Lenard (see general references, Chap. I), but his results are not amenable to interpretation. The activators in these phosphors were found to be bismuth, copper, manganese, and lead, and also certain rare-earth elements such as samarium and europium. The early studies will not be described, but recent work of interest on these phosphors merits some attention. Birus has given some account of these phosphors [7], but until the recent studies by Randall and Wilkins [15] of the electron trapping responsible for their phosphorescence and studies by A. F. Wells, *et alia*, on phosphor constitution the general knowledge of the phosphor mechanisms has been, to a great extent, unsatisfactory. More recent work on the application of alkaline earth phosphors to infra-red detection, by virtue of their stimulability by infra-red radiation, has provided valuable fundamental information and is described in Chapter VI.

Calcium, strontium, and barium sulphides have the rock-salt type of structure. The usual method of formation of the

sulphides is by firing a mixture of the alkaline-earth carbonate or oxide with sulphur and a suitable flux (in small percentage) together with the desired activating impurity. The following is a summary of experimental results by A. F. Wells [37]. It is concerned with conditions of preparation in relation to the crystallinity and luminescence characteristics of the final phosphor product.

(*a*) The preparation of calcium sulphide in the above way results in a mixture of sulphide and sulphate and also complexes of the flux metal. However, by passing carbon disulphide vapour with nitrogen over the carbonate, almost complete formation of the sulphide occurs.

(*b*) Without inclusion of flux, firing of the carbonate or oxide with sulphur does not give rise to a good phosphor and X-ray analysis shows that only a very small quantity of sulphide is formed. The same applies to the carbon disulphide method, with respect to the luminescence and phosphorescence efficiency, although the sulphide formation is in this case almost complete. Reheating of the products of either process with a suitable flux produces a good phosphor.

(*c*) The fluxes effective in the production of efficient calcium sulphide phosphors have been listed in an instructive way by Wells and are given below in Table IV. The specimens prepared by use of these fluxes were all made from calcium oxide and sulphur with bismuth as activator and contain 10 per cent. of the selected flux. They were heated to 900° C. for half an hour in open-ended quartz tubes. The last column of the table gives an estimate, derived from the light sum of phosphorescence or thermoluminescence, of the relative phosphor efficiencies.

TABLE IV

The Action of Fluxes in preparation of CaS—Bi *Phosphors*

Fluxes	*Phosphor efficiency relative to group* (i) (*per cent.*)
i. Sodium oxy-salts: Na_2SO_4, Na_2WO_4, Na_2O_2:$LiCO_3$, $MgSO_4$	100
ii. NaCl, LiCl, NaBr	20
iii. KI, KBr, KCl, K_2SO_4, KH_2PO_4, NaI, $CdSO_4$ . .	5
iv. $ZnSO_4$, $CaCl_2$, $BeSO_4$, $Al_2(SO_4)_3$, YCl_3 . . .	1

The evidence from these studies shows that the different fluxes determine the amount of calcium sulphide formed, but that they also influence the building of the activator into the crystal lattice.

(*d*) The two main functions of the flux are to ensure the formation of calcium sulphide and to aid in its crystallization, but the efficiency of fluxes in this respect does not necessarily mean that they can produce a good phosphor. If the above action is effected, then the material with suitable impurity inclusion will become a phosphor if the flux also facilitates the entry of the activator into the lattice and aids in formation of the emission centres. In this respect the nature of the flux cation is found to be of importance, e.g. Na^+. A flux not efficient in CaS crystal formation will not be effective in the activation process.

(*e*) The above flux action is observed for other activators besides bismuth, such as copper or lead, but for impurities such as manganese and the rare-earth ions mentioned, the activation is not markedly dependent on the flux. This would be expected from the nature of these elements with respect to luminescence, discussed in Chapter I. For barium sulphide phosphors the flux action is similar to that for calcium or strontium sulphides, but potassium salts are also effective in this case, in contrast to their behaviour in the latter phosphors.

The luminescence properties of alkaline-earth sulphides. Calcium and strontium sulphides or mixed sulphides of these two metals show phosphorescence of very long duration lasting for days or even weeks when activated by bismuth. The emission is in the blue-violet region for calcium sulphide, but in the blue-green region for strontium sulphide. The emission bands are broad, as in the case of copper or silver activators in zinc sulphide phosphors. The emission colour and the phosphorescence decay are both characteristic of the particular activator. Randall and Wilkins [15] have studied the thermoluminescence properties of some of these phosphors in relation to their phosphorescence and, as Fig. 18 of Chapter II shows, good correlation between the two phenomena is obtained by neglect of retrapping processes. Thus, the original assumption of Lenard,

that the decay of phosphorescence in these materials could be explained as a sum of exponential terms due to the phosphorescence centres of different lifetimes, was true in some respects. It is, however, certain that the electron traps which are present are not actually within the luminescence centres as in the case of potassium chloride activated by thallium discussed in section

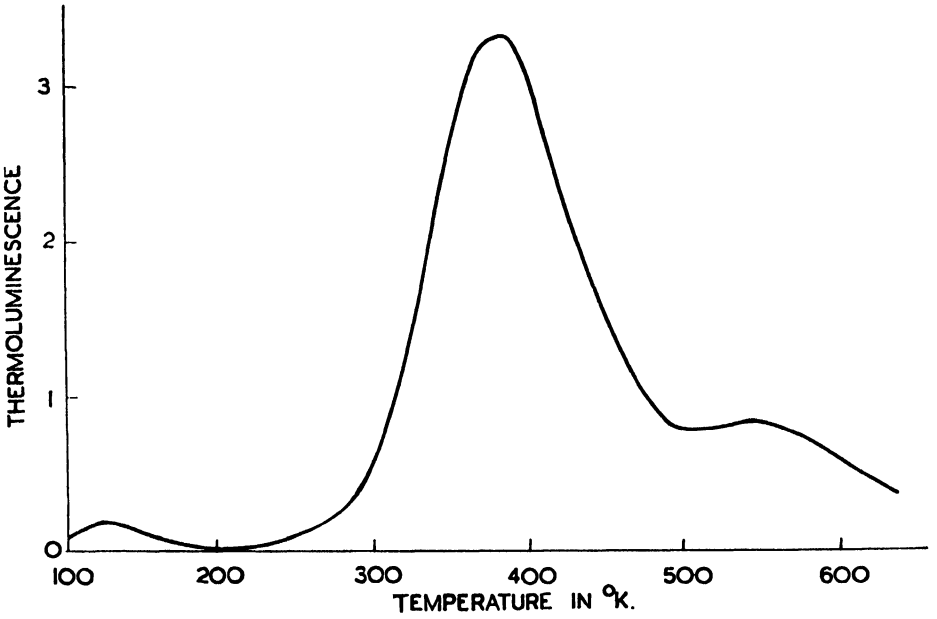


FIG. 35. Thermoluminescence curve of a typical CaS—Bi phosphor.

(*a*) of this chapter but are in the immediate vicinity. This assumption is borne out by the thermoluminescence studies of alkaline-earth sulphide phosphors made by Wells. Fig. 35 shows the thermoluminescence curve for a CaS—Bi phosphor with very long duration phosphorescence. The electron traps responsible for this afterglow are indicated by the broad emission peak above room temperature.

The most useful information obtained in these studies has been from the preparation of phosphors with more than one activator. Observations due to Rothschild [47] showed that the phosphorescence efficiency of bismuth-activated calcium sulphide could be improved by addition of a second activator in smaller concentration, the effect being greatest with samarium. This effect depends on the relative concentration of the activator

since the addition of bismuth to samarium-activated calcium sulphide enhances the emission from the samarium centres. This has a line-spectrum character. The measurement of the thermoluminescence curves of such phosphors shows that, in general, each activator gives rise to its own electron-trap distribution. Fig. 36 gives the thermoluminescence curves for

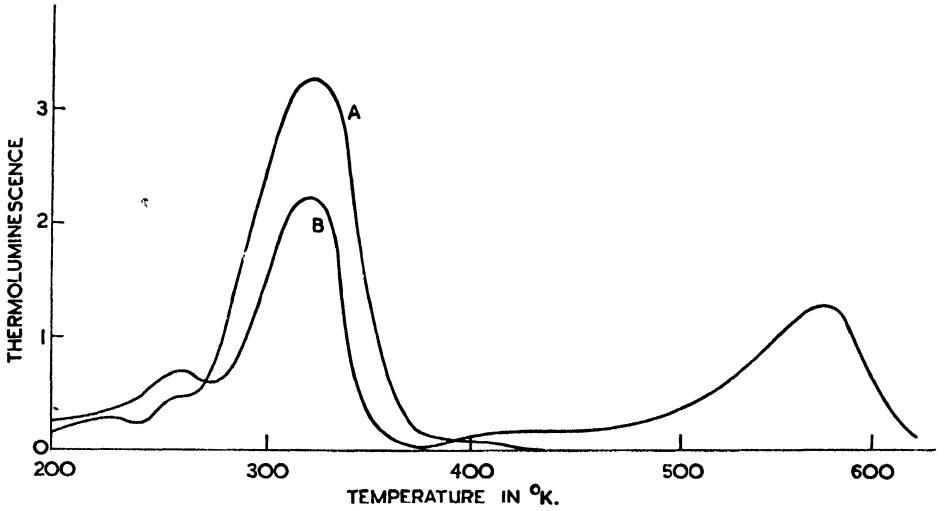


FIG. 36. Thermoluminescence curves for CaS—Cu and CaS—Cu—Bi phosphors showing relation of electron traps to impurity activators. (Wells.) *A*, CaS—Cu phosphor; *B*, CaS—Cu—Bi phosphor.

a CaS—Bi—Cu phosphor. The peak at 310° K. is due to traps created by the copper impurity, whereas the peak at 570° K. is due to bismuth, each peak having an emission spectrum characteristic of the respective activator. Similar behaviour is observed for CaS—Sm—Bi and CaS—Mn—Bi phosphors. The association of traps with the specific luminescence centres accounts for the absence of retrapping, the phosphorescence processes being effectively monomolecular in these phosphors. However, as will be seen from studies of the infra-red radiation sensitivity of these materials to be described in Chapter VI, there is some interaction between the various activator centres which modifies the electron trap-depth distribution. In some phosphors of the alkaline-earth sulphide type the electron traps must be relatively deep since exposure to light causes the materials to darken (i.e. the absorption bands are due to traps of 1 or 2 eV. in optical trap depth). The effect disappears as

phosphorescence or thermoluminescence proceeds. It has been described previously by Rothschild [48], but the explanation in terms of the absorption of light in the electron traps has not been given until now.

(*c*) SILICATE PHOSPHORS

Under this heading we include the manganese-activated silicates of zinc, beryllium, and cadmium, and some alkaline-earth silicates which have been recently investigated. The first group, that is, the zinc, beryllium, and cadmium silicates, are of great practical importance in the manufacture of fluorescent lamps and cathode-ray tube screens for television. Their practical development has led to a large amount of fundamental research on the silicate systems. In general they are in a different category from sulphide phosphors since the activating impurity, in many cases manganese, often forms isomorphous silicates. Thus, when incorporated in the matrix lattice, solid solutions are formed and the emission centres are then substitutional rather than interstitial. The existence of interstitial activator centres in the silicates has only been investigated recently. The studies of manganese-activated silicates has thrown much light on the function of manganese as an activator in other phosphor systems.

i. *Manganese-activated zinc silicate phosphors*

As far as is known with any degree of certainty, pure zinc silicate shows no luminescence after firing, when excited by ultra-violet light. A feeble blue emission is claimed to have been observed by Leverenz and Seitz [49], but such emission is not confirmed by the studies due to Randall [50] or to Kröger [51]. The presence of a very small amount of manganese (0·01 per cent.) is, however, quite sufficient to produce a green emission which is characteristic of the manganese ions. In conventional zinc silicate phosphors the manganese concentration is of the order of 1 per cent. In its mineral form, known as willemite, this phosphor has been known for a long time. More systematic study of the synthesized phosphor has shown that it has the formula Zn_2SiO_4—Mn_2SiO_4 and that the only real compound in

the system ZnO—SiO_2 is the ortho-silicate Zn_2SiO_4 [52]. It is, however, possible to prepare phosphors with excess silica, but they still retain the willemite structure; this structure is rhombohedral. The phosphors with excess silica are discussed below.

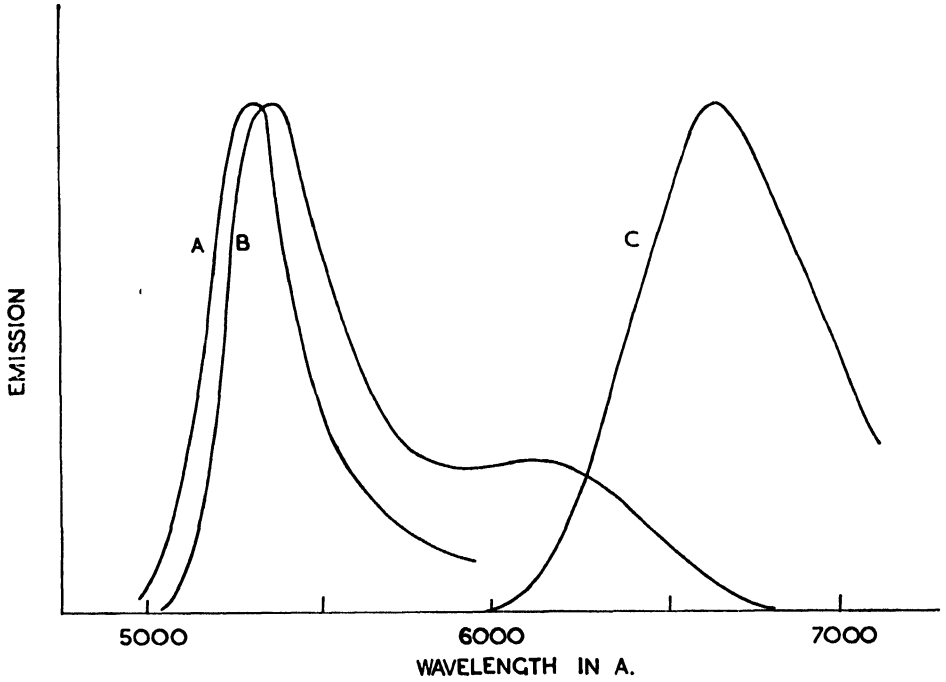


FIG. 37. Luminescence spectra of zinc and manganese silicate phosphors at low temperature (90° K.: 3,650 A excitation). (Kröger.) *A*, Zn_2SiO_4—Mn_2SiO_4 (5 per cent.); *B*, Zn_2SiO_4—Mn_2SiO_4 (20 per cent.); *C*, $MnSiO_3$.

Since zinc silicate and manganese ortho-silicate are isomorphous they form solid solutions, the limit of solubility being about 45 mol. per cent. Mn_2SiO_4, as determined by Kröger [51], the willemite structure is preserved in these solutions. The green luminescence due to the manganese is shown by these phosphors for manganese content up to 5 per cent. at room temperature, but above this concentration the luminescence efficiency decreases rapidly, presumably due to interaction of the impurity centres. At low temperatures the green emission can be observed for manganese silicate contents of 40 mol. per cent. Fig. 37, taken from Kröger's results, shows the effect of the increase in manganese concentration on the low-temperature emission spectrum of zinc silicate phosphors and also includes the

emission for another manganese silicate $MnSiO_3$. At high manganese concentrations a new emission band appears to the long wave-length side of the green emission and has a maximum at 6,100 A for a 20 mol. per cent. concentration of manganese. For concentrations above 40 mol. per cent. structural changes occur in the phosphor and X-ray analysis shows that crystals of the formula $MeSiO_3$, where Me is either zinc or manganese, are formed. These crystals exhibit a red emission at low temperatures which is the same as that of the pure manganese silicate $MnSiO_3$.

Yellow- and red-emitting zinc silicate phosphors can be prepared under suitable conditions, the normal green emission being suppressed. The manganese concentrations are normal (1 per cent.) and the emission occurs at room temperature. As early as 1923 Schleede and Gruhl [53] observed that the rapid cooling of manganese-activated zinc silicates after firing at 1,200° C. produced yellow- and red-emitting phosphors. Kröger has shown, by X-ray analysis, that these specimens still have the willemite structure, but that the emission may be due to local structural changes around the emission centres. It may also be associated with excess silica, particularly in the case of the red-emitting variety. More recently Fonda [54] has prepared such phosphors by firing the constituent materials at a lower temperature (850° C.) in the presence of a flux, such as potassium chloride (15 per cent.), which can later be removed without affecting the phosphor characteristics. Fonda suggests, with respect to the yellow-emitting phosphors, that amorphous complexes of ZnO and SiO_2 are produced which still correspond to the gross formula Zn_2SiO_4; the red emission he associates with excess silica probably present as a complex in association with zinc oxide and zinc silicate. The yellow emission has a maximum at 6,100 A, while the red-emission peak is at 6,700 A; these maxima may be compared with those of Fig. 37, the red emission coinciding with that for $MnSiO_3$. A further study of these phosphors has been made by Froelich [55], who has shown that the rapid cooling method can produce phosphors with luminescence efficiencies up to 65 per cent. of those for normal green-emitting

phosphors; Fonda's values of efficiencies are of the order of 45 per cent. By using steam atmospheres and preformed $MnSiO_3$ inclusions in his phosphors, Froelich obtained phosphors of 65 per cent. relative efficiencies at the normal firing temperatures (1,200° C.). His discussion of the formation of these phosphors is of some interest. In normal zinc silicate phosphors the production involves the important stage of the formation of the oxide or silicate of manganese in the bivalent state. If this step can be eliminated, by preformation or any of the other methods for altering the normal phosphor as described above, then the yellow emission occurs; if excess silica is also present, then the red form is produced. In this respect steam acts as a catalyst. From a general survey of the above studies of Kröger, Fonda, and Froelich it would seem that the red emission is to be identified with the local existence of $MnSiO_3$ at some places in the normal lattice while the yellow emission is due to some intermediate form of the complexes produced.

The absorption characteristics of the zinc silicate phosphors have already received attention in Chapter II as illustrations of the theoretical model for crystal phosphors. They have been measured by Kröger, who has given an adequate explanation of the absorption changes due to the introduction of manganese. A recent discussion of the absorption characteristics has been given by Butler [56] in which he considers the energy states of the zinc and manganese ions and their modification when introduced into the silicate lattice. However, his discussion does not appear to be very satisfactory for the explanation of energy transfer during luminescence, since he assumes this to be due to excitons even when high-energy quanta, or ionizing particles of high velocity such as cathode rays, are absorbed.

The emission of the manganese-activated zinc silicates is characteristic of the divalent manganese ions. The initial decay of the emission after excitation is exponential and independent of temperature. It is thus characteristic of a centre process and a forbidden optical transition. The decay constant is usually of the order of 10 milliseconds, but is affected by the concentration of manganese. The decay has been measured by

Randall and Wilkins [57], by Fonda [58], and by Strange and Henderson [59] (for cathode-ray excitation as described in

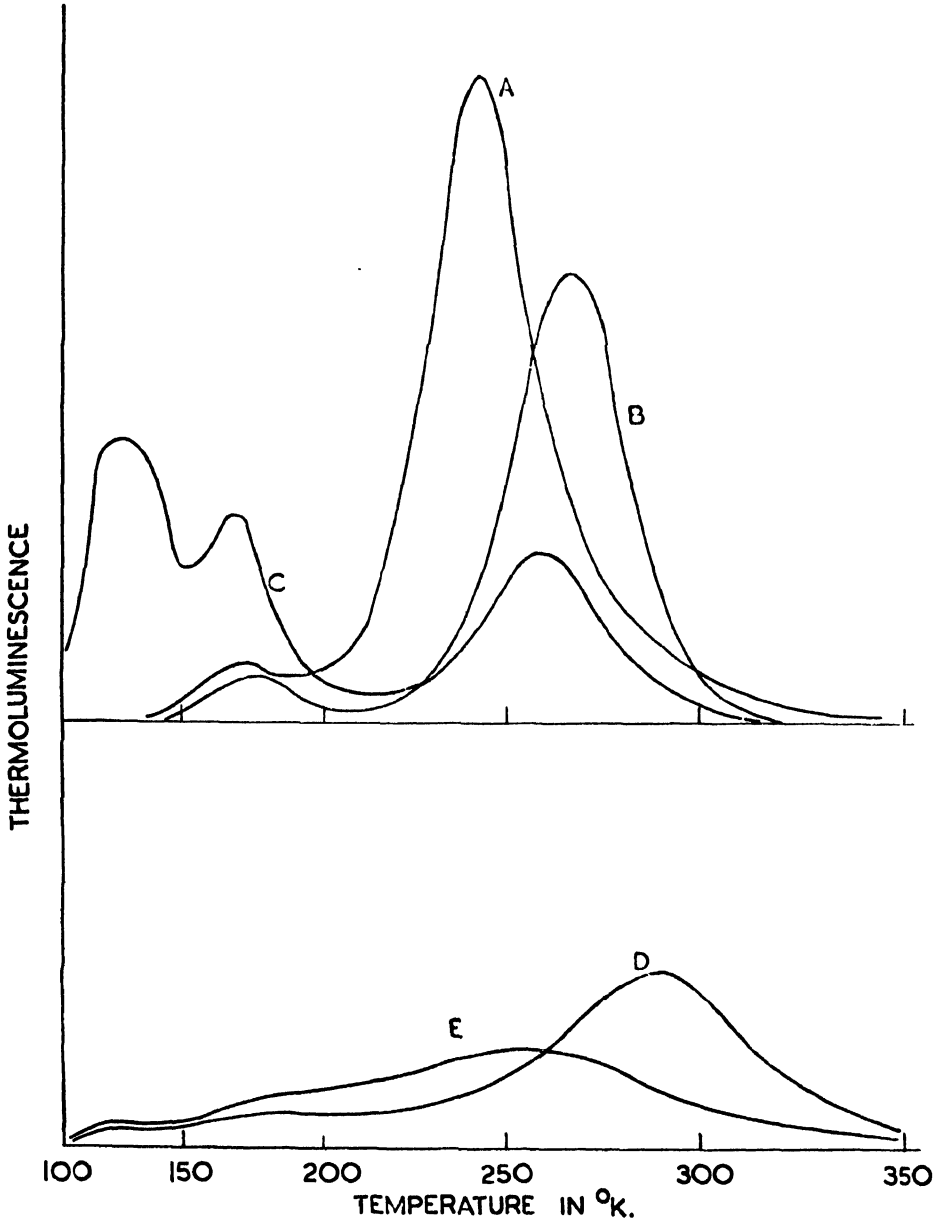


FIG. 38. Thermoluminescence curves for zinc silicate phosphors. (Randall and Wilkins.) *A*, Zn_2SiO_4—Mn (0·5 per cent.); *B*, Zn_2SiO_4—Mn (1 per cent); *C*, Zn_2SiO_4—Mn (0·1 per cent.); *D*, $ZnBeSiO_4$—Mn (2 per cent.); *E*, $ZnBeSiO_4$—Mn.

Chapter VII) among others. The effect of increase in manganese content is to increase the rate of decay (see Chap. VII, Table

III). The later stages of the phosphorescence of the zinc silicate phosphors are governed by electron-trap processes and are hyperbolic in form. Except in certain cases, this portion of the decay is of very feeble intensity (for an exception see Chapter IV) and the number of traps is thus relatively small compared with the number usually obtained in long afterglow phosphors. The electron-trap distributions of several specimens of normal zinc silicate phosphors have been measured by Randall and Wilkins using the thermoluminescence experiment. Examples from their results are given in Fig. 38. It was found by Froelich and Fonda [60] that the phosphorescence of zinc silicate can be enhanced and prolonged by the inclusion of suitable amounts of arsenic. A discussion of the possible action of arsenic in this respect has been given by Schulmann [61]. He suggests that by introducing arsenic ions As^{+5} these are substituted for Si^{+4} ions and that such distributed ions forming AsO_4 groups will give rise to positive holes which can trap electrons. The holes are associated with the neighbourhood of vacant lattice-points. One of these phosphors with enhanced persistence of phosphorescence has recently been studied by Garlick and Gibson [62] and their results, which provide information on the fundamental trapping processes in the phosphor, are given in Chapter IV.

ii. *Manganese-activated zinc-beryllium silicates*

The three compounds Zn_2SiO_4, Be_2SiO_4, and Mn_2SiO_4 form a ternary mixed crystal system with the willemite structure within certain limits of constitution. This system has been thoroughly investigated by Kröger [51] and more recently by Fonda [63] and by Schulmann [61]. Kröger has found that solid solutions of zinc and beryllium silicates occur up to 12 mol. per cent. of beryllium silicate in the absence of manganese, but that introduction of manganese lowers this limit as far as 8 per cent. Fonda's studies extend the range of solubility to 30 mol. per cent. in the presence of manganese of 1 mol. per cent. concentration, this value decreasing to 15 mol. per cent. when 4 mol. per cent. manganese silicate is present. The system preserves the willemite structure, but whereas manganese expands the zinc

silicate lattice, beryllium causes a contraction. Above the solubility limit the beryllium silicate forms a separate phase. According to Kröger, the absorption characteristics of these mixed phosphors are very similar to those of the zinc silicates

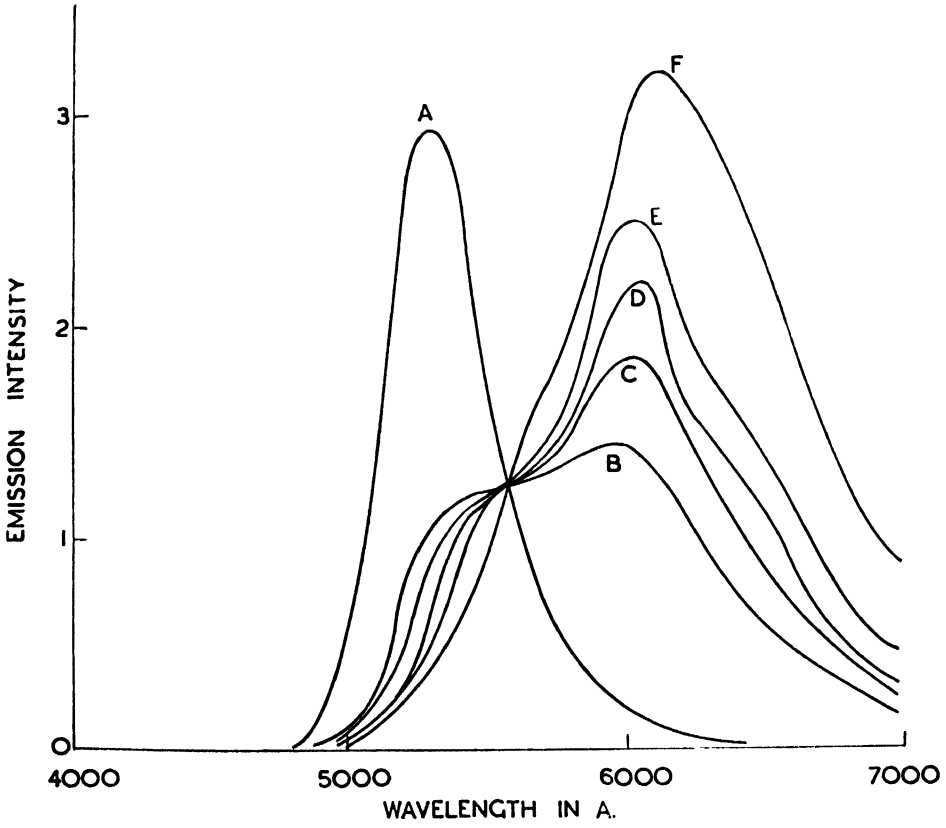


FIG. 39. Luminescence spectra of $ZnBeSiO_4$—Mn phosphors. (Schulmann.) (See Table V for key to curves.)

if allowance is made for differences in lattice parameters. No quantitative absorption measurements appear to have been made on the system.

The inclusion of Be_2SiO_4 in the Zn_2SiO_4—Mn_2SiO_4 system causes the emission colour to shift from the green towards the red, the change being due to the appearance of a new emission band with a maximum at 6,100 A. The effect of increasing beryllium content on the emission spectrum is shown by the curves of Fig. 39 for a series of phosphors prepared by Schulmann [61] and having the compositions given in Table V, which includes measurements of the phosphor efficiencies.

TABLE V

Constitution of Phosphors having the Spectra shown in Fig. 39

	Composition in moles				*Phosphor efficiency*	
Phosphor	ZnO	BeO	MnO	SiO_2	*Lum./watt.*	*Quantum efficiency*
A	2·0	0	0·122	1·18	517	0·77
B	1·8	0·2	0·058	1·11	402	0·89
C	1·8	0·2	0·051	1·10	365	0·89
D	1·8	0·2	0·111	1·17	345	0·84
E	1·8	0·2	0·138	1·20	323	0·84
F	1·6	0·4	0·132	1·19	278	0·84

The beryllium content of 10 mol. per cent. suppresses the normal green band and the new yellow band persists up to 20 mol. per cent. Be_2SiO_4. When beryllium is present the spectral change with increase in manganese content is much more marked than when it is absent. This must be due to the larger disturbance of the symmetry of the manganese ions in the former case. Because of the similar radii of the Zn^{+2} and Mn^{+2} ions (about 0·8 A), the symmetry remains relatively undisturbed, but with the introduction of beryllium, having a much smaller ionic radius (about 0·35 A), the symmetry is much more perturbed for the same manganese concentration. Schulmann associates the change in emission spectrum of the manganese centres with changes in the coordination number of the manganese ions and suggests that the band with maximum at 6,100 A is due to interstitial manganese having a coordination number higher than 4. Thus, for constant ratio of zinc and beryllium silicates, the development of this band with increase in manganese content is probably due to the increase in the interstitial manganese. The interstitial manganese may arise from the occasional substitution of Zn^{+2} for Si^{+4}. In normal willemites this substitution is considered unlikely because of the large differences in size and polarization of the two ions (Zn^{+2} rad. 0·8 A; Si^{+4} 0·39 A), but in zinc-beryllium silicates it may be more probable because of the smaller differences between Be^{+2} and Si^{+4} ions. It is, however, to be noticed that the red band is very similar to that of $MnSiO_3$ shown in Fig. 37. A further

discussion of the emission spectra of manganese ions in various matrices is given later in the chapter.

iii. *Manganese-activated cadmium silicate systems*

Most of the studies of these systems are due to Kröger [51]. The zinc and cadmium silicates (*ortho*) form solid solutions with a solubility limit of about 20 mol. per cent. Cd_2SiO_4 [64]. Cadmium silicate causes a slight expansion of the willemite lattice. With manganese silicate these two silicates form a ternary system and, as in the case of zinc-beryllium silicates, the emission is altered by increase in the cadmium content. The absorption edge of the crystals moves towards the red with this increase, but the manganese absorption bands, occurring at longer wave-lengths, are not disturbed.

iv. *Manganese-activated calcium and magnesium silicates*

These phosphors have been studied recently by Butler [65]. Unlike zinc silicates activated by manganese, these phosphors are only excited by cathode rays; the calcium silicate phosphor emission is in the yellow, and the magnesium silicate phosphor in the red region of the spectrum. According to Butler there is no absorption of the matrix lattices in the region of 2,537 A, which would account for the lack of response to this excitation. The interesting feature of the calcium silicate phosphor is that its emission is altered from yellow to red by the introduction of lead as a secondary activator, and this addition makes it respond to 2,537 A radiation. It is thought that the absorption takes place in the lead impurity; the latter must also perturb the manganese centres to cause the change in emission. Lead also gives rise to a much slower decay of phosphorescence, which in these phosphors is normally much faster than for zinc silicate phosphors.

v. *Lead-activated calcium and barium silicates*

These phosphor systems have also been studied by Butler [66]. Calcium silicate activated by lead and excited by cathode rays and 2,537 A radiation gives a blue luminescence emission according to Butler, but Fonda, as reported by Froelich [67], finds an emission peak at 3,400–3,500 A for such excitation.

Barium silicates may also be activated by lead, giving blue and blue-green emission after excitation by 2,537 A radiation. The emission is markedly dependent on the crystal structure of

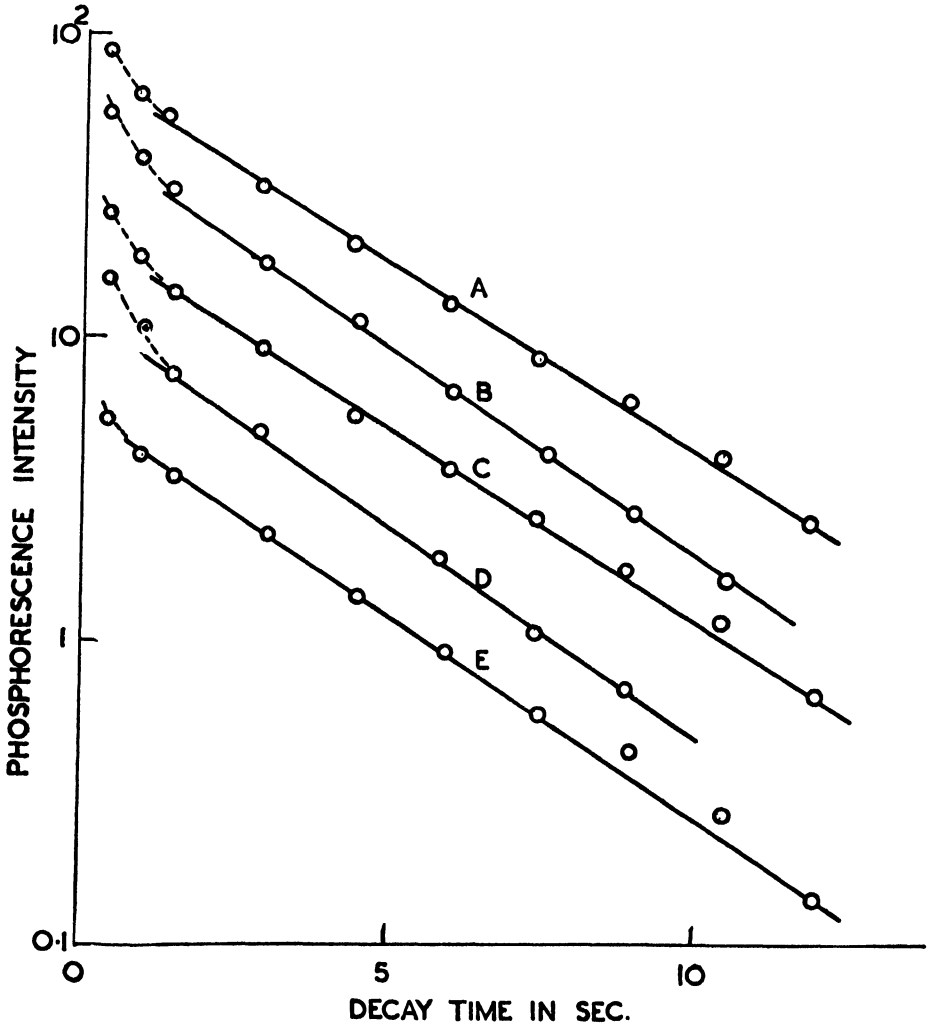


FIG. 40. Phosphorescence decay of a $SrSiO_3$—Eu phosphor at different temperatures after excitation by 3,650 A radiation. (Garlick and Gibson.) *A*, 476° K; *B*, 398° K; *C*, 294° K; *D*, 192° K; *E*, 90° K.

the matrix lattice, on the lead content (which may be very high), and on the presence of excess silica which can be dissolved in relatively large amounts in the lattice.

vi. *Europium-activated silicates*

Calcium, strontium, and barium silicates or mixtures of these silicates may be activated by europium impurity [68]. Garlick

and Gibson [69, 70] have shown that the strontium silicate phosphor with europium as activator has unique luminescence characteristics. Under 3,650 A or 2,537 A excitation the emis-

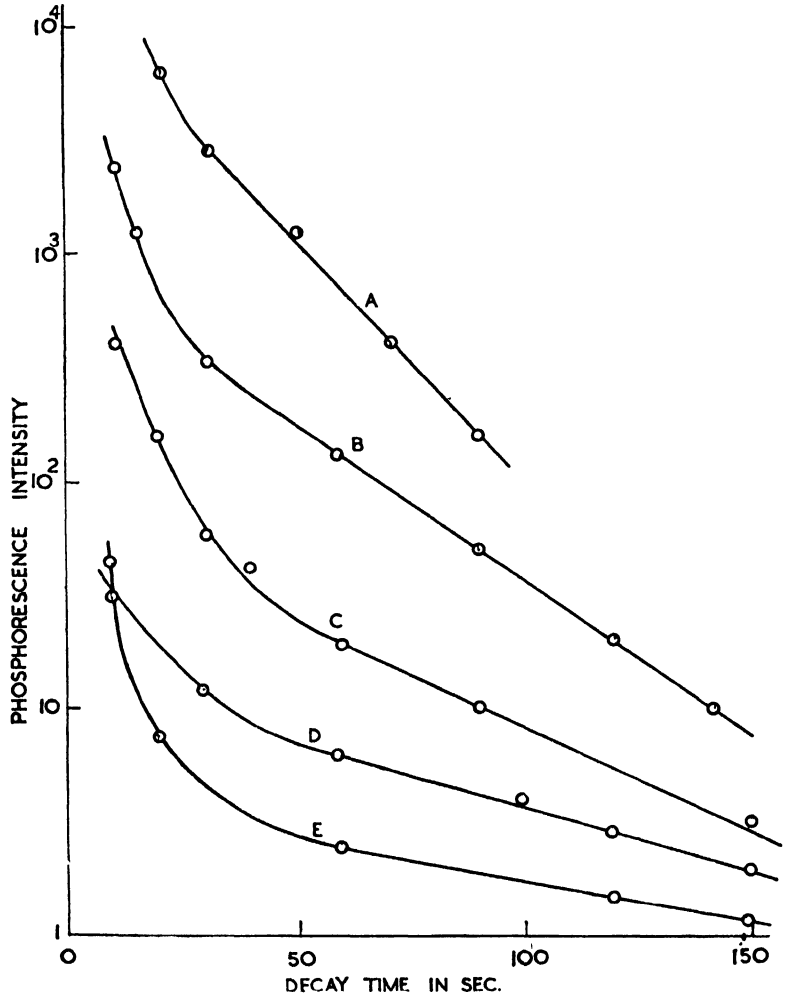


FIG. 41. Phosphorescence decay of a $SrSiO_3$—Eu phosphor at different temperatures after excitation by 2,537 A radiation. (Garlick and Gibson.) *A*, 387° K; *B*, 373° K; *C*, 358° K; *D*, 340° K; *E*, 320° K.

sion is in a band in the green. The decay characteristics are exceptional. For the long wave-length excitation the decay of phosphorescence is initially rapid but is followed by a slower component which is exponential in form, has a rate which is independent of temperature, and is characteristic of a forbidden optical transition within the luminescence centre having a half life-time of 2·3 seconds. The decay curves at different tempera-

tures are shown in Fig. 40. While the same decay occurs for short wave-length excitation, there is also present a slower decay component than this one which is also exponential in form but is very temperature-dependent, as shown by the curves of Fig. 41. This decay is due to electron traps of one depth, as is

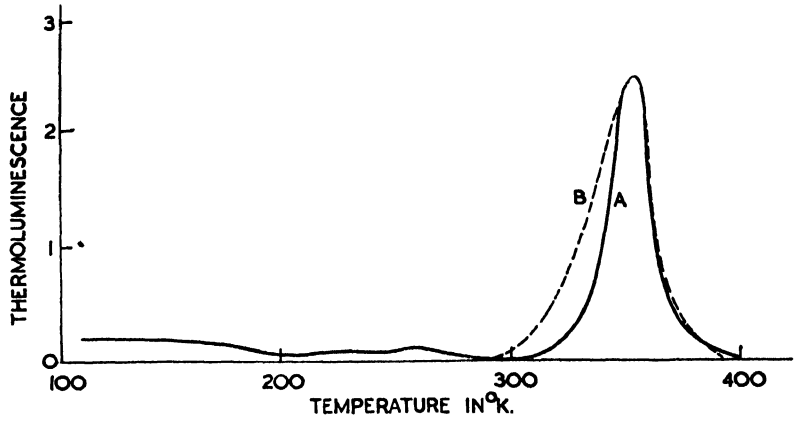


FIG. 42. Thermoluminescence curve of a $SrSiO_3$—Eu phosphor: excitation by 2,537 A radiation. (Garlick and Gibson.) *A*, Experimental curve. *B*, theoretical curve (eq. 2.4): $E = 0{\cdot}72$ eV.; $s = 1{\cdot}5 \times 10^9$ sec.$^{-1}$

evident from the thermoluminescence *versus* temperature curve of Fig. 42 for the phosphor; the decay and thermoluminescence curves also follow the simple equations of Chapter II for single trap depths, assuming no retrapping to occur (eqns. 2.3 and 2.4). The nature of the trapping centres has not yet been ascertained, but it seems probable that they are due to the europium impurity in the divalent state.

(*d*) OXIDE PHOSPHORS

In this section the characteristics of two types of oxide phosphor are described; they are those of zinc oxide and of chromium-activated aluminium oxide (ruby).

Zinc oxide

Phosphors formed by heating pure zinc oxide or by burning zinc in oxygen are of considerable interest from both practical and theoretical aspects. There is no impurity added, and the hexagonal structure is very similar to that of pure zinc sulphide phosphors made at high temperatures (i.e. wurtzite type). It is

also significant that zinc oxide is a well-known semi-conductor of the excess electronic type.

Early studies of the phosphor system were made by Beutel and Kutzelnigg [71]. Randall [1] has shown in later studies that at low temperatures pure zinc oxide excited by short wave-length ultra-violet light or by cathode rays (measurements at 85° K) emits luminescence consisting of narrow bands in the near ultra-violet and a broad band in the visible spectrum with peak at 5,450 A. His measurements for the ultra-violet bands are given in the following table:

TABLE VI

Ultra-violet Emission Bands of a Zinc Oxide

Wave-length in A	*Wave no. in cm.*$^{-1}$	*Wave no. diff. in cm.*$^{-1}$
3,715	26,920	
		310
3,758	26,610	
		570
3,840	26,040	
		540
3,922	25,500	
		530
4,005	24,970	
		580
4,100	24,390	

It is significant that the wave-number differences are of the right order to be associated with vibrational states in the phosphor crystal, though their origin is not known.

Leverenz [72] has given emission spectra for the luminescence of zinc oxide phosphors under cathode-ray excitation. These are shown in Fig. 43. The curve *A* is for a phosphor prepared by burning zinc in an oxygen atmosphere and the emission has its peak at 3,850 A. Curve *B* is for this phosphor after reheating in a reducing atmosphere at about 900° C. for 1 hour. The spectrum is broad, in the visible region with a maximum at about 5,050 A (cf. Randall's value of 5,450 A). Leverenz has reported elsewhere that addition of 0·05 mol. per cent. of lead enhances the zinc oxide emission, while manganese even at concentrations of 0·001 mol. per cent. suppresses it; the last observation was reported earlier by Randall [1]. It is interesting to compare the function of manganese impurity in zinc oxide phosphors with its activation of zinc sulphide.

Other investigations of zinc oxide have been made during the late war by Mollwo in Göttingen [73] using the burning tech-

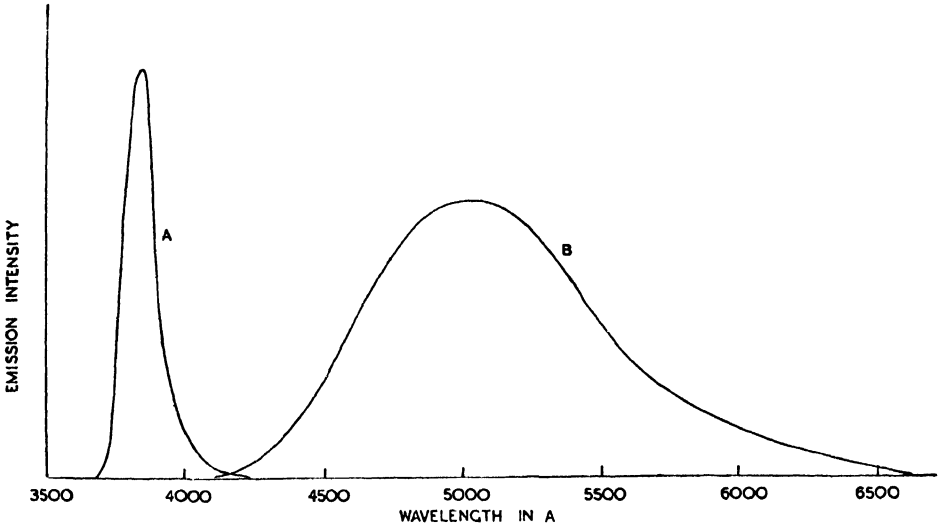


FIG. 43. Cathodoluminescence spectra of ZnO phosphors. (Leverenz.) *A*, from burning Zn in O_2. *B*, ZnO from heating phosphor A in a reducing atmosphere at 900° C. for 1 hour.

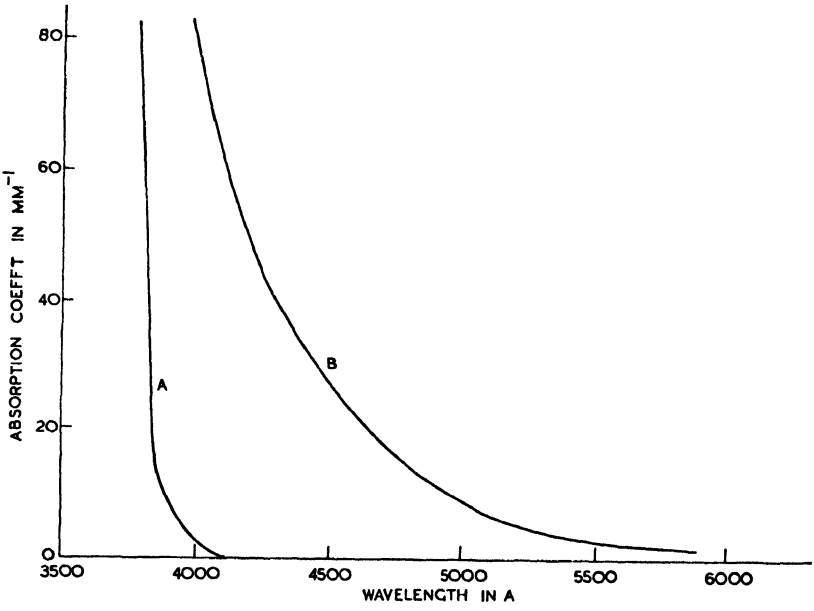


FIG. 44. Absorption spectra of ZnO phosphors. (Mollwo.) *A*, white ZnO. *B*, yellow ZnO (0·5 per cent. excess zinc). Absorption coefficient at 3,860 A is $2{\cdot}7 \times 10^4$ mm.$^{-1}$

nique for phosphor production. He has given absorption spectra for specimens as shown in Fig. 44 which show the effect of excess

zinc on the absorption characteristics. The absorption edge for 'white' zinc oxide, which applies to the Leverenz and Randall phosphors, is about 3,800 A, which is almost coincident with the ultra-violet emission of these phosphors. The narrow-band emission reported by Randall may thus be of similar origin to the edge emission of zinc and cadmium sulphides (Fig. 27) measured

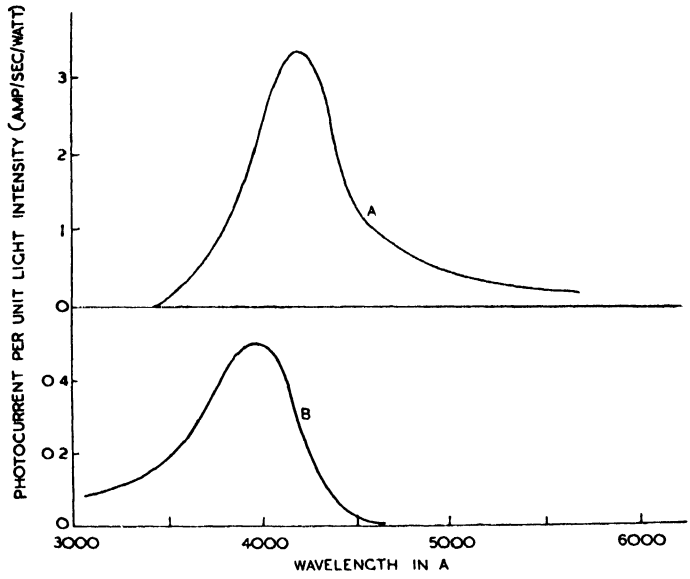


FIG. 45. Spectral sensitivity of photocurrents in ZnO phosphors. (Mollwo.) *A*, yellow ZnO (excess zinc). *B*, white ZnO.

by Kröger. Mollwo's measurements of the spectral sensitivity of photoconductivity in specimens with excess zinc content are given in Fig. 45. The maximum is at about 4,000 A and, according to Mollwo, luminescence is not produced by illumination in this region. Thus it seems likely that interstitial zinc which gives rise to the electrical effects of photoconduction and semiconduction is not responsible for the luminescence. This is of interest when it is compared with the opposite view adopted by some workers [74]. There is little doubt, however, that the luminescence of zinc oxide in the visible spectral region is associated with the deficiency of oxygen.

The decay of luminescence of most zinc oxide specimens is very rapid (decay constant about 1 μsec.), but in some specimens there are shallow electron traps which cause appreciable afterglow at low temperatures. These trap distributions have

been studied by Garlick and Wilkins [45] and a typical variation of thermoluminescence with temperature for a zinc oxide phosphor is given in Fig. 46. Thermoluminescence and other characteristics of these phosphors investigated by Garlick and Gibson (unpublished work) show that the zinc oxide phosphors

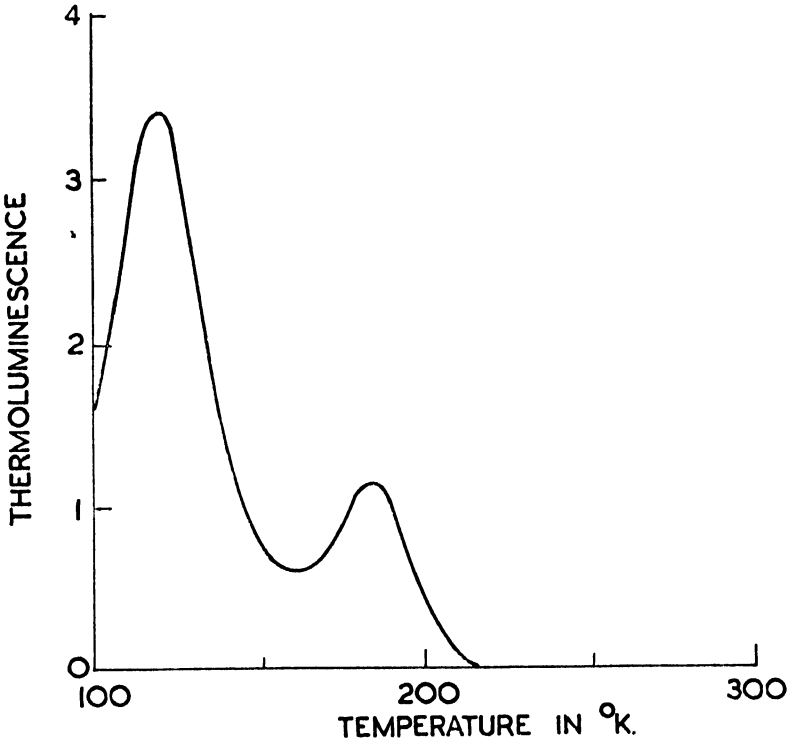


FIG. 46. Thermoluminescence curve for a typical ZnO phosphor.

are of the same category as zinc sulphide phosphors activated by copper, silver, or zinc. They show similar dielectric changes on excitation and anomalous temperature variation of efficiency (see Chaps. IV and V).

Chromium-activated aluminium oxide (ruby)

The spectral distribution of the bright-red luminescence of ruby due to chromium activation was studied by Deutschbein [75]. The emission is due to an intense doublet, the lines occurring at 6,920 A and 6,934 A, respectively. This emission can be excited by radiation of almost the same wave-length, and the resulting decay of phosphorescence is exponential and characteristic of forbidden transitions. Decay curves of ruby

measured by Garlick and Wilkins [45] are given in Fig. 47. The decay rate, measured at different temperatures from 90° to 650° K, only changes at the highest temperature, becoming more rapid and being accompanied by a drop in the luminescence efficiency. The luminescence of pure aluminium oxide which

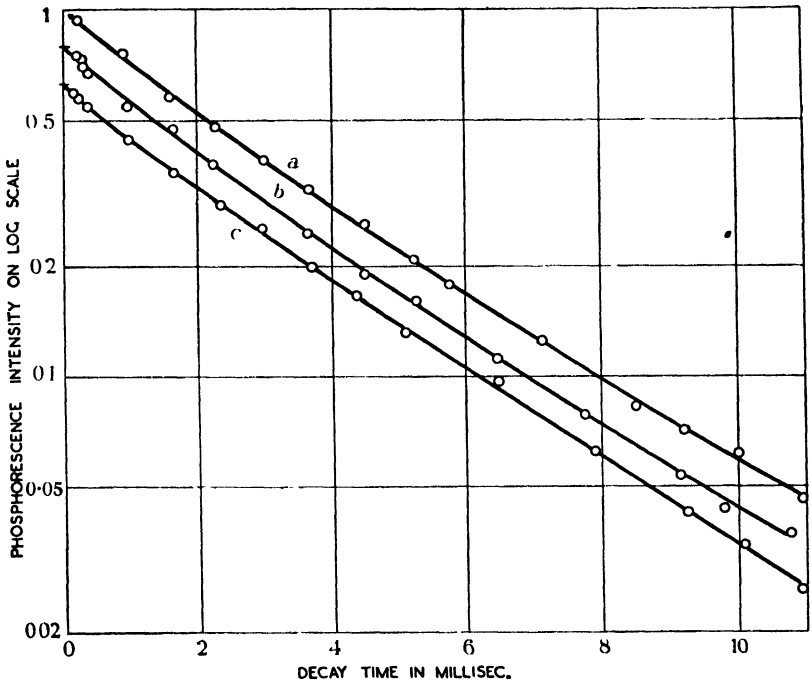


FIG. 47. Phosphorescence decay of a ruby (Al_2O_3—Cr) phosphor at room temperature. (Garlick and Wilkins.) (*a*) 3,650 A excitation; (*b*) 4,358 A excitation; (*c*) 4,358 A excitation: intensity 1/9.

may be stimulated by cathode rays lies in the ultra-violet and consists of a broad band with a peak at 3,000 A.

Deutschbein established the fact that the doublet emission in the red is due to the triply ionized chromium present and to transitions between the ^2G and ^4F states of the ions. These are normally forbidden, which explains the magnitude of the decay constant for the emission (2 millisec.). Thosar [76] has made a very thorough study of this phosphor and has shown that chromium replaces aluminium in the crystal lattice and that the symmetry of its position determines the relative simplicity of the emission spectrum. The interest in chromium ions as activators is due to their similarity to divalent manganese ions in other

matrices. It has been found recently by Kröger [77] that the fluorescence spectra of magnesium titanates activated by chromium and manganese, respectively, are very similar and that it is likely that the manganese is in the quadrivalent state and the chromium in its trivalent state in the matrix, the two ions being iso-electronic in these states.

(*e*) TUNGSTATE AND MOLYBDATE PHOSPHORS

i. *Pure tungstate materials*

The pure tungstates of calcium, strontium, magnesium, zinc, and cadmium form efficient phosphors if given suitable heat

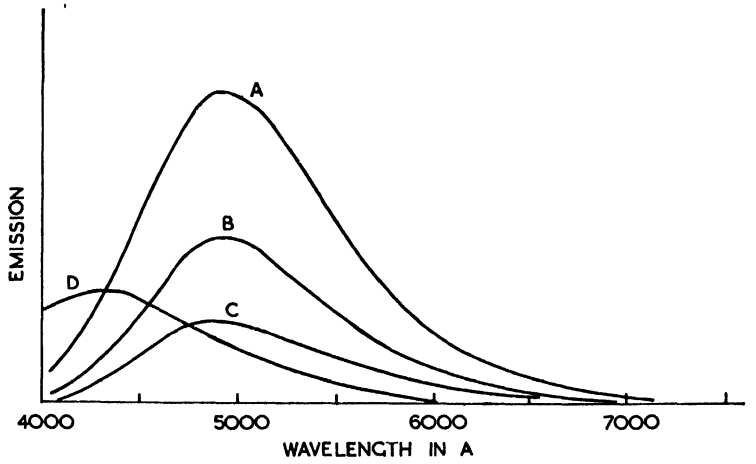


FIG. 48. Cathodoluminescence spectra of tungstate phosphors. (Leverenz.) *A*, $MgWO_4$; *B*, $CdWO_4$; *C*, $ZnWO_4$; *D*, $CaWO_4$. (Relative curve magnitudes are correct.)

treatment, and for this reason it is doubtful whether these prepared solids can be classed as pure. They are more likely to be in the category of self-activated phosphors such as zinc oxide and zinc sulphide. Randall [1] has stated that the seat of the emission is in the tungstate ion and his postulate appears to be supported by later evidence. Fig. 48 shows the emission spectra of a number of tungstates excited by cathode rays as measured by Leverenz [78]. It is seen that the spectra of magnesium, cadmium, and zinc tungstate phosphors are very similar; that of calcium tungstate is different, but this may be due to the different crystal structure of this phosphor from the others. The similarity of emission spectra among tungstate phosphors

was previously noted by Henderson [79]. The influence of phosphor structure and preparation conditions on the luminescence of magnesium tungstate has been investigated in detail by Hill [80] and by Fonda [81]. Hill finds that it is the monoclinic form that is luminescent and that the tungstate ion, as situated in this lattice, is the emission centre. Each tungsten atom is tetrahedrally surrounded by oxygen atoms. Although calcium tungstate has the scheelite structure, the same tetrahedral arrangement holds for the tungstate ion.

In a recent communication Kröger [82] has shown that the absence of luminescence in many other tungstates and in molybdates other than calcium molybdate is due to thermal quenching. Many more become fluorescent if the temperature is lowered sufficiently. The decay of emission of tungstate phosphors without impurity activators is very rapid, being of the order of 10 μsec. [83]. No evidence of electron traps in these materials operative in the luminescence process has been obtained.

ii. *Impurity-activated tungstate phosphors*

It was found by earlier workers that calcium tungstate could be activated by lead [84] and by samarium [85]. The lead-activated tungstate gives a blue emission which is excited by 2,537 A radiation. The addition of samarium gives rise to a red line emission characteristic of the impurity, while at room temperature the normal blue tungstate emission is somewhat suppressed. The blue emission is much enhanced if the temperature is lowered to 85° K, and the phosphorescence at that temperature is due to the samarium ions [1]. The phosphorescence decay of the phosphor has been measured by Garlick and Wilkins [45] over a wide temperature range and is found to be exponential, independent of temperature, and to have a half-life of about 100 μsec., that is, somewhat greater than for the pure materials.

Uranium can function as an impurity activator in calcium and cadmium tungstates. In cadmium tungstate it is responsible for an intense red emission, while in calcium tungstate it

gives rise to green emission and in some cases produces many electron trapping states. It also sensitizes the phosphors so that they can be excited by longer wave-lengths (3,650 A). In the long-afterglow type of uranium-activated calcium tungstate the blue tungstate and the green uranium emission both occur at room temperature, although the self-emission is quenched at

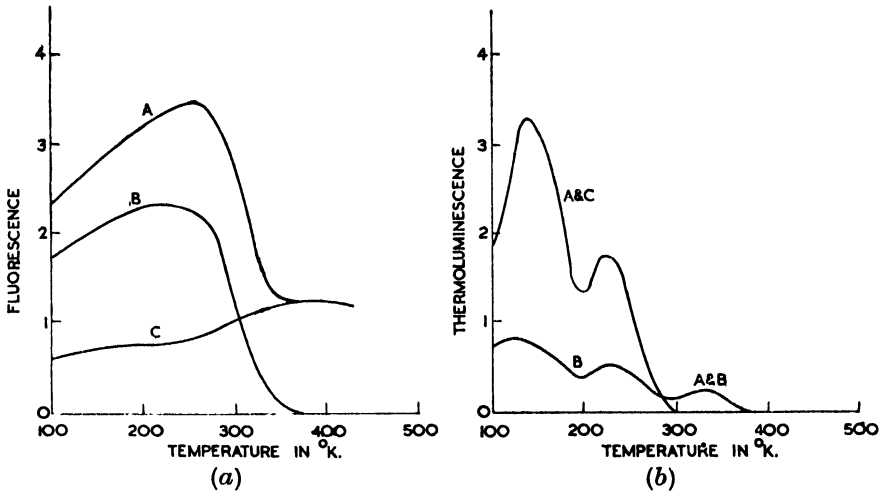


FIG. 49*a*. Fluorescence-temperature curves of a $CaWO_4$—U phosphor. *A*, no filter; *B*, blue filter; *C*, green filter.

FIG. 49*b*. Thermoluminescence curves for a $CaWO_4$—U phosphor. *A*, no filter; *B*, green filter; *C*, blue filter.

slightly higher temperatures, as shown by Fig. 49*a* [86]. The thermoluminescence curves for this phosphor are shown in Fig. 49*b*, optical filters being used to separate the emission of each activator centre. The shallow traps then appear to be associated with the tungstate ions and the deep traps with uranium. This phosphor also shows large dielectric changes on excitation and in almost every characteristic belongs to the category of the doubly activated zinc sulphides (e.g. ZnS—Zn—Cu). The emission spectrum due to the uranium shows some structure in its broad-band system.

(*f*) VITREOUS STATE PHOSPHORS

The study of luminescence produced by the inclusion in glasses of impurities, effective in crystalline phosphors, provides fundamental information on the luminescence processes in solids, and also provides a powerful method of analysis of

structure in relation to other physical states. A comprehensive discussion of the latter development, with respect to the use of line-emission spectra from luminescence activators, has been given by Tomaschek [87], while Kreidl [88] has surveyed its application to the study of glasses alone. In most of the studies of vitreous-state phosphors the glasses formed by oxygen in combination with the elements boron, silicon, or phosphorus have been used. These basic glass constituents provide the network structure of a glass, for example, silicate tetrahedra form the network units in silica glasses; other ions, such as those of the alkali or alkaline earth metals, occupy interstitial positions in the network and act as 'modifiers' by weakening the network bonds and thus altering such physical properties as the melting-point. The impurities which activate luminescence are well known for other phosphors, namely, manganese, the uranyl ion UO_2, lead, and rare earth ions such as Eu^{+3}.

Studies of manganese activation of silicate glasses have been carried out by Weyl and his associates [89], while earlier work by M. Curie [90] included the study of manganese in borate glasses and of the effect of devitrification on the luminescence. Manganese in all these glasses is in the divalent state as an emission centre; its trivalent ion does not produce luminescence, but gives to silica glasses an intense purple coloration. In glasses of high silica content the network is very little disturbed and the manganese has a green emission. As the concentration of modifier ions is increased the emission shifts to the red, being associated with a loosening of the network bonds. This change may be compared with the changes in zinc silicate systems in (*c*) above. Linwood and Weyl associate the change with a change in the coordination number of the manganese ions from four to six. In a fourfold coordination the manganese tends to function as a network former, but in the sixfold state it is more likely to occupy an interstitial position like a modifier ion. In the latter case the red emission is due to the larger thermal disturbance of the centres.

M. Curie has shown that the emission of manganese in borate glasses is in the red and is relatively feeble. However, devitri-

fication of the glasses by suitable heat treatment gives rise to a change of the emission from red to green and a large increase in its intensity; the changes are also accompanied by the creation of electron traps causing phosphorescence and thermoluminescence. Measurements of the phosphorescence show that the decays are hyperbolic of the form given by equation 2.13. Devitrification of the glasses also causes photoconductivity, but this does not seem to be related to the luminescence processes (cf. photoconductivity in silicates, Chap. V). Earlier studies of manganese in borate glasses by Cohn and Harkins [91] showed that the addition of small amounts of cerium (0·05 per cent. Ce for up to 1 per cent. Mn) caused an enhancing of the thermoluminescence, and presumably the phosphorescence, of the phosphors. The precise function of the cerium is not understood; in such small concentrations it is not likely to effect even a partial devitrification. It is more probable that its action is similar to that of auxiliary activators in crystalline phosphors.

Lead, causing intense blue emission, and antimony, giving rise to violet emission, both act as activators in silica glasses (cf. lead activation of tungstates in (*e*)). Uranyl ions provide very suitable centres for structure investigations as shown by the increase of the emission with removal of modifier ions [92], this being due to the increase in network strength. Tomaschek [93] and Deutschbein [94] have made very extensive studies of the line fluorescence of ions such as Eu^{3+} in crystals, glasses, and solution. The effective fields acting on the ions in the different media may be deduced from the line splitting which occurs, and the state of the medium is determined by the sharpness or diffuseness of the lines. Fig. 50 shows the effect of the matrix medium of the phosphor on the 5,790 A line of europium which is not split by electric fields and therefore is very suitable for diffuseness observations. As the effective field is reduced, the wave-length of the line decreases. The figure stresses an important fact, emphasized by Tomaschek, that the vitreous state is not intermediate between those of crystals and solutions. In liquids there can be more symmetry of the emitting ions and stronger bonds than in glasses because of the cushioning effect

of the water molecules of hydration attached to the ions. Randall [95] has pointed out that the diffuse state of the emission lines or bands is due to the fact that no two ions have exactly the same environment. The coordination is only saturated when an average is taken over all ions. The diffuse emission

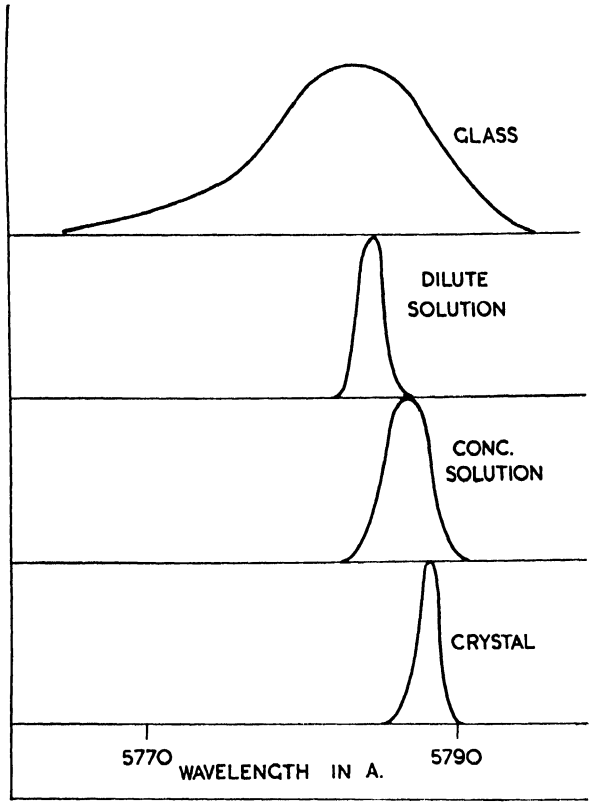


FIG. 50. Luminescence emission spectra of europium centres dispersed in different media. (Tomaschek and Deutschbein.)

corresponds to the lack of definition shown by the X-ray diffraction patterns of glasses [96].

(*g*) It has not been possible in the space of this chapter to discuss all phosphor systems recently investigated. For example, there are other cases of the sensitizing action of auxiliary activators in crystals [97]. In addition, the function of manganese as activator in many different phosphor systems might appear to be worthy of more detailed considerations. We hope that these may be forthcoming in other publications [98].

CHAPTER IV

LUMINESCENCE PROCESSES IN ZINC SULPHIDE AND SOME OTHER PHOSPHORS

1. Nature of recent studies

We have shown in Chapter II that the electron energy-band model for crystalline solids can be satisfactorily applied to the interpretation of luminescence in phosphors. By its use good agreement is obtained, often of a quantitative nature, between experimental and theoretical studies. However, the experimental data so far described in the last two chapters are not sufficiently extensive to give detailed information about the nature of the emission centres and metastable states in phosphors. In this chapter, therefore, we shall discuss some recent studies by several workers which assist the establishment of a more precise theoretical model to explain phosphorescence and thermoluminescence. These relatively new data are supported by other investigations of the electrical changes in phosphors during luminescence which we shall describe in later chapters. We consider here three main aspects of luminescence in zinc sulphide phosphors and in some other materials. They are as follows:

i. The luminescence efficiency of phosphors and its dependence on temperature and on the conditions of excitation.

ii. The determination of the extent to which the retrapping of electrons occurs in phosphorescence and thermoluminescence.

iii. The nature and location of luminescence centres and electron traps in crystalline phosphors.

2. The luminescence efficiency of phosphors

We have already considered in Chapter I the general conditions for luminescence to occur in solids. However, the discussion was limited to the intrinsic efficiency of the emission centres and did not take into account energy losses in the bulk material of the phosphor. Such losses are likely when absorp-

tion takes place in the crystal lattice and is followed by a transfer of the absorbed energy through the lattice to emission centres. Thus for photoconducting phosphors equation 1.1 is only qualitatively in agreement with experiment. It is found that in zinc sulphide and some other phosphors the luminescence efficiency for ultra-violet light excitation is markedly dependent on the wave-length and intensity of the exciting radiation as well as on the temperature. Equation 1.1 does not include any terms which show this dependence, and in fact we shall see that the dependence on the excitation conditions is determined by the non-radiative energy losses occurring outside the emission centres.

According to equation 1.1, the fluorescence intensity should be proportional to the intensity of excitation. Departures from this linear relation were first observed by Gisolf and Kröger [1] and by Riehl [2]. Gisolf and Kröger found that the intensities of the individual spectral emission bands of a manganese-activated zinc sulphide phosphor were not proportional to the excitation intensity. Riehl found a similar effect in copper- and silver-activated zinc sulphides and showed that the non-linear behaviour was more marked at elevated temperatures. Some of the results of Gisolf and Kröger are given in Fig. 51. Curve A is the variation of fluorescence intensity with excitation intensity for the yellow emission band (characteristic of the manganese activator), while curve B gives the variation for the blue emission band (characteristic of self-activation). Both curves follow a relation of the form:

$$F = \text{constant} \times J^n, \tag{4.1}$$

where F is the fluorescence intensity, J is the excitation intensity, and n is a constant: n is greater than unity for the blue emission and less than unity for the yellow emission. Gisolf and Kröger have explained the effect by assuming that electrons excited and freed from blue emission centres become trapped in the neighbourhood of yellow emission centres. After escaping from traps they are more likely to be captured by the adjacent empty centres. This appears to be supported by the fact that

the phosphorescence of the specimen is yellow. This explanation requires a further process to be acceptable, namely, the filling of the empty blue-emission centres with electrons by a non-radiative process. There must also be an additional emptying of the yellow emission centres, apart from that due

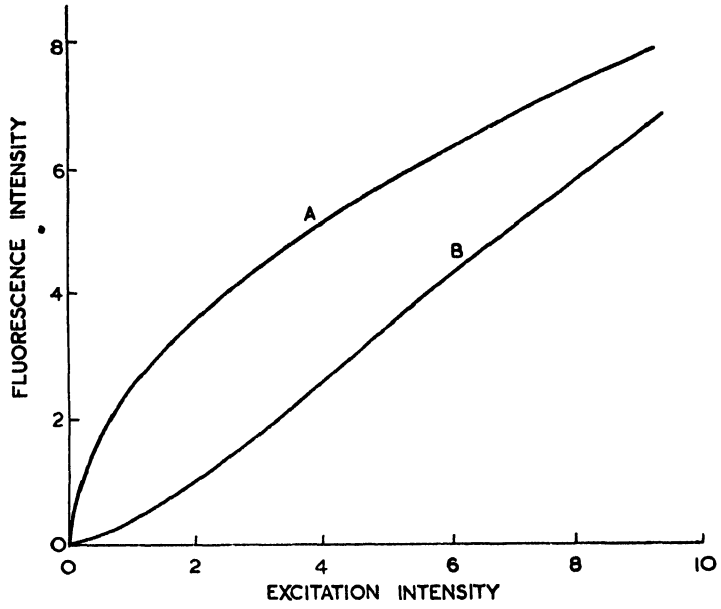


FIG. 51. Non-linear variation of fluorescence with excitation intensity for a ZnS—Mn (0·1 per cent.) phosphor at room temperature. (Gisolf and Kröger.) *A*, yellow band (Mn); *B*, blue band (Zn).

to excitation, in order to accommodate the extra electrons from blue emission centres.

The first satisfactory explanation of the non-linear increase of fluorescence with excitation intensity was given by Schön [3] and elaborated more recently by Klasens [4] and by Klasens et coll. [5]. These authors assume that the non-radiative transfer of electrons between different centres is effected by the migration of positive holes in the phosphor crystal. We shall discuss their theory in some detail before reviewing later experimental evidence which does not show good agreement with it. Fig. 52 shows the energy-band scheme for a phosphor with two different emission centres L_1 and L_2 due to different activating impurities. As already shown in Chapter II, excitation may raise electrons from the ground states of the centres into the con-

duction band. If the excitation is sufficiently energetic it may be able to excite electrons from the full band into the conduction band. This process will also lead to an emptying of luminescence centres, since electrons in the ground states of L_1 and L_2 may fall into the full band to combine with the positive holes created by the excitation. This is equivalent to the trapping of positive

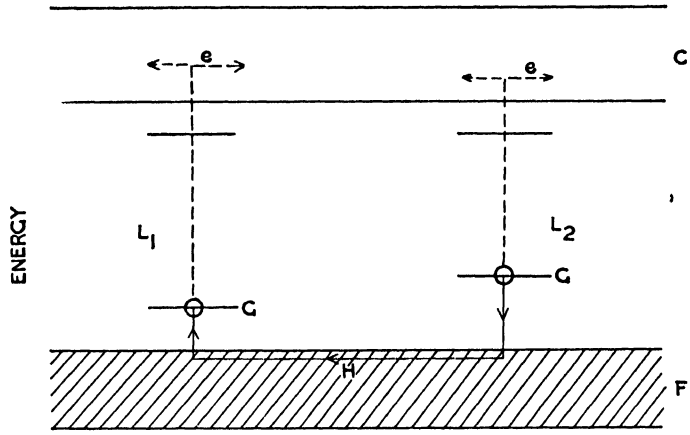


FIG. 52. Energy-band scheme for doubly activated phosphors. C, conduction band; F, filled band; L_1 and L_2, different activator centres; H, positive hole migration; e, excited electrons; G, ground states of luminescence centres.

holes in the emission centres. It can be shown that the luminescence produced by steady excitation of both types of centre will be proportional to the excitation intensity if the temperature is sufficiently low. However, at elevated temperatures there is the possibility that electrons in the full band of the phosphor crystal may be thermally excited into empty ground states of the luminescence centres. The probability of this process will be given by the familiar expression $\gamma \exp(-W/kT)$, where γ is a constant and W is the energy difference between the ground state of a centre and the top of the full band. The value of W will be different for different centres and, according to the positions of the ground states shown in Fig. 52, the centres L_1 will be more readily filled by this process than the centres L_2. The latter will tend to lose electrons which will be captured by positive holes created in the full band by the thermal activation into the centres L_1. There will thus be a transfer of electrons from one type of centre to another during excitation, the

transfer being effected by the positive hole motion. The positive hole migration will be temperature dependent but will not depend on the excitation intensity. Hence it will be significant at low intensities of excitation and at elevated temperatures. The mathematical treatment due to Klasens [4] yields an expression for the fluorescence efficiency (η) of the form

$$\eta = \frac{F}{F_0} = \frac{1}{\{1+c\sqrt{(\alpha J)}\}}, \tag{4.2}$$

where F_0 is the fluorescence at low temperatures at which the positive hole migration is negligible, $c = \gamma \exp(-W/kT)$, and α

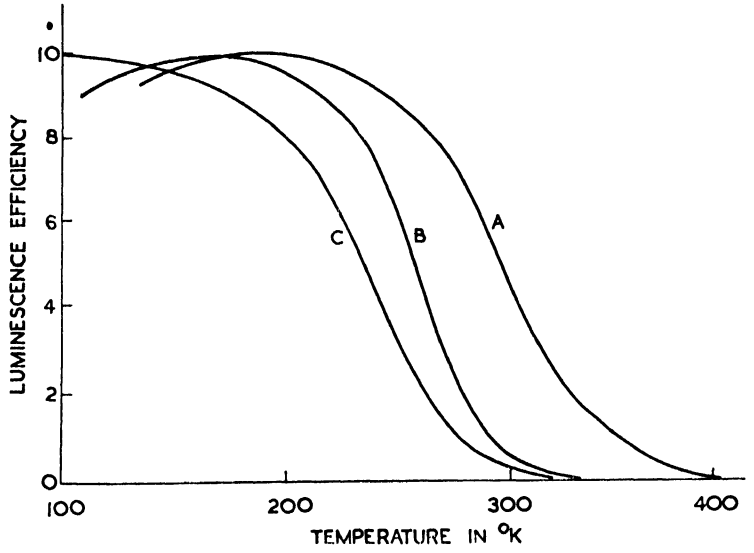


FIG. 53. Luminescence efficiency-temperature curves for nickel-killed ZnS—Ag phosphors. (Klasens.) *A*, unkilled ZnS—Ag (0·01 per cent.); *B*, ZnS—Ag (0·01 per cent.) Ni (0·0002 per cent.); *C*, ZnS—Ag (0·01 per cent.) Ni (0·001 per cent.).

is a constant. For a fixed temperature and for low intensities this equation reduces to the form of equation 4.1 with $n = 1{\cdot}5$.

If one of the impurities in the phosphor does not form an emission centre it may function as a non-radiative centre capturing electrons and thus 'killing' the luminescence. Nickel behaves in this way in zinc sulphide phosphors. Klasens has given typical results for the variation of fluorescence efficiency of such phosphors with temperature which are shown in Fig. 53. The curves follow the form of equation 4.2, but each curve gives a different value of the energy W. We have also found that the

value of W varies with the nickel content [6]; in addition we have found that the index n is variable with the nickel content and with the wave-length of the exciting radiation. These variations are not explained by the above theory.

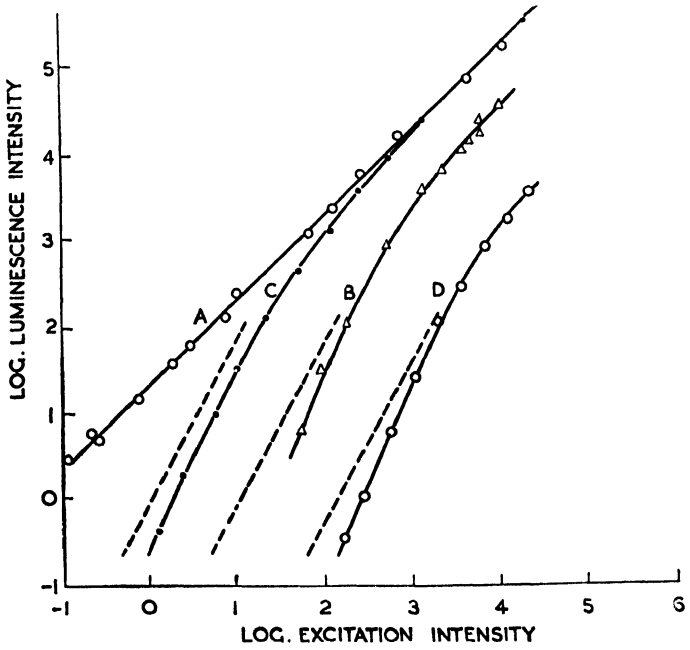


FIG. 54. Fluorescence as a function of exciting intensity for ZnS phosphors. (Urbach, *et al.*) *A*, linear variation of ZnS—CdS—Cu at room temperature; *B*, non-linear variation of ZnS—CdS—Cu at 185° C.; *C* and *D*, non-linear variation at room temperature for ZnS—Ag—Ni phosphors.

Other experimental studies of the above effects have been made by Urbach, Urbach, and Schwarz [7]. Their results are given in Fig. 54. They show that the non-linear variation of fluorescence with excitation intensity occurs in phosphors with only one activator if the temperature is raised sufficiently; the index n can also be as high as 2. These authors have not proposed a detailed theory to explain their results, but suggest the following equation for the processes occurring in the phosphor under constant excitation at a fixed temperature:

$$\frac{dm}{dt} = 0 = aJ - bm^2 - cm, \tag{4.3}$$

where m is the number of excited electrons, J the exciting intensity, and a, b, and c are constants. It is assumed that the

luminescence emission is due to a bimolecular process and is given by bm^2. Thus at low intensities the fluorescence intensity is proportional to the square of the exciting intensity, while at higher intensities it changes to a linear variation. This equation would appear to be more widely applicable if the last term is due to a non-radiative process and the constant c has the form given

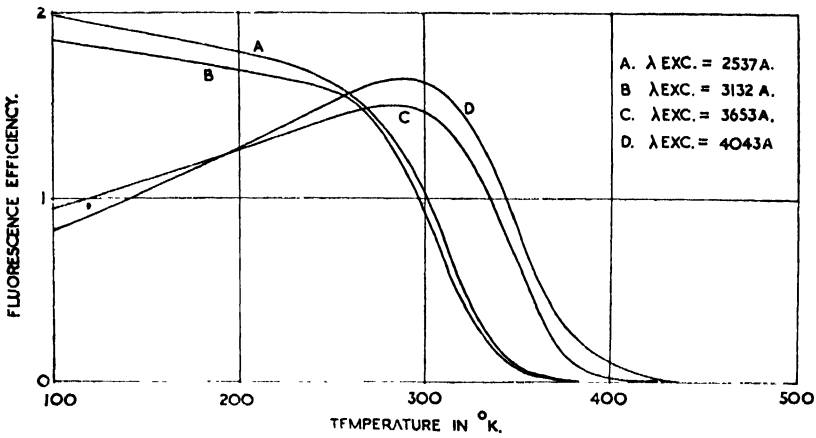


FIG. 55. Luminescence efficiency-temperature curves for self-activated ZnS phosphor for different wave-lengths of excitation.

for equation 4.2. We find, however, that in all the above studies there is a lack of exhaustive experimental evidence. We therefore give below a brief account of extensive investigations made in the author's laboratory [8]. We shall show that the efficiency of a phosphor depends in a fairly definite way on the nature of the exciting radiation as well as on its intensity and on the temperature.

We have found that better agreement with experiment is obtained if the equations 4.1 and 4.2 are replaced by the following empirical formula:

$$\eta = \frac{F}{F_0} = 1 \Big/ \left[1 + \frac{b \exp(-W/kT)}{J^{n-1}} \right] \tag{4.4}$$

with the usual notation, b being a constant. The value of the index n varies between 1 and 2. The phosphor ZnS—Zn, that is, the self-activated zinc sulphide, was chosen as the simplest phosphor of its class in order to investigate the effects in phosphors with only one emission band at normal temperatures. Fig. 55 shows how the fluorescence efficiency varies with

temperature for different wave-lengths of the exciting radiation. Fig. 56 gives this variation for different intensities of excitation of wave-length 3,650 A. The values of the index n and the

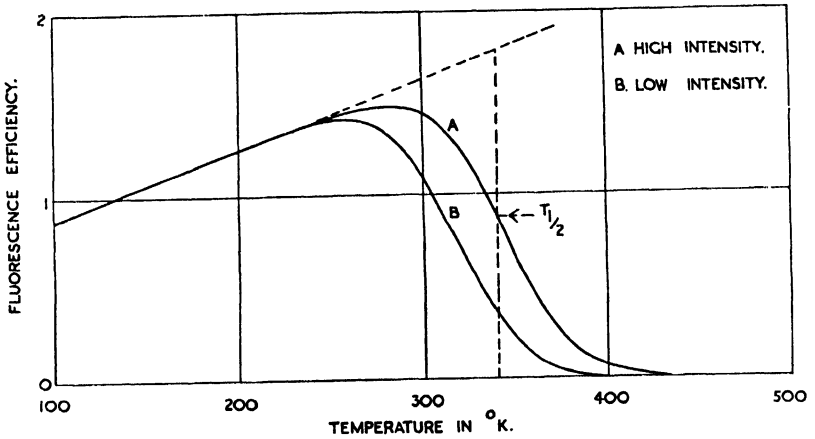


FIG. 56. Luminescence efficiency-temperature curves for self-activated ZnS phosphor for two different excitation intensities (3,650 A excitation).

activation energy W are given in Table I below for different wave-lengths.

TABLE I

Luminescence Efficiency Characteristics of a Self-activated Zinc Sulphide Phosphor as given by the Constants of Equation 4.5

Exciting wave-length in A	*Value of the index n*	*Value of the energy W in eV*
2,537	1·22	0·55
3,132	1·38	0·53
3,653	1·50	0·57
4,043	2·00	0·56

It will be seen that the index n increases with wave-length while the activation energy W remains sensibly constant. Very similar results are obtained for silver-activated phosphors which show almost identical values of n (for a given wave-length) and W. It is noteworthy that the emission spectrum of silver-activated zinc sulphide is almost the same as that of a self-activated specimen.

If measurements are made on the green emission band of copper-activated zinc sulphide phosphors, a similar variation of n with excitation wave-length is observed. However, the energy

W is different, being about 1·0 eV. for all specimens made at temperatures above 770° C. Thus the energy value is independent of the ratio of cubic to hexagonal crystal structure in the phosphor (see Chap. III, § b(i)). The curves of Fig. 57 show the variation of fluorescence efficiency with temperature for phosphors made at different temperatures between 500° and 1,200° C.

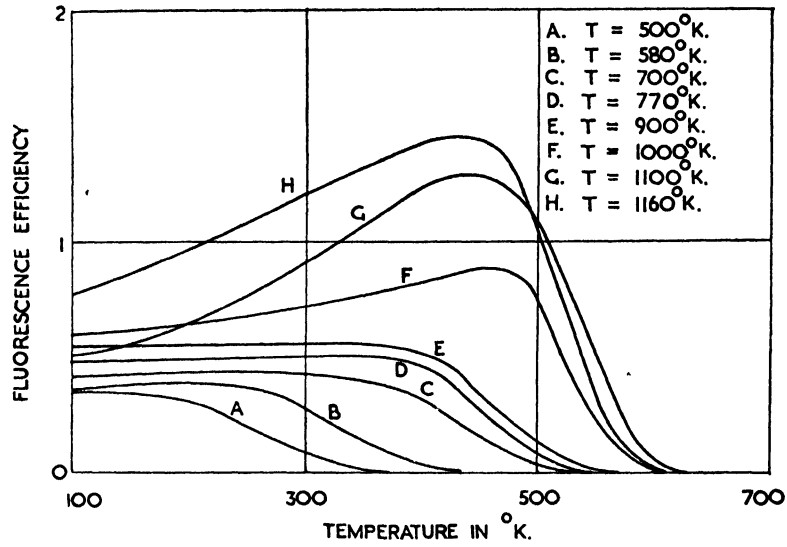


FIG. 57. Effect of preparation temperature on the luminescence-temperature characteristics of ZnS—Cu phosphors.

Investigations of the fluorescence efficiency characteristics of zinc sulphide-cadmium sulphide phosphors show that the activation energy W decreases in a regular way with increase in cadmium sulphide content. The index n increases with excitation wave-length from 1 to 2, but the wave-length range over which this occurs is shifted towards the red. We have already described the change in other properties, such as emission spectrum, when the cadmium sulphide content is increased (see Chap. III, § b(i)). In particular, Fig. 13 shows the change in absorption and hence the change in separation of the full band and conduction band in the energy scheme for the phosphor. We should therefore expect a decrease in the value of W when the energy-band separation decreases.

Summarizing the above results, we see that the activation energy W is a characteristic of the particular phosphor while

the index n is dependent on the excitation wave-length as well. Comparison of the variation of n with wave-length with the absorption spectrum of a phosphor shows that in the region of the lattice absorption (below 3,340 A for ZnS phosphors) its value is usually 1·25, while in the tail to the long wave-length side of the absorption edge it increases with decrease in the absorption coefficient. It is not possible to say yet whether n is dependent on the magnitude of the absorption coefficient only or whether it depends on the different nature of the absorption process above and below the wave-length of the absorption edge of the phosphor.

Some evidence from independent studies

It has been found by Szigeti and Nagy [9] that the rapid drop in fluorescence efficiency with temperature at elevated temperatures is accompanied by a rise in the dielectric loss of phosphors. On the basis of the model of Chapter II and Fig. 52 it is assumed that at these temperatures electrons can leave the excited states of luminescence centres and enter the conduction band, thus contributing to the dielectric loss. The same increase in loss would, of course, be observed if there were an onset of positive hole migration at these temperatures, as suggested in the theory given above. The results obtained by Szigeti and Nagy for a manganese-activated zinc silicate phosphor are given in Fig. 58, showing the good agreement between their experimental curve for the variation of luminescence efficiency with temperature and that derived from their loss measurements. Their measurements of the dielectric loss in relation to the luminescence efficiency do not distinguish between the contributions made to the dielectric loss by conduction electrons and by positive holes. However, recent measurements of the incidence of a thermo-electric potential at temperatures where the emission decreases enable the sign of the current carriers to be determined [8]. We find that for all zinc sulphide phosphors and for many others the thermo-electric effects are predominantly due to electrons and that there is very little evidence of a significant migration of positive holes. The experimental

results were interpreted according to the theoretical treatment of Mönch [10] and as interpreted for such materials as stannous and lead sulphides by Anderson and Morton [11]. It would appear therefore that the activation energy W is associated

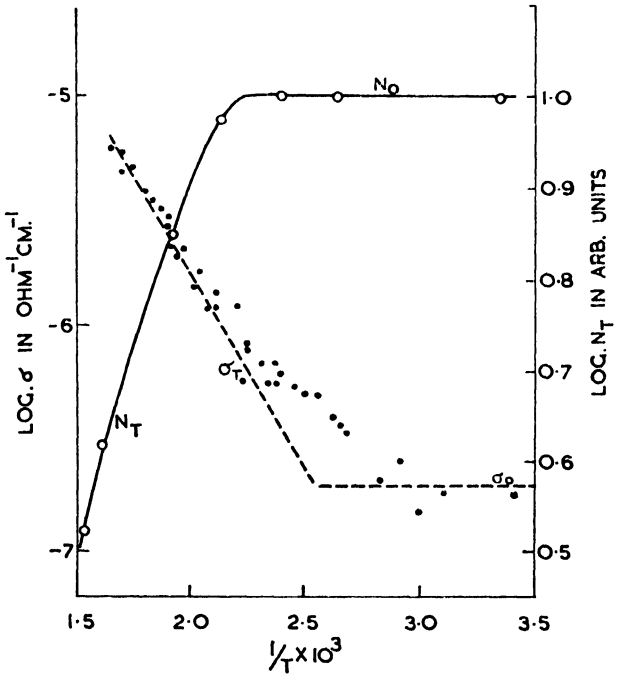


FIG. 58. Comparison of temperature quenching of fluorescence of a Zn_2SiO_4—Mn phosphor with rise in 'dark dielectric losses' in R.F. fields. (Szigeti and Nagy.) N_T is number of quanta emitted (fluorescence) and σ_T the R.F. conductivity at a temperature T.

with the energy difference between the excited states of the emission centres and the bottom of the conduction band of the phosphor crystal.

The variation of luminescence efficiency with temperature at low temperatures and for different excitation wave-lengths

It will be seen from Fig. 55 that the fluorescence efficiency of a phosphor is not entirely independent of temperature or of the excitation wave-length at low temperatures. For the zinc sulphide phosphor of this figure the efficiency shows a slow increase with temperature for wave-lengths longer than that of the absorption edge (3,340 A) but a slow decrease with temperature for shorter wave-lengths. This effect has been

previously observed in several different phosphors such as zinc sulphides [12, 13], and manganese-activated cadmium iodide phosphors [13]. An explanation of these slow variations of efficiency has been put forward by Williams and Eyring [14]. They assume that the change in excitation wave-length, and hence the change in quantum energy, results in different absorption transitions within the emission centres. The conclusions

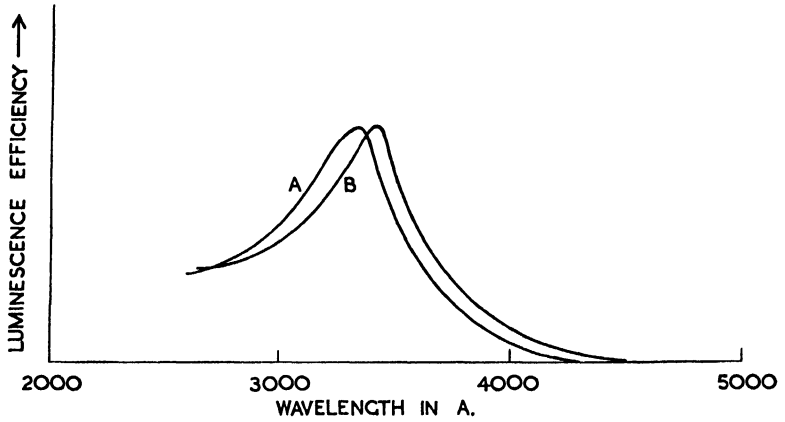


FIG. 59. Excitation spectrum of a self-activated ZnS phosphor at two different temperatures. (Garlick and Gibson.) *A*, 90° K; *B*, 230° K.

they arrive at by this treatment are untenable, since absorption at shorter wave-lengths does not occur in the emission centres but in the matrix lattice. Garlick and Gibson [15] have recently provided a relatively simple explanation of the efficiency changes. They have measured the excitation spectra of various zinc sulphide phosphors (that is, the variation of luminescence efficiency with wave-length of excitation) over a wide temperature range. Spectra measured at 90° K and 230° K for a self-activated zinc sulphide specimen are given in Fig. 59. It is found that as the temperature increases the whole excitation spectrum is shifted to longer wave-lengths. The temperature coefficient of this shift is found to be $0{\cdot}5 \pm 0{\cdot}05$ A/°K, which is the same as that for the shift of the absorption edge of zinc sulphide with temperature. The latter shift was measured by Gisolf in unpublished studies quoted by Möglich and Rompe [16]. The latter workers have associated the absorption-edge shift with the thermal expansion of the crystal lattice. It is

easily seen that the shift in excitation spectrum with temperature causes a fall in efficiency with temperature for short wave-length excitation (curves *A* and *B* of Fig. 55), while at longer excitation wave-lengths it causes an increase in efficiency with temperature (curves *C* and *D* of Fig. 55).

It is of interest to note that the maximum efficiency of excitation occurs for wave-lengths slightly longer than that of the

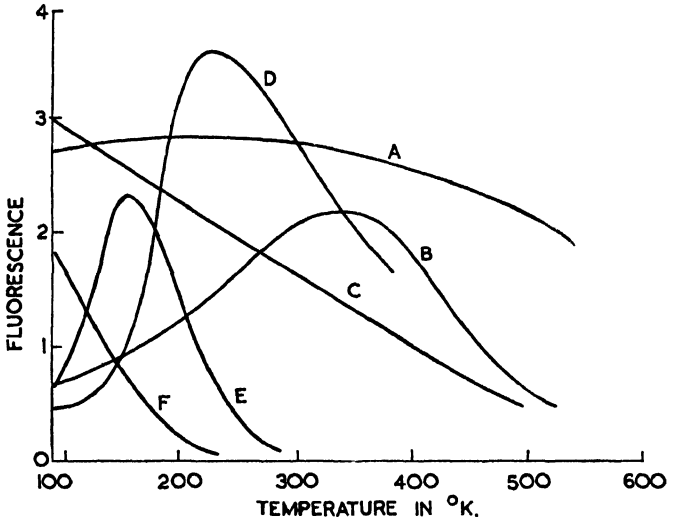


FIG. 60. Fluorescence–temperature curves of ZnS—Mn, CdI_2, and CdI_2—Mn phosphors for different excitation wave-lengths. (Garlick and Wilkins.) *A*, ZnS—Mn: 4,043 A, 4,358 A; *B*, ZnS—Mn: 3,653 A; *C*, ZnS—Mn: 3,342 A, 3,132 A, and 2,537 A; *D*, CdI_2—Mn: 3,653 A; *E*, CdI_2: 3,653 A; *F*, CdI_2—Mn and CdI_2: 2,537 A.

absorption edge. At longer wave-lengths the efficiency falls off, due to the decrease in quantum energy and in the absorption coefficient. However, at short wave-lengths the absorption coefficient is very high, and the drop in efficiency can only be explained by assuming that electrons, being raised into the conduction levels, can be captured by non-radiative systems as well as by luminescence centres. In most zinc sulphide phosphors the efficiency at short wave-lengths falls to about 10 per cent., which is of the same magnitude as the efficiency for particle excitation (see Chap. VII). It is therefore likely that excitation by longer wave-lengths than that of the absorption edge does not raise electrons into the conduction levels, although such a process has generally been assumed by other workers.

We give in Fig. 60 curves for efficiency variation with temperature and wave-length of some cadmium iodide phosphors as measured by Garlick and Wilkins [13]. They show a similar variation with wave-length to that shown by zinc sulphide phosphors, although their lattice has a layer structure. No absorption measurements on these phosphors are available for comparison.

3. The retrapping of electrons during phosphorescence and thermoluminescence

We have seen in Chapter II that the occurrence of retrapping of electrons during the luminescence process in phosphors

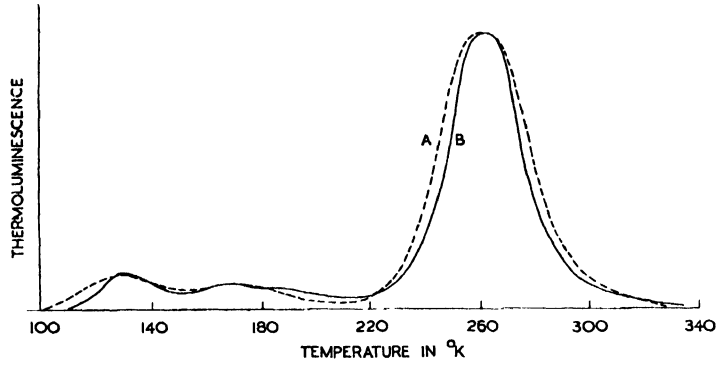


FIG. 61. Comparison of experimental and theoretical thermoluminescence curves for a Zn_2SiO_4—Mn phosphor. *A*, theoretical curve neglecting retrapping (Herman and Meyer); *B*, experimental curve (Randall and Wilkins).

necessitates a modification of the theoretical treatment of phosphorescence and thermoluminescence. We have also observed that although in many phosphors the capture cross-sections of an empty luminescence centre and an empty electron trap are of the same order of magnitude, yet there is little evidence of retrapping [17]. We shall now review experimental evidence of a more conclusive nature than that so far presented, which enables the earlier inference of the absence of retrapping in sulphide and silicate phosphors to be confirmed.

Fig. 22 and Fig. 62 below are thermoluminescence curves for a copper-activated zinc sulphide phosphor. The peaks of these curves are due to a distribution of electron trap depths, according to the theoretical treatment of Randall and Wilkins. However, Herman and Meyer [18] have constructed curves

from calculations which assume that each peak is due to one depth of trap. Such a curve is given in Fig. 61 (curve *A*) together with the experimental curve measured by Randall and Wilkins for a manganese-activated zinc silicate phosphor (curve *B*). Good agreement is shown between the two curves. In order to construct such curves it is necessary to assume low values for

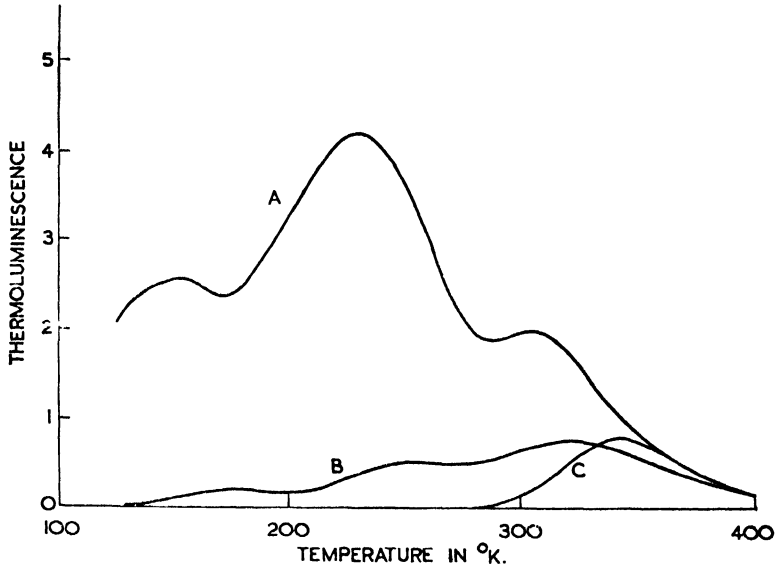


FIG. 62. Thermoluminescence curves of a ZnS—Cu phosphor for saturated and non-saturated filling of electron traps. (Garlick and Wilkins.) *A*, saturated curve; *B*, unsaturated curve due to very weak excitation. Actual area under curve *A* is about 2,000 × that under *B*. *C*, thermoluminescence after some time of phosphorescence decay at 291° K.

the constant s of equation 2.1, whereas the values calculated from measurements for zinc silicates are of the order of 10^8 sec.$^{-1}$ The experiments recently carried out by Garlick and Wilkins [19] show conclusively that the peaks of the thermoluminescence curves for zinc sulphide phosphors are due to a distribution of trap depths, while other exhaustive experiments by Garlick and Gibson [20] show that the same is true for zinc silicate phosphors. Garlick and Wilkins postulate that electron traps and luminescence centres coexist in one centre and that electrons leaving traps may not be free to move through the crystal lattice. Fig. 62 gives some of the experimental results on which

their conclusions are based. Curve A is the saturated thermoluminescence curve of the zinc sulphide phosphor measured after strong excitation at liquid-air temperature. Curve B is the thermoluminescence curve measured after a very small amount of excitation at liquid-air temperature. From the relative areas of the two curves it is estimated that in the second case only 0·1 per cent. of the traps in the phosphor are filled. Thus electrons escaping from traps during the early stages of thermoluminescence will have a very great chance of being retrapped in deeper traps and this should enhance the emission at higher temperatures. Comparison of curves A and B shows that the ratio of the heights of these two curves at various temperatures is not altered very much. From this it is concluded that retrapping is negligible. It is possible that the absence of retrapping may be due to the existence of many empty luminescence centres in the unexcited phosphor. This explanation is ruled out by exciting the phosphor at 90° K with all traps empty. The luminescence increases with time as shown in Fig. 19 and there is no evidence of a rapid initial rise of emission, which would be expected if empty luminescence centres were present. Thus the authors assume that the absence of retrapping is due to the proximity of the traps and luminescence centres in one centre.

The evidence of Garlick and Wilkins for a distribution of trap depths in phosphors is given in curve C of Fig. 62. This curve is the thermoluminescence curve measured after allowing the phosphorescence to decay at room temperature. If the peak of the curve A, at 310° K, is due to a single trap depth, then its position will remain unaltered after phosphorescence decay although its height will have diminished. The large shift of the emission peak shown in curve C indicates that a distribution of trap depths is present and that after phosphorescence decay only the deeper traps remain.

Garlick and Gibson [20] have extended the above measurements to three phosphors of three different classes, namely, a copper-activated zinc sulphide, a manganese-activated zinc silicate, and a europium-activated strontium silicate phosphor.

All three phosphors have thermoluminescence curves with narrow peaks suggestive of single trap depths and are therefore very suitable for experiments which attempt to determine the extent to which retrapping occurs during luminescence. Fig. 63 and Fig. 42 give their thermoluminescence curves after strong

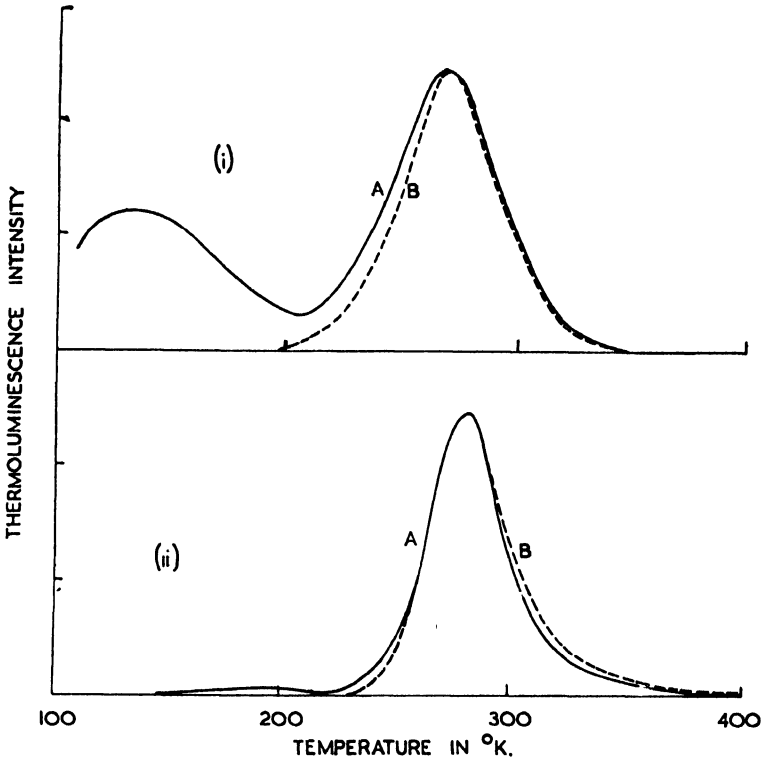


FIG. 63. Experimental and theoretical thermoluminescence curves for zinc sulphide and silicate phosphors. (i), ZnS—Cu. (ii), Zn_2SiO_4—Mn. Curves: *A*, experimental; *B*, calculated assuming retrapping to occur during thermoluminescence process.

excitation at 90° K. In addition, the theoretical curves for these phosphors have been included: they have been calculated by assuming a single trap depth to be responsible for the curve peaks. The calculations for the first two phosphors are based on equation 2.15 which assumes retrapping to be present, while the calculated curve of Fig. 42 for the strontium silicate phosphor is based on equation 2.7 which neglects retrapping. All three theoretical curves show remarkable agreement with the respective experimental curves, but this in itself is not conclusive evidence for the validity of the particular theory used, except

in the case of the strontium silicate phosphor. Its thermoluminescence curve shows a peak so narrow that it is similar to that of the potassium chloride phosphor in Fig. 17. The characteristics of the strontium silicate phosphor have been described in Chapter III, and we shall therefore confine our attention to the zinc sulphide and zinc silicate phosphors. The phosphores-

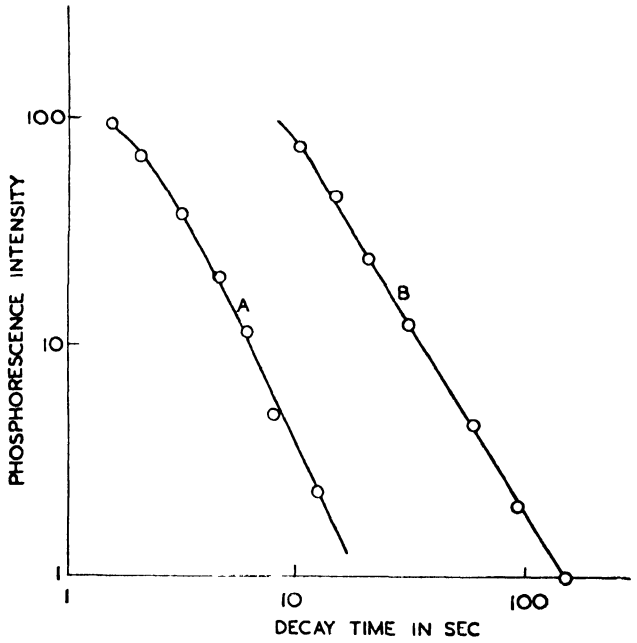


FIG. 64. Phosphorescence decay curves of zinc sulphide and silicate phosphors of Fig. 63 at room temperature. *A*, ZnS—Cu; *B*, Zn_2SiO_4—Mn.

cence decay of these phosphors at room temperature is shown in Fig. 64. If the assumption that retrapping is present is correct, then the decay of both phosphors should be given by equation 2.15. Since the decay curves of Fig. 64 are plotted with logarithmic coordinates, the curves should approach an asymptote of slope 2 at long decay times. Although this is approximately true for the zinc sulphide phosphor, the zinc silicate specimen has a decay curve slope of 1·7. However, in both cases the slopes are those expected from an analysis of the shape of the respective thermoluminescence curves of the phosphors, assuming that there is no retrapping present (see Table I, Chapter II, for other correlations in ZnS phosphors).

In order to reach a more definite conclusion as to the correct

theoretical treatment, the following experiments have been made, based on the derivations of Chapter II:

i. Measurements of the variation in the number of filled electron traps with intensity of excitation at a fixed temperature. If retrapping is not present, then according to equation 2.20 the variation is given by:

$$(N/n_0 - 1) = \text{constant}/J, \tag{4.6}$$

where N is the total number of traps, given by the area under the saturated thermoluminescence curve, and n_0 is the number

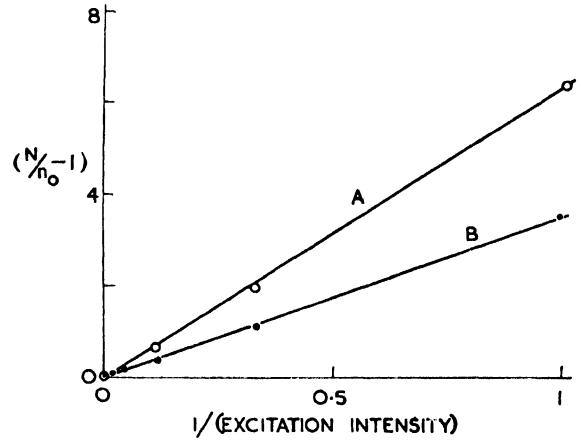


FIG. 65. Dependence of trap filling in zinc sulphide and silicate phosphors on the excitation intensity. (n_0 is number of electrons in the N available traps.) *A*, ZnS—Cu; *B*, Zn_2SiO_4—Mn.

of traps filled at intensity J, given by the area under the thermoluminescence curve for that intensity. When retrapping is present, then equation 2.25 is followed and the right-hand side of equation 4.6 will involve an inverse square root of the intensity J instead of the simple inverse form. Fig. 65 shows the variation of the expression $(N/n_0 - 1)$ with the inverse of the intensity J. Equation 4.6 appears to be followed by both phosphors showing that retrapping is not important.

ii. Measurements of the form of the initial part of the thermoluminescence curve; more specifically, the way in which its height at a fixed temperature varies with the number of filled traps. If retrapping is absent, then equation 2.8 is followed, that is, the curve height is proportional to the number of filled traps n_0. If retrapping occurs, then, according to equation 2.17,

the curve height is proportional to the square of n_0. Fig. 66 shows that the linear relation of equation 2.8 is in agreement with the results and indicates that retrapping does not occur.

All the above results show that in the phosphors investigated retrapping of electrons during phosphorescence and thermoluminescence does not occur to any marked extent. Since these

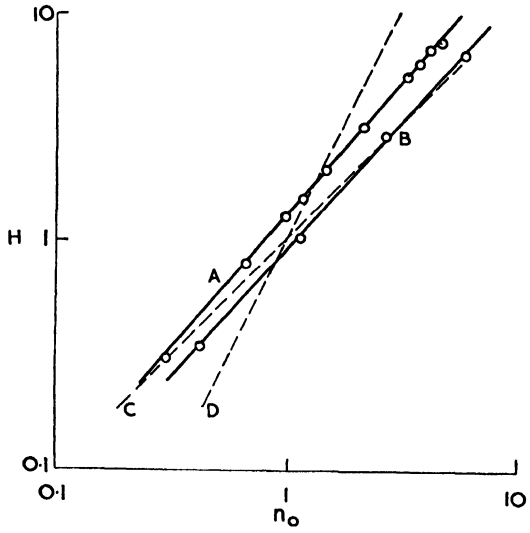


FIG. 66. Variation in height (H) of initial portion of thermoluminescence curves at some fixed temperature with the number n_0 of traps initially filled: phosphors ZnS—Cu and Zn_2SiO_4—Mn of Fig. 64. A, ZnS—Cu; B, Zn_2SiO_4—Mn; C, slope of graph expected for neglect of retrapping of electrons; D, slope of graph assuming retrapping to be present.

specimens are typical of their class, and since similar results have been obtained with other phosphors having less well-defined thermoluminescence characteristics, we must assume that the absence of retrapping is a general feature of the luminescence process in sulphide and silicate phosphors. We now discuss the implications of these experimental findings in establishing the nature of traps and luminescence centres.

4. The relation between luminescence centres, electron traps, and the crystal lattice of phosphors

In the theoretical derivations of Chapter II it was not necessary to consider in detail the spatial location of luminescence centres and electron traps in phosphors but only the energy

relations between them. Distinction has been made between two types of phosphor, those of the thallium-activated potassium chloride type, in which the phosphorescence and thermoluminescence processes are entirely confined to the emission centres, and those of the sulphide type, in which excitation is assumed to free electrons from centres. In the case of the latter phosphors it has been assumed that the emission centres and electron traps are separate entities and that electron transit between them involves movement through the conduction band of the phosphor crystal. It is clear from the evidence given above that there must be a spatial association of traps and emission centres in order to explain the absence of retrapping during luminescence. Further support of this hypothesis has been given in Chapter III (§ *b*), where it has been shown that the activating impurity in sulphide phosphors also gives rise to specific distributions of electron traps. It is therefore probable that the traps are near to the impurity centres. These studies have also shown that certain other ions, particularly the halogen ions exclusive of fluorine, are essential for the formation of an emission centre. Thus we may assume that the emission and the trapping states occur in relatively large complex centres in the crystal. It is then probable that phosphorescence and thermoluminescence will only involve the movement of electrons within these centres and that excitation into the conduction band of the matrix will only occur for excitation of short wave-length or for particle excitation. The large size of the centres is also suggested by the broad, structureless nature of the emission spectra of sulphide phosphors. In the next chapter we shall discuss independent evidence in support of this hypothesis from measurements of photoconductivity and dielectric changes in phosphors.

The luminescence efficiency of phosphors

We shall now consider the application of the above concept of a luminescence centre to the explanation of the dependence of luminescence efficiency upon temperature and upon the intensity and nature of excitation as described in § 2. We have already concluded in the above section that when excitation

frees electrons from luminescence centres into the conduction levels of a phosphor they can be captured by non-radiative centres. For this reason the efficiency for excitation of short wave-length, involving absorption in the matrix, and for particle excitation, will be smaller than that for excitation processes confined to the emission centres. Since thermo-electric power measurements show that the fall in efficiency at high temperatures is accompanied by a predominantly electronic conductivity (that is, electrons in conduction levels rather than positive holes in the full band), it is probable that the increased temperature causes a thermal activation of electrons from the excited states of the complex centres into the conduction levels. They are then captured by non-radiative centres rather than by luminescence centres. In order to make this assumption rigorous, we must provide for the return of excited electrons which are captured in non-radiative centres to their ground states in the complex centres. As yet there is only one piece of experimental evidence which helps in this respect. We refer to the occurrence of edge-emission spectra in zinc and cadmium sulphides at low temperatures when excited in the lattice absorption band [21]. This emission only occurs when electrons are first raised into the conduction levels, and has a vibrational structure characteristic of a large complex in the lattice. Since it is quenched at ordinary temperatures, we may assume that its transitions become non-radiative. Hence the existence of non-radiative transitions for electrons which reach the conduction levels follows from the properties of the emission centres themselves, and it may not be necessary to assume the existence of other impurities in the phosphor which function as 'killers'. In specific cases such as the inclusion of nickel in zinc sulphide there is no doubt that the 'killer' impurity can capture electrons. However, there is considerable overlap of these 'killer' centres with the normal emission centres at the usual concentrations present, as shown by their effect on the electron trapping states pertaining to the emission centres. This overlap vitiates the simple assumptions made by Klasens [4] for the process of 'nickel killing' of sulphide phosphors. It explains in a qualita-

tive way the change in the activation energy W when the complex centre is perturbed by the nickel inclusion.

The experiments described in this chapter and the inferences drawn from them are still of a preliminary nature. However, they serve to emphasize the limitation of the simple energy-band model for phosphors. They also stress the need for more careful experimental investigation into the detailed structure of the emission centres of the sulphide type of phosphor.

CHAPTER V

THE ELECTRICAL PROPERTIES OF PHOSPHORS

1. The chief electrical phenomena

THERE are three main electrical phenomena associated with the luminescence of solids which have been investigated in recent researches. They are:

i. Changes in electrical conductivity during luminescence.
ii. Changes in the dielectric constant and dielectric loss of phosphors during luminescence.
iii. The production of luminescence by the application of strong electric fields to phosphors.

We shall consider these phenomena in the sections of this chapter which follow.

2. The electrical conductivity of phosphors

In the previous chapter we have already mentioned the increase in phosphor conductivity which accompanies the decrease of the luminescence efficiency at elevated temperatures. We have also considered in Chapter II the general relations between conductivity and luminescence. In this section we shall review some of the early studies of photoconductivity in phosphors and then discuss more recent studies.

Early studies of photoconductivity

Although the phenomenon was observed by Lenard and Saeland [1] in 1909, the earliest significant studies of photoconductivity were made by Gudden and Pohl [2]. Since that time the progress made in its investigation has been reviewed by various workers [3, 4, 5]. The experimental difficulties attendant on the use of phosphors in powder form have hindered the development of a precise, quantitative treatment of the results. More information of a quantitative nature has been obtained by the study of photoconductivity in single crystals of the alkali halides and the silver halides [5]. However, it is of interest here to summarize the results of the early work on phosphors as follows:

i. Excitation which produces luminescence in zinc sulphide phosphors also gives rise to a photocurrent when the phosphor is placed in an external electric field. According to the theoretical model of Chapter II, this photocurrent will be due to the excitation of electrons into the conduction band of the phosphor crystal, the electrons then moving under the influence of the applied field.

ii. This photocurrent, known as the primary current, decreases rapidly with time, and it has been assumed that this is due to the setting up of a space charge by the empty luminescence centres and by the trapping of electrons.

iii. The primary current is proportional to the intensity of excitation provided that this is sufficiently small. In the spectral region where the photoconductivity effect is a maximum, quantum equivalence is shown; this means that each quantum absorbed gives rise to one conduction electron.

iv. The space charge set up by continued excitation can be dissipated by heating the phosphor or by irradiating it with long wave-length light.

v. Prolonged excitation gives rise to a secondary current which increases with time and is assumed to be due to a breakdown of the resistance of the phosphor.

vi. The rise and decay of the primary current is normally very rapid, but the secondary current decays relatively slowly after excitation ceases. In many cases it is similar in its behaviour to the phosphorescence decay and has therefore been associated with the escape of trapped electrons and their return to luminescence centres.

This summary serves to indicate the qualitative relations between luminescence and photoconductivity. In these early studies it has been assumed that electrons must be excited into the conduction band before they can contribute to the observed photoconductivity. We have concluded in the previous chapter that in zinc sulphide and zinc silicate phosphors excited electrons may be confined to the large complex centres formed by the activating impurity. However, electrons so limited could give rise to a rapidly polarized photocurrent, and this is in fact

observed in these phosphors at ordinary temperatures. We shall see also in the following section that the trapping of electrons causes a large displacement current which might account for most of the photoconductivity current observed for static applied fields. It should be emphasized that the available information on photoconductivity in phosphors does not enable us to distinguish between conduction due to electrons in the conduction band and that due to the displacement of electrons in the excited states of the relatively large luminescence centres. It is of interest to note that Lenard interpreted the electrical effects in his phosphors according to the latter process.

Recent studies of conductivity in phosphors

The photoconductivity of phosphors has been studied more recently by several workers, such as Herman and Hofstadter [6], Gisolf [7], Reimann [8], Hill and Aronin [9], Randall and Wilkins [10], and Hardy [11]. Herman and Hofstadter have investigated the photoconductivity of zinc silicates, using radiation of wave-lengths from 2,300 to 4,100 A and at temperatures as low as −150° C. The effect has a maximum for excitation of 2,965 A wave-length at low temperatures. The photocurrent is proportional to the applied field strength for fields up to 900 V/cm. in magnitude. Measurements made by Hill and Aronin, using specimens of pure and manganese-activated zinc silicate phosphors, show that the photocurrents are of the same order of magnitude in the pure and in the activated phosphors and that the effect seems to be characteristic of the matrix crystal. Randall and Wilkins have confirmed these results and have made measurements of the photoconductivity of other phosphors, such as borates, tungstates, and chlorophosphates. Photocurrents of relatively large magnitude are only found in the sulphide and silicate types of phosphor. Recent measurements made in the author's laboratory show that photoconductivity in calcium and strontium silicates is independent of the activating impurity.

The effect of long wave-length light on photoconductivity

in zinc sulphide phosphors has been investigated by Gisolf [7], Reimann [8], and Hardy [11]. Gisolf's results suggest that this radiation frees electrons from traps and, as the electrons return to luminescence centres, the resistance increases with time. Reimann has shown for one phosphor that this increase in resistance proceeds linearly with time for steady irradiation.

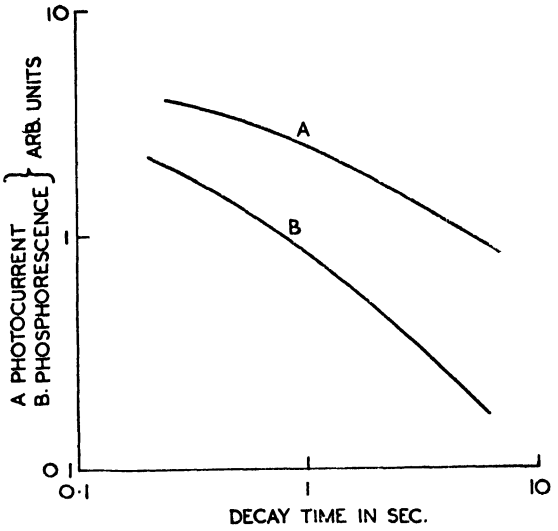


FIG. 67. Decay of phosphorescence (B) and corresponding decay of photocurrent (A) after cessation of excitation for a ZnS(85 %)CdS(15 %)—Cu phosphor. (Hardy.)

Hardy has made measurements of the photocurrents during fluorescence and phosphorescence, and in both cases with and without the presence of infra-red irradiation. Fig. 67, constructed from his data, gives the relation between the decay of the photocurrent and the decay of phosphorescence. His results cannot be used to interpret the processes involved since they are not sufficiently extensive with respect to time and intensity of excitation. However, our use of logarithmic coordinates shows that the decay of photocurrent does not follow the same law as the phosphorescence decay. We shall find similar differences for the decays of phosphorescence and the dielectric changes in phosphors given in Fig. 76 and discussed in the next section.

Hardy has given results of some interest for the photocurrent decay in a cadmiu msulphide phosphor after excitation by long wave-length light. It is thought that this phosphor emits in

the infra-red [12]. The current decay, shown in Fig. 68, is relatively slow, while the decay of the visible part of the emission is quite rapid. It is likely that the slow decay of the

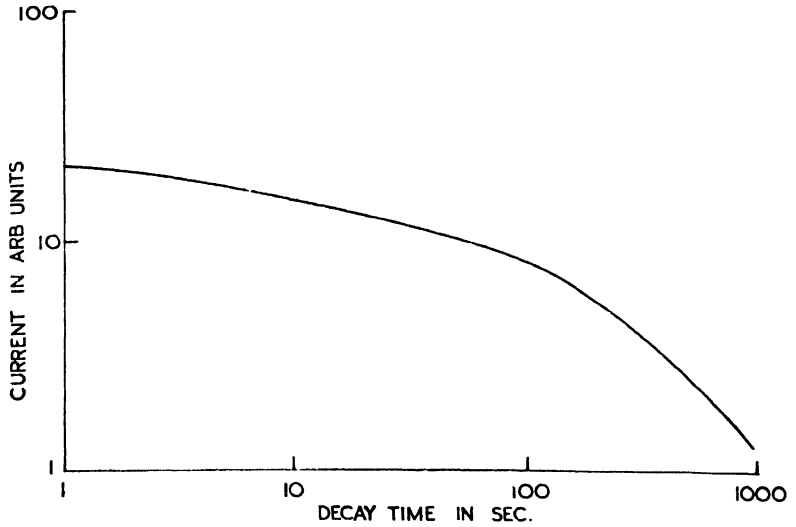


FIG. 68. Photocurrent decay in a CdS—Cu phosphor after excitation by long wave-length light. (Hardy.)

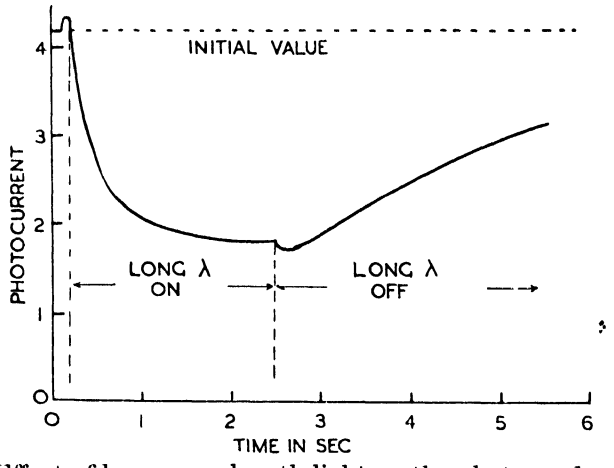


FIG. 69. Effect of long wave-length light on the photoconductivity of a ZnS—CdS—Cu phosphor during steady excitation by ultra-violet radiation. (Hardy.)

current is due to the slow release of electrons from deep traps present in cadmium sulphide and in zinc-cadmium sulphide phosphors having high cadmium sulphide content. These traps are shown by curve *D* of Fig. 32. Hardy has found that application of infra-red light during excitation of phosphors causes a

decrease in the photocurrent. This is shown in Fig. 69, which also shows the initial transient rise in the current when infra-red irradiation begins and a corresponding transient decrease when irradiation ceases. The effect produced by irradiation with infra-red light during phosphorescence is shown in Fig. 70. Although the two specimens appear to behave differently, this

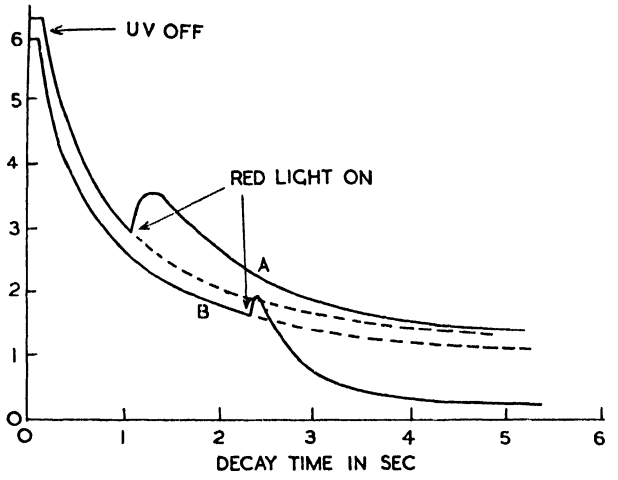


FIG. 70. Effect of long wave-length light on the decay of photo-current in two different ZnS—CdS—Cu phosphors (*A* and *B*). (Hardy.)

is not significant as the use of heterochromatic infra-red radiation does not enable us to distinguish the effects of quenching wave-lengths and stimulating wave-lengths on the photocurrents. These would be different for different phosphors.

Theoretical discussion of photoconductivity

Because of the experimental difficulties involved in the use of powders, we shall find that it is only possible to attempt a qualitative theoretical explanation of the above results. It is certain that photoconductivity in phosphors is due to the movement of excited electrons, but it is not certain whether this movement is restricted to the centres formed by the activating impurity or whether it is unrestricted in the conduction band of the crystal. Whichever hypothesis is correct, the decay of the photocurrent during phosphorescence may be associated with the escape of electrons from traps and their subsequent return to the unexcited state. We therefore expect that there will be an increase in conductivity during thermoluminescence

due to the release of trapped electrons. Herman and Hofstadter [6] have observed increases in the 'dark' current of zinc silicate phosphors when warmed after excitation at low temperatures. The current is found to reach a maximum at about the same temperature as the maximum of the thermoluminescence emission. More recent studies by Garlick and Gibson [13] in-

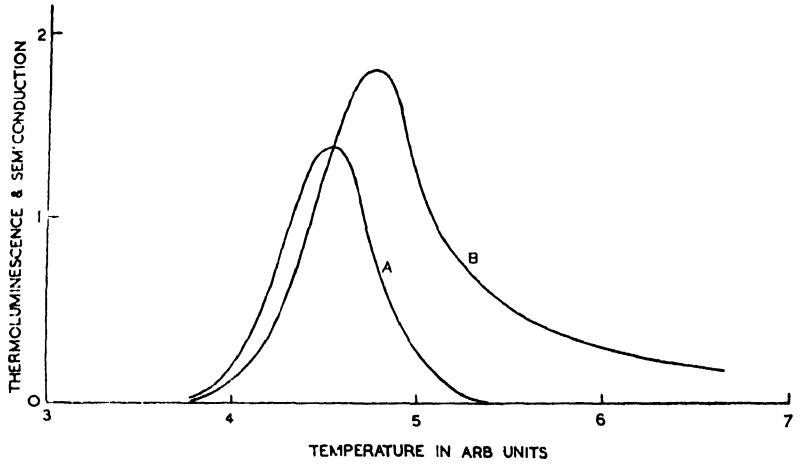


FIG. 71. Thermoluminescence (A) and accompanying semiconduction current (B) of a phosphor with a single trap depth predicted theoretically. (Herman and Meyer.)

clude measurements of the conductivity changes during thermoluminescence in zinc sulphide phosphors, and a typical curve showing the variation of current with temperature is included in Fig. 77 below. Herman and Meyer [14] have attempted to establish theoretical relations between the conductivity changes and the thermoluminescence: Fig. 71 shows their theoretical curves for the variation of current and thermoluminescence with temperature for a phosphor with one depth of electron trap. According to their theory, the maximum current should occur at a higher temperature than the maximum emission. However, the experimental curves of Fig. 77 do not indicate any marked difference in the positions of these two maxima.

Herman and Meyer have also considered the effect of infrared radiation on the decay of photocurrent in phosphors. They show that when irradiation with long wave-length light begins there should be a temporary decrease in phosphor resistance, since electrons are ejected from traps and become available for

conduction, but that, since the supply of electrons from traps will always be decreasing, the initial fall in resistance will be followed by an increase in resistance. Theoretical curves

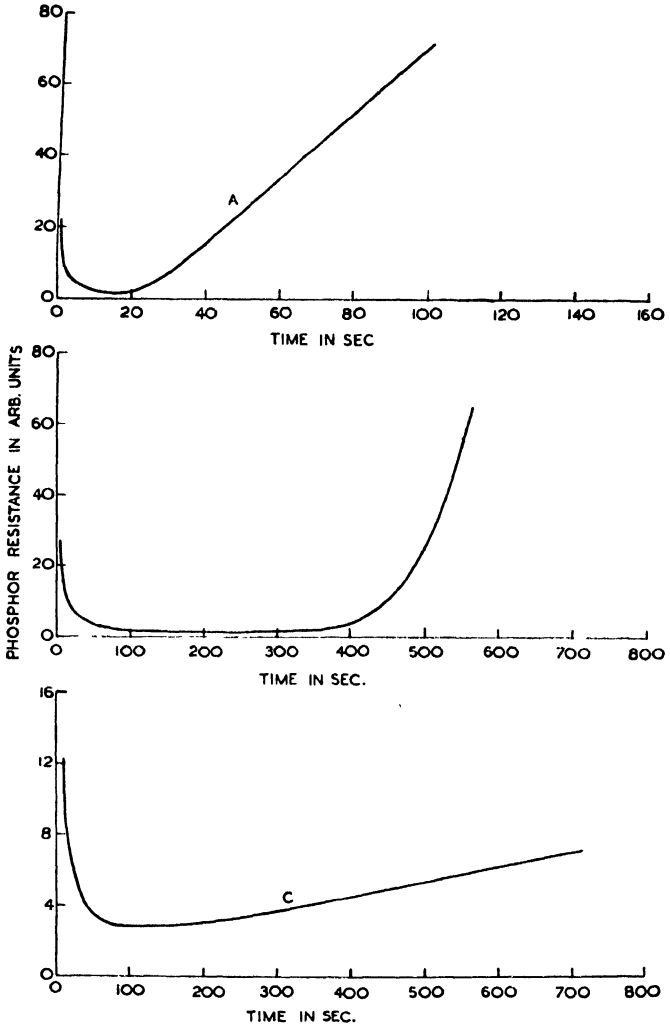


FIG. 72. Change in electrical resistance of a phosphor with time under different intensities of infra-red radiation (I) after excitation: curves also show effect of the number of traps initially filled on the change (N is number of traps filled). (Herman and Meyer.) A, $N = N_a$: $I = 0{\cdot}1$; B, $N = N_a$: $I = 0{\cdot}01$; C, $N = 0{\cdot}1N_a$: $I = 0{\cdot}001$.

showing this change in resistance with continued irradiation, for different intensities of irradiation and for different numbers of electron traps initially filled, are given in Fig. 72. In their theory Herman and Meyer assume that liberated electrons

return to the emission centres via the conduction band and also that retrapping is negligible. However, their relations will follow from different assumptions, such as those made in Chapter IV that the electrons do not normally pass through the conduction levels when in transit from traps to emission centres. It is not possible to use Hardy's results to test the validity of their theory as his experiments do not include the effect of different infra-red intensities on the decay of the photo-current.

We should note that in all experiments which involve the sudden emptying or filling of electron traps a transient and rapid change in current is observed. It is probable that this is due to the polarization effects, associated with the electron traps, which we shall discuss in the following section.

3. Dielectric changes in phosphors during luminescence

The increase in the dielectric constant of impurity-activated phosphors, such as zinc sulphide, when excited was first observed by Lenard and Saeland [1]. More extensive studies were carried out by Gudden and Pohl [2], Herweg [15], Wilde [16], and Schmidt [17]. Later investigations include those of Gisolf [18], who measured the corresponding increase in dielectric loss, Goos [19], and Wesch [20]. We may summarize the results of these studies as follows:

i. Dielectric changes are only shown by those phosphors which also show photoconductivity during luminescence. No effect is observed in the thallium-activated alkali halides.

ii. For some zinc sulphide phosphors the increase in dielectric constant may be as much as its normal value (about 8), this being for quite normal excitation intensities.

iii. Wilde's experiments show that the changes are dependent on the temperature and on the frequency of the applied alternating electric field.

iv. The dielectric changes decay as phosphorescence proceeds and are sensitive to infra-red irradiation in a similar way to the phosphorescence processes.

v. There is no simple relation between the dielectric changes and the intensity of excitation and emission.

In these studies we find no adequate explanation of the origin of the dielectric changes in phosphors. It has been thought that they will occur if electrons are present in the conduction band. This idea has been suggested recently by de Groot [21], although it fails to explain his experimental results. Recent extensive studies by Garlick and Gibson [13] of the dielectric changes in relation to fluorescence, phosphorescence, and thermoluminescence have provided an adequate interpretation of the dielectric effects in terms of the properties of filled electron traps. It has been shown by these authors that dielectric changes occur when electrons are trapped, the traps constituting highly polarizable systems when filled by electrons. Their work is described in some detail below.

Some theoretical observations on dielectric changes in phosphors

At the beginning of the investigations by Garlick and Gibson it was found that the dielectric changes were independent of the number of electrons excited at any instant, that is, independent of the number of electrons which might be in conduction levels according to the accepted theory at that time. They were, however, markedly dependent on the number of trapped electrons. We shall discuss here some of the most significant facts which lead to the conclusion that trapped electrons are responsible for the dielectric changes in phosphors. It is evident that electrons raised into the conduction band should contribute to an increase in the dielectric loss of a phosphor. If these electrons are subject to any constraints when moving in the conduction levels, so that they move out of phase with the field, then they may also cause an increase in dielectric constant. We also expect that trapped electrons will cause an increase in dielectric constant since they have a low binding energy in the trap (0·1 to 1·0 eV.), and can thus be easily displaced by an applied field. Some of the experiments which show that the effects observed are almost entirely due to trapped electrons are summarized as follows:

i. Although the fluorescence and the primary photocurrent of phosphors show a more or less linear increase with intensity of

excitation at ordinary temperatures, the dielectric changes show saturation effects at relatively low excitation intensities, as shown in Fig. 73. However, the saturation is similar to that shown by the variation of the number of filled electron traps with intensity.

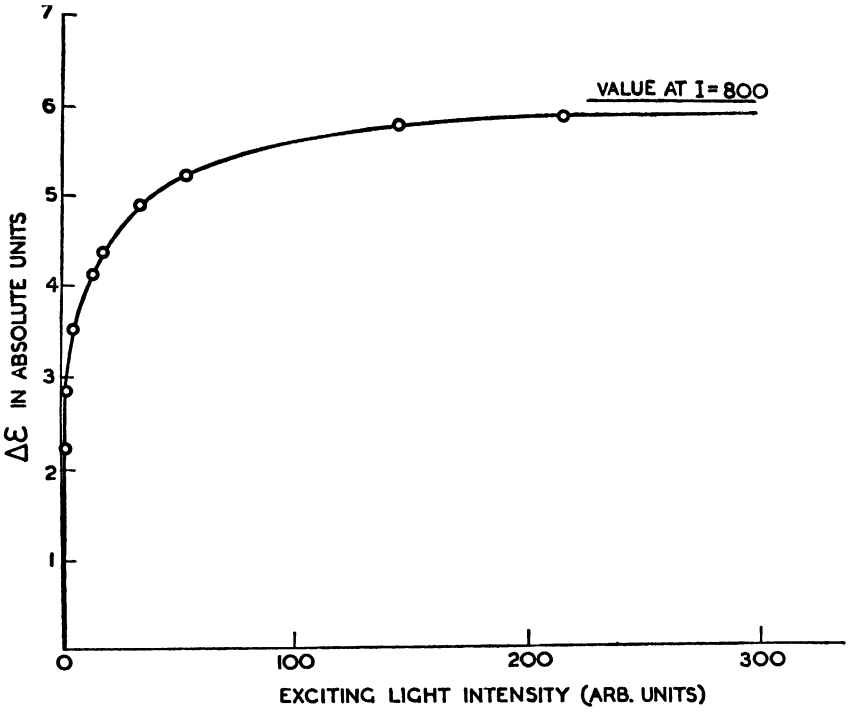


FIG. 73. Variation of dielectric constant change ($\Delta\epsilon$) with exciting light intensity for a ZnS—Ag phosphor at 291° K. (3,650 A exc.)

ii. After excitation at low temperatures the phosphorescence decay of a phosphor reaches a very low value at long decay times but the dielectric changes only fall during this decay to about 80 per cent. of their initial value. Since no appreciable phosphorescence occurs, very few electrons are in transit between traps and emission centres and so the dielectric changes cannot be due to these electrons. If infra-red radiation is applied there is often an enhancing of phosphorescence, but in all cases there is no corresponding increase in the dielectric constant or loss; the latter show only a decay to zero under irradiation.

iii. The variation of the dielectric changes with the frequency

of the applied field shows that the polarizable systems giving rise to the dielectric changes have a relaxation time of the order of 10^{-7} sec. Such a large value is hardly likely to be characteristic of electrons in the conduction band, but it seems to be characteristic of electron trapping systems as discussed below.

We may estimate, from a knowledge of the number of traps in a phosphor and the magnitude of the dielectric changes, the contribution to these changes from each filled trap. In most phosphors the number of traps is about 10^{18} per c.c. [22]. In order to explain the loss changes (often from 10^{-8} to 10^{-5} ohm^{-1}), we must assume that the filled electron trap can take up very small amounts of energy from the field. This implies that the electronic energy-levels in a trap are very close together, and thus the effective size of the trap must be large compared with the crystal lattice spacing. The applied fields used in experiments were not sufficient to eject any trapped electrons at ordinary temperatures. Since the escape of electrons from traps is a highly temperature-dependent process (see equation 2.1), and depends on the binding conditions, we should expect the dielectric changes due to trapped electrons to show a marked temperature dependence. This is borne out by the experimental results below.

The above discussion shows that, if dielectric changes are due to filled traps, then their magnitude will depend on the number of filled traps, on the depths of the traps, on the applied field frequency, and on the temperature. We now consider in detail the experimental evidence which upholds the validity of the assumptions made above. The results are for a few selected phosphors which are typical of their class.

Variation of the dielectric changes with intensity of excitation

If a phosphor is excited by radiation of constant intensity at a fixed temperature, the fluorescence is generally proportional to the excitation intensity. However, the dielectric changes show saturation, even for low intensities of excitation. A typical result showing this saturation is given in Fig. 73 for a silver-

activated zinc sulphide phosphor. Examination of many phosphors has shown that the dielectric constant change ($\Delta\epsilon$) and the dielectric loss change ($\Delta\gamma$), which is expressed as the change in equivalent parallel conductance, are related to the excitation

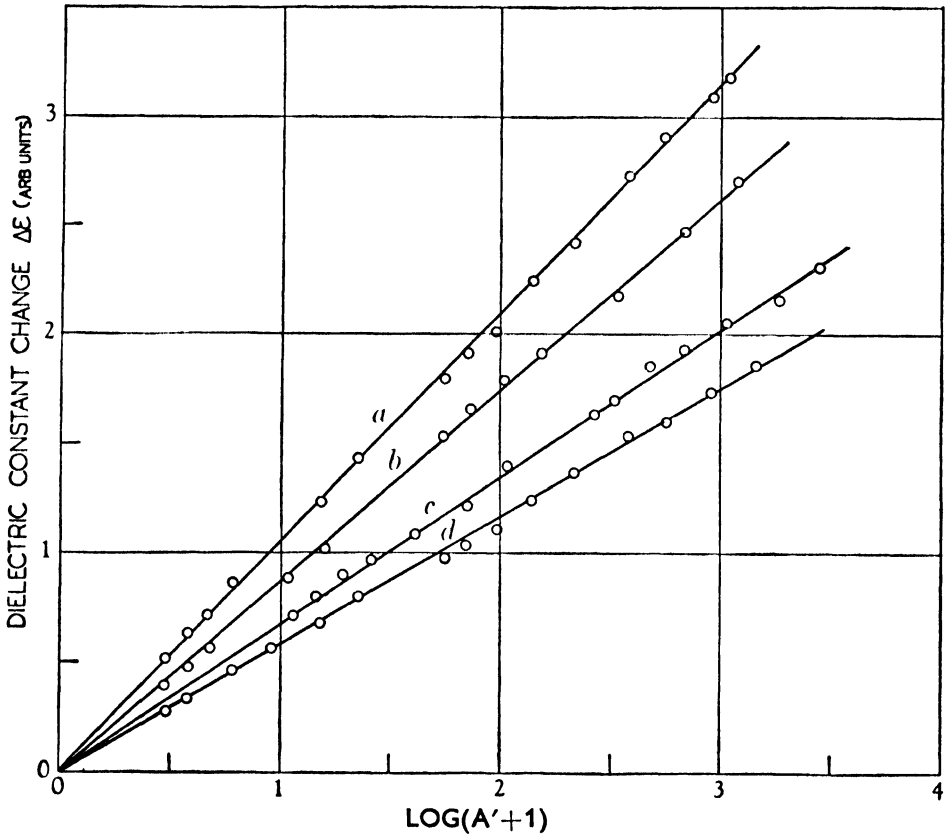


FIG. 74. Variation of dielectric constant change with excitation intensity for various phosphors at room temperature. (*a*) ZnS—CdS—Cu: short afterglow; (*b*) ZnS—Cu: long afterglow; (*c*) ZnS—Ag: short afterglow; (*d*) ZnS—Zn: short afterglow. (A' is equal to a constant factor b times the exciting light intensity I.)

intensity by similar expressions. The form of the expressions is as follows:

$$\Delta\epsilon \text{ or } \Delta\gamma = \text{constant} \times \log(Ib+1), \qquad (5.1)$$

where b is a constant. At high excitation intensities where $Ib \gg 1$ the equation reduces to the following:

$$\Delta\epsilon \text{ or } \Delta\gamma = \text{constant} \times \log(Ib). \qquad (5.2)$$

Thus by plotting $\Delta\epsilon$ or $\Delta\gamma$ against $\log(Ib)$ for these intensities

a straight line is obtained, whose intercept with the abscissa gives the value of b. Figs. 74 and 75 show experimental results plotted to indicate the validity of equation 5.1. Equation 5.1 is of the same form as equation 2.22 which describes the variation of the number of filled traps with excitation intensity. Thus the dielectric changes depend on the number of filled

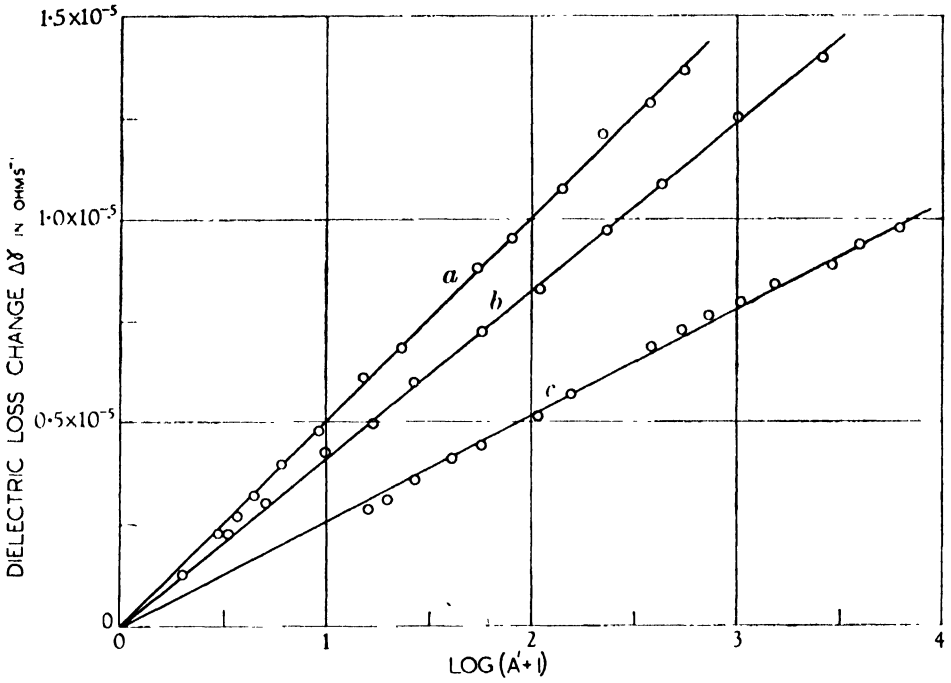


FIG. 75. Variation of dielectric loss change with excitation intensity for various phosphors at room temperature. (*a*) ZnS—Cu: long afterglow; (*b*) ZnS—Ag: short afterglow; (*c*) ZnS—CdS—Cu: long afterglow. (A' is as for Fig. 74.)

traps. Values of the constant b obtained from thermoluminescence measurements (using equation 2.22) show good agreement with those obtained from dielectric measurements on the same phosphor.

The decay of the dielectric changes with phosphorescence

The form of the phosphorescence decay after excitation ceases depends on the extent to which traps of different depths are filled as shown in Chapter II. The corresponding decay of the dielectric changes will also depend on the trap filling. To determine the relation between the phosphorescence decay and

the decay of the dielectric changes the following experiments were carried out:

i. Measurement of the phosphorescence decay with time.
ii. Measurement of the decay of the dielectric changes with time.
iii. Measurement of the decrease in the number of trapped electrons with time by means of thermoluminescence experiments.

These decay measurements are given in Fig. 76: they are plotted with logarithmic coordinates to show the form of the curves in relation to each other. The dielectric changes decay parallel to the decay of the number of trapped electrons, but the decay curve for phosphorescence shows a marked difference in slope. This difference should be about unity, according to the derivations of Garlick and Gibson. A slight increase in slope of the dielectric change curves at long decay time is ascribed to the effect of trap depth on these changes. Deeper traps will contribute a smaller amount to the changes since the electrons trapped in them have a stronger binding energy than in shallow traps.

Dielectric changes during thermoluminescence

Since thermoluminescence is due to the release of trapped electrons, we should expect that the dielectric changes would decrease as thermoluminescence proceeds. Typical results of dielectric measurements during thermoluminescence in a zinc-cadmium sulphide phosphor are shown in Fig. 77. It appears that the dielectric changes actually show an increase during part of the emission and that the curves for the dielectric constant and loss changes are not simply related to each other or to the thermoluminescence curve. However, relations can be established between them if it is assumed that the dielectric changes have a marked temperature variation, due to the change in the binding conditions of the trapped electrons with temperature (eq. 2.1). If we use the previous assumptions that the dielectric changes at any instant are proportional to the number of trapped electrons at that time but that they have a

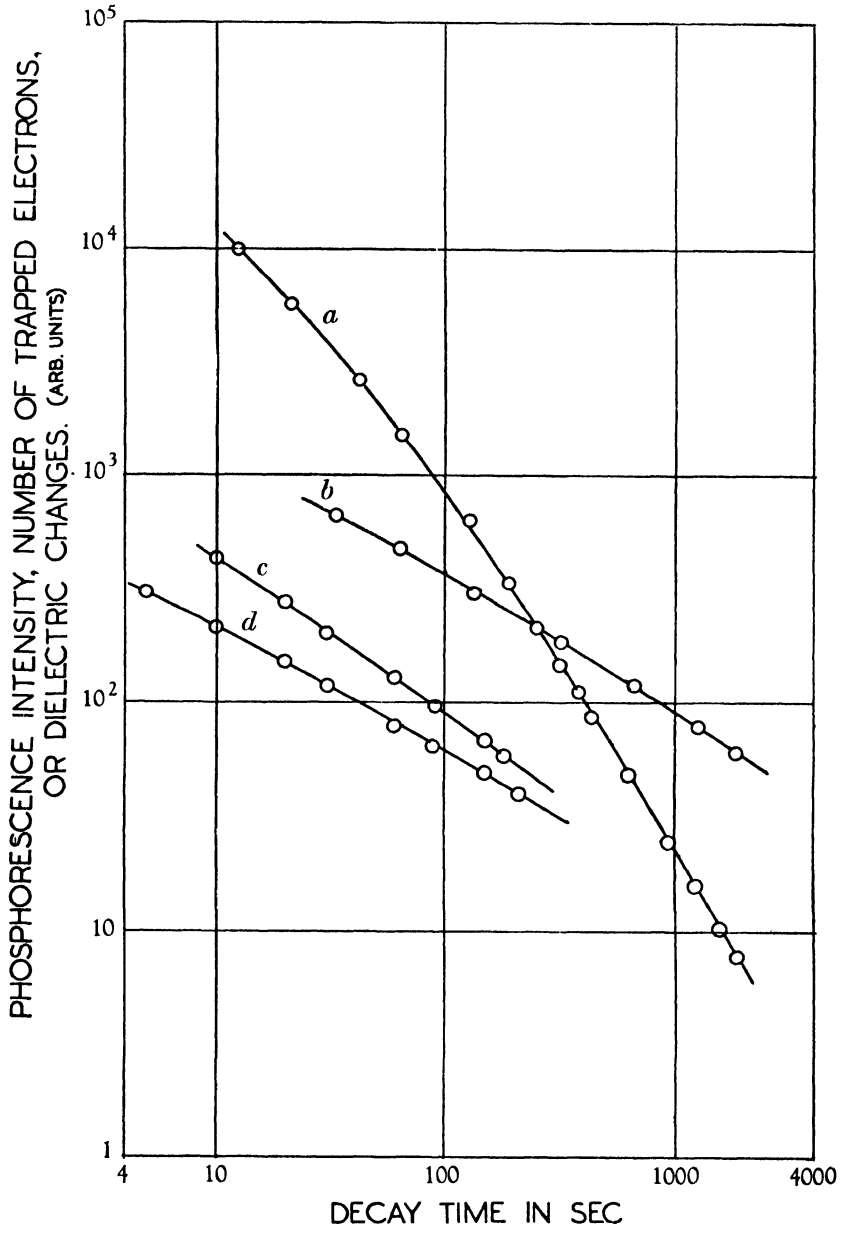


FIG. 76. Decay of dielectric changes, phosphorescence, and number of trapped electrons with time for a ZnS—Cu phosphor at room temperature. (*a*) Phosphorescence decay; (*b*) decay of number of trapped electrons; (*c*) decay of dielectric loss change; (*d*) decay of dielectric constant change.

temperature variation as well, then the temperature functions for the dielectric constant and loss changes are obtained from the curves of Fig. 77 as follows. The magnitude of the dielectric

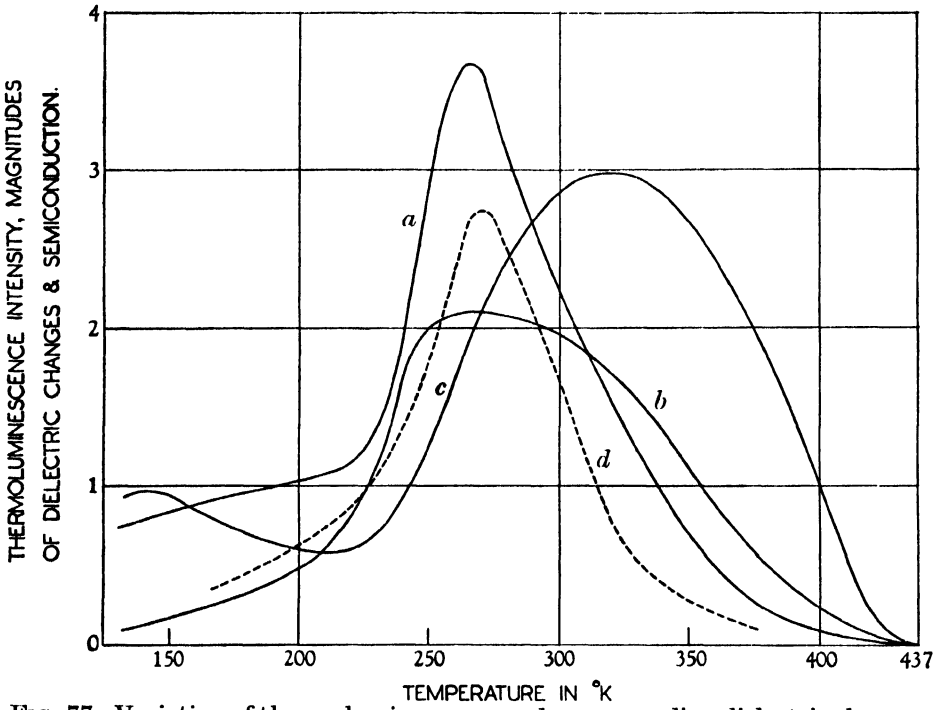


FIG. 77. Variation of thermoluminescence and corresponding dielectric changes with temperature. (*a*) Thermoluminescence curve; (*b*) dielectric loss-change curve; (*c*) dielectric constant-change curve; (*d*) current flowing in static applied field during thermoluminescence.

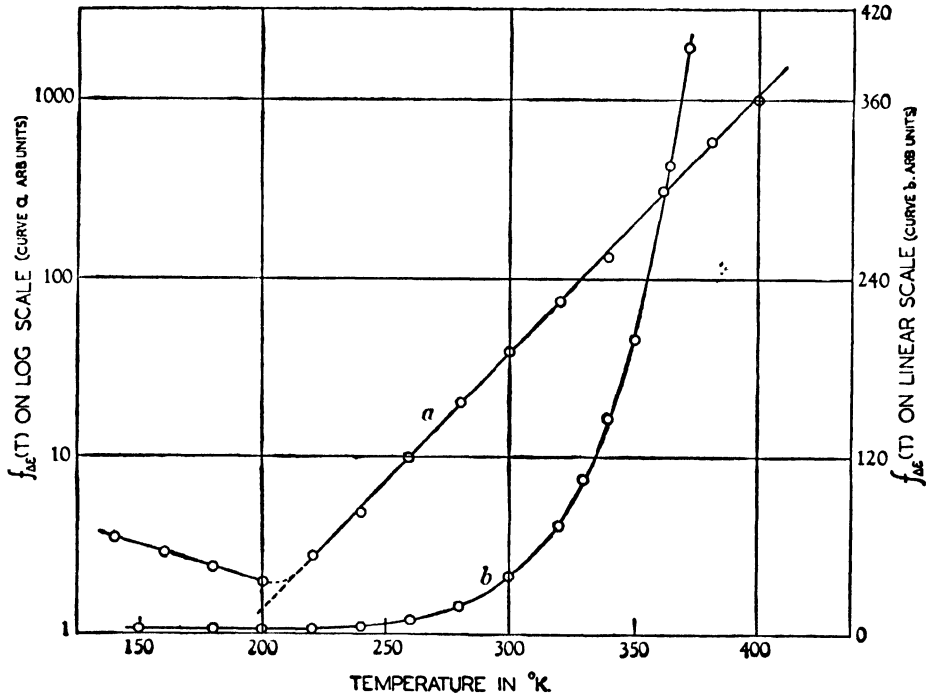


FIG. 78. Temperature function $f_{\Delta\epsilon}(T)$ for dielectric constant change with temperature for a ZnS—CdS—Cu phosphor: curve derived from Fig. 77.

change at a given temperature, which represents the number of trapped electrons multiplied by the appropriate temperature function, is divided by the area remaining under the thermoluminescence curve, which gives the number of trapped electrons. The results when plotted against temperature give the

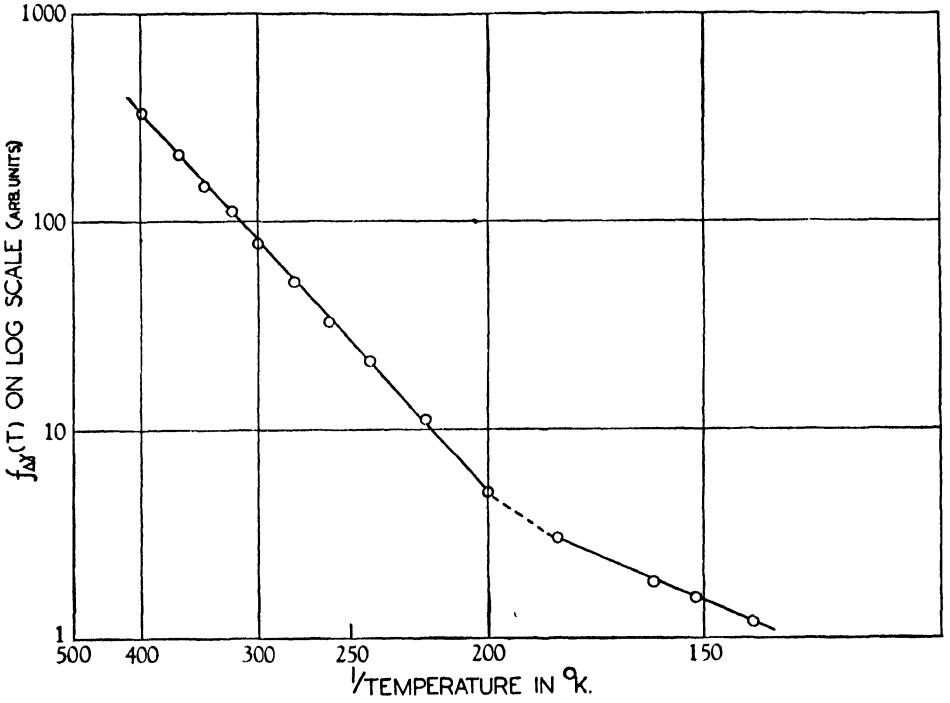


FIG. 79. Temperature function for dielectric loss change $f_{\Delta\gamma}(T)$ with temperature for ZnS—CdS—Cu phosphor: curve derived from Fig. 77.

form of the temperature functions. These curves are given in Figs. 78 and 79. The form of the temperature functions is as follows:

$$f_{\Delta\epsilon}(T) = \text{constant} \times \exp(\alpha T) \tag{5.3}$$

$$f_{\Delta\gamma}(T) = \text{constant} \times \exp\left(-\frac{\beta}{T}\right), \tag{5.4}$$

where α and β are constants. They do not appear to be markedly different for different phosphors as shown by their values for a number of phosphors in Table I below.

No adequate explanation of the temperature functions has yet been given, but there is no doubt that they are due to properties of the electron traps of a phosphor.

TABLE I

Values of the Constants α and β for the Temperature Functions of the Dielectric Changes in Phosphors

Phosphor	*Phosphorescence*	α (*degrees K*)$^{-1}$	β (*degrees 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

The variation of the dielectric changes with the applied field frequency

For a given excitation at a fixed temperature the change in the dielectric constant decreases as the applied field frequency increases, while the dielectric loss change shows an increase with field frequency. Typical results for a zinc-cadmium sulphide phosphor are given in Fig. 80. The variation of these effects with frequency is characteristic of simple polarizable systems having finite relaxation times as treated by Debye [22] and other workers. The results obtained by Garlick and Gibson have been interpreted by the use of theoretical relations due to Murphy and Morgan [23]. The latter assume that the polarizable system consists of a charged particle of small mass bound to a larger charged system of much higher effective mass. In the present case we assume that the electron trap is the large mass in the system and that the bound particle is the trapped electron. The anomalous frequency effects are not found when the phosphor is unexcited.

According to the derivations of Murphy and Morgan, the dielectric change $\Delta\epsilon$ at an angular frequency ω of the applied field is related to its values at static and high frequencies, $\Delta\epsilon_0$ and $\Delta\epsilon_\infty$ respectively, by the following equation:

$$\Delta\epsilon = \Delta\epsilon_\infty + \frac{\Delta\epsilon_0 - \Delta\epsilon_\infty}{1+\omega^2\tau^2}, \tag{5.5}$$

where τ is the relaxation time of the filled trap. This equation

may be rewritten as follows:

$$\frac{\Delta\epsilon_0 - \Delta\epsilon}{\Delta\epsilon - \Delta\epsilon_\infty} = \omega^2\tau^2 = 4\pi^2 f^2 \tau^2, \tag{5.6}$$

where f is the applied field frequency in cyc./sec. In practice, $\Delta\epsilon_0$ and $\Delta\epsilon_\infty$ are obtained by extrapolation at the ends of the

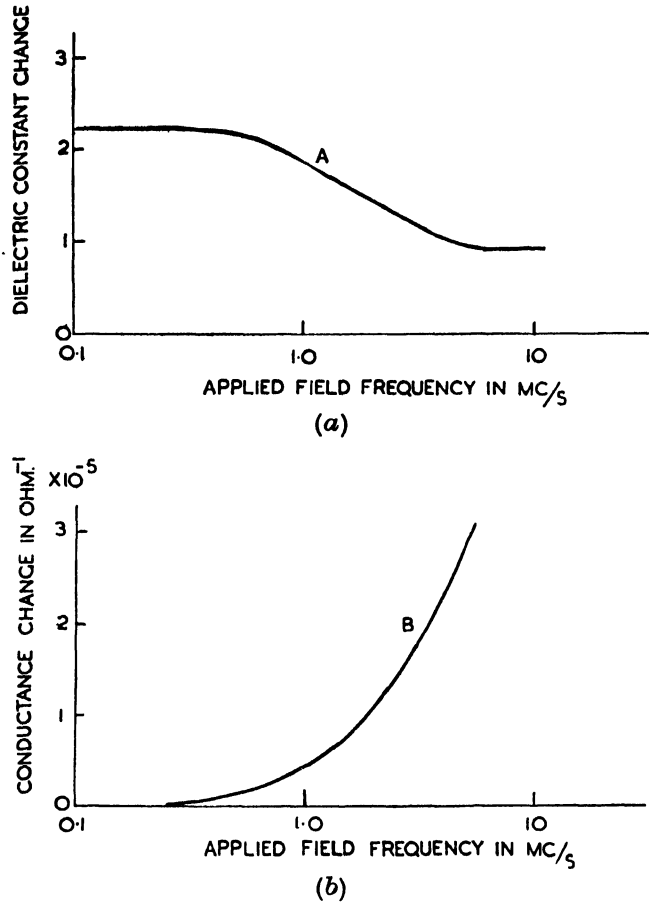


FIG. 80. Variation of dielectric changes in a ZnS—CdS—Cu phosphor with applied field frequency. *A*, dielectric constant change; *B*, dielectric loss change (measured as conductance).

frequency range (see Fig. 80). The variation of the change in dielectric constant with field frequency follows equation 5.6, as shown by Fig. 81, in which $(\Delta\epsilon_0 - \Delta\epsilon)/(\Delta\epsilon - \Delta\epsilon_\infty)$ is plotted against the square of the field frequency. The slopes of the straight lines obtained for two different temperatures give values for the relaxation time τ. These values are included in Table II below.

The variation of the dielectric loss change $\Delta\gamma$ with applied

field frequency is given by the following expression, due to Murphy and Morgan:

$$\Delta\gamma = \frac{(\Delta\epsilon_0 - \Delta\epsilon_\infty)\omega^2\tau}{3{\cdot}6\pi \times 10^{12}(1+\omega^2\tau^2)} \text{ohm}^{-1}, \tag{5.7}$$

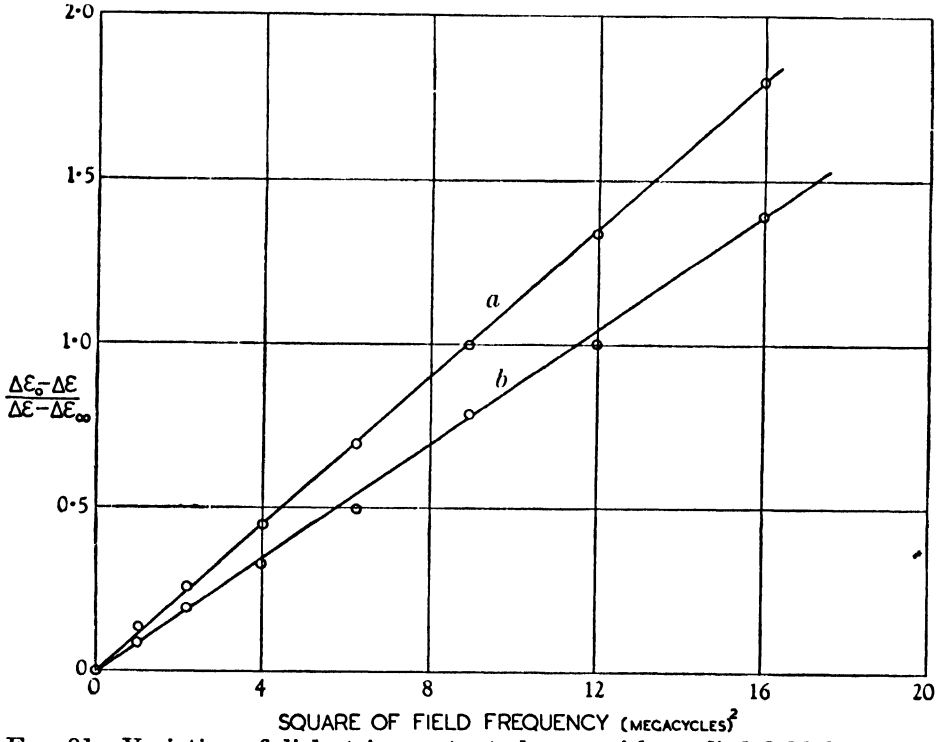


FIG. 81. Variation of dielectric constant change with applied field frequency for a ZnS—CdS—Cu phosphor at two different temperatures (constant excitation intensity). *A*, 291° K; *B*, 361° K. $\Delta\epsilon_0$, dielectric constant change at zero frequency; $\Delta\epsilon_\infty$, that at infinite field frequency; and $\Delta\epsilon$, that for intermediate frequency.

which can be rewritten thus:

$$\frac{\tau}{\Delta\gamma}\frac{\Delta\epsilon_0 - \Delta\epsilon_\infty}{3{\cdot}6\pi \times 10^{12}} = \frac{1}{\omega^2} + \tau^2 = \frac{1}{4\pi^2 f^2} + \tau^2. \tag{5.8}$$

We thus expect the inverse of the loss change to vary as the inverse square of the field frequency. Fig. 82 shows that experimental results agree with this relation. Although values of the relaxation time τ cannot be obtained from these curves because of the arbitrary nature of the units for $\Delta\epsilon_0$ and $\Delta\epsilon_\infty$, a value of τ can be obtained from the loss factor which is given by

$$\Delta\epsilon'' = \frac{4\pi\Delta\gamma}{\omega} = \frac{(\Delta\epsilon_0 - \Delta\epsilon_\infty)\omega\tau}{0{\cdot}9 \times 10^{12}(1+\omega^2\tau^2)}. \tag{5.9}$$

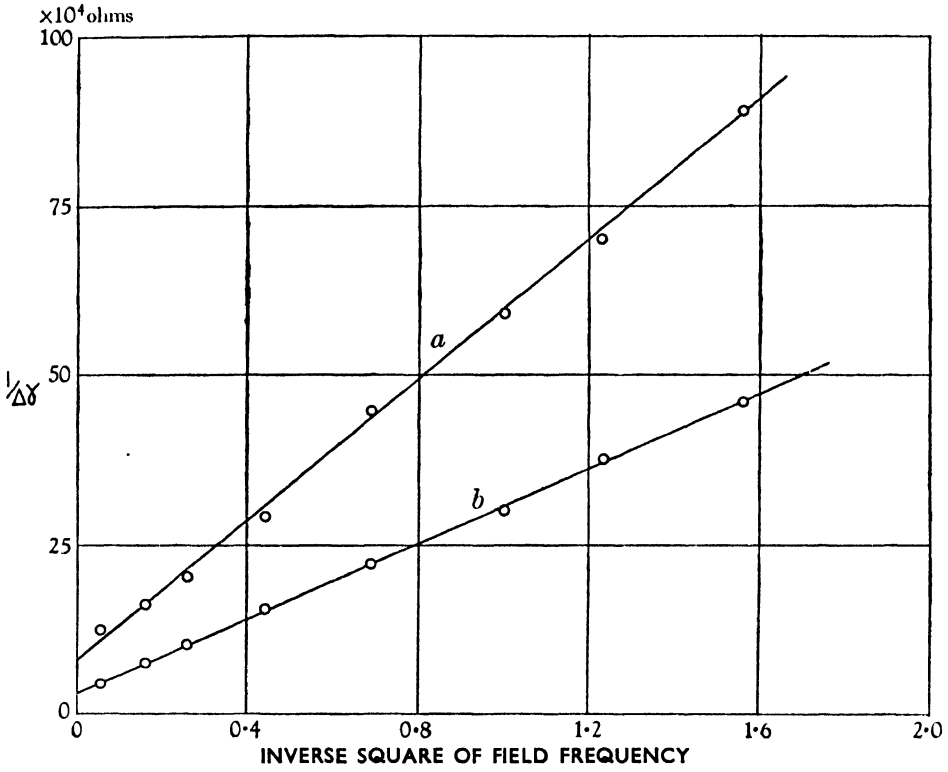


FIG. 82. Variation of dielectric loss change with applied field frequency for a ZnS—CdS—Cu phosphor at two different temperatures (constant excitation intensity). *A*, 291° K; *B*, 361° K.

This has a maximum when $\omega\tau = 1$. The following table gives values of the relaxation time τ obtained in this way and from the variation of the dielectric constant change with frequency.

TABLE II

Experimentally Derived Values of the Relaxation Time τ for Filled Electron Traps in Phosphors

Phosphor	*Temperature (degrees K)*	*τ, derived from dielectric constant change*	*τ, derived from loss factor*
ZnS(70%) CdS(30%)—Cu	90	$9{\cdot}0 \times 10^{-8}$ sec.	$8{\cdot}0 \times 10^{-8}$ sec.
	291	5·3 ,,	7·8 ,,
	361	4·7 ,,	5·3 ,,
	457	4·3 ,,	4·0 ,,
ZnS—Cu	291	13·3 ,,	16·0 ,,
ZnS—Ag	291	5·8 ,,	4·7 ,,

The significance of the relaxation time τ

Experimental results show that the relaxation time τ does not vary markedly with temperature or with the particular phosphor. According to the theory of Murphy and Morgan the relaxation time is the reciprocal of the natural frequency of the polarizable system. It is difficult, in view of the relatively large 'size' of an electron trap, to think of its possessing a single natural frequency. However, the reciprocal values of the relaxation time are of the same order of magnitude as the constant s for trapped electrons given in equation 2.1. Randall and Wilkins [24] have thought of s as a simple function of the natural frequency of the system formed by a filled electron trap. We must emphasize that it is not possible to give a precise discussion of the relaxation time τ or of s until more is known of the detailed structure of luminescence centres and the trapping states associated with them.

The variation of the dielectric changes with wave-length of excitation

The variation of the dielectric constant change in phosphors with the wave-length of excitation was investigated by Gudden and Pohl [2] and the variation for the loss change by Gisolf [18]. It is found that the dielectric changes only occur if the exciting radiation fills electron traps and that the spectral variation for the effects is similar to that for photoconductivity. Thus in manganese-activated zinc sulphide phosphors there are no dielectric changes when 4,358 A radiation is used since this causes only the manganese centres to be excited and no traps are filled. In zinc sulphides the dielectric changes show a maximum for 3,500–4,000 A radiation. At shorter wave-lengths they decrease because only a small number of traps in the surface layers of the phosphor are filled. Increase in the cadmium sulphide content of zinc-cadmium sulphide phosphors extends the long wave-length limit for the effects to longer wave-lengths.

A general discussion

There are two important conclusions which we may draw from these studies of the dielectric changes in phosphors. The

first is that agreement between theory and experiment is good when retrapping is neglected. This is shown by the validity of equation 2.22 when applied to the dielectric changes as well as to the filling of traps. The second is that electron traps have a large effective size. This is consistent with our conclusions reached in Chapter IV concerning the large dimensions of the complex centres which include the emission and trapping states. The large increase in dielectric loss which occurs when electrons are trapped may account for the large initial currents measured in photoconductivity experiments. In this case it is not necessary to assume that the 'primary' current is due to conduction electrons. In addition, its saturation at all but low intensities of excitation may be explained by the relations of equation 5.1.

As a general result, these studies show that electrons in the conduction band of a phosphor do not make significant contributions to photoconductivity and to dielectric changes at ordinary temperatures. Their significance at high temperatures has been discussed in Chapter IV.

4. The production of luminescence by strong electric fields

It was found by Gudden and Pohl [2] that the application of a strong electric field during phosphorescence enhanced the emission of zinc sulphide phosphors. This effect has since been studied by Schmidt [17], Hinderer [25], and by Destriau [26, 27]. The applied field strengths involved are of the order of 10^4–10^5 volts per centimetre. The general form of the experimental results shows, without doubt, that the action of the field is to release trapped electrons: according to Destriau, the field may also influence the emission centres since it causes extinction of phosphorescence with no initial enhancing in some phosphors. The effect of a strong electric field on a trapped electron can be treated in the same way as its effect on ionic conductors, as discussed by Mott and Gurney [5]. It may cause a lowering of the potential barrier for the electron in the trap. As yet no precise experiments to determine the way in which the field strength required depends on the trap depth have been

made and there is thus little to discuss beyond the above qualitative observations. We therefore consider here the production of luminescence in previously unexcited phosphors, due solely to the action of strong electric fields. The phenomenon is known as *electrophotoluminescence.*

The possibility of exciting luminescence by the application of an intense electric field to a phosphor was first investigated by Destriau [28]. He found that the effect was transient for static applied fields, but was sustained if alternating fields were used. It occurred in conventional phosphors such as the sulphides, silicates, and tungstates. The alternating fields used by Destriau were of mains frequency (50 c./sec.), but other frequencies have been used. The emission varies in intensity with time, having twice the frequency of the applied field: a typical result is shown in Fig. 83. The main characteristics of electrophotoluminescence may be summarized as follows:

i. As stated above, the emission varies in a periodic manner with time, having twice the frequency of the applied field.
ii. The maximum emission does not necessarily occur when the field is a maximum but may be out of phase by an amount dependent on the particular phosphor.
iii. The maximum emission intensity during a cycle varies exponentially with the peak field strength.
iv. If the applied field is suddenly removed there is very little phosphorescence, even in specimens which show long afterglow for ultra-violet light excitation.
v. The emission increases with temperature in a complex manner.

We now consider these effects in some detail.

The dependence of the effect on phosphor constitution

Most of the conventional phosphors, such as zinc sulphide, show electrophotoluminescence, but the required field strengths are rather high, being of the order of 10^5 V/cm. Destriau and Soddy [29] found that the effect was increased for phosphors which had received repeated firings. They attributed this to

the increase in the oxide content of their zinc sulphide phosphors. Deliberate additions of zinc oxide resulted in an increase of

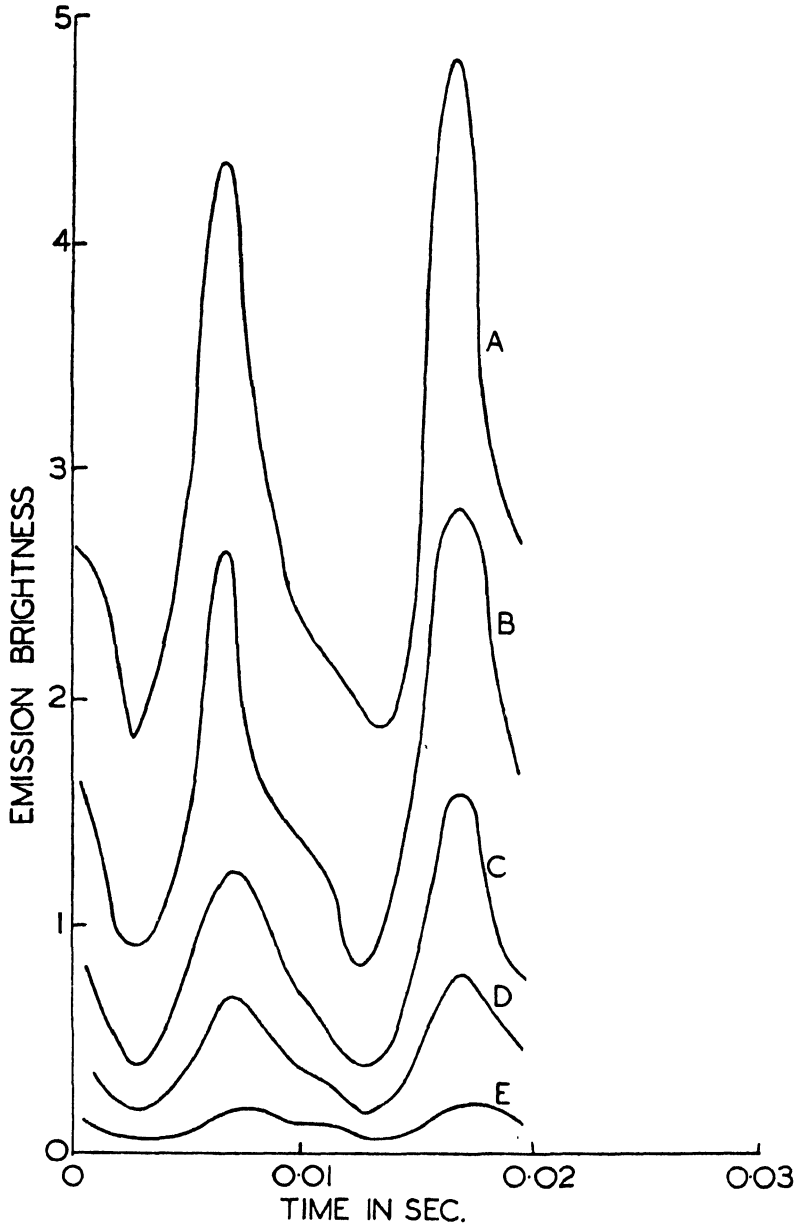


FIG. 83. Variation of electrophotoluminescence intensity with time and field strength for a ZnS—Cu phosphor. (Destriau.) *A*, $V = 40$ volts; *B*, $V = 35$ volts; *C*, $V = 30$ volts; *D*, $V = 25$ volts; *E*, $V = 20$ volts.

sensitivity of a large order. The threshold field strength was also found to be lowered when the copper impurity in zinc sulphide

phosphors was increased, but this had a deleterious effect on the emission efficiency. From their work it appears that the optimum phosphor constitution is ZnO (75 per cent.) ZnS (25 per cent.)—Cu (0·2 per cent.). Table III gives some results which show the effect of increase in zinc oxide content.

TABLE III

Effect of Phosphor Constitution on the Threshold Field Strengths for Electrophotoluminescence in ZnS—ZnO—Cu *Phosphors*

ZnO *Per cent.*	ZnS *Per cent.*	*Threshold field strength in volts/cm.*
0	100	23×10^3
10	90	20 ,,
25	75	18 ,,
50	50	6 ,,
75	25	6·2 ,,
90	10	5·6 ,,
100	0	9 ,,

Although the emission efficiency of the phosphors with high zinc oxide content is lower than that of a zinc sulphide phosphor, the electrophotoluminescence effect is much greater and the threshold field strengths required are much lower. Destriau has also studied the effect of the variation in copper content for a phosphor with optimum ZnO—ZnS ratio. As the copper content increases the phase difference between the emission maximum and the field maximum decreases. There is a corresponding increase in the electrical conductivity of the phosphor which may produce this phase change, since it will cause the internal field of the phosphor to alter.

The empirical laws of electrophotoluminescence

The maximum emission intensity B of a phosphor increases exponentially with the field strength V as follows:

$$B = aV^n \exp(-b/V), \qquad (5.10)$$

where a, n, and b are constants, n being about 2. Fig. 84 shows the agreement between experimental results for a ZnS—Cu phosphor and the curve calculated from equation 5.10. The brightness for a given field strength appears to increase with

field frequency, but this is a visual observation and may be due to the increase in light output per second. If it is a real effect,

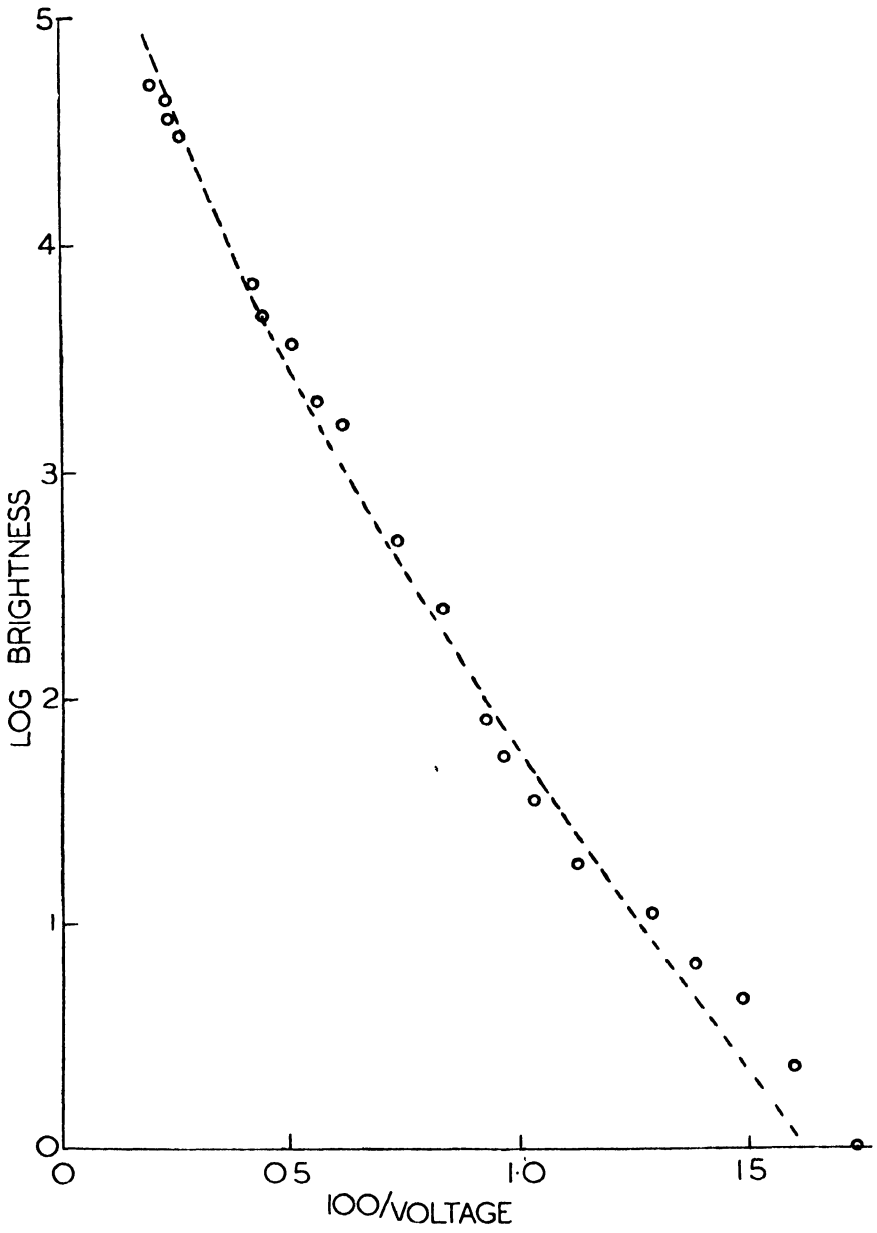


FIG. 84. Variation of electrophotoluminescence intensity with applied field strength (peak emission measurements). (Destriau.)
○ Experimental points; – – – – theoretical curve. (Eq. 5.10.)

which is not clear from Destriau's results, then it may be due to a change in the internal field of the phosphor with its frequency.

The effect of temperature [30]

As the temperature is increased the emission for a given field strength increases and the temperature variation can be expressed by a change of the constant b with temperature as follows:

$$b = \frac{\delta}{T - T_1}, \tag{5.11}$$

where δ and T_1 are constants. Thus the complete expression for the emission is given by

$$B = aV^n \exp\left(-\frac{\delta}{V(T - T_1)}\right). \tag{5.12}$$

It will be evident that a critical temperature T_1 will give rise to a change in the form of equation 5.12 if the phosphor temperature is lowered sufficiently. No experiments in the region of the critical temperature appear to have been made. Fig. 85 shows the variation of emission with temperature for a phosphor and its agreement with the theoretical curve derived from the above equation. The critical temperature assumed is 225° K.

The theoretical interpretation of electrophotoluminescence

There is no doubt that the effects recorded by Destriau are real and are not due to discharge excitation of the phosphors. They can also be produced by rotating a phosphor in a static electric field. Destriau interprets the exponential increase of emission with field strength as due to an internal field emission effect. He assumes that the field raises electrons from the ground states of impurity centres into the conduction levels. Since this process normally requires a few electron volts to accomplish it, it is doubtful whether his hypothesis is correct for the field strengths effective in producing the emission. It is more likely that there are always a few electrons in traps in unexcited phosphors which can be freed by the field and accelerated to produce excitation of luminescence centres. The absence of afterglow when the field is removed may be due to the peculiar nature of the excitation process or to the liberation of electrons, which may happen to be trapped, by the action of the field. The fall in threshold field with increase in impurity content may be due to the

decrease in the required energy for excitation caused by mutual perturbation of the emission centres.

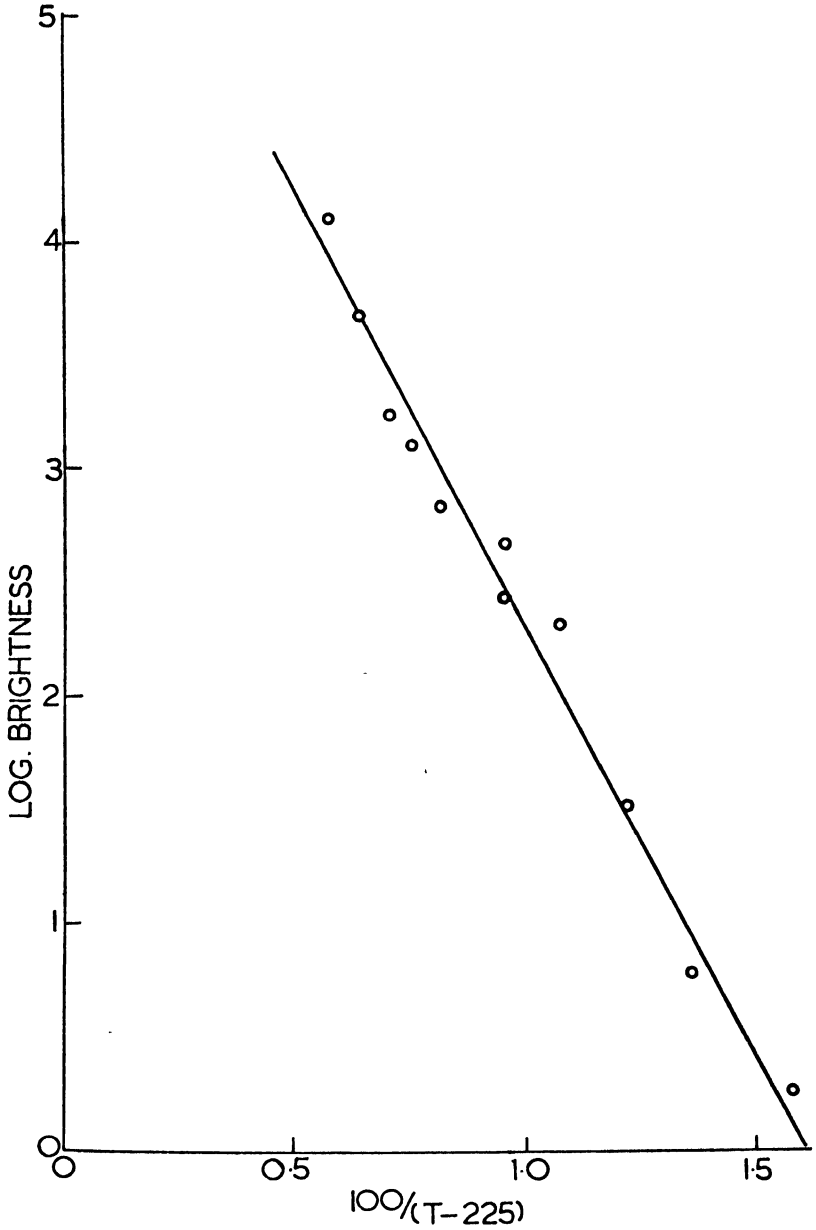


FIG. 85. Variation of electrophotoluminescence with temperature for a given applied field strength. (See eq. 5.12.) (Destriau.)
○ Experimental points; ——— theoretical curve.

It would appear from the above discussion that at present insufficient data of a precise nature exist for an adequate theoretical explanation to be given for the effects.

CHAPTER VI

PHOSPHORS AND INFRA-RED RADIATION

1. The effects of infra-red radiation

MOST luminescent solids which show long afterglow after excitation by ultra-violet light are sensitive to the action of long wave-length light or infra-red radiation. These long wave-length radiations cause the ejection of electrons from traps, and their effect is in some ways similar to that produced by heating or by strong electric fields. However, there appear to be two different effects of such irradiation; it may cause a temporary enhancing of the phosphor emission or it may suppress it. These two effects depend on the wave-length of the infra-red radiation and also on the particular phosphor specimen. In general it is found that radiation of longer wave-lengths tends to enhance phosphorescence while that of shorter wave-lengths tends to suppress or, as it is termed, *quench* the emission. The two effects were distinguished in the very early studies of Lenard, described in the general references of the first chapter. Fig. 86 gives the enhancing and quenching spectra for a bismuth-activated calcium sulphide phosphor taken from these studies. The different wave-length regions for the effects are quite distinguishable.

The recent war-time development for practical use of phosphors having a marked response to infra-red irradiation has enabled a more systematic study of the processes in these phosphors to be made. It has provided more precise data from which a more adequate theoretical treatment of the phenomena of quenching and enhancing can be established. It is with these phosphors that we are concerned in this chapter, and for the purpose of describing their properties a definition of terms is essential. In the literature concerned with infra-red sensitive phosphors the normal phosphorescence of the material is usually referred to as the *background*. The enhancing of the luminescence by infra-red radiation is referred to as *stimulation*, while the suppression of emission retains the term 'quenching'. The two effects of stimulation and quenching both lead to an

exhaustion of the energy stored in the phosphor and therefore to an *extinction* of phosphorescence.

All phosphors having a marked infra-red sensitivity, and which are also of practical interest, belong to the impurity-activated phosphor classes. For the most part they are confined

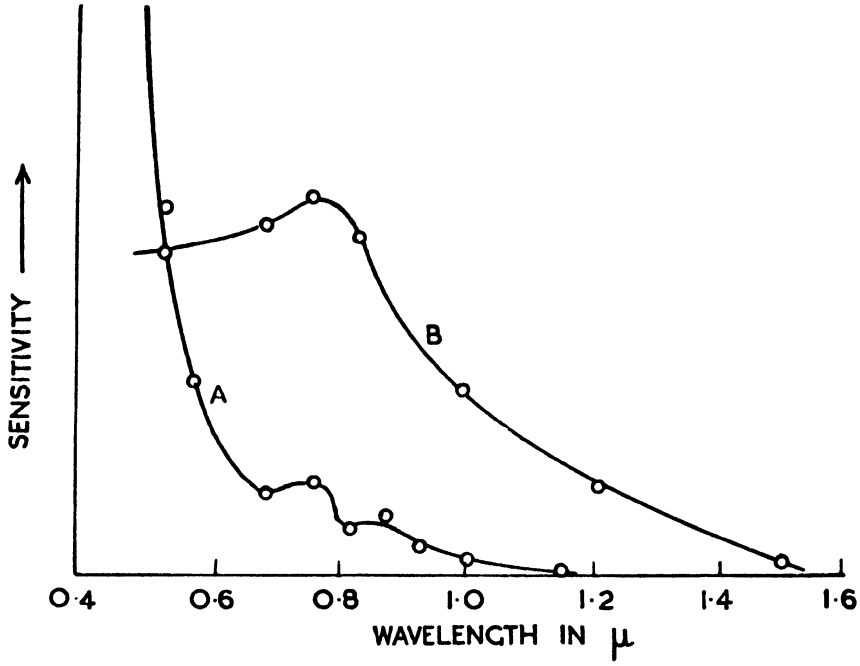


FIG. 86. Spectral sensitivity of quenching and stimulation of a CaS—Bi phosphor. *A*, quenching spectrum; *B*, stimulation spectrum.

to zinc sulphide and alkaline earth sulphide types. As has been seen already in Chapter III, these phosphors have characteristics which are very dependent on their constitution, mode of preparation, and on the excitation conditions. This same dependence is also shown by their infra-red sensitivity. In addition it is found that all phosphors possessing such sensitivity at room temperature owe it to the presence of a second or *auxiliary* impurity in addition to that producing the normal emission and phosphorescence, which is referred to here as the *dominant* activator. We shall consider first the alkaline earth sulphide phosphors having two different activators.

2. Infra-red sensitive alkaline earth sulphide phosphors

We have already seen in Chapter III that a second activating impurity added to an alkaline earth sulphide phosphor can

improve the emission efficiency of the luminescence centres formed by the dominant impurity. We have also seen that the additional activator can give rise to new trapping states for electrons in the phosphor, as revealed by selective thermoluminescence experiments. The systematic study of such doubly activated phosphors is due to Urbach and his collaborators [1]

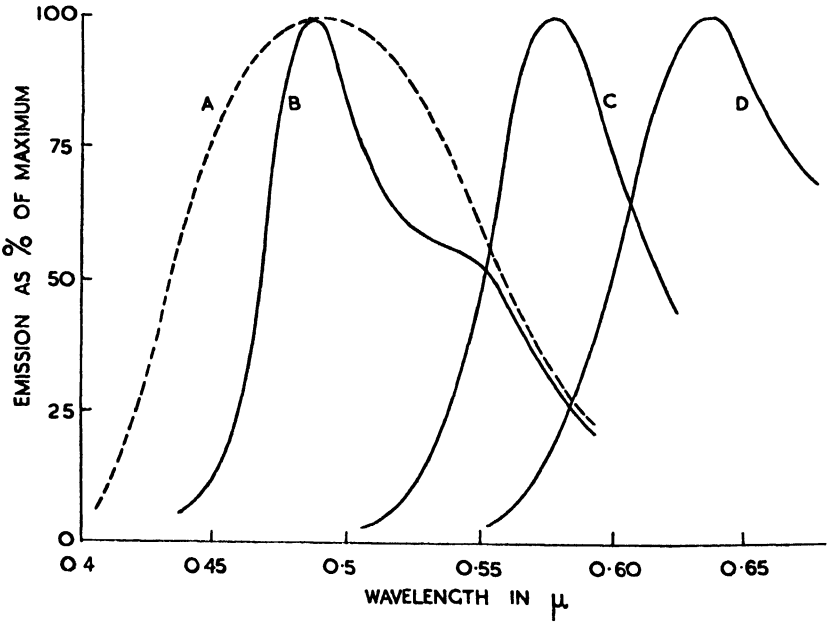


FIG. 87. Emission spectra of strontium sulphide phosphors with different activators. *A*, copper; *B*, cerium; *C*, manganese; *D*, europium. (Urbach, *et al.*).

and to Ward [2]. These studies show that the important auxiliary activator in calcium and strontium sulphides, activated by such dominant impurities as cerium, manganese, and europium, is samarium. The latter improves the *infra-red stimulability* of such materials by a large factor at ordinary operating temperatures. The addition of samarium also suppresses the normal phosphorescence or background of the phosphors, that is, in some way it inhibits the action of electron traps of moderate depths (of the order of 0·5 eV.). We shall discuss these effects in more detail later. For the present it is useful to give one or two examples from experimental results of the effect of the auxiliary activator in these phosphors. Fig. 87 shows the emission spectra of strontium sulphide phosphors activated by

copper, cerium, manganese, and europium. If samarium is added as the auxiliary activator to each phosphor, in smaller concentration than the dominant activator, then the phosphors are made sensitive to stimulation by infra-red radiation. In each case the emission spectrum due to stimulation is characteristic of the dominant activator, but the stimulation spectrum is

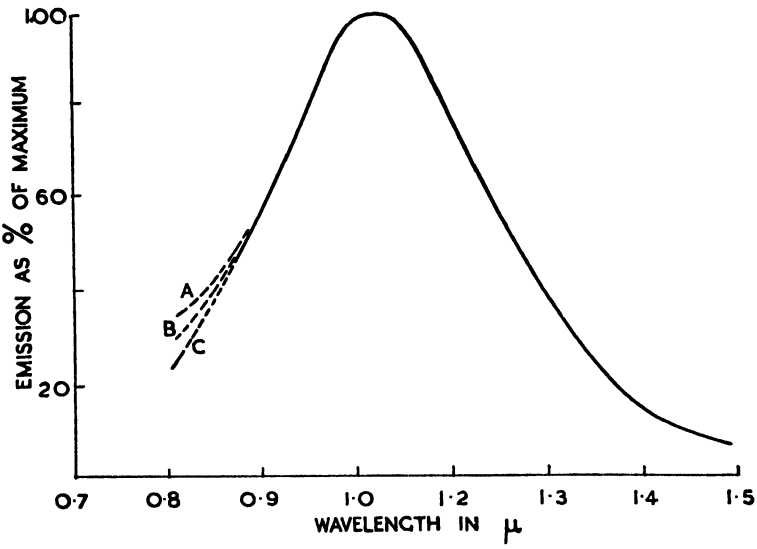


FIG. 88. Stimulation spectra of strontium sulphide phosphors with different dominant activators but the same auxiliary activator. *A*, manganese; *B*, europium; *C*, cerium. (Urbach, *et al.*).

characteristic of the auxiliary activator. This spectrum is given in Fig. 88 for the manganese-, cerium-, and europium-activated specimens of Fig. 87. It will be seen that the stimulation spectrum is the same for each phosphor although the emission spectrum is different. Fig. 89 shows the stimulation spectra for phosphors having three different auxiliary activators. These auxiliary activators, when present alone in alkaline earth sulphide phosphors, have their own characteristic luminescence spectra, but when functioning as auxiliary activators, their normal emission is almost completely quenched, at least at room temperature. At high temperatures phosphors with samarium as an auxiliary activator show an orange-red emission which is due to the samarium present. The thermoluminescence curves of Fig. 36 have already shown that the electron traps due to each

activator are of different depths and produce their individual effects at different temperatures.

The work of Urbach and his collaborators [1] has shown that there is no definite empirical rule which can be used to select pairs of activators to give optimum performance in infra-red sensitive phosphors. It is evident, however, that certain impurities, such as samarium, function best as auxiliary activators.

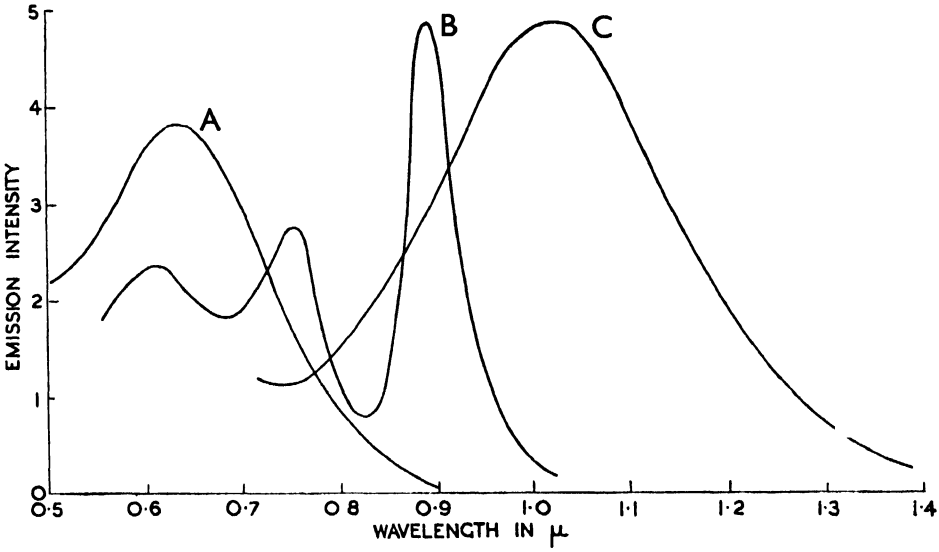


FIG. 89. Stimulation spectra due to different auxiliary activators in strontium sulphide. *A*, tin; *B*, bismuth; *C*, samarium. (Urbach, *et al.*)

There appear to be many factors which determine the optimum performance for a phosphor, amongst which the most important are the preparation conditions. Some account of the effect of fluxes in the preparation of alkaline earth phosphors has already been given in Chapter III. In the case of infra-red sensitive phosphors, it was found by Urbach and Ward and their collaborators that the amount of sulphate present in the sulphide lattice of the phosphor was of considerable importance in increasing the stimulability of the phosphor. This means that some degree of oxidation is necessary to produce good phosphor specimens. Besides the effect of partial oxidation it was found that other small changes in phosphor constitution, such as the presence of a small amount of calcium sulphide in a strontium sulphide phosphor, could improve the stimulability.

In addition to the stimulation spectra shown in the above figures we shall consider other important properties of the doubly activated alkaline earth sulphide phosphors. These include their total energy-storage capacity, the creation of new absorption bands in the phosphors by excitation, and the decay of the stimulated emission with time. With respect to the storage capacity of such phosphors, estimates have been made by measuring the light sum of the emission during stimulation. Results show that for optimum phosphor specimens 10^{17} light quanta are emitted per cubic centimetre of the phosphor. This is equivalent to a storage of one electron in a trapping state per activator atom. This estimate is not accurate and may be in error by a factor of 10.

The absorption characteristics of infra-red sensitive phosphors of the alkaline earth sulphide type

Urbach and his co-workers [3] have found that excitation of the alkaline earth sulphide phosphors with samarium as auxiliary activator gives rise to new absorption bands which disappear again when the phosphor is irradiated with light lying in these bands. One of the two bands found in these phosphors has a maximum at about $1\,\mu$ and is almost identical in form and position with the stimulation spectrum of Fig. 88. The other band which is associated with quenching of the phosphor emission occurs at about $0{\cdot}6\,\mu$, but it overlaps the excitation spectrum of the phosphor. The magnitude of the absorption in both bands increases with the samarium concentration and with the intensity of excitation. It is considered likely that the bands are due to electron transitions in the centre formed by the samarium impurity.

The decay of the stimulated emission

The emission of stimulated phosphors decays with time and the rapidity of the decay depends on the intensity of the stimulating radiation. Ellickson [4] has measured the decay of typical phosphors. His results for a cerium–samarium-activated strontium sulphide phosphor are shown in Fig. 90. From these results he suggested that the decay followed the relation

$$B = B_0(1+at)^{-2}, \qquad (6.1)$$

where B_0 is the initial brightness and B is the brightness at a time t after stimulation has begun. The constant a is proportional to the intensity of the infra-red radiation. However, as

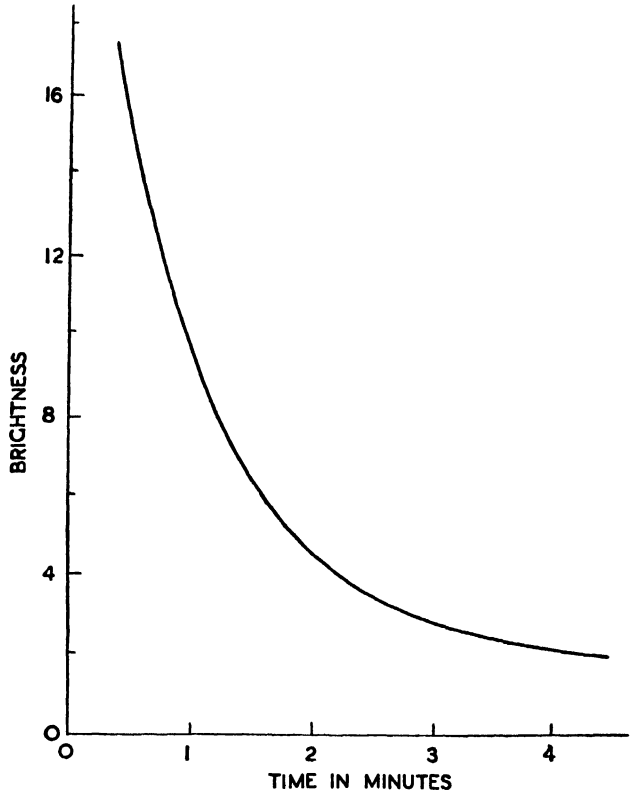


FIG. 90. Stimulated decay of a SrS—Ce—Sm phosphor due to infra-red radiation. (Ellickson.)

Ellickson has since shown, this relation is not followed at long decay times and a more correct form is as follows:

$$B = B_0(1+at)^{-n}, \tag{6.2}$$

where n is a constant less than 2. In Fig. 91 the value given by the slope of the final asymptote is 1·25, but it is different for other phosphors. Ellickson and Parker have attempted a theoretical explanation of this decay law which we shall discuss in a later section.

3. Infra-red sensitive zinc sulphide phosphors

It has been found that zinc sulphide phosphors can also be made sensitive to the stimulating action of infra-red radiation if they are made with inclusion of an auxiliary activator.

These doubly activated phosphors have been investigated by Fonda [5], Miller and Barnett [6], and others [7]. Fonda has found that the chief activators which enhance the infra-red stimulability of zinc sulphide phosphors are manganese, copper, and lead. Although Riehl [8] has concluded that lead does not

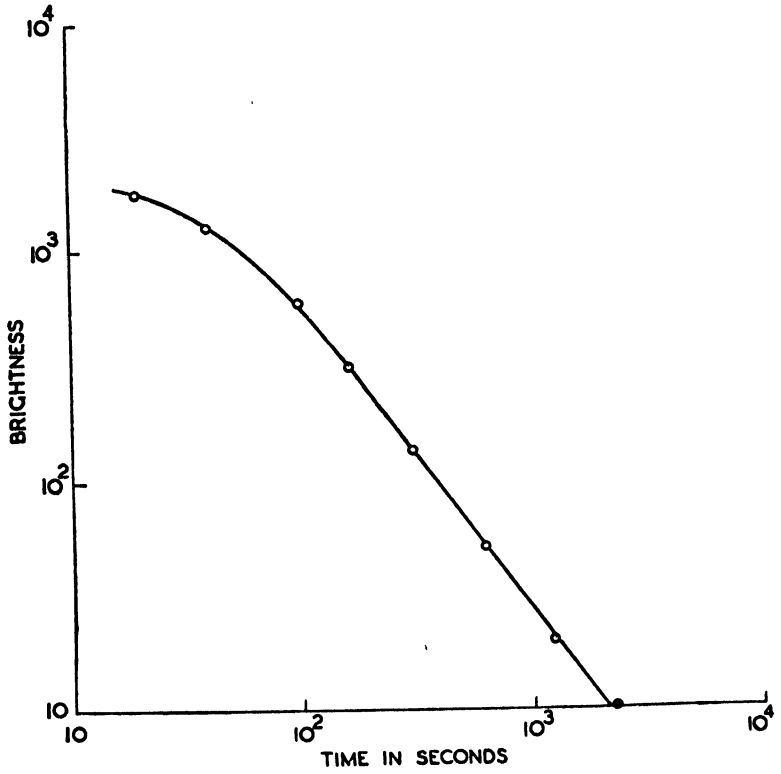


FIG. 91. Stimulated decay of a SrS—Ce—Sm phosphor over a wide range of decay time. (Plotted from Ellickson's results.)

function as an activator in zinc sulphide because it cannot diffuse into the crystal lattice, yet Fonda has measured the emission spectrum characteristic of lead inclusion in such phosphors. It is given, together with the emission spectra for manganese and copper activation, in Fig. 92. It appears from his work that these activators function as auxiliary activators if their concentration is low compared with the dominant activator. The emission characteristic of lead activation is produced by the same ultra-violet excitation spectrum as for the emission due to copper or manganese. It has two distinct bands, but the emission due to infra-red stimulation consists

only of the green band. The variation of the emission spectrum due to lead with temperature does not appear to have been studied.

The stimulation spectrum of phosphors with lead as auxiliary activator consists of two bands, a relatively weak one at 1·25–1·6 μ and a strong one at 0·7–1·0 μ. Fonda has found that

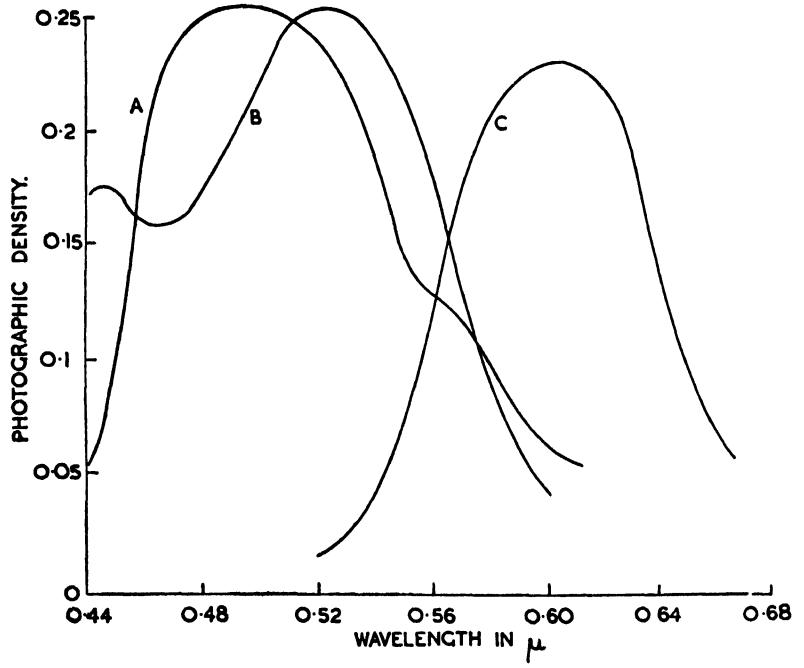


FIG. 92. Emission spectra of zinc sulphide phosphors with different activators. *A*, lead; *B*, copper; *C*, manganese. (Fonda.)

the spectrum is very much the same for manganese activation and suggests that it is a characteristic of the matrix lattice; the introduction of the secondary activator renders the absorption effective in stimulation. Fig. 93 gives the stimulated emission spectra of lead-activated zinc sulphide phosphors with copper and manganese as auxiliary activators respectively. It is important to notice that the characteristic emission of copper is suppressed and only its storage effects remain operative. However, when manganese is present as an auxiliary activator the emission spectrum contains its band as well as that of lead.

At low temperatures (77° K) the stimulation characteristics

of zinc sulphide phosphors with and without lead as auxiliary activator appear to be similar. The stimulation spectrum of those containing lead does not differ much from that at room temperature and there is no evidence of a shift of the spectrum

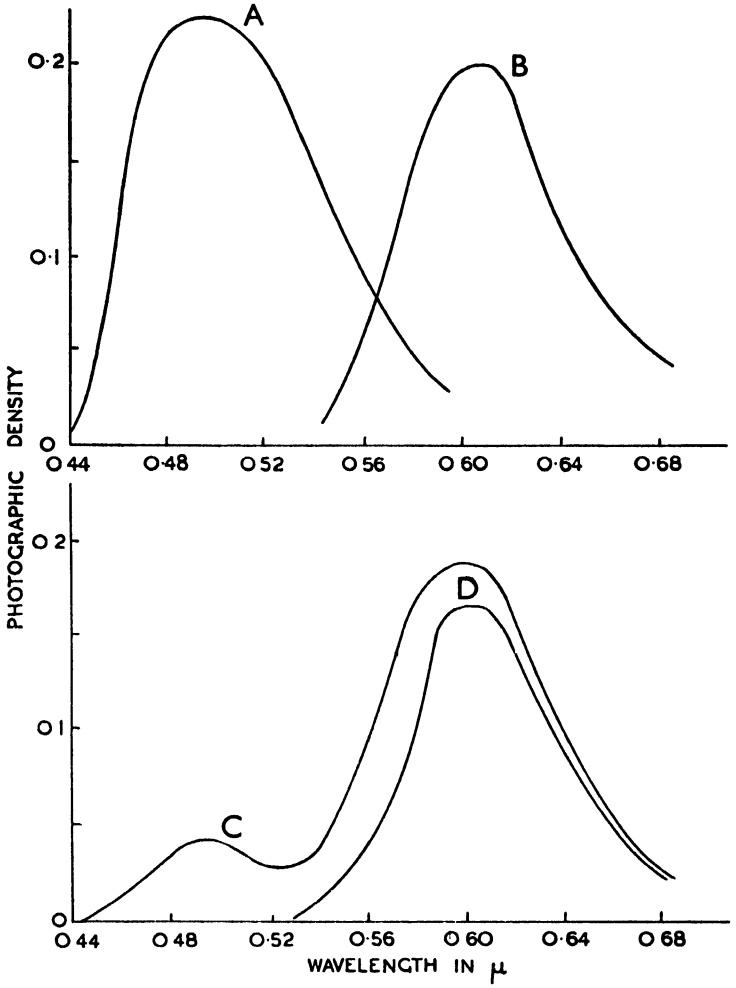


FIG. 93. Stimulated emission spectra of ZnS phosphors with two activators. *A*, ZnS—Pb—Cu; *B*, ZnS—Mn—Cu; *C*, ZnS—Pb—Mn; *D*, ZnS—Mn. (Fonda.)

to longer wave-lengths. Experiments made recently in the author's laboratory show that the shallow traps in phosphors are used for storage at low temperatures, but do not seem to be associated in any direct way with the characteristics of the stimulation spectra.

The decay of the stimulated emission of zinc sulphide phosphors

In contrast to the alkaline earth sulphide phosphors, Fonda has found that the stimulated emission of zinc sulphide phosphors decays exponentially with time. Some of his decay curves are shown in Fig. 94. The normal phosphorescence of

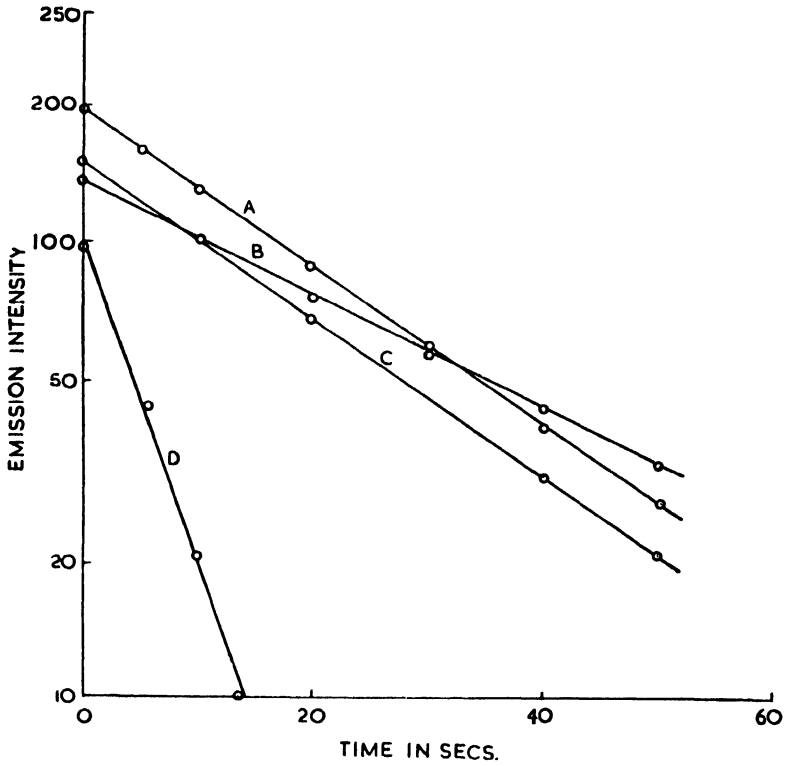


FIG. 94. Stimulated decay of zinc sulphide phosphors. *A*, ZnS—Pb (4 per cent.)—Mn (0·12 per cent.); *B*, ZnS—Pb (4 per cent.); Cu (0·001 per cent.); *C*, ZnS—Pb (4 per cent.)—Cu (0·0001 per cent.); *D*, ZnS—Mn (0·12 per cent.)—Cu (0·001 per cent.) (Fonda.)

these phosphors retains its usual hyperbolic form. However, it is found that the exponential form of the curves of Fig. 94 is not general for infra-red sensitive zinc sulphide phosphors [3].

Absorption bands due to excitation in zinc sulphide phosphors

When zinc sulphide phosphors are excited new absorption bands occur in the visible and infra-red regions of the spectrum. Although these bands are relatively weak they have been detected in some specimens by Hoch [9], and some of his results are given in Fig. 95. The bands are different for phosphors with

different activators and in general appear to have no definite relation to the stimulation and quenching spectra for zinc sulphide phosphors. The absorption due to excitation has only been measured at room temperature.

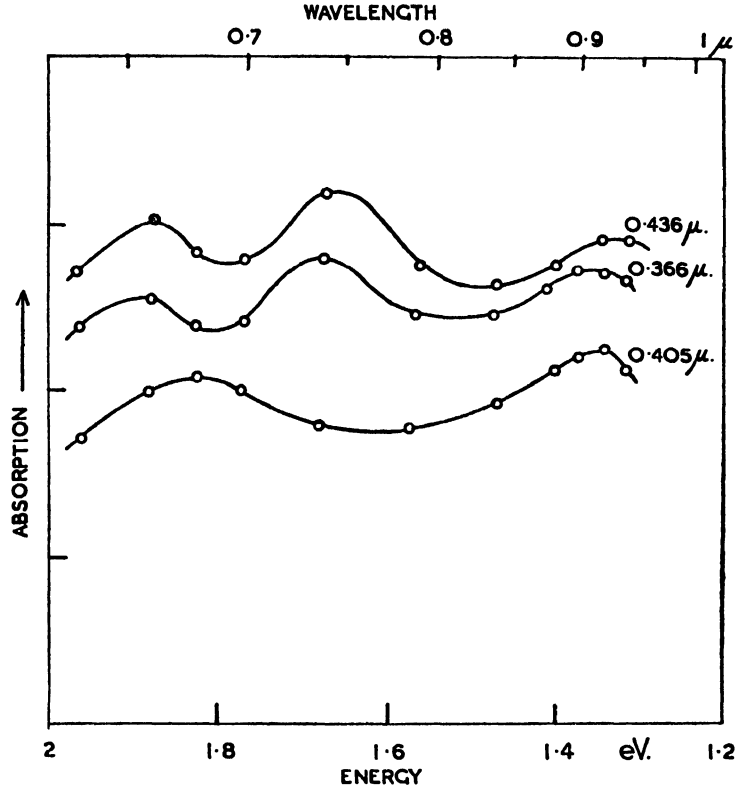


FIG. 95. Absorption spectra of a silver-activated zinc sulphide phosphor in the excited state. (Hoch.)

4. Theoretical studies of infra-red stimulation and quenching

Any adequate theory of infra-red stimulation and quenching of phosphors must be able to explain at least the following facts:

i. The sensitizing action of the secondary activator.
ii. The difference between the stimulation and quenching processes.
iii. The various forms of the decay of stimulated emission with time.
iv. The variation of the infra-red effects with temperature.

In the following sections we shall consider the application of the simple energy-band model to the interpretation of the infra-red phenomena and its limitations. We shall also show that the modified theoretical concepts discussed in Chapters IV and V may provide a more adequate explanation of the effects described above.

Infra-red absorption processes in phosphors

There is no doubt that the absorption of stimulating or quenching radiation by a phosphor leads to the ejection of trapped electrons. We would therefore expect that if the infra-red radiations are absorbed directly by these electrons, the filling of electron traps by excitation should give rise to new absorption bands in appropriate regions of the spectrum. The creation of absorption bands by the trapping of electrons gives rise to the well-known coloration of the alkali halides by X-rays or electron bombardment. In this case the absorption bands are in the visible region. Rothschild [10] has described the visible darkening of alkaline earth sulphide phosphors when excited, the darkening disappearing as phosphorescence proceeds. However, in most phosphors the electron traps are relatively shallow compared with those in alkali halides and we should therefore expect to find the absorption bands due to excitation in the infra-red region of the spectrum. The experimental facts do not support this simple idea of absorption due to trapped electrons. We have seen above that the excitation of alkaline earth sulphide phosphors containing samarium as an auxiliary activator creates an absorption band in the near infra-red, but also another in the visible region which overlaps the excitation spectrum and is associated with quenching. Fig. 95 for a zinc sulphide phosphor, having very few deep electron traps, shows that absorption bands occur in the visible region as well as in the infra-red region of the spectrum. Fonda's measurements show that the stimulation spectrum of zinc sulphide phosphors at low temperatures is not much affected by phosphor constitution. Hence we must abandon the simple hypothesis that absorption of infra-red or long wave-length visible radiation

affects the trapped electrons directly. If such a process existed, then at very low temperatures the stability of electrons in the very shallow traps would cause the appearance of new absorption bands at much longer wave-lengths than those which occur at room temperature. There is at present no evidence of such bands [4].

The idea that the absorption process for infra-red radiation is related to some system in the phosphor, which does not change with the electron-trap distribution, is thus more acceptable. Lenard in his early studies assumed that absorption of infra-red radiation took place in special regions, the absorbed energy being subsequently transported to the phosphorescence storage centres which we have called electron traps. If we adopt the hypothesis, developed in previous chapters, that the emission and trapping states form part of a complex luminescence centre, then this centre may also have electronic states in which the infra-red absorption takes place. If these states are associated with lattice ion constituents of the complex centre, then the absorption spectra will be characteristic of the phosphor lattice and will be relatively independent of the particular activating impurity. In some cases the action of the auxiliary activator is more specific and we shall discuss this in the next section.

The function of the auxiliary activator

In the alkaline earth sulphides the auxiliary activator does determine to a large extent the stimulation spectrum, as shown by Fig. 89. It also removes or reduces the normal background or phosphorescence of the phosphor. This means that it inhibits the action of relatively shallow traps and also provides deeper traps for the stimulation process. The suppressive action on the electron trapping states already present, which are usually produced by inclusion of the dominant activator, must involve a perturbation of the dominant activator centres by the auxiliary activator centres. Such interaction between different types of centres is not unexpected since it occurs in zinc sulphide and other phosphors not markedly sensitive to infra-red radiation. As early as 1930 it was found by Cohn and Harkins [11] that the thermoluminescence of manganese-activated, vitreous zinc

borate could be greatly enhanced by the addition of small amounts of cerium as a secondary activator.

In zinc sulphide phosphors the stimulation spectrum does not appear to depend markedly on the auxiliary activator, but there is no doubt that at room temperatures the latter causes an increase in the stimulation efficiency. It also affects the relative magnitudes of the bands of the stimulation spectrum of these phosphors. At low temperatures the stimulation efficiency is relatively independent of the presence of the auxiliary activator. From such characteristics it must be concluded that the states responsible for absorption of infra-red radiation in zinc sulphide are due to the matrix lattice and that the auxiliary activator renders them operative in the stimulation process at ordinary temperatures. It is likely that in some way the auxiliary activator prevents the non-radiative loss of the absorbed energy; this would account for its small effect at low temperatures when the non-radiative processes are less likely. We require much more precise experimental evidence of the infra-red stimulation and quenching processes in zinc and alkaline earth sulphide phosphors in order to define more clearly the action of the auxiliary activator in these phosphors.

Stimulation and quenching processes in phosphors

One marked distinction between quenching and stimulation processes in phosphors is the difference in the wave-length of the radiation producing the two effects. Möglich and Rompe [12] have attempted to explain this by the use of the energy-band model for phosphors. They assume that in the quenching process electrons are ejected from traps by the absorbed radiation into much higher levels of the conduction band than those which are reached by electrons ejected by stimulating radiation. In these higher levels electrons are more likely to make non-radiative transitions to their ground states than when in the lowest levels of the conduction band. Their hypothesis is not attractive since it is usually assumed that electrons in high levels of the band will first reach lower levels before returning to ground states. In this case they would be indistinguishable

from electrons released by stimulating radiation after their initial loss of energy. A more satisfactory use of the band theory has recently been put forward by Brauer [13]. He attempts to explain the action of auxiliary activators, particularly samarium in the alkaline earth sulphide phosphors, and the difference between quenching and stimulation processes. He assumes that, in quenching, the irradiation not only releases trapped electrons but also raises electrons from the filled band of the crystal lattice into the ground states of the dominant and auxiliary activator centres, thus filling the centres by a non-radiative process. In stimulation the radiation again releases trapped electrons, but cannot fill the ground states of the dominant activator centres because the quantum energy is not sufficient. This theory is very similar to that proposed by Schön and by Klasens to explain the thermal quenching of fluorescence in such phosphors and the action of nickel and other 'killer' impurities (see Chapter IV). This model is inadequate to explain the suppressive action of the auxiliary activator on the traps due to the dominant activator, and it is still necessary to assume some mutual perturbation of the centres. Such a model would be difficult to apply to non-crystalline phosphors, such as the borates studied by Cohn and Harkins, where the absence of a regular structure vitiates the basic assumptions of the energy-band model.

Some studies by Becker [14] of the quenching effects in zinc sulphide phosphors show that the degree of quenching for a given quenching radiation decreases with the wave-length of the excitation. He has measured the quenching by observing the drop in emission intensity during excitation. This decrease may be due to the decrease in the effective excitation intensity with wave-length since the absorption coefficient also decreases with wave-length. Becker found that variation of the exciting intensity caused a change in the efficiency of quenching, the latter decreasing as the intensity of excitation increased. Thus Becker's results, which were of a preliminary nature, may be explained by the change in absorption coefficient. They do not therefore add anything to our knowledge of the quenching process.

An alternative hypothesis based on the concept of the large complex emission centres in sulphide phosphors might provide a more satisfactory explanation of the difference between quenching and stimulation. Stimulation may consist of the absorption of radiation and the excitation of electrons into the upper levels of the centre. From these levels the electrons would make radiative transitions to their ground states. Quenching radiation, which is of higher quantum energy, may eject electrons into the conduction levels when they would be prone to capture in non-radiative centres. Overlap of quenching and stimulation spectra would be explained by the probability of thermal activation of the electrons excited from higher states of the emission centres into the conduction band and their behaviour then as electrons ejected by quenching radiation. Such a process would be temperature-dependent and would be revealed by a change in the relative configurations of the quenching and stimulation spectra in their overlapping region. No experiments to test this hypothesis appear to have been made.

The decay of stimulated emission with time

In the studies of phosphorescence described in previous chapters the form of the decay of emission with time has been used to help in determining the nature of the phosphorescence process. It might be thought that, in the same way, the measurement of the decay of stimulated emission with time could be used to indicate the mechanism of the decay. The hyperbolic form of the decay of the stimulated emission of alkaline earth sulphide phosphors led Ellickson and Parker [15] to assume that the process was bimolecular in nature, that is, the electrons are ejected from traps by the radiation and then recombine with empty emission centres. For the simplest bimolecular process and for a very thin phosphor layer they assume that the decay relation of equation 6.1 would be followed. The more correct empirical form given in equation 6.2 they ascribe to the thickness of the phosphor layers used in their experiments. According to their hypothesis both the stimulating

and emitted light will be absorbed in passing through a finite thickness of phosphor. If the ratio of the absorption coefficients for the emitted and stimulating light is p, then the following decay law is derived:

$$B = B_0 \frac{p+1}{(at)^{p+1}} \int_0^{at} \frac{y^p}{1+y^2} dy, \tag{6.3}$$

where y is a variable. By assuming a value for p the authors obtain good agreement with experiment. However, no attempts have been made to obtain values of p by independent measurements of the respective absorption coefficients. It would seem that a crucial test of the validity of the theory would be given by measurements of the decay of stimulated emission for different thicknesses of phosphor layer, particularly for very thin layers. Ellickson and Parker [16] have observed that the stimulation spectrum does not change noticeably as the decay proceeds. This would not be expected if the emission was due to ejection of electrons from traps of different depths by a direct absorption process in the traps. Their experimental measurements are shown in Fig. 96.

As an alternative hypothesis, the hyperbolic decay characteristics of these phosphors could be explained by assuming a number of monomolecular processes as in the treatment of thermoluminescence and phosphorescence described in Chapter II. At present the experimental data are insufficient to distinguish the correct hypothesis. Valuable data might be obtained by measuring the decay of the stimulated emission at different temperatures from room temperature over a wide range. The exponential decay of the stimulated emission of zinc sulphide phosphors shown in Fig. 94 suggests a simple monomolecular process for these phosphors. However, Fonda's results lack evidence of the effect of infra-red radiation intensity on the rate of decay which would help to test the theory. If a simple process occurred, then the decay rate should be proportional to the radiation intensity. Other experiments, which show that the exponential form of the decay is not general, indicate that the decay processes are not simple [3]. Experiments made in the

author's laboratory show that the decay due to stimulation in the long wave-length band for lead-activated zinc sulphide phosphors is often more rapid than that due to stimulation at shorter wave-lengths. As in the case of the alkaline earth sul-

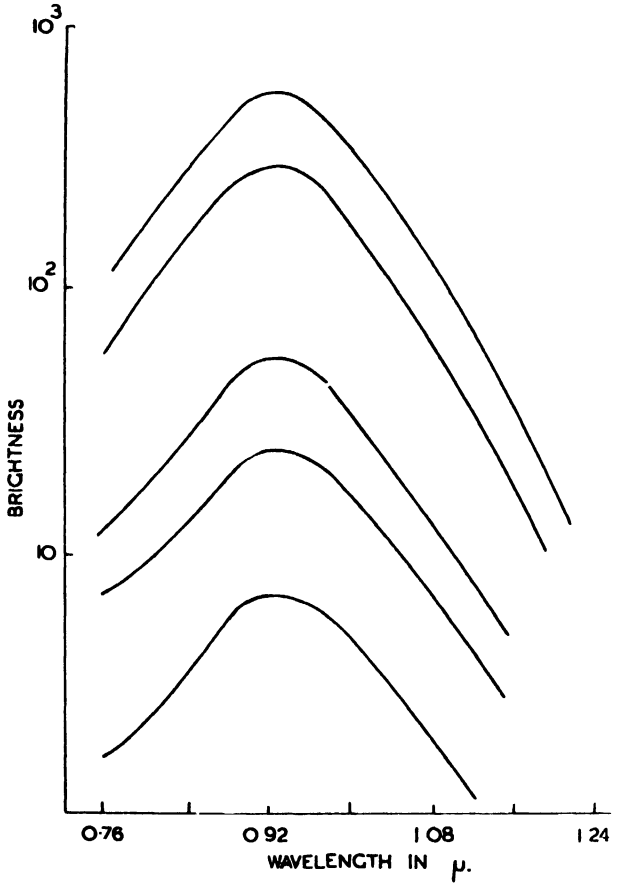


FIG. 96. Stimulation spectra of SrSe phosphor at various stages of stimulated decay. (Ellickson and Parker.)

phides, the evidence so far obtained for zinc sulphide phosphors is not precise enough to determine the decay process.

5. A general discussion of the effects of infra-red radiation in phosphors

We have already discussed the Franck–Condon principle in Chapter I with respect to optical and thermal transitions of electrons in luminescence centres. Mott and Gurney [17] and Frenkel [18] have applied the same principle to explain the difference between the thermal and optical activation energies of

trapped electrons in semiconductors and insulators. According to the treatment given by Mott and Gurney for semiconductor impurity levels, the ratio of the optical and thermal trap-depths will be given approximately by the ratio of the dielectric constants for static and optical frequencies respectively. If the principle is applicable to phosphors, then there should be marked similarity between the trap distributions as given by thermoluminescence experiments and the energy spectrum for stimulation and quenching. As we have seen, there is no direct relation between the two and it may be that the same holds for the cases considered by Mott and Gurney, namely, semiconductors and *F* centres in the alkali halides. According to Bünger and Flechsig [19], the electrons in the metastable states of the thallium centres of thallium-activated potassium chloride have a thermal activation energy of 0·67 eV. They also found that radiation of wave-lengths up to that corresponding to 0·67 eV. could eject the trapped electrons. Thus there is very little difference between the thermal and optical activation energies in this case. However, the dielectric constants of thallous halides are markedly different from those of the alkali halides.

In order to obtain a more precise picture of the irradiation processes in infra-red sensitive phosphors the following experiments need to be carried out:

i. Measurements of the stimulation and quenching spectra of phosphors at different temperatures over a wide temperature range.

ii. Measurements of stimulated emission decay for a wide range of temperatures and irradiation intensities and for various wave-lengths of monochromatic radiation.

iii. Measurements of the absorption spectra of phosphors when excited at different temperatures and for different intensities of radiation.

iv. Measurements of the electrical changes during quenching and stimulation for variation of the phosphor conditions as in the above experiments.

CHAPTER VII

CATHODOLUMINESCENCE

LUMINESCENT solids of the inorganic, impurity-activated type have found extensive application as screen materials in the cathode-ray tubes used in television, radar, and other electronic apparatus. The materials used for these purposes are usually zinc sulphide and zinc silicate phosphors, and extensive investigation of their properties as cathode-ray tube screens has been made. However, the experimental studies have provided very little information about the fundamental processes of cathodoluminescence. This is especially true with respect to the process of electron penetration into phosphors and the mechanism by which the primary electron energy reaches the luminescence centres of the phosphors. One of the chief hindrances to an understanding of these processes is the fact that the phosphors of commercial interest exist only as microcrystalline powders and therefore the screens made from them have very complex surface conditions for the incident electrons. This so complicates the experimental results, particularly the characteristics of the secondary electron emission from the phosphor screen, that theoretical interpretation is almost impossible. Because of these difficulties we shall separate in the following sections the experimental observations from the discussion of theoretical studies of cathodoluminescence. We shall find, however, that some useful discussion can be derived from observations on other insulating solids having more suitable physical form.

1. Experimental studies of cathodoluminescence

The practical use of phosphors as screens in cathode-ray tubes has necessitated some specification of the desirable properties of the screen material. We may enumerate these as follows:

i. The screen material must have a high luminescence efficiency for excitation by electrons under the particular operating conditions.

ii. The screen must possess the required degree of afterglow and the decay of the afterglow must satisfy the particular needs of the application. These properties are of great importance in radar applications [1].
iii. The screen must have good secondary emission for the given operating conditions, that is, it must not charge up when bombarded with electrons.
iv. The screen phosphor must be stable under electron and ion bombardment, that is, its luminescence efficiency and its afterglow must not change with prolonged usage.

These are the chief requirements for cathode-ray tube screens and they have determined to a large extent the research made on phosphors for screen production. We shall now consider the characteristics of such screen materials obtained from these studies. The experimental data fall into the following main categories:

i. Measurements of the variation of luminescence intensity with the energy and density of the incident electrons. These have been made for static and for pulsed excitation of the phosphor.
ii. Phosphorescence measurements for various excitation conditions.
iii. Measurement of the secondary electron emission characteristics of screen materials over wide ranges of primary electron energy and density.
iv. Observations of the stability of cathode-ray tube screens under electron bombardment and their resistance to ion bombardment.

These measurements are considered in the sections below.

Luminescence due to static cathode-ray excitation

The experimental techniques for the measurements of this and later sections will be found in the appropriate references. The simplest type of experiment is that made to find the relations between the luminescence intensity and the energy and density of the primary electron beam in the cathode-ray tube. We shall use the cathode to screen voltage as a measure of

electron energy in discussions. Experiments of this kind were carried out as long ago as 1903 by Lenard [2]. For constant excitation and in the absence of deterioration of the phosphor, the luminescence remains constant. Measurements of the variation of this emission with the cathode-ray tube voltage and

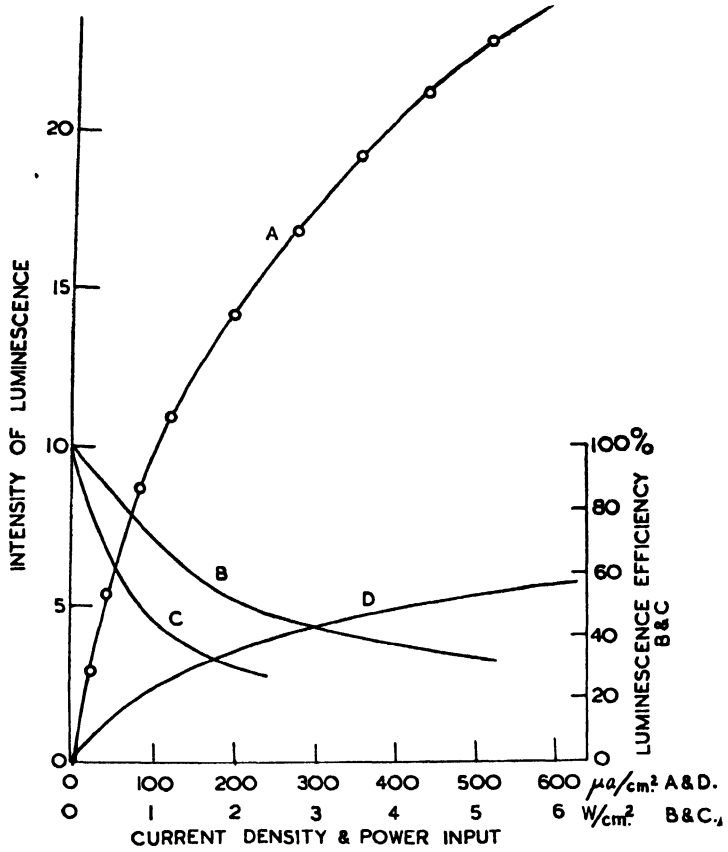


FIG. 97. Current saturation effect for cathodoluminescence of a Zn_2SiO_4—Mn phosphor. (Strange and Henderson.) *A*, 10 kV.: ○ experimental points: continuous line calculated from *D*. *B*, 4 kV. *C*, 10 kV. *D*, 4 kV.

current have been made by various workers [3, 4, 5, 6, 7]. From their results certain empirical relations have been obtained as follows:

i. The luminescence intensity L per unit area of the phosphor screen is proportional to the cathode-ray current density i for sufficiently small values of current. As the current density increases a saturation effect occurs. The value of the current density at which this occurs appears to be specific to the

particular phosphor. For example, for manganese-activated zinc silicate phosphors it is about 10 μamp./cm.^{2}, but for silver-activated zinc sulphide phosphors it is about 200 μamp./cm.^{2} We may conveniently express the degree of saturation at a given current as the ratio of the light output per unit current density

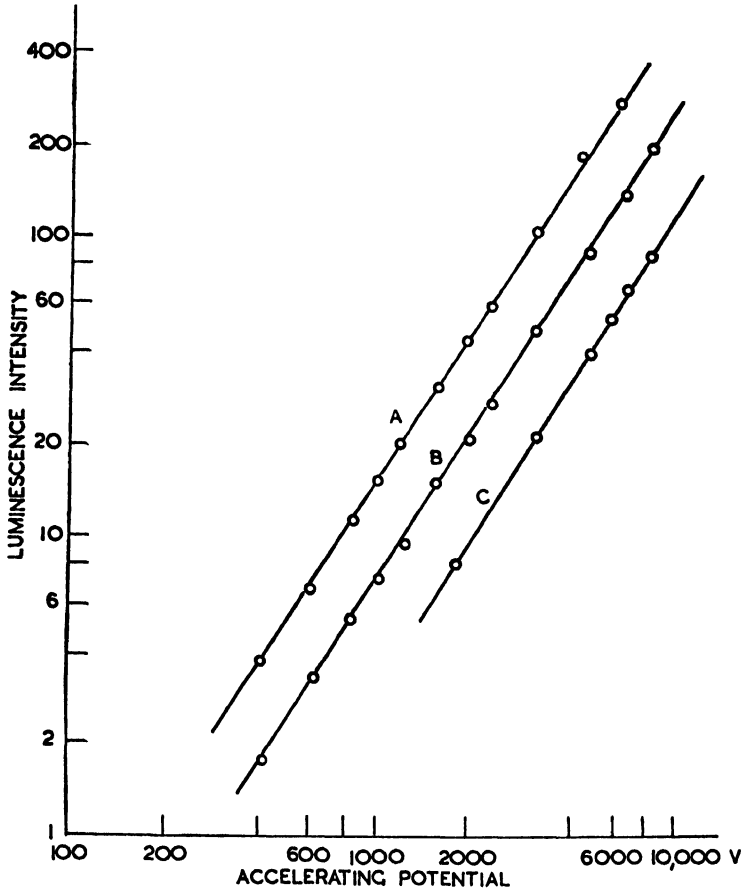


FIG. 98. Variation of cathodoluminescence with electron accelerating potential for a Zn_2SiO_4—Mn phosphor. (Strange and Henderson.) *A*, current density 5 μa/cm.^{2} *B*, current density 100 μa/cm.^{2} *C*, current density 550 μa/cm.^{2}

at that current density to the light output per unit current density at values below that at which the saturation begins to appear. It is found that the saturation effect is almost independent of the electron energy; it tends to decrease slightly with increasing electron energy.

ii. For a given current density the luminescence emission L increases as a power function of the cathode-ray tube voltage

V if a certain *dead voltage* V_0 is taken into account. The relation may be stated as follows:

$$L = kf(i)(V-V_0)^q, \tag{7.1}$$

where k is a constant for a given screen material and $f(i)$ represents the variation of the emission with current density as

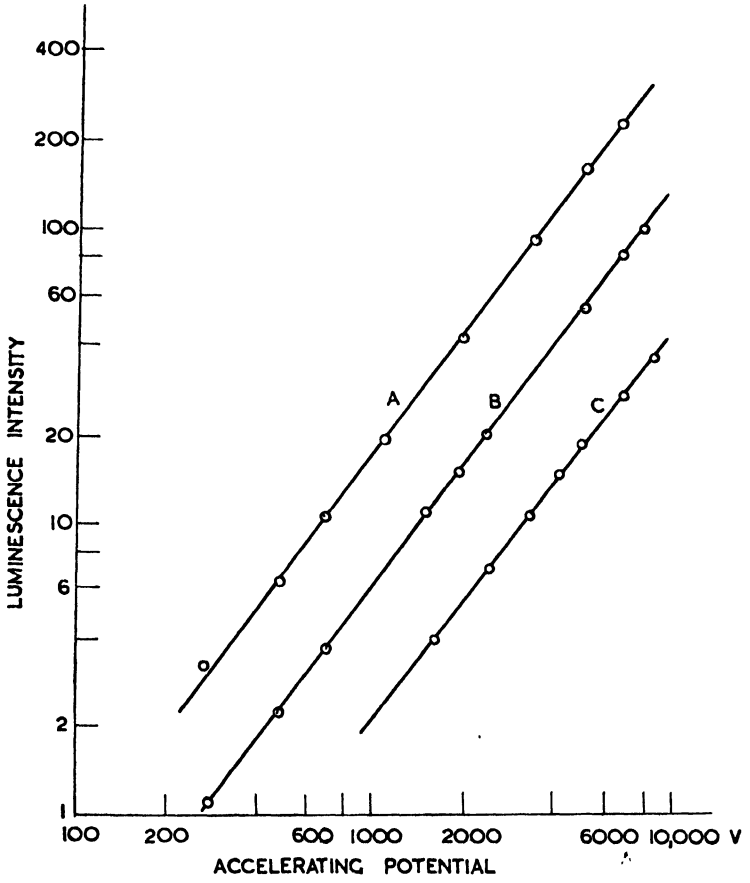


FIG. 99. Variation of cathodoluminescence with electron accelerating potential for a ZnS—Ag phosphor. (Strange and Henderson.) *A*, current density 10 μa/cm.^{2} Light from front of screen. *B*, current density 10 μa/cm.^{2} Light from back of screen. *C*, current density 550 μa/cm.^{2} Light from front of screen.

discussed above. This empirical relation was first put forward by Lenard [2] in a simpler form: he assumed q to be unity and L to be proportional to i. He attributed the dead voltage V_0 to surface contamination of the phosphor [8]. Later experiments due to Strange and Henderson [6], made with very carefully prepared screens, appear to support this assumption since they showed little or no dead voltage. In the results of later studies

it has been shown that the value of q, although specific for a given phosphor, may have values lying between one and three.

As an example of the current saturation effect we take results due to Strange and Henderson for a manganese-activated zinc silicate phosphor. The results are presented in Fig. 97. Com-

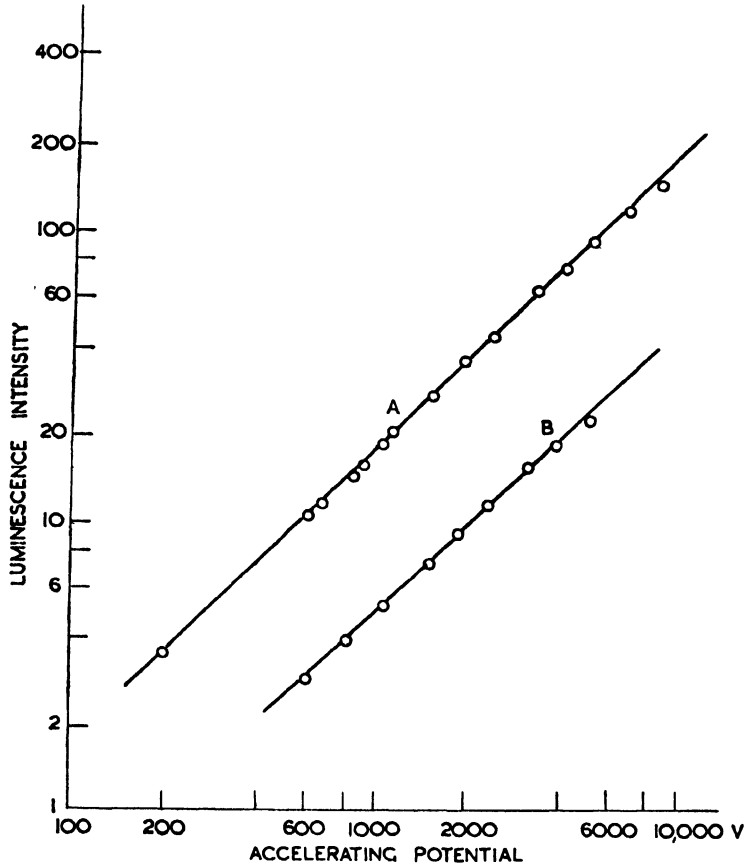


FIG. 100. Variation of cathodoluminescence with electron accelerating potential for a ZnS—Mn phosphor. (Strange and Henderson.) *A*, current density 10 μa/cm.^{2} *B*, current density 200 μa/cm.^{2}

parison of curves *A* and *D*, which show the variation of emission with current density for two different tube voltages, by taking the ratio of intensities at a given current density shows that the saturation effect does not vary appreciably with voltage. A similar comparison may be made by taking the difference in the ordinates of curves *B* and *C* at a fixed power density. We now consider the increase in emission with tube voltage. The straight-line graphs of Fig. 98 show that the

empirical relation 7.1 is obeyed even when current saturation is present in the manganese-activated zinc silicate phosphor. Results for other phosphors are given in Figs. 99 and 100. As Fig. 99 shows, the relation holds whether the light is measured from the back or front of the screen, that is, the depth of penetration of the electrons and light absorption in the phosphor layer do not affect the relation. We may summarize the results for several phosphors by different workers in the following table, using the notation of equation 7.1:

TABLE I

Characteristics of some Cathodoluminescent Materials

Phosphor	*i in μamp./cm.^{2} for 20% light loss per unit current*	*q*	*V_0 in volts*	*V_L in kilovolts*	*Reference no.*
Zn_2SiO_4—Mn	10	1·5	..	..	7
Zn_2SiO_4—Mn	10	2·0	0–100	6·5	2
Zn_2SiO_4—Mn	10	2·0	~100	6·5	4, 5
Zn_2SiO_4—Mn	25	1·53–1·6	0	9·0	6
ZnS—Ag	200	2·8	~100	>10·0	5
ZnS—Ag	500	1·36	150	>10·0	6
ZnS—Ag	150	1·8–2·0	..	6·0	7
ZnS—CdS—Ag	10	Variable	..	>10·0	5
ZnS—Mn	70	1·0	200–300	>10·0	6
$CaWO_4$	30	2·0	100	5·0	5

The second column of the table gives an estimate of the current saturation effects, while the fifth column gives values of the limiting voltage at which the secondary emission begins to be inadequate. From this table it would seem that there is some measure of agreement between the results of various workers, but in some cases considerable differences are shown. This is particularly true for the values of q.

Luminescence due to intermittent excitation

In most practical applications of cathode-ray tubes the excitation of the screen is intermittent in form, and because of this the characteristics of the rise and decay of the luminescence for given excitation conditions are of interest. Thus for television the initial rise and decay of emission during the first few milliseconds is of greatest interest, while for many radar applications

the growth and decay processes up to several seconds' duration must be included. Experimental studies fall into two categories, namely, the study of initial processes and the study of longer period processes in the phosphors. The growth and decay of

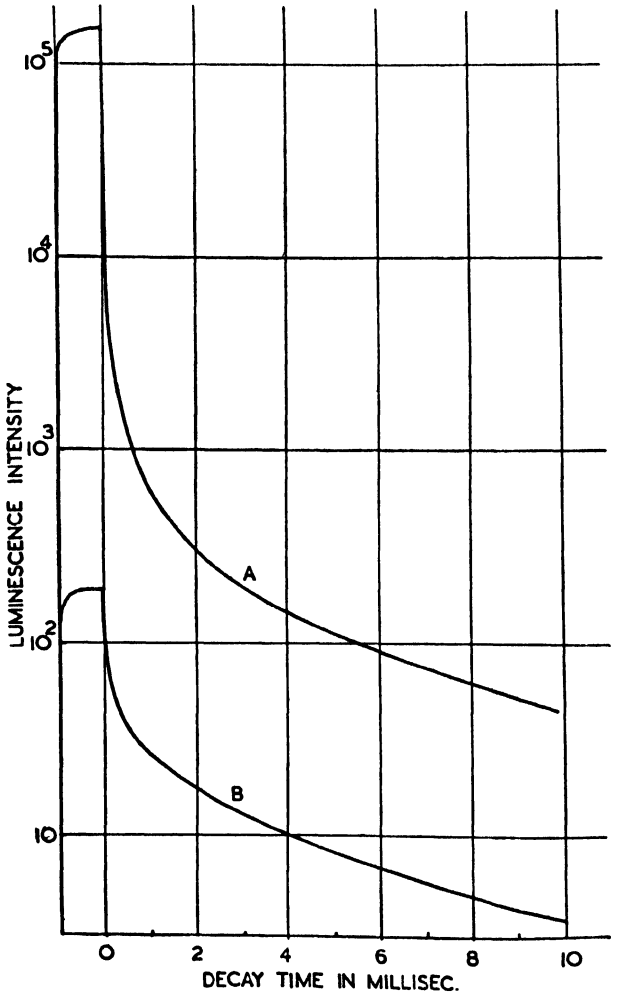


FIG. 101. Initial decay processes for a ZnS—Ag phosphor at 10 kV. (Nelson, Johnson, and Nottingham.) *A*, current density 1,180 μa/cm.^{2} *B*, current density 0·25 μa/cm.^{2}

luminescence for electron excitation are markedly different from those for ultra-violet excitation.

The publications of various workers show that the growth and decay of luminescence may be divided into initial and later processes [6, 7, 9, 10]. The initial components increase or decay exponentially with time, but the later stages of each process may

or may not be exponential according to the phosphor under study. Strange and Henderson [6] have called the faster initial component the α-process and the slower initial component the β-process. The rapid component has been measured in manganese-activated zinc silicate phosphors by Nelson, Nottingham.

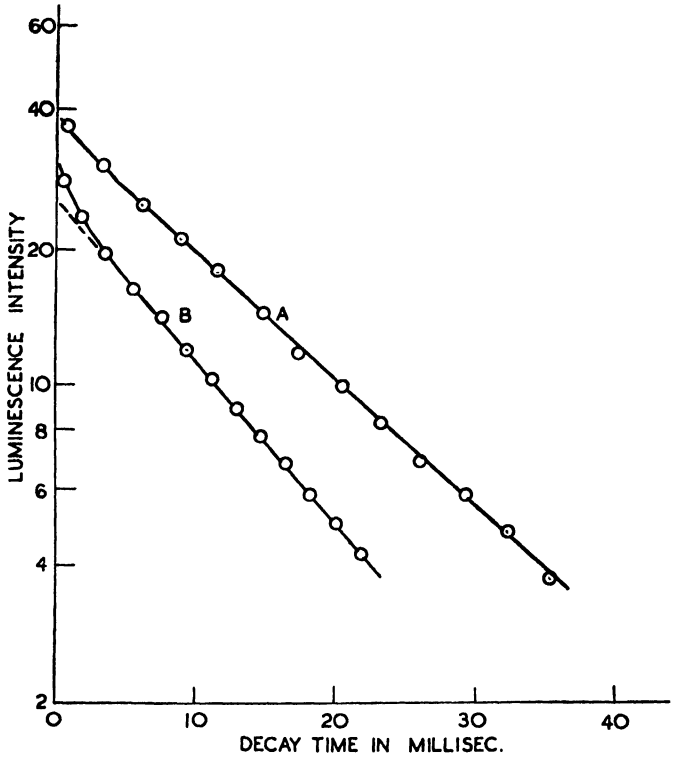


FIG. 102. Initial decay processes for a Zn_2SiO_4—Mn phosphor at 5 kV. (Strange and Henderson.) *A*, current density 1 μa/cm.^{2} *B*, current density 200 μa/cm.^{2} (Scale units different for each curve.)

and Johnson [9] and by Strange and Henderson. The rapid α-process in this phosphor increases with the current density at any electron potential, but it is not marked when compared with the α-process in zinc sulphide phosphors. Fig. 101 shows the rise and decay of luminescence in a silver-activated zinc sulphide phosphor for two different current densities but for the same tube voltage [9]. Fig. 102 shows the less-marked initial α-process of decay in manganese-activated zinc silicate, but still indicates the increase of the initial decay rate with current density [6]. This initial component is not seen when the willemite phosphor is excited by ultra-violet light. A discussion

of its origin is given below in the theoretical section. The measurements made by Strange and Henderson have shown that the initial processes in zinc sulphide phosphors are exponential in form although later stages of the phosphorescence decay are almost invariably hyperbolic. Table II gives some of the decay constants for the α- and β-processes in a zinc sulphide phosphor obtained by these workers. These results show the effect of an increase in current density on the proportions of the α- and β-processes present. (These proportions are given as relative percentages in the table.)

TABLE II

Characteristics of the Initial Decay Processes in Silver-activated Zinc Sulphide

Current density in $\mu amp./cm.^2$	*Decay constant of* α*-process in* $sec.^{-1}$	*Decay constant of* β*-process in* $sec.^{-1}$	% α-*process*	% β-*process*
5	1×10^5	$1{\cdot}3 \times 10^4$	50	50
12	1×10^5	$1{\cdot}45 \times 10^4$	63	37
60	1×10^5	$1{\cdot}65 \times 10^4$	75	25
180	$1{\cdot}2 \times 10^5$	$4{\cdot}1 \times 10^4$	87	13
700	$1{\cdot}8 \times 10^5$	$5{\cdot}0 \times 10^4$	90	10
5,000	$4{\cdot}6 \times 10^5$	1×10^5	95	5

These results show that, except at very high current densities, the decay constants of the α- and β-processes change little with current density although their relative proportions alter considerably. Other experiments in the same series show that the decay constants do not change with the cathode-ray tube voltage or with the phosphor temperature, although there is some evidence that the proportion of α-process increases at low temperatures. A further significant observation by these workers is that the inclusion of 'killer' impurities, such as nickel, in zinc sulphide phosphors has no marked effect on the decay constants of the α- and β-processes, although their presence affects the long afterglow and even the luminescence efficiency of the phosphors.

Because of the large difference in the order of magnitude of the decay constants of the β-process, phosphors may be divided into two classes. The first class has been called the 'Ag' class

since silver-activated zinc sulphide is representative. In phosphors of this class the β-process occurs during the first few microseconds of growth or decay of emission. The second class has been termed the 'Mn' class since it may be represented by the characteristics of manganese-activated phosphors of sulphide and silicate types. In this class the β-process persists for milliseconds: the α-process is usually very small in proportion to the β-process in these phosphors, as shown by Fig. 102. It is found that the decay constant of the β-process in phosphors of the second class varies with the concentration of manganese in the phosphor. This variation occurs for both ultra-violet and for electron excitation and has been studied by Strange and Henderson [6] and by Fonda [11] for the different types of excitation. Table III provides a comparison of the results of the studies made with ultra-violet and electron excitation.

TABLE III

Variation of the Phosphorescence Decay Rate of Willemite Phosphors with the Manganese-activator Concentration

% *Mn*	*Decay constant in sec.*$^{-1}$	*Relative efficiency*	*Mode of excitation*	*Reference*
0·01	63	..	u.v.	Fonda
0·05	67	8·4	c.r.	Strange and Henderson
0·2	67	10·0	c.r.	" "
0·4	73	..	u.v.	Fonda
0·5	67	9·7	c.r.	Strange and Henderson
1·0	80	6·0	c.r.	" "
1·0	73	..	u.v.	Fonda
2·0	113	5·5	c.r.	Strange and Henderson
2·0	170	..	u.v.	Fonda
5·0	550	1·3	c.r.	Strange and Henderson
5·0	540	..	u.v.	Fonda

The rate of rise of emission with time in the growth processes is very high and is found to depend on the current density. In both Ag and Mn type phosphors the rates of rise do not bear any simple relation to the respective decay constants. However, both appear to be independent of the electron potential.

Fig. 103 shows how the luminescence increases with time during excitation for a willemite phosphor. We shall discuss the mechanism of the growth process and the various curves of this figure in a later section.

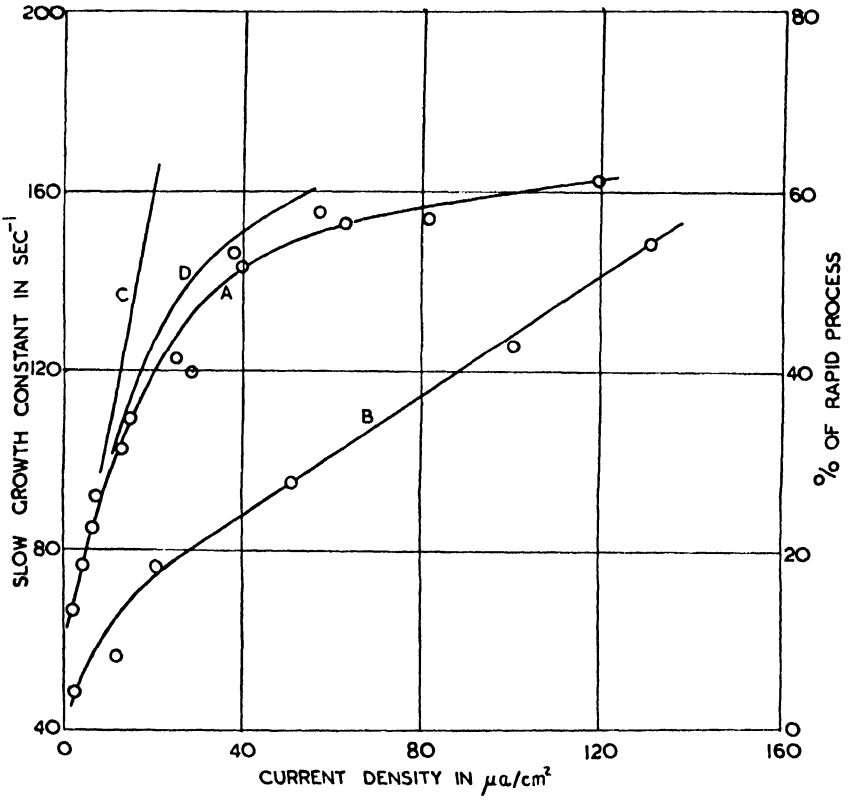


FIG. 103. Growth processes for Zn_2SiO_4—Mn phosphor: changes with current density at 5 kV. (Strange and Henderson.) *A*, observed slow growth constant. *B*, percentage of rapid process. *C*, initial slope of curve *A* from eq. 7.4 $(Ai+B)$. *D*, curve *A* corrected for effect of efficiency of slow process.

Phosphorescence of long duration due to electron excitation

Zinc sulphide and other phosphors which show long afterglow after ultra-violet excitation also show it after cathode-ray excitation. However, the characteristics of the afterglow in the two cases are markedly different. After cathode-ray excitation of a phosphor the initial decay of emission is often much more rapid than after ultra-violet excitation. The intensity of the emission at long decay times is much smaller for cathode-ray excitation. We give, as an example of the different decay

characteristics after cathode-ray and after ultra-violet excitation, the decay curves of Fig. 104. The phosphor, a copper-activated zinc-cadmium sulphide specimen, has been excited to the same brightness of luminescence by ultra-violet radiation and by cathode rays, and in each case the decay curve has been measured. As stated in Chapter II, the afterglow at long decay

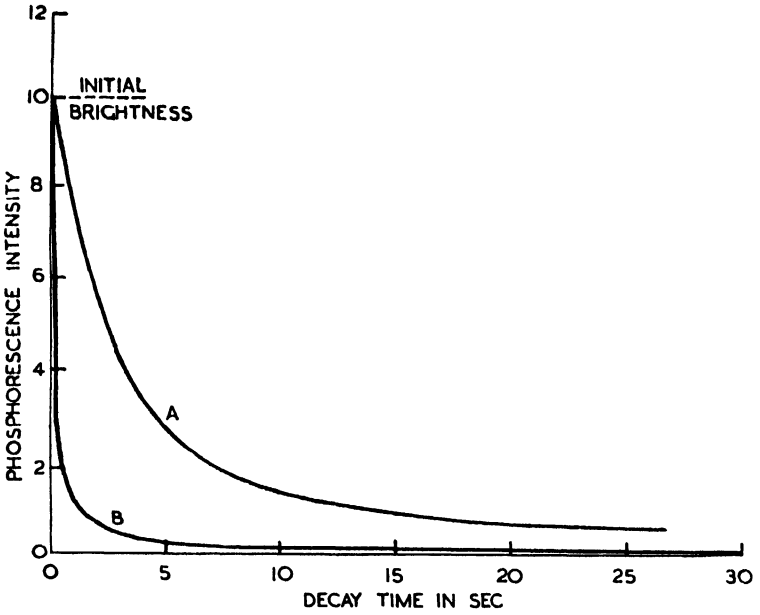


FIG. 104. Phosphorescence decay of a ZnS—CdS—Cu phosphor. *A*, excitation by 3,650 A radiation. *B*, excitation by cathode rays (6 kV). Phosphor excited to same initial brightness in each case.

times shows saturation and becomes independent of the excitation intensity. In the case of cathode-ray excitation the saturation effect occurs at relatively low current densities. However, as in the case of current-saturation effects described above, the saturation of the afterglow is less marked at high voltages.

A survey of the measurements of afterglow characteristics of cathode-ray tube screens shows that there is no evidence of a simple bimolecular decay process; the decay is, however, of the hyperbolic form shown by such phosphors after ultra-violet excitation.

The emission spectra of phosphors excited by cathode rays

Henderson [12] has made studies of the spectral characteristics of phosphors which can be excited by cathode rays and by

ultra-violet light. It appears that the spectra are generally independent of the particular type of excitation. Extensive studies of many phosphors have been made by Leverenz [13, 14]. In general, cathode-ray screen phosphors show broad, structureless, emission bands as shown by Figs. 43 and 48.

The electrical characteristics of cathode-ray tube phosphors

We have stated earlier that a phosphor for use as a cathode-ray tube screen must have good secondary electron emission characteristics. Unless the screen emits a sufficient number of secondary electrons it will charge up negatively and will therefore decrease the effective electron potential of the primary beam. This will have obvious effects on the luminescence intensity. In order to avoid this charging of the screen the ratio of the secondary electron current from the screen to the primary beam current must be greater than, or equal to, unity. At ordinary cathode-ray tube voltages, that is, between 1 and 10 kilovolts, there is usually no difficulty in obtaining adequate secondary emission from the phosphor screen, but at higher voltages the fall in secondary emission constitutes a serious practical difficulty. Special techniques of screen mounting have been developed to overcome the difficulty [15], but we shall only consider here the behaviour of conventional screens. The ratio of the secondary electron current to that of the primary beam current will be denoted by η. The ratio behaves in a characteristic way, which is similar for both metals and insulators, as the cathode-ray tube voltage is increased. This is shown by the two curves of Fig. 105, one for nickel [21] and the other for potassium chloride. The secondary emission characteristics of metals have been investigated by many workers and their studies have been reviewed by Kollath [16], by Bruining [17], and by Trey [18]. Recently studies have been made of the characteristics of insulators by Geyer [19] and by Knoll, Hachenberg, and Randmer [20], from whose experimental results the curve A of Fig. 105 is taken. It is usually found that the maximum value of the ratio η is greater for insulators than for metals and occurs at higher voltages. After reaching this

maximum the value of η decreases with increase in tube voltage until it becomes much less than unity. The voltage at which it is unity is known as the *sticking potential* and is generally much higher for insulators than for metals. It is known as the sticking potential because the secondary emitting material begins to

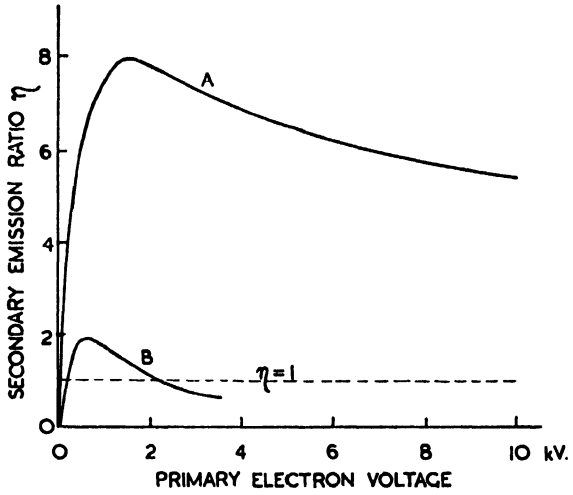


FIG. 105. Secondary emission characteristics of insulators and metals. *A*, potassium chloride at 20° C. (Knoll, *et al.*) *B*, nickel. (Hagen.)

charge up when the overall tube voltage is further increased and therefore tends to remain at the voltage for which η is unity.

It is found that the secondary emission ratio η increases as the inverse of the temperature for insulators, but that it is independent of temperature in the case of metals. Both in metals and in insulators the ratio η increases as the angle of incidence of the primary electrons departs from the normal. This must be of some significance in studies of phosphor screens since these are composed of very small crystals presenting faces at all angles to the incident electron beam. For this reason the measurements of secondary emission do not lend themselves to easy interpretation when made on conventional phosphor screens.

The fatigue and deterioration of cathode-ray tube screens

Prolonged bombardment of a cathode-ray tube screen usually produces a decrease in its luminescence efficiency and sometimes a visible darkening of the screen material. There are several

factors which can contribute to this process of deterioration. The chief of these are:

i. Physical destruction of the phosphor by the bombarding electrons.

ii. Physical and chemical destruction of the phosphor by ionic bombardment. The ions originate in the cathode-ray

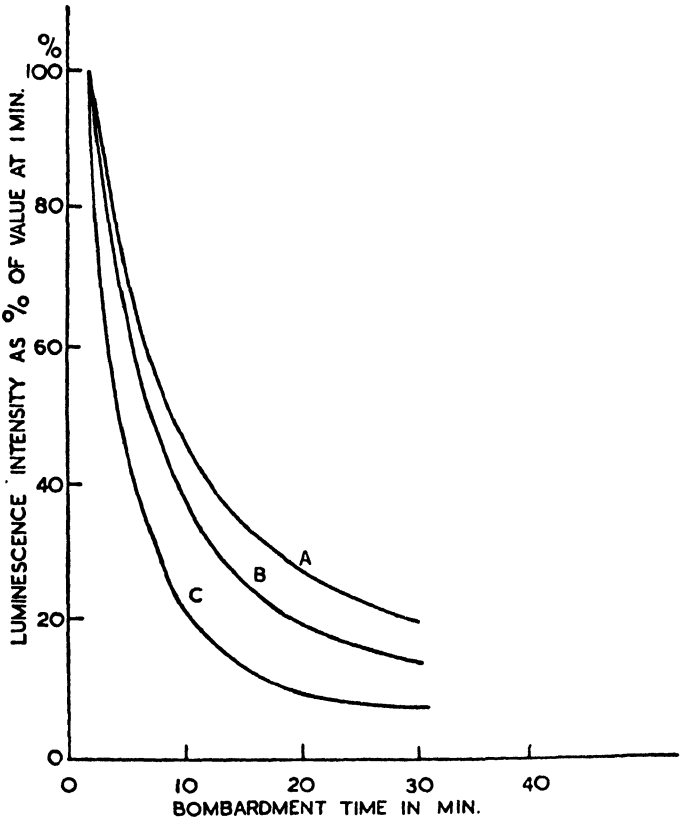


FIG. 106. Low-voltage electron burn of phosphors at 1,600 V, 700 μa/cm.^{2} (Grotheer.) *A*, ZnS phosphor. *B*, $CaWO_4$ phosphor. *C*, Zn_2SiO_4—Mn phosphor.

tube walls, electrodes, etc., and are accelerated to the screen by the applied voltage. Similar positive ion contamination causes the cathode of the tube to deteriorate.

iii. The saturation of the screen material by electrons at low voltages. This results in a fatigue of the material which may later disappear again.

We shall consider only the effects of electron bombardment. As stated above, both slow and fast electrons can produce a

decrease in luminescence efficiency. However, the effects of slow electrons can sometimes be removed by heating the screen. The deterioration effects, commonly known as *electron burn*, decrease with voltage for a given current density. This may be explained by the decrease in density of the excitation per unit volume of the screen as the electrons penetrate deeper into it.

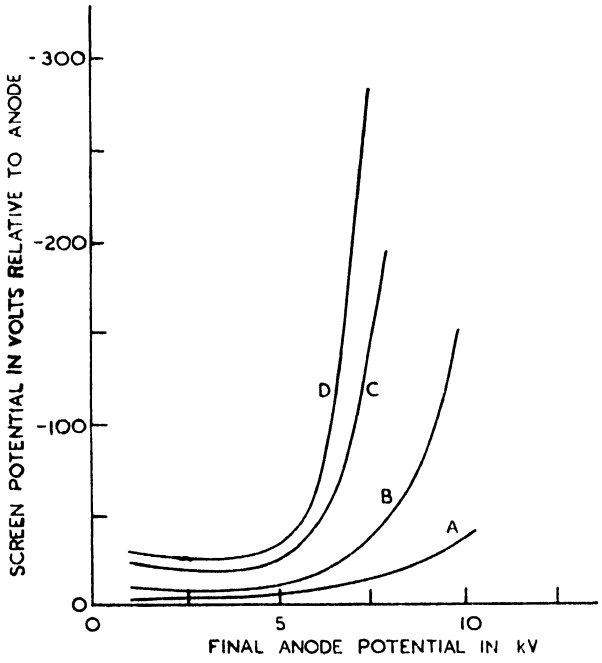


FIG. 107. Decrease in secondary emission shown by variation in screen potential of $ZnBeSiO_4$—Mn phosphor with continued excitation at 6 kV. (Nelson.) *A*, initial curve. *B*, after 300 hours' excitation. *C*, after 500 hours' excitation. *D*, after 765 hours' excitation.

The fall in luminescence efficiency with bombardment at a fixed voltage often shows an exponential decrease with the *dosage* which is the product of current density and time of excitation. Typical curves for three different phosphors showing the deterioration effects are given in Fig. 106, due to Grotheer [22]. In this case the burn is of the low-voltage type and it will be noticed that it is more marked in phosphors of the Mn class. The calcium tungstate screen shows an intermediate behaviour between the Ag and Mn classes, and this corresponds to the intermediate nature of its β-decay process (10^{-5} sec. mean decay time).

Leverenz [13] has made a study of the burn due to high-voltage electron bombardment. In this case the effects are usually irreversible, and in some cases there must be thermal destruction of the screen. Experimental results show that at high electron voltages the oxide types of phosphor are more resistant to bombardment than the sulphide types. This places a serious limitation on the choice of materials for the screens of projection cathode-ray tubes. Prolonged bombardment produces changes in the secondary electron emission characteristics of phosphors. Fig. 107, due to Nelson [23], shows how the sticking potential decreases with the time of bombardment.

2. The theory of cathodoluminescence and related phenomena

Comparison of optical and electronic excitation processes

It will have been evident from the description of the experimental studies of cathodoluminescence that the excitation process is much more complex than that for ultra-violet light excitation of phosphors. In the latter case the absorption characteristics of the phosphors are relatively well defined, particularly those with such impurity activators as manganese. The absorption coefficient for such exciting radiation may also be quite small when absorption is confined to the impurity centres. In cathodoluminescence the incident electrons interact with all the atoms or ions of the phosphor along their path and the effective absorption coefficients are of the same order as those for absorption of radiation lying in the fundamental absorption bands of the phosphor lattice. However, there is no selective absorption change with electron energy as occurs for a change in energy of ultra-violet radiation. Electrons penetrating into a phosphor will have a range of penetration dependent on their initial energy. Whereas for ultra-violet radiation one quantum produces one excited electron, the primary electrons incident on the phosphor will produce many secondary electrons along their paths in the solid. For slow electrons there are also relatively large surface forces to overcome before penetration is possible. This will give rise to the dead voltage which may

be of considerable magnitude in some phosphors (see Table I above).

For the purpose of this theoretical discussion we may divide the whole process of cathodoluminescence into several stages and consider them in turn. We shall therefore consider the following processes:

i. The way in which surface conditions affect the electron penetration.

ii. The way in which the electrons lose their energy along their path in the phosphor. This involves a knowledge of the variation of the maximum penetration depth with electron energy, the variation of electron current with depth, and the relation of the secondary electron production to the electron energy at any point along its path.

iii. The mechanism for the transport of energy from excited secondary electrons to luminescence centres and to other centres in the phosphor.

iv. The non-radiative loss of energy in phosphors and the deterioration effects due to electron bombardment.

The mechanism by which the electrons penetrate into the phosphors

We have already mentioned the effect of surface forces on the electron penetration. There is a great need for further careful study of these forces and their effect on slow electrons. Some of the earliest studies of the penetration of electrons into matter were made by Lenard [24], Leithauser [25], and by Whiddington [26], the latter studying the decrease in energy of electrons passing through thin metal foils. Whiddington's work led to the formulation of the Thomson–Whiddington law which relates the depth of electron penetration x to the velocities of the electrons at incidence and at this depth. Using the electron potential instead of the velocity, the law may be stated as follows:

$$x = a(V_0^2 - V^2), \tag{7.2}$$

where V_0 is the incident electron potential and V is the potential at the depth x. The constant a is specific to the particular material and is approximately proportional to the reciprocal of its density. The maximum depth of penetration will therefore be proportional to the square of the electron energy, a conclusion reached by Bethe [27] from similar theoretical considerations. Most of the experimental support for the above law is derived from studies of metal foils and for electrons of 50 kilovolts potential. It is not certain that for insulating crystals and at lower voltages this law is still valid. A discussion involving the above relation has been given by Strange and Henderson [6], who also discuss the possible ways in which the electron current decreases with depth of penetration. Stinchfield [28] has assumed that the current decays exponentially with the depth of penetration, as follows:

$$i = i_0 \exp(-\alpha x), \tag{7.3}$$

where i_0 is the initial current and α is a constant dependent on the electron velocity at incidence and on the density of the material. Support for these assumptions is given by the experiments of Terrill [29], but the electron potentials in these studies were again of the order of 50 kilovolts. We shall discuss the relations 7.2 and 7.3 in a later section.

We must include in this discussion the secondary electron emission from the phosphor crystals. The general characteristics given in Fig. 105 for metals and for insulators can be given a qualitative explanation. At low voltages the primary electrons will have difficulty in overcoming the surface forces and this will also apply to the secondary electrons. Thus we do not expect slow electrons to produce adequate secondary emission because the residue of energy left to them is small after penetration and because the secondary electrons they can produce will have even lower energies and will not be able to penetrate the surface layers. Trapping states for electrons in the surface layers of the phosphor will capture electrons and therefore diminish secondary emission and primary electron penetration. The importance of surface states with respect to electron

emission has been emphasized by Bloembergen [30]. As the primary electron energy increases, the surface states become less important and the secondary electron emission rises. It will reach a maximum as shown in the figure because of the increased depth of the electron penetration. Secondary electrons produced at considerable depths in the solid will have a small

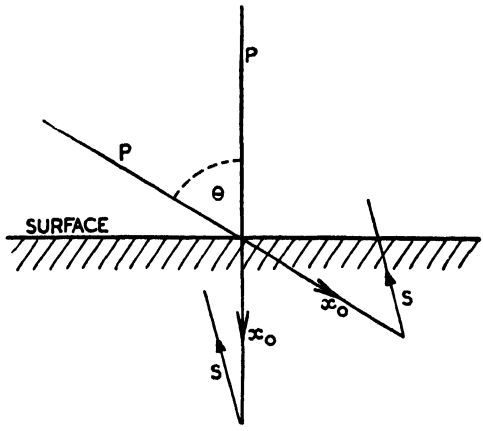


FIG. 108. Effect of angle of incidence of primary electrons on the secondary emission from a surface. *P*, primary electrons. x_0, penetration depth. θ, angle of incidence. *S*, secondary electrons all assumed to have the same range.

chance of reaching the surface and so the emission of electrons will begin to decrease again with increase of primary electron energy. We may also explain in a qualitative way the change of secondary emission with the angle of incidence of the primary electrons. The emission will increase as this angle becomes more glancing, since the secondary electrons are produced nearer to the surface than for normal incidence. This effect is shown schematically in Fig. 108. Since phosphor screens are composed of small crystals of irregular shape the angles of incidence for primary electrons will rarely be normal and thus the surface states will become important. It is the complex incidence conditions which constitute one of the chief difficulties in understanding the relations between primary electron energy and current density and the luminescence produced.

We have seen that there are significant differences between the secondary electron emission characteristics of metals and

insulators, inclusive of phosphors. In the case of insulators we have to explain the following facts:

i. The higher sticking potentials compared with those of metals.
ii. The change in secondary emission with temperature.
iii. The decrease in secondary emission with increasing imperfection of the crystal.

In both metals and insulators primary electrons produce secondary electrons by collisions with lattice atoms or ions. These secondaries, if of sufficient energy, will produce further secondaries, the average energy of all secondary electrons thus decreasing with the number of collisions. For secondary electrons having several electron volts of energy the only impedance to motion in an insulating crystal at low temperature will be due to departures from the perfect periodicity of the lattice. In a metal the secondaries will always be interacting with other conduction electrons. Thus we expect the sticking potential for insulators to be relatively high since more secondary electrons from deeper levels below the surface can reach and penetrate the surface than is the case in metals. An increase in temperature will increase the thermal vibrations of the lattice and so decrease the mean free path of secondary electrons and the resulting secondary emission. This is known to occur in the alkali halides, the range of photo-electrons from F centres showing a decrease with temperature [30]. Knoll and his collaborators [20] have shown by experiment that an increase in the number of defects in an alkali halide crystal causes a decrease in the secondary emission. In cathodoluminescence we are concerned with the way in which the secondary electrons produced can lose their energy since some of it must be taken up by luminescence centres. The production of secondary electrons will be dependent on the primary electron energy and path length and on the internal ionization potential. We know that electrons with energies less than 10 volts can produce luminescence in some phosphors [31]. However, the process is most inefficient. We would expect that for higher velocity

electrons the production of secondary electrons would be greatest towards the end of the electron path in the phosphor, by analogy with ion production in gases. Stinchfield [28] has suggested that the curves of Fig. 109, derived from the relations 7.2 and 7.3, represent the variation in electron energy current and power expenditure with penetration depth in the phosphor.

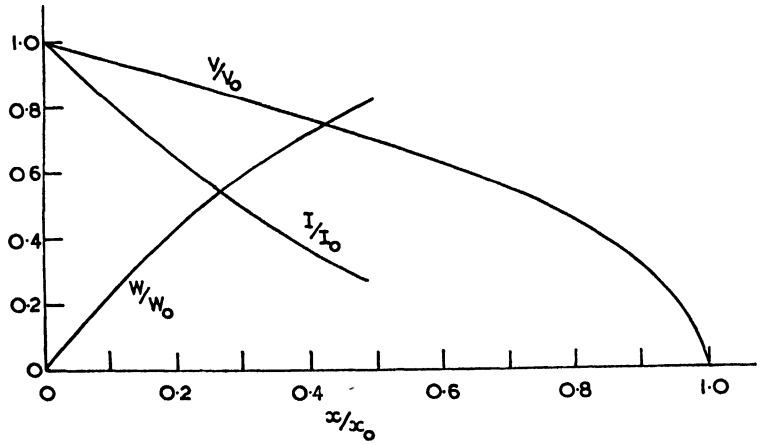


FIG. 109. Variation of residual voltage (V/V_0), residual current (I/I_0), and expended power (W/W_0) of electron beam with penetration distance (x/x_0) into matter: x_0 is maximum range. (Stinchfield.)

However, these relations are not adequately supported by experiment and their use does not help in explaining the dependence of luminescence on electron energy and density, as we shall see later.

The efficiency of cathodoluminescence

The ratio of the light output energy to the incident electron energy rarely exceeds 10 per cent. for a cathode-ray tube screen. In photo-excitation the efficiency of the same material may be as high as 95 per cent. if absorption takes place in the luminescence impurity centres. However, as shown by Fig. 59, the efficiency of photo-excitation decreases when the absorption takes place in the matrix crystal. In zinc sulphide phosphors the efficiencies for cathodoluminescence and photoluminescence due to short wave-length ultra-violet excitation are comparable. It is therefore possible to explain the low efficiencies of both processes by using the concepts developed in Chapter IV. We

have assumed in the latter that when electrons are raised into the conduction levels of phosphors they may lose their energy by being captured in non-radiative centres or states. The relative probabilities for capture in non-radiative centres and in luminescence centres may be given by the excitation spectra of phosphors, and also by their quenching and stimulation spectra (see Chap. VI). In the case of cathodoluminescence we also have electrons excited into conduction levels and so we expect similar efficiencies to those for ultra-violet excitation of short wave-length. The very low efficiencies found for excitation due to very slow primary electrons must be associated with the greater prevalence of non-radiative centres in the surface of crystals where the crystal imperfections are most pronounced. Fano [32] in his theoretical treatment of cathodoluminescence suggested that excited electrons in surface states of phosphor crystals would not contribute to the luminescence. He assumed that energy was transferred to luminescence centres from the secondary electrons by an exciton process, but it is more likely that electron capture in the centres is responsible for the energy transfer.

The relation between luminescence and electron energy and density

In view of the complex excitation conditions it is surprising that such a simple formula as that of equation 7.1 should give the relation between the electron energy and current density and the resulting luminescence emission. We consider first the variation of luminescence with electron current density. The occurrence of saturation at higher current densities is a process not clearly understood. Several workers have suggested that it may be due to the saturation of luminescence centres because at any instant those excited are unavailable for excitation [6, 7, 9]. If this is so, then we should expect that phosphors falling into the Mn class would show saturation at lower current densities than those of the Ag class. This is in fact the case, as Table I shows, but the explanation adopted fails to explain why the saturation effects are almost independent of electron energy.

High-voltage electrons give rise to a lower energy density in the phosphor than low-voltage electrons, but the saturation of the centres appears to be unaffected.

The variation of luminescence with electron energy also lacks a satisfactory explanation. Fano [32] has attempted an elaborate mathematical treatment which yields an expression similar to that of equation 7.1 but having a q-value of two. Since q varies from phosphor to phosphor, his derivations seem to have little value. Strange and Henderson [6] have given a fairly comprehensive discussion of the relation 7.1. They have shown that if current saturation effects are neglected and the electron current is assumed constant throughout the excited volume of the phosphor screen, then any penetration law for the electrons will give a value of unity for the index q. If the current is assumed to vary linearly along the primary electron path, or assumed to vary with path length according to a simple power law, they again find that the index is unity. If q is assumed to be different from unity, then it must also be assumed that it will vary with current density. This is not supported by experiment, as the curves of Figs. 98, 99, and 100 show. The objection which we must make to the arguments put forward by these workers is that while they apply the principle of the conservation of energy to the problem, they do not include energy lost by non-radiative processes in the phosphor. If such losses are included, then the fact that they decrease with electron energy means that the luminescence efficiency can increase with electron energy, and thus give rise to a value of q greater than unity when the principle of conservation of energy is applied.

We do not expect that further progress will be made in establishing a theoretical explanation of the relation 7.1 until experimental conditions are much simplified. This will mean the use of single phosphor crystals with simple surfaces.

Growth and decay processes

We have already described the distinctive features of the α- and β-decay processes in Ag and Mn type phosphors. In both cases it is likely that these are characteristic of transitions

within the emission centres. In the case of Mn class phosphors this is supported by the correlation between the decay constants of the phosphors after excitation by ultra-violet radiation and by electrons. For phosphors of the Ag class no measurements of the α- and β-processes have been made for ultra-violet excitation, and so it is not possible to be certain that the processes are dependent only upon the nature of the emission centres. The large increase in the α-process relative to the β-process with increase in current density is not clearly understood. Strange and Henderson [6] have suggested that collisions of the second kind can account for it. It would seem that the increased electron density can perturb the emission centres so that the transitions for the α-process become more likely than those for the β-process.

An important consideration in a theoretical discussion of the decay constants is their relation to the constants of the growth processes during excitation. Fig. 103 shows that the rate of rise of luminescence increases with current density. This would be expected from very simple theoretical considerations as proposed by Strange and Henderson [6]. They assume that a thin layer of phosphor is excited. A is the probability of excitation of a luminescence centre, B is the probability of its return to the ground state, i is the current density, and n the number of luminescence centres per unit volume: x of these centres are assumed to be excited at any instant. They then derive the following relation between luminescence intensity L, time of excitation t, and the current density:

$$L = Bx = \frac{ABin}{(Ai+B)}[1-\exp\{-(Ai+B)t\}]. \qquad (7.4)$$

According to this equation the luminescence rises exponentially with time, having a rate which is dependent on the current density, namely, $(Ai+B)$. This equation does not agree with experiment since measurements show that there are two components of the growth processes similar to the two components α and β of the decay process. Fig. 103 shows the way in which the proportion of each process changes with current density.

It also includes the calculated form of the initial slope of the growth curve, derived by insertion of appropriate values in the rate constant $(Ai+B)$. Although the theoretical and experimental curves show some agreement in their initial slope, there is no general agreement between them.

Phosphorescence of long duration

The later stages of the decay processes following electron excitation may be explained by the action of electron traps. As shown by Fig. 104, the decay after electron excitation is much more rapid and less intense than that after ultra-violet excitation to the same initial brightness. This difference is mainly due to the different densities of excitation per unit volume of phosphor in the two cases. The exciting electrons are absorbed in a relatively thin layer of the phosphor and so the excitation is relatively intense and tends to saturate the deep traps in the layer, and also to fill a comparatively large number of shallow traps. The ultra-violet radiation excites a much larger volume of phosphor and, because of the resulting lower density of excitation, more deep traps are filled relative to shallow ones, as expected from an application of equation 2.19. Thus the decay is more intense at long times than that due to electron excitation. Ultra-violet radiation of short wave-length produces a similar effect to electron excitation since it is also confined to a very thin layer of the phosphor. As the electron energy is increased the excitation by electrons more nearly approaches that due to ultra-violet excitation, since the excitation is taking place in a larger volume of the phosphor and is therefore of lower density for a given current density.

The processes of electron burn

We consider first the deterioration of the phosphor which occurs at low electron energies. This electron burn is most marked in phosphors of the Mn class which have initial decay components lasting for milliseconds. In these phosphors the degree of burning for a given dosage decreases with increase of electron energy. This is presumably due to the lowering of

the density of excitation with increasing electron penetration. Since low-voltage burn effects can often be partly removed by heating the phosphor, they must involve some metastable state of the screen material. The permanent effects which are generally accompanied by darkening of the phosphor are probably due to the reduction of the phosphor by the electron bombardment and the formation of colloidal metal particles in the crystals. The association of this type of burn with phosphors of the Mn class is not understood at present.

At high electron energies the Mn class phosphors are more stable than those of the Ag class. We must assume that the burn effects are somewhat different from those at low voltages. It is certain that their irreversible nature is due to a destruction of the phosphor crystal structure. It has been suggested that prolonged bombardment of alkali halides with electrons creates a mosaic structure in the crystals [33]. A similar effect may occur in phosphors. Although much experimental knowledge of the electron burn effects is available, no attempt has been made to provide a precise theoretical interpretation of the processes involved. Some preliminary investigations in the author's laboratory on phosphors of the Mn class show that the low-voltage burn of these phosphors is independent of temperature over the range 90° K to 600° K. The change in secondary emission characteristics with electron burn shown in Fig. 107 can be explained by the increase in the disorder of the phosphor crystals as discussed above.

3. Future studies of cathodoluminescence

We end this chapter with some suggestions of future approaches to the study of cathodoluminescence processes. It is of importance that research shall be made using large crystals with optically worked faces or with carefully evaporated layers of suitable luminescent materials. This will simplify the surface conditions of the phosphor, giving a relatively well-defined angle of incidence for primary electrons. In view of the availability of multiplier photocells of high gain, the alkali halide crystals could be used in spite of their feeble luminescence.

Phosphors of the fluoride type might prove suitable for forming evaporated layers of phosphor [34].

There is also a need for secondary emission studies using insulating materials, including phosphors, of simple well-defined form. These studies would enable the validity of the penetration laws for electrons at relatively low voltages (less than 10 kV) to be tested.

A note on the excitation of phosphors by α-particles

It has been affirmed by Riehl [35] that the efficiency of excitation of phosphors by α-particles may be as high as 80 per cent., to be compared with the value of 10 per cent. for cathode rays. A critical review of experimental evidence has been given recently by Klasens [36]. He has shown that Riehl's estimates of the efficiency of α-particles, together with those of some other workers, are in error and that correct estimates give an efficiency comparable with that for electron excitation.

CHAPTER VIII

THE LUMINESCENCE OF ORGANIC MOLECULES

1. Introduction

THE investigation of the occurrence and characteristics of luminescence in organic molecules has not only increased our general knowledge of such processes but has provided a powerful method of determining molecular structure. Earlier studies of luminescence in organic systems are described in the general literature referred to at the end of Chapter I. During the last decade or so more extensive and precise studies have been made and have been reviewed by various workers [1, 2, 3, 4]. In addition to these experimental investigations there has been a parallel development of the wave-mechanical approach to the theory of organic molecules [5, 6, 7, 8, 9]. This has enabled such phenomena as colour, photochemical activity, and luminescence to be related to the structural form and physical state of molecules. As in the case of inorganic phosphors, one of the primary interests has been the determination of the conditions necessary for luminescence to occur in molecules. Other interests have been centred in such phenomena as the polarization and quenching of fluorescence, photochemical sensitization in relation to luminescence, and the occurrence of long-period phosphorescence in molecular systems adsorbed on to solid surfaces or dispersed in solids. In this chapter we shall consider these recent developments. The phenomena of chemiluminescence and bioluminescence will not be included: Newton Harvey [10] has provided a comprehensive series of references to the work in the field.

2. The conditions for luminescence in organic molecules

It is possible to provide for organic molecules general considerations of the conditions for luminescence to occur such as we have described in Chapter I. These considerations include the use of potential energy diagrams to describe the normal and excited states of the molecule. In fact, the treatment of organic molecules is an extension of the ideas represented by the diagrams of Figs. 1 and 2. As in inorganic solids, absorption of

energy leads to excitation of the molecule and a new configuration for its nuclei. An organic molecule not only possesses electronic energy but also vibrational and rotational energy. These extra degrees of freedom are subject to quantum con-

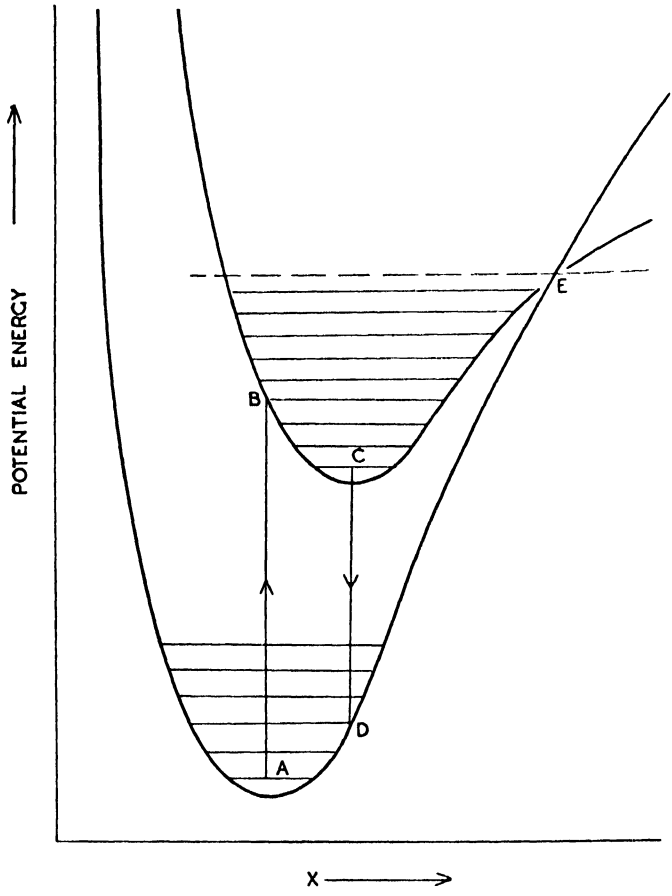


FIG. 110. Energy-configurational diagram for a luminescent organic molecule. (Bowen.) *AB*, absorption transition; *CD*, luminescence emission transition; *CED*, non-radiative transition.

ditions as in the case of the electronic energy. The upper and lower curves of Fig. 110 represent the potential energy configuration of the molecule in its excited and normal states respectively. Vibrational states are represented in this diagram by horizontal levels proper to each curve, but rotational states are not included here. At ordinary temperatures the unexcited molecule will not possess more than one or two vibrational quanta. Absorption of light causing electronic excitation will

raise the molecule into its excited state by the transition AB which produces a compressed molecule. Coupling between the electronic and vibrational states of the molecule in this excited condition will lead to a degradation of energy as the molecule expands until the state C is reached. There is always a probability of a resonance transition BA taking place before the molecule has begun to expand, but this becomes unlikely if coupling is present. When once in the excited state the molecule may lose all its energy by dissociation or by collision with another molecule; we shall consider such cases later. After the state C is reached luminescence will occur with transition CD to the ground state and further loss of energy by coupling with vibrational states so that the initial state A is once more reached. The lifetime of the excited state of the molecule will depend on several factors, including the transition probability for luminescence and the disturbance by external agents. As in inorganic phosphors, there is always a probability of a non-radiative return to the ground state if the state E is reached. It must therefore be assumed that in non-luminescent molecules, and in the absence of chemical change or dissociation, the vibrational states of the normal and excited molecule overlap so that radiationless transition from E to A is possible. In luminescent molecules the vibrational states will only effect such transitions at high temperatures and a formula for this quenching similar to that of equation 1.1 is obtained. In most cases of quenching in organic molecules the above process is obscured by other influences, such as collisional quenching or photochemical changes.

From this brief discussion of the molecular configurations favourable to luminescence we may infer some general conditions for luminescence to occur in organic systems. It is necessary that in the excited state of a molecule there should not be too much coupling between the electronic and vibrational states. It follows from this that excitation should not involve any marked change in the structure and stability of the system [2]. We may thus indicate those organic molecules which are likely to satisfy these conditions. The simplest molecules which

show luminescence are those of benzene, its homologues, and some of its derivatives, and those of heterocyclic ring compounds. All these molecules have a common feature in their structure, namely, the presence of conjugated double bonds and the resulting ring systems of electrons which have non-localized orbitals [1, 2, 9]. More complex molecules also have these characteristics, in particular many organic dyes and the polymers they form in aqueous solution [4]. Since excitation of these molecules must involve little structural change or changes of molecular symmetry, it follows that the optical transitions due to absorption are of a forbidden nature, involving very small change of dipole moment. As an example we give the case of benzene, cited by Bowen [2]. Electronic transitions between the normal and excited states which involve totally symmetrical vibrations of type A_{1_g} are forbidden. However, the symmetrical electronic transition for 2,600 A radiation, coupled with A_{1_g} vibrations, is allowed if vibrations of type E_g^+ are also excited. The latter are vibrations along an axis and the process becomes analogous in some ways to an $s \rightarrow p$ transition. These theoretical predictions agree with the observed form of the absorption and emission spectra for benzene. The widths of the spectral bands are due solely to the different environments of the individual molecules. Solid benzene shows spectra which contain the bands which are normally forbidden, this being due to a distortion of the symmetrical hexagonal form of the molecules by the binding forces of the crystal.

It will be evident from Fig. 110 that the absorption and emission spectra of molecules will consist of a system of regularly spaced bands corresponding to the vibrational levels of the normal and excited states. The frequency differences between adjacent bands will be those between the vibrational states. A mirror-image effect is shown between the absorption and emission spectra if excitation does not alter, to any marked extent, the symmetry of the molecule. Fig. 111 gives the absorption and emission spectra of anthracene in different physical states as an example of this effect [1]. Exact correspondence does not occur since absorption involves transitions

from the lowest or next lowest vibrational level of the ground state to any of the vibrational levels of the excited state, while

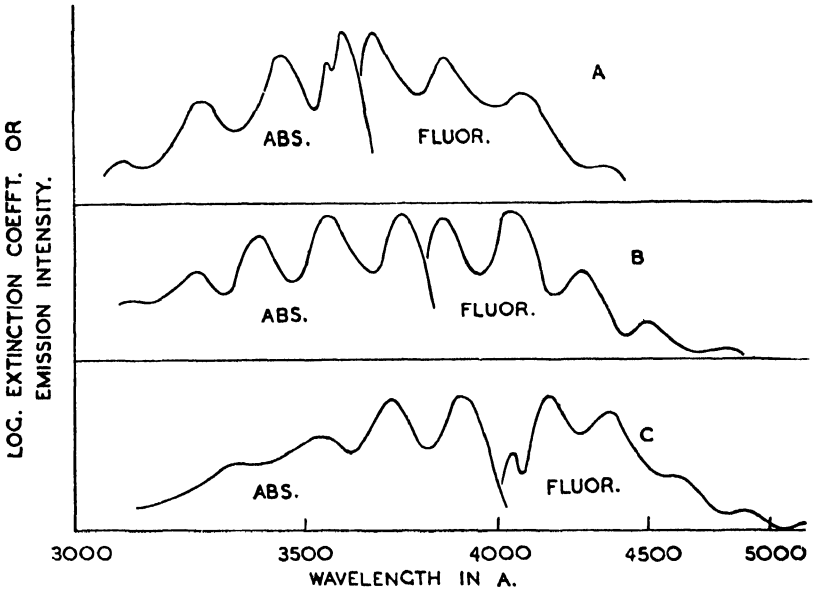


FIG. 111. Absorption and emission spectra of anthracene. (Bowen.) *A*, vapour; *B*, solution in dioxane; *C*, solid.

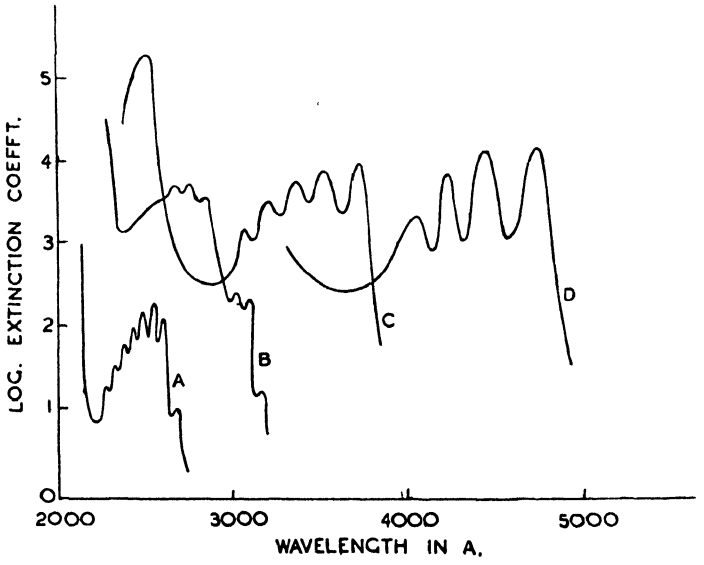


FIG. 112. Absorption spectra of benzene and some of its homologues. (Bowen.) *A*, benzene; *B*, naphthalene; *C*, anthracene; *D*, naphthacene.

emission is due to transitions to any of the vibrational levels of the ground state. The absorption spectra of the homologous series formed by benzene, naphthalene, anthracene, etc., are

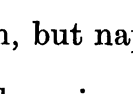
not markedly different from each other in general appearance, but as the number of conjugated rings increases in the molecule both the absorption and emission spectra move towards longer wave-lengths. Fig. 112 gives the absorption spectra of the first few members of the series, while Table I below summarizes the absorption and emission characteristics of these and other members.

TABLE I

Absorption and Emission Spectral Characteristics of Benzene and its Homologues [11]

Substance	*Limit of long wave-length absorption*	*Wave-length range of emission bands*
Benzene	2,600 A	2,600–3,000 A
Naphthalene . . .	3,300 A	3,000–3,650 A
Anthracene . . .	3,800 A	3,800–4,550 A
Naphthacene . . .	4,360 A	4,500–6,500 A
Pentacene . . .	5,800 A	Bands in the red

The increase in wave-length in the series is presumably associated with the effect of increase in chain length on the π-electron orbitals.

The absorption and emission spectra of such hydrocarbons will be altered by substitution in the ring systems. Introduction of groups such as NO_2 or the halogens causes a decrease in luminescence efficiency, while other groups, such as NH_2, enhance the efficiency and shift the emission to longer wave-lengths. For example, naphthalene ( ) absorbs and emits in the ultra-violet region, but naphthionic acid (

) emits and absorbs in the visible region. Comparison of the characteristics of anthracene and quinoline indicates a similar behaviour [11]. These changes of emission or absorption with substitution can be explained by the effect of the latter on the non-localized π-electrons. Nitro groups and halogens are electron-attracting groups while amino groups are electron repelling. Thus the first type of group will tend to localize the π-electrons which will lead to a greater coupling between the electronic and

vibrational states of the molecule and a loss of symmetry. This will decrease the luminescence efficiency according to our considerations above. An opposite effect is produced by the electron-repelling groups. Similar quenching effects by attractive groups are shown in the case of dye molecules. A well-known example of the effect is given by the series, fluorescein (efficiency 0·8), eosin or tetrobromo-fluorescein (efficiency 0·2), erythrosin (efficiency 0·02) [12]. The quenching effect of the halogens increases with their polarizability, that is, according to their ability to localize the π-electrons. They show a similar behaviour when used as quenchers in solutions of luminescent molecules [13]. They have a similar effect on the luminescence of uranyl salts in solution.

Having provided a brief outline of the general relations between molecular structure and the occurrence of luminescence, we may consider now special aspects of luminescence in organic systems as mentioned in the first paragraph.

3. The quenching of fluorescence in solution

In the previous section we have shown how internal processes in a molecule can lead to a non-radiative dissipation of the absorbed energy. This is known as *internal quenching*. The luminescence of molecules may also be quenched by external agents, particularly when in solution, and this is known as *external quenching*. The simplest type of external quenching is that by which a quencher molecule present in the solution takes away the energy of an excited molecule during a collisional encounter with it. The luminescence may be quenched if the excited luminescent molecule initiates a photochemical action or acts as a sensitizer for such action, so that its absorbed energy is used in the photochemical change. At high concentrations of fluorescent molecules in solution, interaction among the molecules may result in the formation of loose association compounds which are only feebly luminescent, or even non-luminescent. Even without the formation of such compounds, the interaction by collisions between molecules at high concentrations will produce what is known as *concentration*

quenching. We shall consider these various quenching processes in more detail in the following sections.

Collisional quenching

In the absence of photochemical activity, the simplest form of collisional quenching will be due to an encounter and an energy exchange between a fluorescent molecule and a quencher molecule. This may occur during the absorption process or during the lifetime of the excited molecule. Distinction between these two states has been made by Franck and his collaborators [14]; they term the first a *statical* encounter and the second a *diffusional* encounter. These authors have made detailed attempts to derive theoretical expressions for the quenching process in terms of such factors as the solution viscosity, the concentration of quencher molecules, the temperature, and the lifetime of the excited fluorescent molecules. The following equation is due to them:

$$\frac{L_0}{L} = \exp(pVNc)\left[1+\frac{NkTxz\tau c}{\eta}\right], \qquad (8.1)$$

where L_0/L is the ratio of unquenched to quenched emission intensity, p is the interaction probability in collision, V is the volume of the interaction sphere, z is the ratio of effective to kinetic collisional distances, x is a function of the radii of the molecules, τ is the mean lifetime of excited molecules, N is Avogadro's number, T is the temperature in degrees K, η is the viscosity, and c is the concentration of quencher molecules. This relation is an improvement on that developed by J. and F. Perrin [15]. It shows that for weak quenchers, which are only effective at high concentrations, only the exponential term of the relation is important and the solution viscosity is not significant. For strong quenchers, which are effective at weak concentrations, the second term of the equation which includes the viscosity is important. Some examples of the different effects of strong and weak quenchers have been given by Bowen [16] for anthracene solutions.

The above relation is not fully adequate to explain the experimental facts, and Bowen [2] has put forward the following

expression which is in better agreement with experimental studies [17, 18, 19]:

$$\frac{L_0-L}{L} = 3pVc\left[\frac{D\tau}{R^2}+\frac{\sqrt{(D\tau)}}{R}\right], \qquad (8.2)$$

where in addition to the factors given in equation 8.1, D is a diffusional constant given by

$$D = \frac{kT}{6\pi\eta}\left(\frac{1}{r_a}+\frac{1}{r_b}\right), \qquad (8.3)$$

which assumes the validity of Stokes's law. R is the sum of the radii r_a and r_b of the fluorescent and quencher molecules respectively: V is given by $4R^3N/3000$. The agreement with experiment for anthracene solutions shows that for a more polar solvent larger values of p are obtained and so the quenching efficiency increases. This again emphasizes the fact that the effectiveness of external quenching depends upon the polarization and the resulting distortion of molecular orbitals.

The advance which is made by the use of equation 8.2, rather than that due to Franck and his collaborators, is shown by consideration of the variation of the luminescence efficiency with solution viscosity for a given quencher concentration. According to equation 8.1 the efficiency, represented by L_0/L, will vary inversely as the solution viscosity. This is not shown by experiment and, in order to explain the discrepancies, Franck and Wawilow postulate that the effective quenching sphere increases with viscosity. Bowen [20] has suggested that the different natures of the collisional processes for solutions of high and low viscosities must be considered when formulating expressions such as 8.1 and 8.2. Equation 8.2, which includes a more precise consideration of the collision processes, does not give a simple inverse form for the variation of efficiency with viscosity. The square root term of this equation takes into account the change in the collision process with viscosity, and provides a closer correlation with experiment. However, insufficient investigations of solutions of high viscosity have been carried out to allow a complete test of these equations to be made.

Fluorescence quenching and photochemical action

The quenching of fluorescence in solution very often involves a photochemical reaction which either affects the fluorescent molecule or sensitizes photochemical changes in other molecules present in solution. A simple example of photochemical action accompanying the quenching of fluorescence is the formation of dianthracene at high concentrations of anthracene in solution. In this case, and in the absence of foreign quencher molecules, the decrease in fluorescence efficiency with increase in concentration is commensurate with the dimeric reaction as demonstrated by Weigert [21]. Some general observations may be made concerning the occurrence of photochemical activity in conjunction with fluorescence quenching. Molecules of high luminescence efficiency are usually highly efficient in initiating photochemical changes when their emission is quenched. However, there does not appear to be a simple relation between the several processes, particularly in the case of complex dye molecules [16, 22]. The simplest behaviour is shown by systems containing aromatic hydrocarbons such as benzene and its homologues in solutions containing quenching agents [16, 22, 23]. Experiments made by Bowen and his co-workers [16] show that for solutions of rubrene in benzene the fluorescence efficiency is about unity when no oxygen is present. When oxygen is present in the solutions the fluorescence is quenched and photo-oxidation of the rubrene takes place. In rubrene solutions of high concentration the quantum efficiency of the oxidation process is about unity. However, this does not mean that fluorescence and photo-oxidation are reciprocal processes. For naphthalene in solution quenching by oxygen is not accompanied by photochemical activity.

Aromatic compounds have also been studied by West and Miller [23]. They have shown how naphthalene may act as a sensitizing agent for the photodissociation of ethyl iodide in benzene solution when it is excited but when its fluorescence is quenched. In the absence of naphthalene the photodissociation of ethyl iodide is produced by 2,600 A radiation, and radiation of longer wave-length (particularly 3,130 A radiation) has little

effect. When naphthalene is present in the solution photodissociation is effected by 3,130 A radiation. The authors have proposed energy diagrams to describe this sensitization process, but it may be briefly described as follows: in the absence of naphthalene the ethyl iodide molecule cannot reach its excited state unless it absorbs 2,600 A radiation. When in the excited state dissociation follows. When naphthalene is present it absorbs in the region of 3,130 A but its fluorescence is quenched. This is because it encounters an ethyl iodide molecule when in the excited state and hands over to the latter its absorbed energy, which raises the ethyl iodide into a high-vibrational level of its ground state. In this state the ethyl iodide molecule can absorb 3,130 A radiation and so the excited state in which dissociation occurs is reached.

In relatively early studies of photochemical action relative to fluorescence Weiss [3, 24] assumed that the collision between the fluorescence and quencher molecules might involve electron transfer from one to the other. In the excited state the ground state of the molecule is empty and might be filled by an electron transferred from a neighbouring molecule. An alternative mechanism proposed was the capture of the excited electron of the fluorescent molecule by the quencher molecule. It is a little difficult to justify these hypotheses unless the normal and excited states of a molecule are non-combining. If, however, the quencher molecule can donate an electron to the fluorescent molecule, the molecule will be reduced: if it takes an electron from the fluorescent molecule, then the latter is oxidized. The first mechanism proved successful when applied to certain dye molecules such as methylene blue. In solution the fluorescence of this molecule is quenched by ferrous ions and the reactions may be described thus:

i. *Excitation process* (D represents the dye molecule):

$$D + h\nu \rightarrow D^* \text{ (excited state).}$$

ii. *Quenching process*:

$$D^* + Fe^{++} \rightarrow D^- + Fe^{+++} \text{ (reduced dye).}$$

iii. *Bleaching process*:

$$D^- + H^+ \rightarrow 2DH + DH_2,$$

where DH_2 is the leuco base of the dye.

iv. *Further reactions.* Pairs of the semiquinone react thus:

$$2DH \rightarrow D + DH_2.$$

Most of these reactions which occur in dye molecules are reversible for certain conditions, such as suitable excitation intensity. Although the electron-transfer mechanism cannot be applied extensively to photochemical action, there is no doubt that it plays an important part in processes such as that described above. The possibility of explaining energy transfer in biological systems by it has been suggested by Weiss [25] and has been discussed by others [3, 4].

Concentration quenching of fluorescence

In the previous section we mentioned the quenching of anthracene at high concentrations in solution due to photochemical formation of the dimeric form of the molecule. In other cases molecules show quenching of fluorescence with increase in concentration of solutions, and Walter [26], in very early studies, attributed this to the formation of association compounds by the molecules. Since that time the formation of these compounds in concentrated dye solutions has been studied by several workers [1, 2, 4, 27, 28, 29, 30, 31]. In solution there is always a likelihood of relatively strong van der Waals' forces (dispersion forces) between molecules with non-localized electrons. By their attraction these forces lead to the formation of molecular complexes which are usually non-fluorescent or only feebly so. Thus these complexes, when formed from fluorescent molecules, will give rise to a quenching of fluorescence known as the *inner filter effect.* This type of quenching is not dependent on diffusional processes, as in the usual concentration quenching by collisions between molecules, and is equally effective in solutions of high or low viscosity [32]. In the case of the simpler aromatic hydrocarbons this inner filter type of quenching often occurs [33]. In dye solutions an

increase in the concentration favours the formation of dimers, but only when aqueous solutions are employed, no effect being observed in alcoholic solution. In aromatic hydrocarbon solutions the absorption spectrum is not much changed by the presence of complexes, but in dye solutions marked changes occur and departures from Beer's law are observed. Dimer

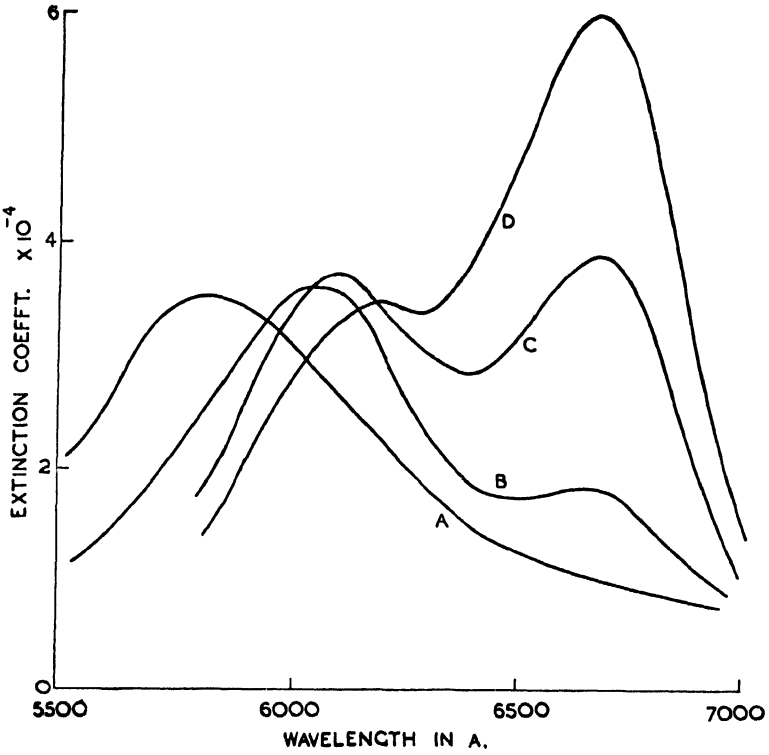


FIG. 113. Absorption spectra of methylene blue 2B dye in aqueous solution. (Lemin and Vickerstaff.) *A*, conc. $3{\cdot}13\times10^{-2}$ mol/litre; *B*, conc. $2{\cdot}5\times10^{-3}$ mol/litre; *C*, conc. $2{\cdot}0\times10^{-4}$ mol/litre; *D*, conc. $2{\cdot}0\times10^{-5}$ mol/litre.

formation results in the appearance of a new absorption band to the long wave-length side of that for the single molecules [28, 29, 30, 31]. Fig. 113 gives a typical example of this change of absorption spectrum with concentration for solutions of methylene blue in water [29]. In this case the dimer absorption band becomes as strong as the normal band for 10^{-3} molar concentrations, but for most dyes its intensity is only a fraction of that of the band for the single molecule at these concentrations. Shift of the dimer band to short wave-lengths as the

concentration is further increased is associated with the formation of polymers of the dye. Other effects may accompany the formation of dimers in solution. Solutions of benzoflavin in water normally exhibit fluorescence of short duration (10^{-8} sec.), but at higher concentrations when dimers are formed the lifetime of the fluorescence is increased to 10^{-2} sec. Under these conditions the enhanced lifetime of the molecule makes it

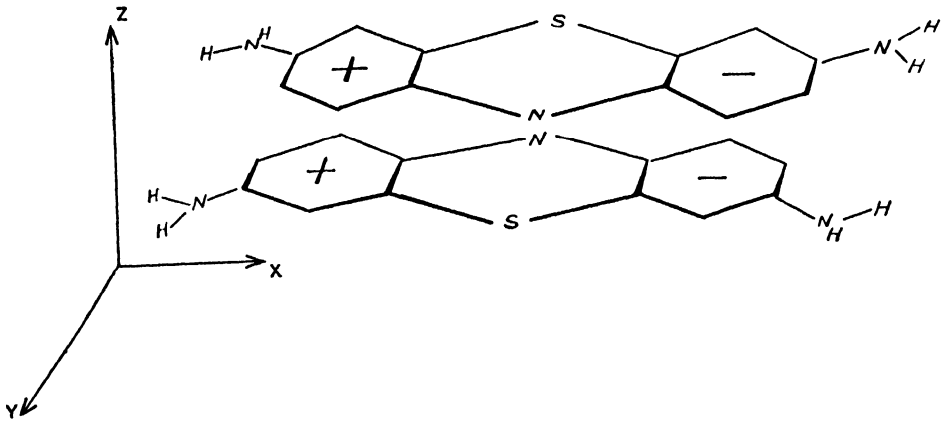


FIG. 114. Schematic diagram of dimeric form of methylene blue dye molecules. (Förster.)

much more sensitive to external quenching by oxygen [1]. The changes in absorption with dimer formation show that the energy states of the system are changed and the dimer possesses two excitation states for each single state of the individual molecules. This should lead to two new absorption bands, but only one is observed, as shown in Fig. 113. This may be explained on the grounds of molecular symmetry. The smaller energy transition is forbidden and only the short wave-length band is observed. Förster [4] has treated in some detail the case of dimer formation in methylene blue. The dimer is shown schematically in Fig. 114, the benzene rings lying in the same plane one above the other. The momentary charge distribution is represented by the plus and minus signs of the figure. Such a system will execute coupled electronic oscillations of two different kinds. In one case the electrons of one molecule move in phase with those of the other molecule, while in the other case they move out of phase with each other and give rise to a

repulsive effect. The first type of oscillations will possess a resultant dipole moment of transition when excited by incident radiation but in the second case there is no resultant dipole moment and the corresponding optical transitions are forbidden. The latter are evidently the slower oscillations corresponding to the long wave-length absorption band. Fig. 115 compares the energy-levels of a dimer with those of a single molecule.

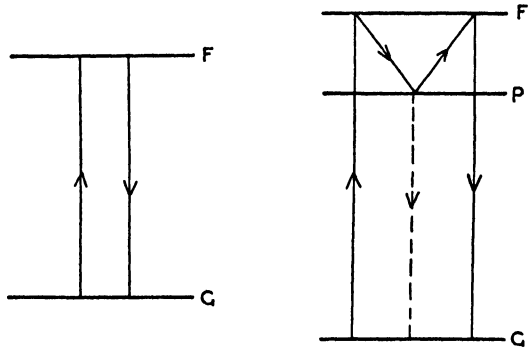


FIG. 115. Energy-levels for single and dimeric molecules. *G*, ground state; *F*, excited state; *P*, metastable state.

The transitions *G–P* and *P–G* are forbidden. If excitation gives rise to the transition *G–F* and the system goes over to the state *P*, its lifetime will be prolonged and phosphorescence of long duration may be observed. This energy diagram was first proposed by Jablonski [34] to explain the phosphorescence of organic molecules: Kautsky [35] applied it to dimer formation and to dye aggregation in solution. It may account for the enhanced lifetime of the benzoflavin molecule when excited in solutions of high concentration. If the enhanced phosphorescence has the same spectral characteristics as the fluorescence, then it must occur by thermal activation of the system from the state *P* to the state *F* followed by the transition *F–G*, and in this case it will be strongly temperature-dependent (see Chap. II, equation 2.3). If, however, the afterglow is of longer wavelength than the fluorescence it may be due to the transition *P–G*, in which case it will have a rate which is independent of the temperature and dependent on the forbidden nature of the transition. We shall consider the phosphorescence states of molecules in sections 5 and 6 below.

4. The polarization of fluorescence

Absorption and emission of light by molecules will depend on the nature of the elementary oscillators which are excited by the absorption or give rise to emission. In general the orientation of the oscillators will make these processes highly directional with respect to the molecular axes. Thus light will only be absorbed if the resulting electronic transition raises an electron to a new orbital which has a nodal plane perpendicular to the electric vector of the incident light. Only those molecules which are suitably orientated will take part in absorption, and if they do not rotate appreciably between absorption and emission then the luminescence will be similarly polarized. A lucid and comparatively simple treatment of polarization has been given by Bowen [1]. The mathematical treatment has been given recently by Wawilow in a comprehensive form [36].

Polarization of fluorescence will be dependent on many factors, such as the lifetime of the excited molecules, rotation due to Brownian motion, solution viscosity, and the occurrence of quenching. Experimental studies furnish information, not only about the elementary oscillators, but also about the quenching processes which may be present. There are two main experimental methods for investigation of the polarization of fluorescence. In one case an attempt is made to fix the orientations of the molecules being studied, so that their major axes are all parallel to each other and at a suitable angle to the incident radiation which need not be polarized: the resulting anisotropy of the system will select the incident radiation having its vector at the required angle to the molecular system, and this will then be shown by the polarization of fluorescence. In the other method of study the molecules are left in random orientation but the incident light is polarized and is only absorbed by molecules which are suitably orientated. This method has been the most widely used, but methods of orientating dye molecules have not been neglected. Jablonski [37] has used anisotropic systems of dye molecules by dispersing the dye in cellophane and drying it under tension applied in one direction only. More recently Zocher [38] has studied the polariza-

tion of fluorescence of dye molecules dissolved in mesophases, such as ammonium oleate, whose molecules form fibrous structures by aggregation : in these fibres the molecules of the dye are constrained to lie with their axes parallel to one another and to the fibre threads.

Early theoretical treatment of the results obtained by the more usual method of irradiation with polarized light were given by Wawilow and Lewschin [39] and by Perrin [40]. These workers assumed that the oscillators of the molecules were simple linear dipoles. Their expression for the degree of polarization in terms of other factors is given below with the usual notation :

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3}\right)\frac{RT\tau}{V\eta}, \tag{8.4}$$

where p is the degree of polarization and p_0 its maximum value in solutions of high viscosity. The polarization p is defined as follows :

$$p = \frac{(I_{\parallel} - I_{\perp})}{(I_{\parallel} + I_{\perp})}, \tag{8.5}$$

where $I_{\parallel}$ is the amplitude of the electric vector of the emission parallel to the electric vector of the incident light and $I_{\perp}$ is the amplitude of the light vector perpendicular to the electric vector of the incident light. In systems involving such simple oscillators p_0 was assumed to be 0·5. In the experimental arrangements it is usual to have the electric vector of the incident light in a vertical plane and to observe the polarization either along the direction of incidence or at right angles to it. The simple formula 8.4 is not adequate to account for the dependence of the polarization on other factors. The theoretical reasons for this inadequacy are several, among them being the fact that the elementary oscillators are assumed to be simple. In molecules which have an appreciable lifetime in the excited state the luminescence is likely to be due to forbidden optical transitions and therefore to oscillator systems of quadripole or even octipole type. This means that the maximum degree of polarization p_0 will be less than 0·5 for all but dipole systems. In recent studies Wawilow [36] has attempted to overcome the

deficiencies of the earlier theoretical treatments and has given mathematical analyses of the effects of dipole and quadripole oscillators on the polarization of fluorescence. Some of his

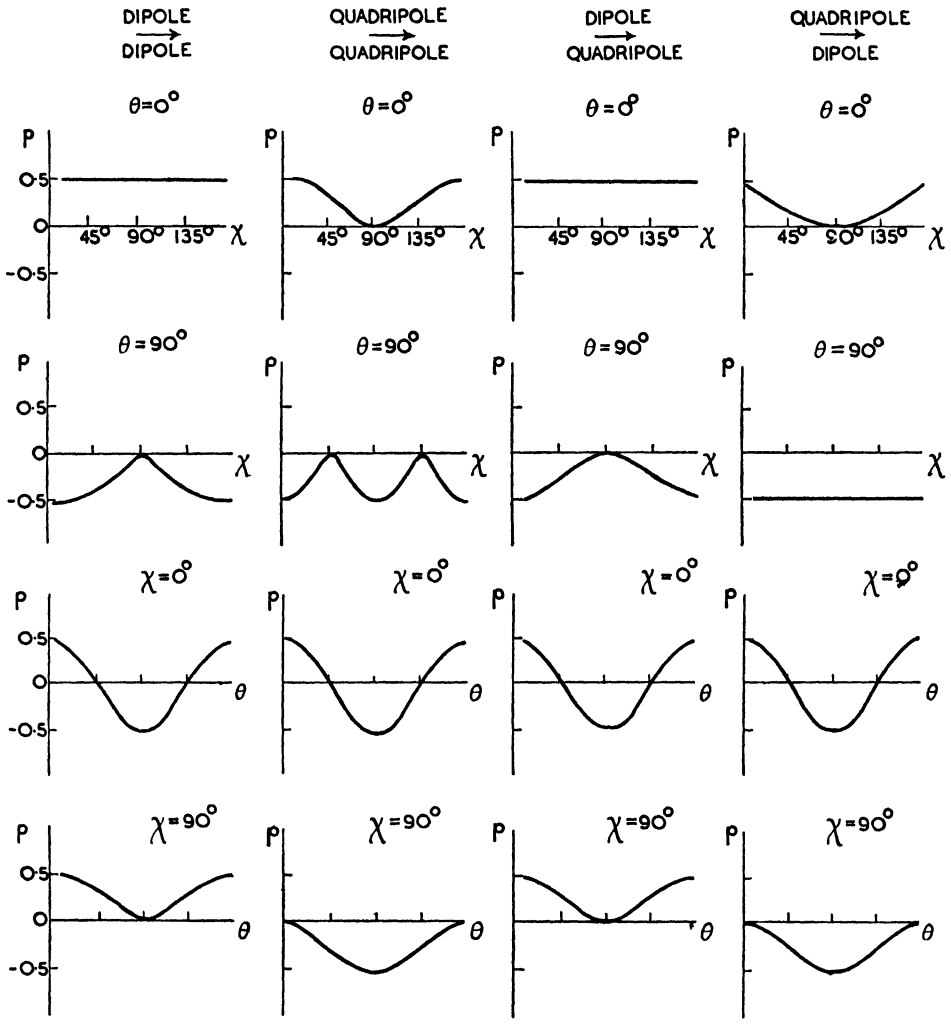


FIG. 116. Dependence of polarization of fluorescence of molecules on the nature of the elementary oscillators for absorption and emission. (Wawilow.) θ is inclination of electric vector of incident radiation to z-axis. Incidence direction is along x-axis. χ is the angle between observation direction for fluorescence and the x-axis. Observations in the xy-plane.

deductions are of practical importance, for they show that the nature of the oscillators cannot be determined only by observation along the direction of incidence of the exciting light or perpendicular to it. They also show that negative polarization

(that is $I_\perp > I_\parallel$) can occur for some conditions. Wawilow's findings are summarized in Fig. 116. The inclination of the electric vector of the exciting radiation is given by θ relative to the vertical axis (z-axis) and the inclination of the observation direction to the direction of incidence (x-axis) by χ. Observation is in the xy-plane. The natures of the oscillator systems for absorption and emission are given at the top of each column of figures. The first oscillator named is that for absorption and the second that for emission. The change from one type of oscillator to the other presumably takes place during the excited lifetime of the molecule when it loses some energy by electronic-vibrational coupling.

We shall now describe some of the experimental studies which illustrate the general characteristics of polarization of fluorescence in molecules and show how they correlate with the theoretical predictions.

Experimental studies of the polarization of fluorescence

Although many investigations of the polarization of fluorescence have been made since its discovery by Weigert [41], we shall find it more useful here to review some of the more recent investigations. We have seen from equation 8.4 that the polarization of fluorescence will depend on many factors. The studies of Pringsheim and Vogels [42] have shown how the above relation for the variation of polarization with solution constitution and viscosity breaks down. The equation predicts a linear relation between the reciprocal of polarization and the viscosity when other factors remain constant. For dilute solutions of fluorescein or trypaflavin in glycerin–water mixtures this relation is followed. It also holds for wider ranges of concentration if other solvents, such as octanol–ether or butanol–ether mixtures, are used. Some results for trypaflavin are given in Fig. 117. However, the values of p_0 which are deduced from the results are much lower than the expected value of 0·5. They are as follows:

Water–glycerin solutions . . .	$p_0 = 0{\cdot}27$
Octanol–ether solutions . . .	$p_0 = 0{\cdot}135$
Butanol–ether solutions . . .	$p_0 = 0{\cdot}1$

Pringsheim and Vogels infer from these low values that the dye has an appreciable mobility of a rotational type in relatively rigid surroundings. It is known that the fluorescence of molecules in highly viscous solutions of gelatin, or in solution in organic plastics, is often unpolarized. Here the molecules freely rotate in regions of almost pure solvent, since the viscosity is a

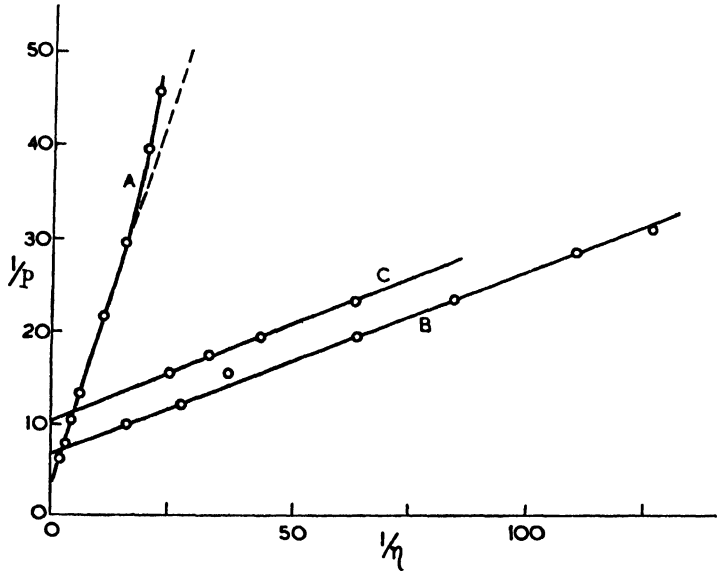


FIG. 117. Variation of the degree of polarization (p) with solution viscosity (η) for trypaflavin molecules. (Pringsheim and Vogels.) A, glycerin–water solutions; B, octanol–ether solutions; C, butanol–ether solutions.

'macro' effect due to widely spaced polymer molecules criss-crossing the solution. The results of the above investigations show that the effective volume V and the lifetime τ of the excited molecule will be variable from one solution to another and for changes in viscosity of the same solution. We remember that for similar reasons the quenching relations of section 3 proved to be inadequate to explain experimental results. It is clear that the use of the macroscopic values of solution viscosity in such cases is not justified, since it may not be of the same order as the localized viscosity around the dye molecules. The departure of p_0 from the expected value of 0·5 is presumably due to the existence of oscillators of greater complexity than those due to simple dipole systems in the molecules. Perrin [40] has given the value of p_0 as 0·143 for a circular oscillator: this may

be qualitatively analogous to a rotating system within some kind of van der Waals' complex formed by the dye in solution. It would seem that the theoretical derivations of Wawilow [36] are sufficient to show that in all cases, except those of simple oscillators, p_0 will be less than 0·5.

The dependence of the polarization of fluorescence on the concentration of the solution and on the presence of quenching agents has been demonstrated by the experiments of Pheofilow and Sveshnikow [43]. They have used solutions of fluorescein, eosin, rhodamine B, and trypaflavin dyes in glycerin. According to equation 8.4 the degree of polarization depends on the life-time of the excited state τ and is improved if τ is shortened, for example, by quenching [44]. However, an increase in concentration causes depolarization and so must be explained by mechanisms other than those of simple collisional quenching due to the concentration. Depolarization also occurs at lower concentrations than those at which quenching due to concentration is evident. In the investigations of the above workers precautions of an extensive nature were taken so that such effects could be carefully distinguished. Corrections were made for the depolarizing effect of secondary fluorescence emission (that is, emission caused by overlap of the absorption and emission frequencies) and in the experiments very thin layers of solution were used. Fig. 118 shows the decrease in polarization and decrease of fluorescence efficiency with increase in concentration of the solution over a wide range of concentrations. Fig. 118*a* is for fluorescein in glycerin and Fig. 118*b* is for trypaflavin in glycerin. For rhodamine B solutions, and using radiation of 3,600 A instead of the usual 5,460 A wave-length, negative polarization decreasing with concentration is observed. A similar change of sign for the polarization is observed for other dyes, and it is presumably due to the different natures of the absorbing and emitting oscillator systems in the molecules [1]. For high concentrations the depolarization in trypaflavin reaches a stationary state and then begins to decrease as shown by Fig. 118*b*: this effect is discussed later. From the above experimental results it is found that the reciprocal of the

degree of polarization p varies linearly with the concentration c as shown in Fig. 119. Pheofilow and Sveshnikow suggest a

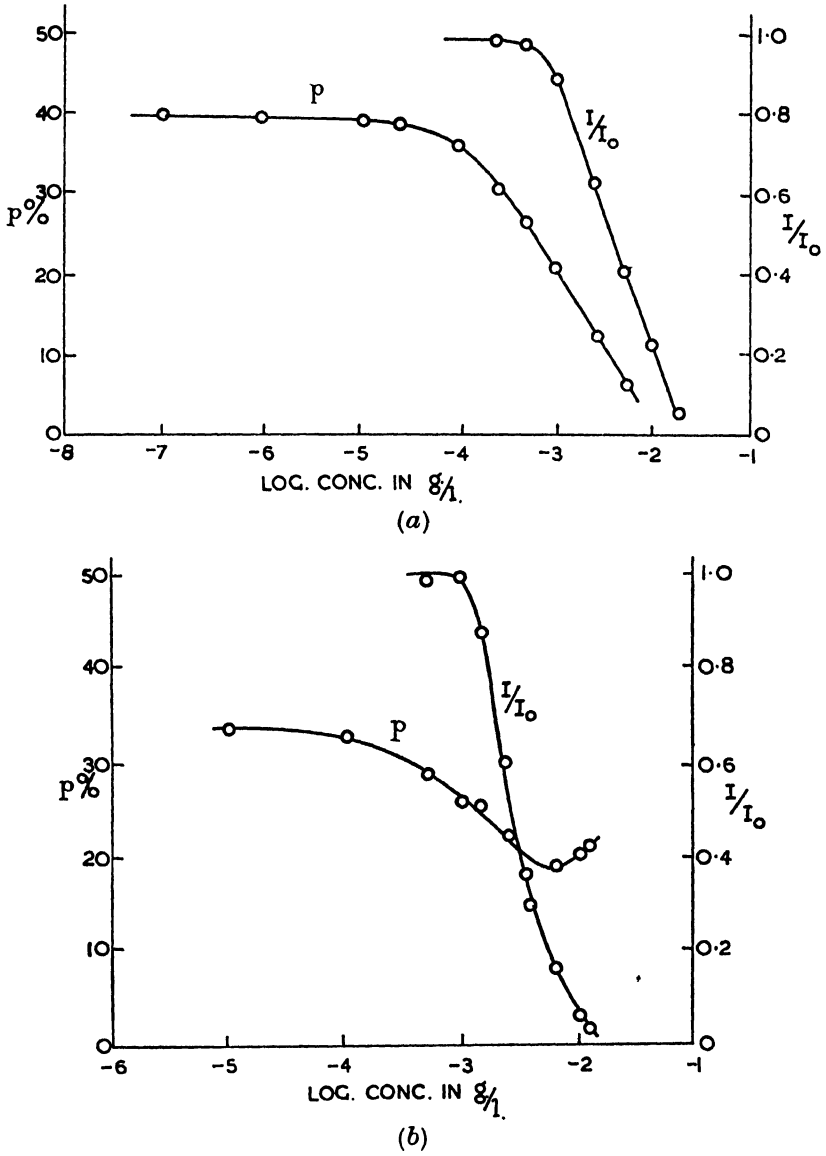


FIG. 118. Variation of degree of polarization (p) and efficiency (I/I_0) of fluorescence with dye concentration in solution. (Pheofilow and Sveshnikow.) (a) Fluorescein in glycerin; (b) trypaflavin in glycerin.

modified form of equation 8.4 to include this effect of the concentration which is as follows:

$$\frac{1}{p} = \frac{1}{p_0} + \left(\frac{1}{p_0} - \frac{1}{3}\right)\frac{RT\tau}{V\eta} + Ac, \tag{8.6}$$

where A is a constant. Other experiments in which quenchers were present in solution show that the depolarization effects decrease as the degree of quenching increases, which may be

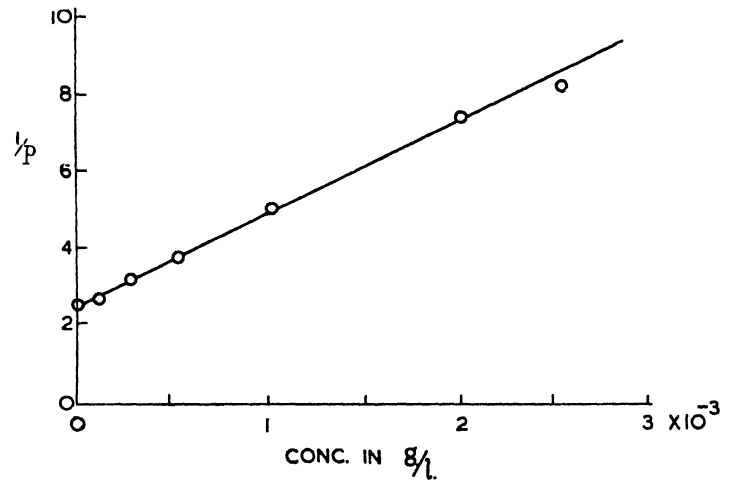


FIG. 119. Variation of degree of polarization (p) with solution concentration showing hyperbolic relation. (Pheofilow and Sveshnikow.)

ascribed to the decrease in the lifetime τ. When the temperature of the dye solutions is increased two effects are observed:

(a) The depolarization due to rotation is increased because of the lowering of the viscosity and the increase in Brownian motion.

(b) The increase in temperature shortens the excited lifetime of the dye molecules and so counteracts the first effect.

At low concentrations the effect (a) predominates, but at higher concentrations the second effect (b) increases and the depolarization is diminished. This explains the behaviour of trypaflavin shown in Fig. 118b. The authors suggest that all dyes should behave in this way, but that in most cases the effect occurs at concentrations for which the fluorescence efficiency is too low for polarization measurements to be made.

An important problem has been raised by these results and has been discussed by Förster [4]. Since the depolarization due to concentration of solution occurs at concentrations lower than those necessary for concentration quenching, and since depolarization is due to the effect of collisions, then the interaction

distances for the encounters between molecules must be very large. It is certain that collisions occur between excited and unexcited molecules and not between two excited molecules. We shall discuss other polarization effects which occur in molecules in rigid media in section 6.

5. The luminescence of polymerized dye systems

The tendency of dyes to form dimers in aqueous solution and its effect on luminescence have been described in section 3. In this section we shall consider the properties of dye solutions when polymers are formed. In the previous sections the luminescent systems discussed have consisted of a few molecules at the most, but in this section we shall consider systems containing thousands of molecules which behave as one unit with respect to their absorption and emission.

In 1936 Jelley [45] reported new absorption and emission bands for dye molecules which appeared during the salting out of cyanine dyes from solution. In this process a phase occurred in which the dye molecules formed aggregates having a thread-like structure; this was visible with the ultra microscope [46]. Confirmation of the phenomena was given by the independent studies of Scheibe and his collaborators [47]. When this thread-like phase appeared a very sharp absorption band appeared at long wave-lengths as shown by curve *A* of Fig. 122. An emission having a spectrum coincident with that of the absorption was also observed. The absorption was only for light incident on the threads with its vector parallel to the thread axis. The fluorescence was polarized with similar orientation of vector. Further salting out of the dye caused these bands to disappear and weaker bands to occur at still longer wave-lengths. Scheibe ascribed the threads to long chains of polymerized dye molecules and since the first studies there have been many investigations of such systems. A review of the experimental results has been given by Förster [4]. Experiments on dye absorption on silver halide crystals made by Sheppard and his collaborators [48] show that in this case the dyes form similar structure and lie in 'card-pack' formation on the crystal surfaces. The mole-

cules have their planes approximately parallel and are separated by a distance of about 3·8 A. Recent X-ray analyses by Scheibe and his co-workers [49] indicate a structure for the polymer threads which is shown schematically in Fig. 120 for pseudo-isocyanine. The molecular planes of adjacent molecules are thus not exactly perpendicular to the thread axis. The momentary charge distribution in the molecules is indicated by

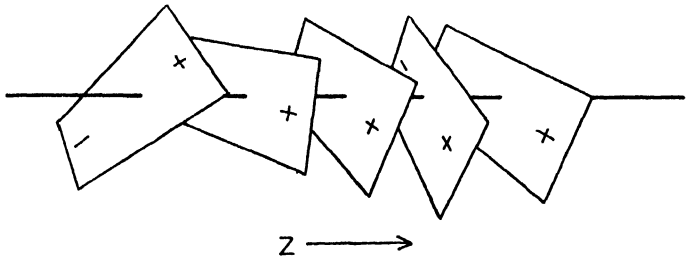


FIG. 120. Schematic diagram of a polymer thread formed by cyanine dyes in aqueous solution. (Förster.)

the plus and minus signs. Scheibe assumes that the molecules of the thread are held together by van der Waals' forces due to the hydrocarbon systems, but that the electronic states of the thread may be treated collectively [50]. However, Sheppard [51] has suggested that water molecules are involved in the thread structure, making the essential links between adjacent molecules. He disagrees with the collective electron treatment proposed by Scheibe. There are other experiments due to the latter which give support to the collective treatment [52, 53]. For instance, the fluorescence of the polymers is extremely sensitive to quenching agents when compared with that of single molecules. The fluorescence of cyanine dye polymers is quenched by one molecule per 10^3–10^6 dye molecules. Thus it appears that collision of the quencher molecule with any part of the polymer thread, which may consist of thousands of molecules, can remove the excitation energy. Such effects are only likely in a collective system. The very sharp nature of the absorption and emission bands and their coincidence indicates a resonance transition for the luminescence, which has a very short duration (less than 10^{-9} sec.). It also indicates very little coupling between the electronic and vibrational states of the polymer thread.

A theoretical discussion of the polymers described above has been attempted by Förster. He proposes an energy-level scheme which is given in Fig. 121 and may be compared with that of Fig. 115. The n molecules of the polymer are assumed to give rise to n excitation states, and if n is of the order of thousands, then these levels will form a continuum whose

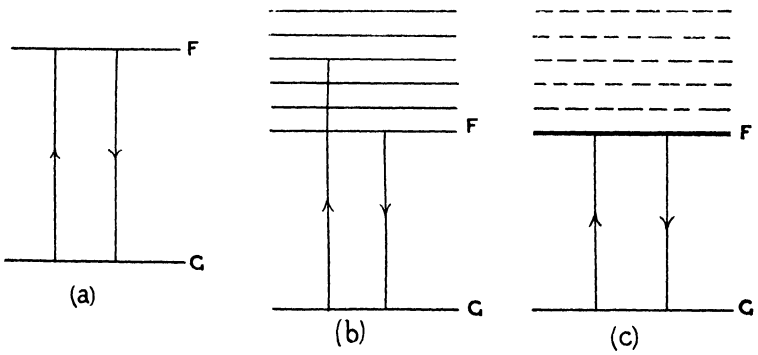


FIG. 121. Energy-level scheme for single molecules and for polymer threads. (Förster.) (*a*) Single molecule. (*b*) Polymer threads: oscillations perpendicular to thread axis. (*c*) Polymer threads: oscillations parallel to thread axis. The F state has a very short lifetime (10^{-9} sec.). The transition FG has a very high probability.

width depends on the strength of the coupling between molecules in the thread. The narrow absorption and emission bands are assumed to be due to transitions between the ground state G and the lowest state of the continuum F. These correspond to oscillations parallel to the thread axis which are permitted from symmetry considerations. Thus the lifetime of the state F is short. For light incident on the thread having its vector perpendicular to the thread axis, transitions to the continuum from the ground state are permitted, but the state F is finally reached by degradation of the energy. Thus for either mode of absorption the emission is the same. This means that in the second case negative polarization should be observed. This is found to be so in experiment. Förster estimates that the time of transit of energy from one end of the polymer chain to the other is about 10^{-14} sec. Thus the oscillations of the collective system appear to be greater than those of the atomic nuclei of the individual molecules.

Mixtures of cyanine dyes in polymer form are stated to give

one absorption band lying at an intermediate position between those of the separate polymers [54]. Scheibe uses this fact as evidence for his collective electron model. Other studies by Sheppard [51] show that discontinuities occur in the absorption-band shift as the ratio of the two dyes is altered. It is probable that the intermediate band may be due to the superposition of

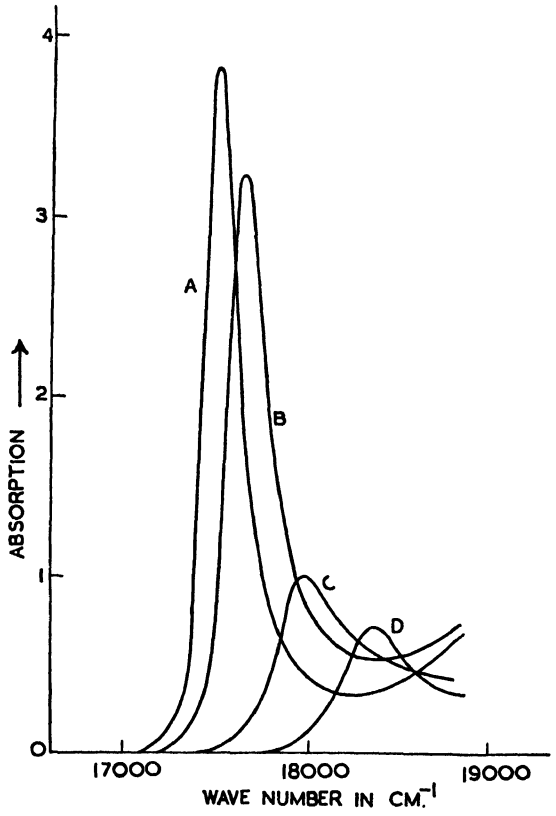


FIG. 122. Absorption spectra of mixed polymer threads. (Scheibe.) Dye I is diethyl-ψ-cyanine. Dye II is diethyl-ψ-selena cyanine. *A*, 100 per cent. I: 0 per cent. II. *B*, 67·2 per cent. I: 32·8 per cent. II. *C*, 25·5 per cent. I: 74·5 per cent. II. *D*, 0 per cent. I: 100 per cent. II.

more than one band since it is not as sharp as those for the individual polymer solutions. Absorption spectra for the dye mixtures are given in Fig. 122 which show this difference. At present there does not appear to be sufficient evidence to distinguish between the different theories of Scheibe and Sheppard. However, there is no doubt that the unusual properties of the polymerized dye systems are due to a resonance effect in the polymer chains.

6. Fluorescence and phosphorescence of rigid organic systems

When dye molecules are dispersed in solid solution or adsorbed to solid surfaces they often exhibit phosphorescence. In a rigid environment many of the usual quenching influences are absent since diffusional processes are inhibited. The occurrence of phosphorescence in rigid systems has been known for a long time [55], but systematic study begins with the work of Jablonski [34] and Kautsky [56]. Some of the most precise investigations have been those of G. N. Lewis and his collaborators [57]. We shall discuss below some of their results for the system comprising fluorescein in boric acid. In acid solution the fluorescein exists as a cation and has a different molecular form from that in the more usual sodium salt (uranin).

The phosphorescence of fluorescein in boric acid

The energy-level scheme of Fig. 115 *b* for dimers is so successful in the interpretation of the phosphorescence characteristics of fluorescein in boric acid that it might indicate the existence of pairs of fluorescein molecules giving rise to phosphorescence. This idea is supported by recent studies of Kautsky and Müller [62] which we shall describe later. The luminescence transition F—G in fluorescein gives rise to a blue emission, while the transition P—G corresponds to a yellow emission. Phosphorescence may be due to either transition, but it will have quite different characteristics in each case. Phosphorescence due to thermal activation from P to F will be intensely temperature-dependent, but that due to the transition P—G will be independent of temperature and will be governed by the forbidden nature of the transition. These two processes have been denoted by the symbols α and β respectively. The general characteristics of phosphorescence are as follows:

(*a*) At room temperature the fluorescence emission is blue and in phosphorescence the α-process (blue emission) predominates, as shown by curve A of Fig. 123.

(*b*) At low temperatures the fluorescence emission is the same as that at room temperature but the phosphorescence emission

is yellow and due entirely to the β-process, as shown by curve B of Fig. 123.

(*c*) Phosphorescence decay curves for fluorescein in boric acid at room temperature and at liquid-air temperature are given in Fig. 124. In the measurements the α- and β-processes

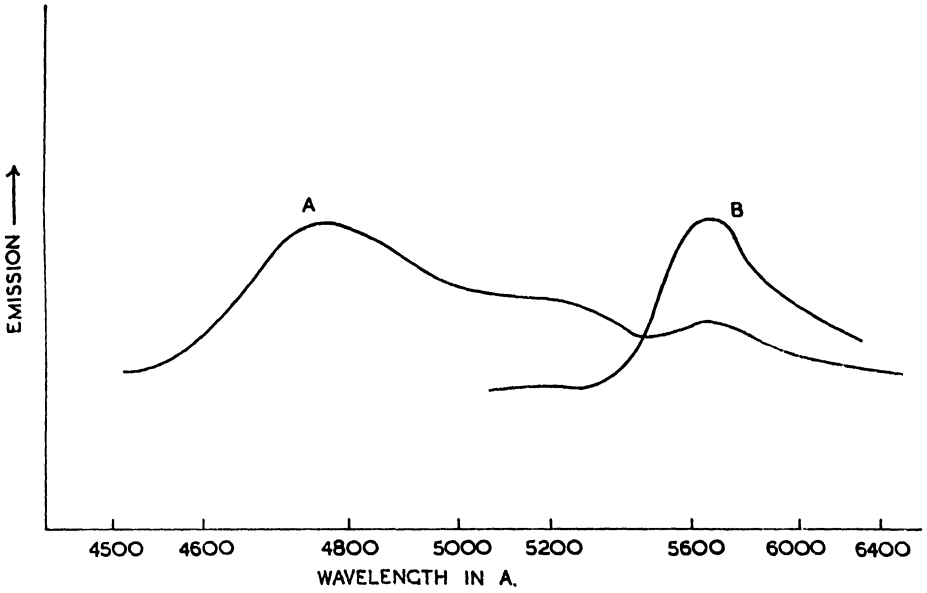


FIG. 123. Phosphorescence spectra for fluorescein in boric acid. (Lewis *et alia.*) *A*, 20° C.: *B*, −40° C.

are measured separately by means of optical filters. The decay curves for both processes are exponential in form, but the decay rate of the α-process varies exponentially with temperature. The thermal activation energy for the α-process, as obtained from the exponent, is about 0·37 eV. The value for the energy difference between the P and F states obtained from the emission spectra is about 0·4–0·45 eV. The thermal and optical values show good agreement if the Franck–Condon principle is borne in mind. The β-process is independent of temperature, having a half-lifetime of about 2 sec. It is characteristic of a multipole oscillator.

The polarization of phosphorescence

In rigid systems the molecular orientation will be fixed and hence, if polarized light is used to excite the molecules, the

emission may also be polarized. For fluorescein in boric acid the phosphorescence of the α-process is polarized, but not to any high degree (max. 15 per cent.): the β-process exhibits very little polarization. Since polarization is observed for the α-process, which involves a considerable lifetime in the *P*-state,

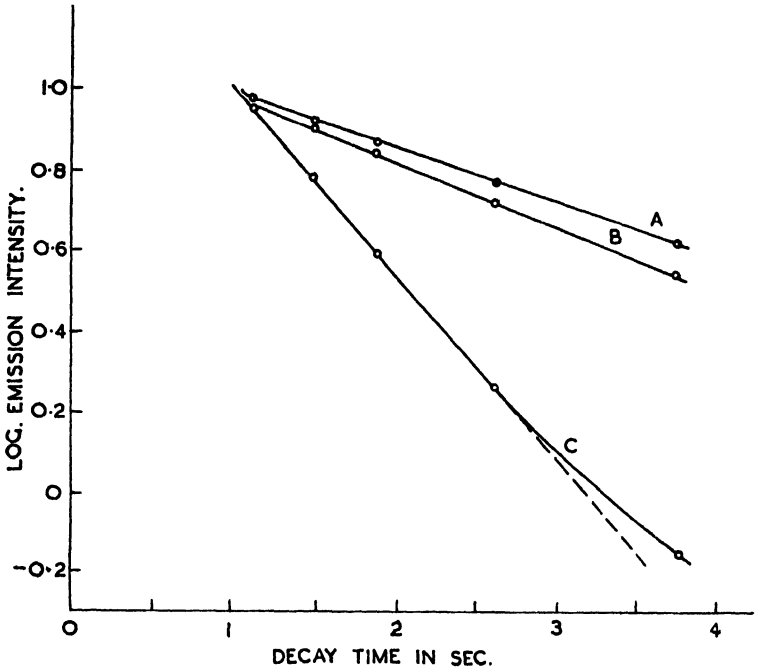


FIG. 124. Phosphorescence decay of fluorescein in boric acid measured with optical filters. (Lewis *et alia.*) *A*, 20° K. (orange filter): β-process; *B*, 88° K. (orange filter): β-process; *C*, 296° K. (blue filter): α-process. Arbitrary light units different for each curve.

the molecules cannot have any freedom of rotation and appear to be free from external depolarizing influences. In some cases the β-process shows negative polarization, but the degree of this is always small (0·05 per cent.) [37, 59]. We can understand the absence of polarization in this process since the elementary oscillators are of multipole order.

The absorption characteristics of phosphorescent molecules

When fluorescein in boric acid is subjected to strong excitation its normal absorption band decreases in intensity and new bands appear at longer wave-lengths. This effect is shown by the absorption spectra of Fig. 125 for an unexcited molecule

and for a fully excited molecule. The reason for the appearance of new bands and the decrease of the normal absorption band is that, with increasing excitation, the number of molecules in P-states increases and the number available for normal absorption diminishes. The new absorption bands are ascribed to transitions from P-states to higher excitation states P' and P'',

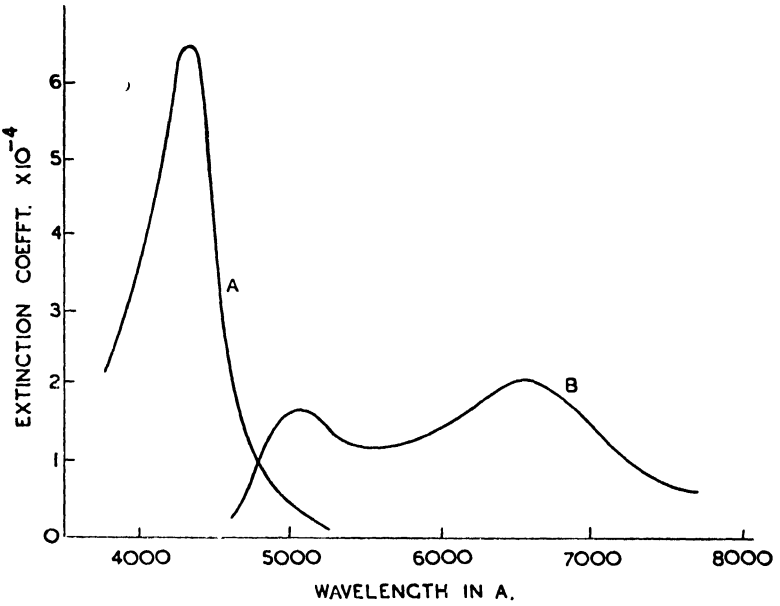


FIG. 125. Absorption spectra of fluorescein in boric acid. (Lewis *et alia*.) *A*, all molecules in normal state. *B*, all molecules in phosphorescence (P) states.

which have been shown to be triplet states [57, 58]. The energy-level scheme suggested for these new states by Lewis is given in Fig. 126. In the P-states the molecule exists as an isomer of the normal molecule and the system becomes paramagnetic. The two long-wave-length absorption bands of Fig. 125 are due to the transitions P—P' and P—P''. Transitions from P' and P'' states to the ground-state P of the isomer will give rise to luminescence having different characteristics from that due to F—G or P—G transitions described above. For example, crystal violet ion in solution in glycerol at low temperatures is changed to other isomeric forms when excited. The new luminescence emission for the P'—P transition is green, but the normal α-process in crystal violet has a red luminescence. Some workers [60] have attributed

the P-states to tautomers of the molecule, but Lewis considers this hypothesis to be unlikely. A full review of the work of Lewis and others on the P-states of molecules in rigid media has been given recently by Kasha [58].

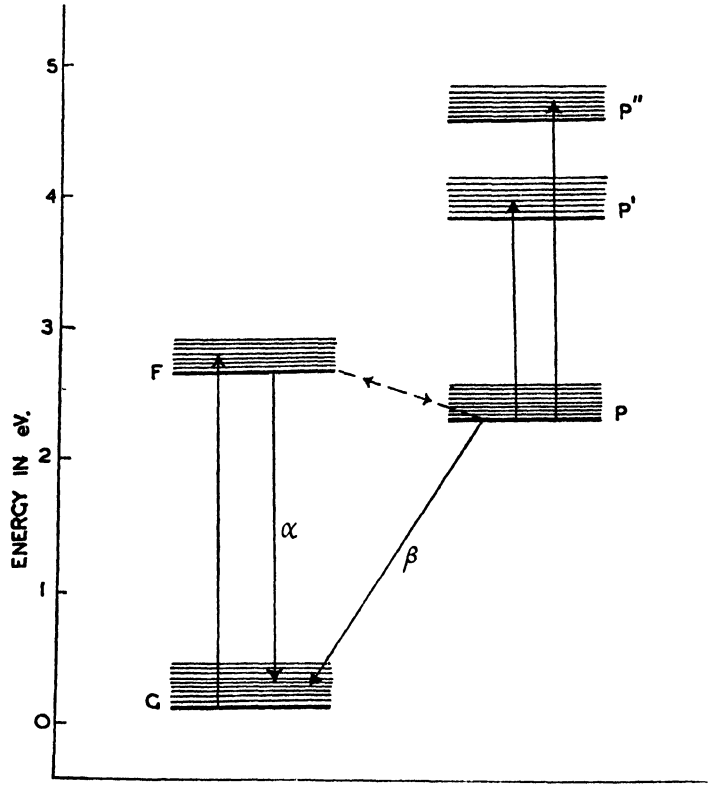


FIG. 126. Energy-level diagram for fluorescein in boric acid. (Lewis *et alia.*) The excitation states of the normal and isomeric (P) molecule are shown.

The quenching of luminescence in rigid molecular systems

When luminescent molecules are held in rigid media the normal quenching due to diffusional processes is not present. However, in adsorbed systems *in vacuo* quenching can often be produced by the admission of a very small amount of oxygen. The quenching effect is observed in fluorescence and phosphorescence. The luminescent molecules can also act as sensitizers for photochemical reactions as in liquid solutions. Some of the most interesting studies in this field are due to Kautsky [56, 61]. He has shown that the phosphorescence of dye molecules

adsorbed on surfaces such as those of silica gel is much more sensitive to quenching by oxygen than the fluorescence. Complete extinction of phosphorescence occurs at oxygen pressures which do not have any noticeable effect on the fluorescence. This is because the long lifetime of the excited molecules (in P-states) increases the probability of interaction with oxygen molecules. Kautsky has shown that in oxygen-free liquid solutions the excited lifetime of benzoflavin molecules is prolonged [35].

Kautsky has studied the photochemical sensitization by luminescent molecules by introducing the leuco base of a non-fluorescent dye. This leuco base, adsorbed together with the luminescent molecules on the solid surface, will be colourless. When oxygen causes quenching a coloration is observed, and it is assumed that the oxygen takes up the excitation energy of the fluorescent molecules and passes into an excited state, probably $1\Sigma_{O_2}$ or $1\Delta_{O_2}$; it can then oxidize the leuco base, which is spatially separate from the fluorescent molecules, producing dye molecules. There is no water present in the evacuated system used. In some more recent experiments on quenching by oxygen Kautsky and Müller [62] have discovered a new effect and have suggested its practical application as a very sensitive oxygen detector. At low temperatures excited fluorescent molecules show only β-phosphorescence, but on warming in the dark they emit thermoluminescence with the same spectral distribution as the fluorescence due to the P—F—G transitions. Kautsky and Müller have found that at low temperatures, when phosphorescence is proceeding, introduction of oxygen causes an intense burst of emission as in thermoluminescence. This effect, having the same emission spectrum as the fluorescence, is only observed when high intensities of excitation are used. It is not observed after long times of phosphorescence. Kautsky and Müller have suggested that the stimulating effect of the oxygen occurs in paired molecules, but their evidence does not appear to justify this assumption. The mechanism of interaction of the oxygen with the fluorescent molecules is not yet understood.

7. Luminescence characteristics of pure and impurity-activated organic solids

Some organic solids exist which closely resemble the pure and impurity-activated phosphors of inorganic type. The best known among these are such hydrocarbons as naphthalene and anthracene. These solids show luminescence characteristic of their own molecular structure when in a very pure state. However, they are very sensitive to traces of other members of the homologous series. Naphthalene, which contains a small trace of anthracene, has a luminescence which is characteristic of the anthracene molecules present in solid solution. A similar effect occurs in anthracene crystals which contain traces of naphthacene and in naphthacene crystals containing pentacene. Of these systems, which we may think of as impurity-activated organic phosphors, that comprising anthracene with inclusions of naphthacene has been studied in detail [63, 64].

When very pure anthracene is excited its absorption and emission spectra are as shown in Fig. 111. All the absorption bands have wave-lengths less than 4,000 A. In its pure state naphthacene is only feebly luminescent, as shown by Fig. 127*b* [65]. It has absorption bands at 4,250, 4,530, and 4,850 A and emission bands at 4,980, 5,530, and 5,740 A. When naphthacene is introduced into anthracene in small amounts (1 part in 10^4), it suppresses the emission of the pure anthracene and gives rise to luminescence of high efficiency having spectral bands at the wave-lengths given above for pure naphthacene. Excitation can take place in either the absorption region due to anthracene or that due to naphthacene. The curves of Fig. 127*a* show that the emission reaches a maximum efficiency as the naphthacene concentration is increased. At the optimum concentration the quantum efficiency for the luminescence process is about 85 per cent. at low temperatures and about 75 per cent. at room temperature. When the two hydrocarbons are present in liquid solutions they do not show the effect. The curves of Fig. 127*b* show that in liquid solution the two different molecules behave as separate entities. Energy transfer, which is possible between them in solid solution, is inhibited

in liquid solutions by the presence of intervening solvent molecules. Experiments in which the hydrocarbons were dissolved in gelatin indicate, by the absence of the transfer effect, that the crystalline state is necessary for efficient energy transfer between the different molecules. Bowen has suggested that

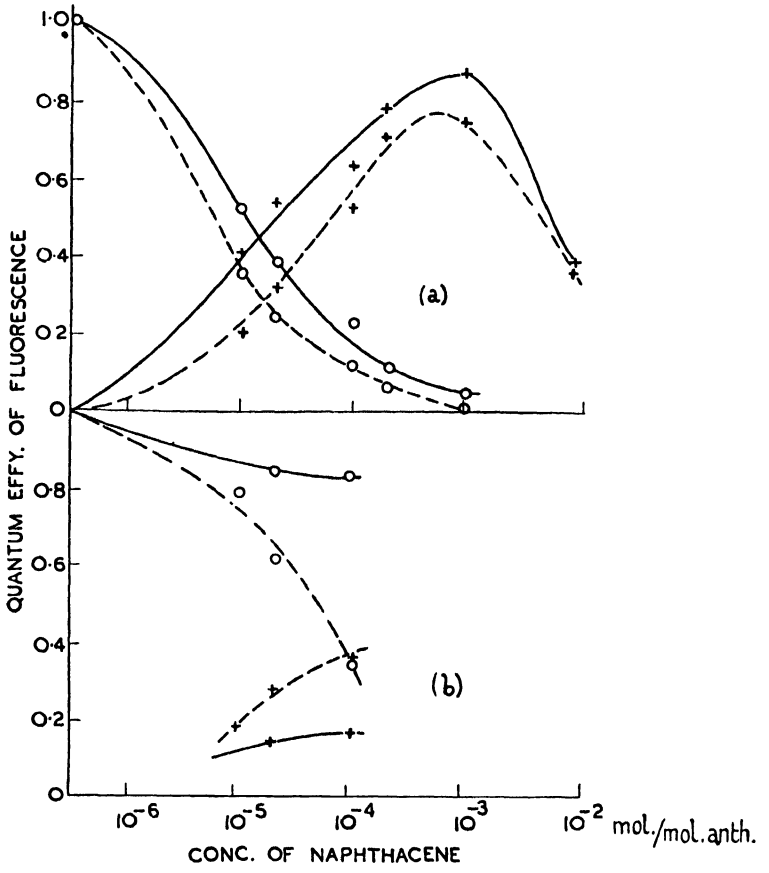


FIG. 127. Fluorescence of naphthacene in anthracene. (Bowen and Mikiewicz.) ○ anthracene fluorescence. + naphthacene fluorescence. (*a*), solid solution: —— at −180° C.; – – – at room temperature. (*b*), In gelatin sol: —— sol mixture; – – – solid solution.

the transfer of energy from anthracene to naphthacene molecules after absorption in the anthracene molecules is due to a resonance process similar to the exciton process in inorganic solids. It has been shown that it does not occur by reabsorption of the anthracene fluorescence by the naphthacene molecules, for such a process would not explain the high quantum efficiency

found in experiment. The low efficiency of the fluorescence of pure naphthacene when compared with that in solid solution in anthracene may be connected with the different environments in the two cases. Pure naphthacene crystals have a triclinic structure, but in anthracene crystals the naphthacene molecules are embedded in a monoclinic system.

Scheibe and Kandler [66] have observed that in pure naphthalene a new absorption band appears at longer wave-lengths than those for the molecules in liquid solution. This band only occurs for light incident with its vector in the plane of the crystal face. Their observations have been confirmed by Sheppard [51]. Since the molecular planes are parallel to each other in these crystals, and stacking effects similar to those for dyes adsorbed on surfaces can occur, it might be thought that bands similar to those of the polymers of section 5 above would be present. However, the observed band corresponds to electron oscillations in the molecular planes and not perpendicular to them, as is the case for the polymer threads. The use of polarization measurements to determine the orientations of impurity molecules embedded in organic crystals began with the studies of Krishnan and Seshan [67]. They found that the naphthacene molecules in anthracene take up positions with their planes parallel to those of the matrix molecules. Chakravarti and Ganguly [68] have reviewed the polarization characteristics of the simple aromatic hydrocarbons in the solid state. The absorption bands of such crystals as anthracene in the near visible region are for light having its vector in the plane of the molecules. The fluorescence is similarly polarized.

Some organic crystals show phosphorescence, for example, tetraphenylmethane, whereas for anthracene-naphthacene systems the emission is of very short duration (10^{-8} sec.). The phosphorescence of tetraphenylmethane and of some of its derivatives has been studied by Clapp [69]. His results, which are of a qualitative nature, are given below in Table II.

The decay is evidently due to an α-process involving P-states. No estimates of the purity of the specimens have been given: the emission colour is stated to be blue-green.

Table II

Phosphorescence in Tetraphenylmethane at Different Temperatures

Temperature in °C.	*Approximate decay time in sec.*
130	No visible persistence
125	2
80	4
40	9
20	23
−20	35

CHAPTER IX

SYNOPSIS

In this chapter we shall consider briefly some of the outstanding problems of luminescence which will have become evident from the substance of preceding chapters. We shall also suggest future experimental approaches which may help in their solution. We first discuss the inorganic phosphors.

1. Inorganic luminescent materials

The majority of inorganic phosphors which are of interest to the research worker and to the practical user are of the impurity-activated type and are usually only obtainable in the form of microcrystalline powders. Exceptions to this are diamond and the alkali halides activated by heavy metals. The relatively precise data which we possess on the latter are due to the accuracy with which optical absorption and emission measurements can be made on such large and homogeneous crystals. It would therefore seem desirable to make renewed efforts to obtain other phosphors in the form of single crystals of useful size or in the form of uniformly evaporated layers. Some success in evaporating fluoride types of phosphor appears to have been achieved already [1]. The absorption bands of the matrix crystals of zinc sulphides and zinc silicates have already been determined in spite of their intractable physical form, but, as later paragraphs emphasize, it is the detailed structure of the lattice absorption-edge and the very weak absorption due to impurity centres which need investigation.

The nature of luminescence centres

The most important entities in any phosphor are the luminescence centres. In some solids these are relatively well-defined systems of atoms or coordination groups. However, in most impurity-activated materials the luminescent centres have no well-defined structure. It is these materials, which include zinc sulphides and zinc silicates, which show the most interesting luminescence characteristics. We have seen in Chapter IV that

such properties as long afterglow, photoconductivity, and sensitivity to long wave-length radiation are very dependent on the phosphor constitution, particularly on the specific impurity activators. We also know that the efficiency of the luminescence does not behave as if it were an intrinsic property of a simple luminescence centre but is very dependent on the conditions of excitation, including the intensity and wave-length of the radiation absorbed and the phosphor temperature. At present we have no adequate explanation of its behaviour and much more exhaustive studies are necessary on more types of phosphor.

Some recent studies mentioned in previous chapters suggest that luminescence centres in zinc sulphide phosphors can be very large and might include as many as a thousand lattice atoms. This is of theoretical importance since it calls into question the validity of the energy-band scheme for crystalline phosphors. It cannot be assumed, as in the past, that the lattice energy-states will remain unperturbed in the region of the impurity atoms. A further problem, which is usually neglected in theoretical considerations, is that of the mosaic structure of crystals. If the mosaic blocks of phosphor crystals are of the same order of size as the luminescence centres, then a drastic modification of theory will be necessary. In the next paragraph we consider these questions further in discussing electron trapping-states.

Phosphorescence and electron traps

The development of the thermoluminescence experiment by Randall and Wilkins [2] has provided a powerful method of studying the metastable trapping-states for electrons in phosphors and their effect on phosphorescence. However, their experimental studies have furnished very little information about the physical nature of the trapping systems or their location in phosphors. We have reviewed some more recent experiments in Chapter IV which suggest that the trapping-states in many phosphors are produced by the introduction of the activator impurity and that they may be contained within

the large complex emission centres discussed above. We know from the studies of dielectric changes in phosphors due to electron traps that the effective size of the traps is of the same order as that of the emission centres and that they cannot be ascribed to any one atom. However, the present data are not at all precise and we need larger phosphor crystals to make a more accurate study. Recently there have been many different investigations of the action of long wave-length radiation in emptying electron traps [3]. Numerous measurements of the stimulation and quenching spectra are included in these measurements, but there have been very few attempts to measure directly the absorption spectra which occur when electron traps are filled. In all these studies the experiments have been made on rather complex phosphors having more than one activating impurity, the reason for this being their practical importance. What is needed to understand these ejection processes is a thorough study of simple phosphor systems. For example, it is known that the alkali halide phosphors and diamond can be stimulated by infra-red radiation, but no quantitative measurements have been made on these solids. A reversion to these materials might provide a better appreciation of the marked difference between the mechanisms of thermal and optical activation of trapped electrons.

Cathodoluminescence

Our knowledge of cathodoluminescence processes is very small when compared with that obtained for photoluminescence mechanisms, although the experimental studies have been quite as extensive. The reason for this is, as stated in Chapter VI, the use of complex layers of phosphor powders in experiment. While the majority of workers have been concerned with the improvement of phosphors for practical uses, they have attempted to give some qualitative theoretical explanation of their results. A fundamental approach to cathodoluminescence will demand a simplification of experimental conditions which is, however, not beyond realization at present. Here again the production of large phosphor crystals or of evaporated

layers is essential. By this means the complex surface conditions would be removed to a great extent. There is also a need for independent studies of the mechanisms of secondary emission and electron penetration in phosphors and in non-luminescent insulators. At present theoretical studies make use of penetration laws which were only verified for thin metal foils and for electrons of much higher energies than those used in cathodoluminescence experiments.

Another investigation which will be necessary to an understanding of cathodoluminescence is that of the destructive effects of electrons and other particles on insulating materials.

2. The luminescence of organic molecules

We have seen in Chapter VIII that the characteristics of luminescence in organic molecules are better defined than in inorganic phosphors. As a result of the application of wave-mechanical theory to organic molecules we can now relate the luminescence of a molecule to certain characteristics in its structure. For example, we associate the occurrence of luminescence with the structural stability due to the presence of conjugated ring systems and non-localized electron orbitals. We can also relate the phosphorescence characteristics of molecules to their isomeric forms and to other changes in their properties such as absorption and magnetic susceptibility variations [4].

The recent discovery of long-chain dye polymers having unique luminescence characteristics has raised the problem of explaining the energy-transfer processes along the polymer chains. A similar problem occurs for the solid aromatic hydrocarbons, such as naphthalene and anthracene. In both these systems a very large number of molecules are held together in a regular formation by dispersion forces. This results in a very efficient electronic resonance between the molecules and the systems may be treated collectively. It is not likely that there is any electron sharing among the molecules and the very rapid transit of energy from one extremity of the system to another excludes any process involving movement of atomic nuclei.

The application of the hydrocarbon crystals of naphthalene and anthracene to the counting of nuclear particles by observation of the scintillation produced has shown that the transfer of energy from the incident particle to the emitting molecules is very efficient. Since in this case there will be considerable production of free electrons in the crystals, a further problem is raised. It is that electron excitation of most materials of inorganic type is relatively inefficient while in some scintillation counters particle excitation may be quite efficient. It is clear that there is room here for considerable study of these processes.

3. Luminescence and phenomena in non-luminescent solids

Since luminescence involves the excitation of valence electrons in solids, it will be closely related to other processes which result from these electrons, and which are not confined to luminescent materials. Among these we would make brief mention of photoconductivity, dielectric effects, and semi-conduction. It is known that at elevated temperatures where the luminescence has disappeared, phosphors become semi-conductors. Some very preliminary experiments show that they are of the excess type. The detailed investigation of these high-temperature characteristics of phosphors still remains to be made. We would suggest that in such studies more use should be made of thermo-electric experiments which can indicate the sign of the charge carriers in materials for which measurements of the Hall coefficients are very difficult.

It is well known that electron traps are operative in other processes than luminescence—for example, the F-centre effects in alkali halides and the low-temperature effects suggestive of trapping states in the silver halides. It may be very fruitful to study the electron traps in non-luminescent solids by means of their effect on the photoconductivity or on the dielectric properties of the materials. Some preliminary experiments made in the author's laboratory show that when silver halides are excited at low temperatures they show similar dielectric changes to those produced by excitation of phosphors. With

respect to semi-conductors, the ideas developed for trapping-states in phosphors may prove useful in understanding the physical structure of the electron donor or acceptor systems of these solids.

4. Conclusion

The last few years have witnessed a large extension of the studies of luminescent substances prompted largely by their practical usefulness. Future improvements of phosphors for practical purposes will depend less upon empirical methods of investigation and more upon the attention given to the fundamental mechanisms of luminescence. The theoretical concepts in the past have been based on relatively few experiments on a comparatively small number of phosphors. What is needed now is an exhaustive study of the various types of phosphors, using carefully prepared specimens of controlled constitution and, in addition, investigations of the luminescence of more simple solids such as the pure alkali halides.

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CHAPTER IX

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