

Phosphorescence and electron traps

I. The study of trap distributions

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The fundamental connexion between thermoluminescence, phosphorescence and electron traps in solids has been investigated. Thermoluminescence and long-period phosphorescence arise from the release of electrons from metastable levels or traps. By studying the thermal stability of trapped electrons and the probability of release from traps of different depths, methods have been developed for finding the depths of electron traps in phosphors. The main experiment consists in exciting the phosphor at low temperatures until all the traps are filled; the phosphor is then warmed at a steady rate and the light emitted while warming is measured as a function of the temperature. The results show that the trap distribution in impurity phosphors such as willemite and the alkaline earth sulphides are, in general, complex, and extend over a range often as wide as 0.2–1.0 eV. The probability of release of an electron from a trap of depth E at temperature T is of the form $se^{-E/kT}$, where s is a constant. Values of s for alkaline earth and zinc sulphides are in the neighbourhood of $10^{8\pm 1}$ sec.⁻¹.

INTRODUCTION

As an introduction we shall give an outline of those ideas which are now generally accepted concerning the nature of a phosphor. The basis of a phosphor is a pure insulating crystal which is made luminescent by the addition of a small proportion of impurity atoms; these additional atoms are supposed to occupy interstitial or substitutional positions in the matrix lattice. The energy states of electrons in the crystal may be considered, partly, as being derived from states which exist in the individual atoms or ions which compose the crystal. The narrow energy levels which exist in the ions in free space are, in the lattice, broadened into bands (A and B , figure 1) by the field due to surrounding ions. These bands in an insulator are filled; and although the electrons in these bands may move fairly freely from ion to ion, the total state of motion cannot be altered by an electric field, and electrical conduction cannot take place. Some distance above the filled bands there is an empty band C corresponding to the states of an electron freed from an ion; this band is called the conduction band, because, if an electron is raised from B to C , the movement of the electron in C and

of the positive hole left in B can give rise to a current. Impurity atoms or lattice irregularities give rise to localized electron states (such as D , E , and F) with narrow energy levels which may occur between the energy bands of the pure crystal. An electron may be raised into the conduction band from B , D , or F by light absorption: this is the case of photoconduction; but if the electron is not given sufficient energy it may remain bound to its positive hole in an excited state at E , and then no photoconduction is observed. In the case of semi-conduction, the levels F are only a small way below the conduction band and electrons from F may be excited by thermal motion into the conduction band. In a phosphor the excited electrons return to the ground state at luminescence centres; the electron dropping

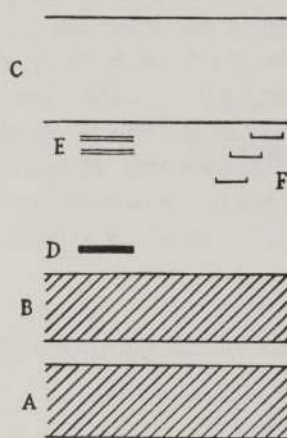


FIGURE 1. Energy levels in a phosphor.

first from C to E and then from E to D ; the second transition being associated with the radiation of luminescent light. The levels F are normally empty, and are called traps, and may capture electrons excited into C . The release, by thermal agitation, of electrons from these trap levels gives rise to a delayed luminescent emission called phosphorescence. Also short period phosphorescence (not dealt with in this work) lasting not longer than a few milliseconds may arise owing to the finite time an electron spends in the excitation level E .

All non-metallic solids appear to contain some electron traps and many may be made to phosphoresce to some extent if suitably excited. In the case of alkali halides, the traps, called colour centres, have been studied in great detail by Pohl and his school (Pohl 1937); and a satisfactory picture has been evolved of their nature by Mott and Gurney (1940), who believe

that colour centres exist at points in the crystal lattice where a negative ion is missing. Traps in silver halides play a role in photographic processes; and have in this connexion been studied by several workers (e.g. Berg 1939). The presence of luminescence centres in a solid makes possible new methods of studying traps. This paper deals with the thermal stability of trapped electrons and its relation to thermoluminescence and with methods of finding the distribution of the trap levels at different depths below the conduction band. A second paper relates this work to long-period phosphorescence, and provides a quantitative explanation of phosphorescence in terms of the trap distribution. Previous work on phosphorescence (e.g. Lenard, Schmidt and Tomaschek 1928, Ives and Luckeish 1911, Mulder 1938) has been extensive, but has not been very susceptible to theoretical interpretation. An exception is the work on phosphorescent potassium chloride (Bünger and Flehsig 1931 *a, b*, Seitz 1938), which substance, however, differs in several respects from the more usual type of phosphor. The chemical and physical nature of traps in phosphors is not yet known: further work is required in this direction. It appears likely, however, that the traps are independent of the luminescence centres and exist in the pure matrix crystal like colour centres in alkali halides.

THE STUDY OF THERMOLUMINESCENCE GLOW

The glow experiment

It is a well-known fact that if a phosphor is excited while cold and is then warmed, light is emitted while warming. Such emission of light has all the properties of thermoluminescence; though, in the past, the term thermoluminescence has been used only for light emitted when a solid is heated above room temperature. In the present work thermoluminescence emission is referred to briefly as glow. The glow experiment consists in measuring the light emission when a thermoluminescent solid is warmed at a uniform rate; and the curve obtained of light emission against temperature is referred to as the glow curve. It has been generally assumed (e.g. Johnson 1939) that glow is due to release of electrons from traps; the probability of escape from a trap increasing with temperature and the shallower traps being emptied at lower temperatures. We have found that a study of the glow curve provides a means of showing how the traps are distributed in depth.

The experimental method is now described. A thin layer of the powdered phosphor is spread on the surface of a small copper box. A suitable phosphor

layer is made by putting a slight smear of glycerol on the copper and shaking the powder on. A copper-constantan thermocouple is soldered to the surface of the box, and an electric heater coil is arranged inside. Figure 2 shows two types of apparatus which have been used. Apparatus 1,

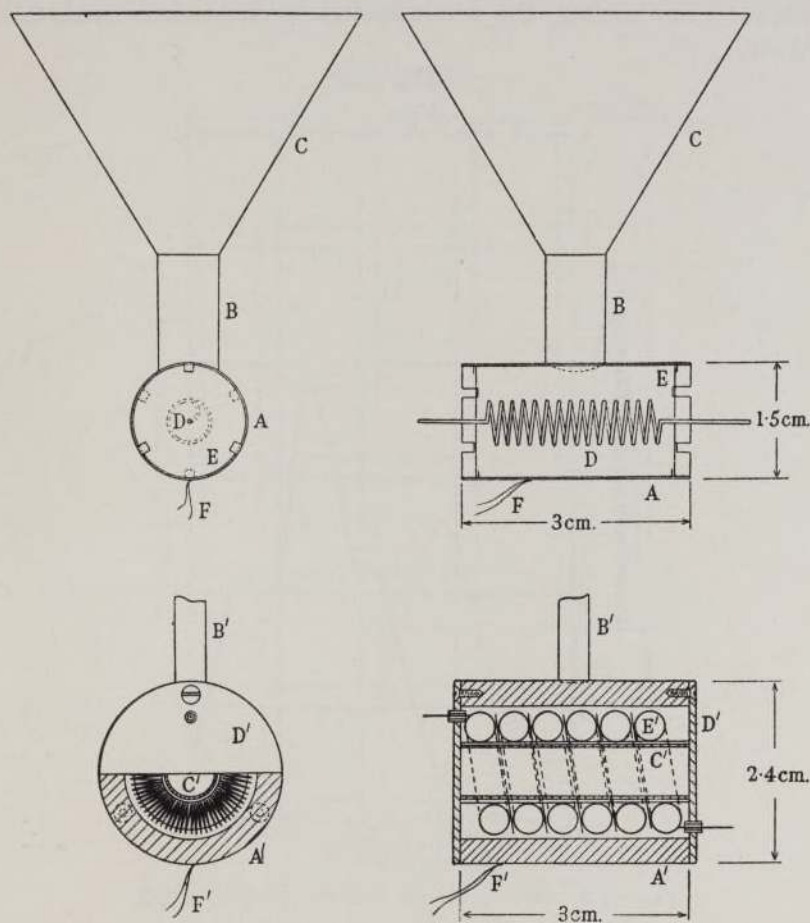


FIGURE 2. Apparatus

Apparatus 1

- A*, copper tube 0.2 mm. thick
- B*, german silver tube 0.05 mm. thick
- C*, copper funnel 0.04 mm. thick
- D*, heater coil 5 Ω , 6 V
- E*, mica discs 0.2 mm. thick
- F*, thermocouple leads 0.1 mm. diam.

Apparatus 2

- A'*, copper tube 3.2 mm. thick
- B'*, german silver tube 0.2 mm. thick
- C'*, copper tube 0.5 mm. thick
- D'*, copper end-plates
- E'*, coiled helical heater*
- F'*, thermocouple leads

* In *E'* the turns are separated by thin mica and insulated from *D'* by quartz tubes and from *C'* by asbestos. Coil resistance 100 Ω , 100 V.

in which liquid air is poured into the funnel *C*, is very convenient to use; but the rate of warming varies considerably with the temperature. Apparatus 2 was designed so that heat losses from the surface of the box would not affect the rate of warming, and so that high temperatures could be reached. For cooling, the whole system is placed in a beaker full of liquid air.

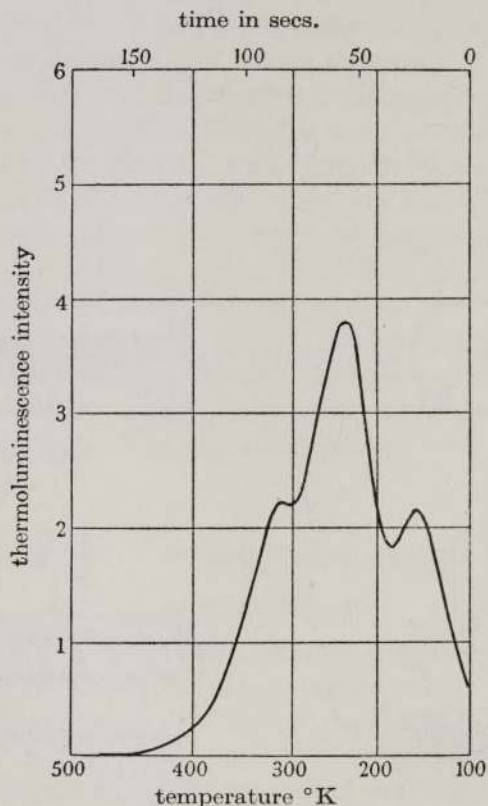


FIGURE 3. Glow curve for ZnS-Cu phosphor no. 2.

When the box is cooled with liquid air, the phosphor is excited with a mercury arc until all the traps are filled. The arc is then switched off, and the apparatus is placed in the dark in front of an electron multiplier type of photocell. The current in the heater is then switched on (in the case of apparatus 1 this is not done until the liquid air in the funnel *C* has all boiled away). The glow produced during the warming is observed as the deflexion of a galvanometer connected to the multiplier.

The galvanometer light spot is followed by a pointer connected to a pen which writes a trace on paper on a rotating drum. Marks are made on the

trace every 10 sec., and the thermocouple current is noted at the same time. The 10 sec. times are given by an electric bell connected to a clock. For accurate work two observers are required, one to follow the glow curve and the other to note the thermocouple readings. If the speed of the drum is constant the clock and bell can be dispensed with, and marks made on the

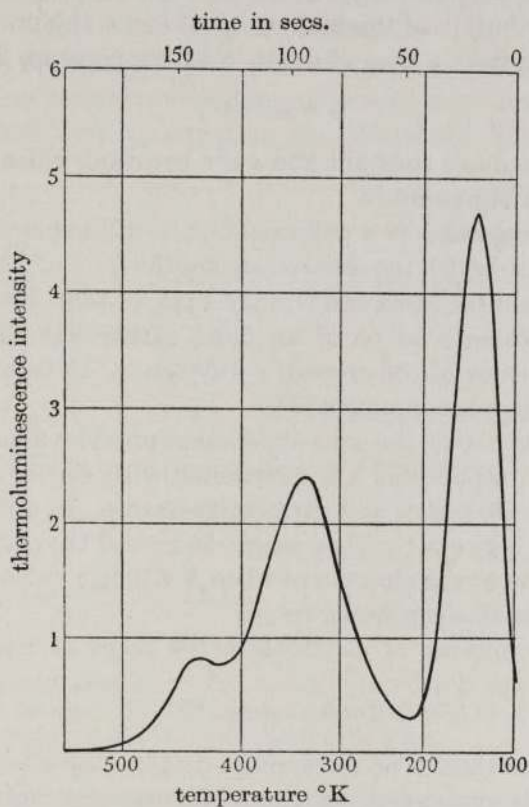


FIGURE 4. Glow curve for SrS-Bi phosphor no. 1.

trace when the thermocouple current takes certain values. (To avoid displacement of temperature readings relative to the glow curve, it is best to use the same period and damping for both the galvanometers employed.)

Glow curves of common phosphors are shown in figures 3 and 4. Before we begin to discuss the experimental results it is necessary to consider in more detail the theory of the form of the glow curve and the theory of some of the properties of trapped electrons.

THEORY OF THE GLOW CURVE

If the energy level of a trapped electron is E eV below the conduction band, the electron must absorb at least energy E before it can escape from the trap. By analogy with the case of a gravitational field acting on a ball in a hole, E is called the trap depth. The electrons in the traps have a Maxwellian distribution of thermal energies; hence the probability p of an electron escaping from a trap of depth E at temperature T is of the form

$$p = se^{-E/kT}, \quad (1)$$

where k is Boltzmann's constant and s is a constant which may, however, vary slowly with temperature.

If the trap is regarded as a potential box, s will express the product of the frequency with which the electron strikes the sides of the box and of the reflexion coefficient (cf. Mott and Gurney 1940, p. 136). There is, therefore, reason for supposing s to be of an order rather less than that of the vibrational frequency of the crystal, $\sim 10^{12}$ sec.⁻¹. In fact s is found to be $\sim 10^8$ sec.⁻¹ in the phosphors studied.

As we have said above, the glow experiment provides a method of finding how the traps in a phosphor are distributed with depth, since traps of a given depth provide a glow at a given temperature. In order that we may find the relation between the glow temperature and the trap depth, we will calculate the form of the glow curve when E is single valued and when the temperature rises at a constant rate.

Let n be the number of electrons in the traps at time t , then from equation (1),

$$dn/dt = -nse^{-E/kT} \quad (2)$$

This assumes that there is no retrapping: that is, if an electron is liberated from a trap it always goes straight to a luminescence centre and does not on the way fall into another trap. We shall see in Paper II that this assumption of negligible retrapping is largely justified. The intensity of glow I is proportional to the rate of supply of electrons to the luminescence centres,

$$I = Cdn/dt = -Cnse^{-E/kT}. \quad (3)$$

Now from (2), $dn/n = -se^{-E/kT}dt$;

then writing $dT = \beta dt$, where β is the rate of warming, and integrating, we have

$$\log n/n_0 = -\int_0^T 1/\beta \cdot se^{-E/kT} dT,$$

and

$$n = n_0 e^{-\int_0^T 1/\beta \cdot s e^{-E/kT} dT};$$

hence

$$I = Cdn/dt = n_0 C e^{-\int_0^T 1/\beta \cdot s e^{-E/kT} dT} s e^{-E/kT}. \quad (4)$$

This expression represents the glow curve for a phosphor containing traps of one depth. The curve has been calculated for $s = 2.9 \times 10^9 \text{ sec.}^{-1}$ and $E = 0.67 \text{ eV}$, and for two different rates of warming (see figure 5).

Beginning at low temperatures, the curve rises exponentially according to the exponential term in equation (3). When the light emission has

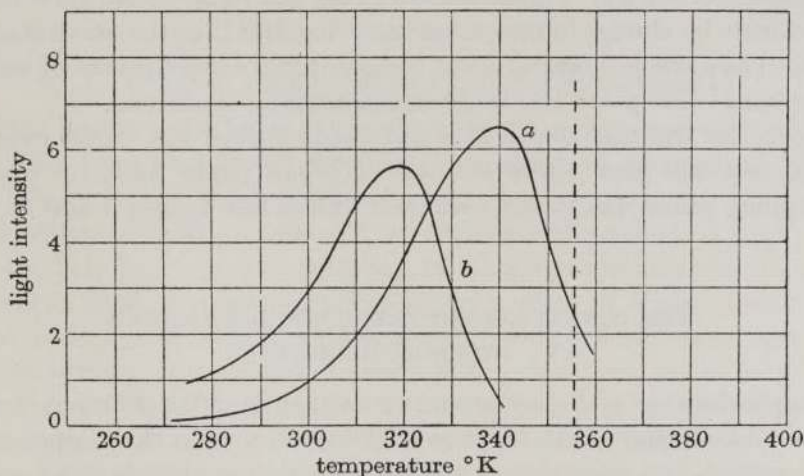


FIGURE 5. Theoretical glow curve for a single trap depth and for two rates of warming, (a) 2.5° per sec., (b) 0.5° per sec. $E = 0.67 \text{ eV}$; $s = 2.9 \times 10^9 \text{ sec.}^{-1}$; at 356° K the decay period of the trapped electrons is 1 sec.

continued for some time the number of trapped electrons (n in equation (3)) becomes appreciably diminished and the curve, after reaching a maximum, falls, and when all the traps have emptied reaches zero. The maximum intensity of glow occurs at a temperature somewhat below the temperature at which the probability of an electron escaping from the trap is 1 per sec. In figure 5 the probability is 1 per sec. at 356° K ; hence we may write

$$s e^{-L/kT_G(1+f(s, \beta))} = 1,$$

where T_G is the temperature of maximum glow and $f(s, \beta)$ has a value small compared with one.

Hence

$$E = T_G \{1 + f(s, \beta)\} k \log s. \quad (5)$$

The temperature of maximum glow varies only slightly with the rate of warming. We will refer to this temperature as the temperature which corresponds to the trap depth. From equation (5) we see that the trap depth is proportional to the corresponding temperature; so it is possible to establish a relation between trap depth in electron volts and temperature of glow in °K, and thus to calibrate the thermal glow spectrum in units of trap depth. The above calculation shows that 0.67 eV corresponds to 340° K at the rates of warming normally used. Hence the relation is approximately that 50° K corresponds to 0.1 eV or that the trap depth is approximately $25kT$. Thus the glow near liquid air temperature (90° K) corresponds to trap depths of 0.2 eV. Figure 5 shows that the form of the glow curve is altered little by change in the rate of warming, but that the curve is slightly displaced as a whole towards lower temperatures when the rate of warming is decreased: this point has been experimentally confirmed.

In practice the trap depth E is not single valued but varies over wide ranges, and the glow curve consists of broad peaks built up from the overlapping peaks due to the various E values (see figures 3 and 4).

THE CONNEXION BETWEEN PHOSPHORESCENCE AND THERMOLUMINESCENCE

Phosphorescence and glow are terms used to describe different forms of the same phenomenon. In the case of phosphorescence the temperature is kept constant, but when glow is produced the temperature is rising rapidly. There is, however, a correspondence between the phosphorescence curve and the glow curve; for it is the deep traps which contribute both to the phosphorescence after long times and to the thermal glow at high temperatures, and similarly the shallow traps contribute to the short times of phosphorescence decay and to the glow at low temperatures.

A given temperature of glow corresponds to a given trap depth, and if phosphorescence takes place at a given temperature it is possible to calculate the mean time an electron stays in the trap of given depth.

From equation (4) we have seen that the trap depth E corresponds to a temperature of glow given by equation (5). If phosphorescence takes place at a constant temperature T , the mean time t that an electron spends in a trap is the reciprocal of its probability of release, and is by equation (1):

$$t = 1/p = s^{-1} e^{E/kT}.$$

Hence

$$\log t = E/kT - \log s,$$

and substituting for E from equation (5),

$$\log t = \log s \frac{T_G \{1 + f(s, \beta)\} - T}{T}, \quad (6)$$

where T_G is the glow temperature.

This expression provides the required relation between the time of phosphorescence decay t and the temperature of glow. It also shows at what rate different parts of the glow curve will decay if the phosphor is kept at a constant temperature.

EXPERIMENTAL RESULTS

1. Traps in some phosphors activated by manganese.

All the powders in this group were excited by short wave-length ultra-violet from a quartz mercury arc. The phosphorescent properties have been described by Randall and Wilkins (1945).

The willemite powders (zinc silicate-Mn) give the brightest glow; figure 6e is typical. The various peaks can be observed qualitatively in a very convenient way. The powder is spread on a piece of copper foil which is dipped in liquid air and illuminated by ultra-violet radiation; the foil is then withdrawn and allowed to warm in the dark; the liquid air hanging on the bottom edge of the foil causes a temperature gradient to be formed in the copper; the glow peaks are observed as bands of light moving rapidly downwards across the foil. Different powders can be compared by spreading them side by side in vertical strips on the foil.

All willemites gave peaks at the same temperatures, except a fluorescent mineral specimen which gave no visible glow at all. There are two characteristic small peaks at 125° and 170° K; there is also a trace of a peak nearer liquid air temperature, but this peak decays rapidly and gives rise to phosphorescence at liquid air temperature. There is a larger peak with a maximum which varies in position from 245° to 260°; the height of this peak also varies considerably. By applying equation (6), we see that at room temperature the traps in the temperature range of the large peak give rise to phosphorescence of period ~ 0.1 sec. This is the temperature dependent phosphorescence tail observed by Fonda (1939). At temperatures much higher or lower than room temperature this phosphorescence disappears. The glow peak in question was almost entirely absent in specimen A (Randall and Wilkins 1945); and this accounts for the absence of a noticeable phosphorescence tail in this specimen. If the peak extends much

above room temperature a phosphorescence lasting seconds and minutes may be observed.

The zinc beryllium silicates (figure 6 *h, i*) appear to have a trap distribution similar to that of the willemites. The phosphorescence is similar.

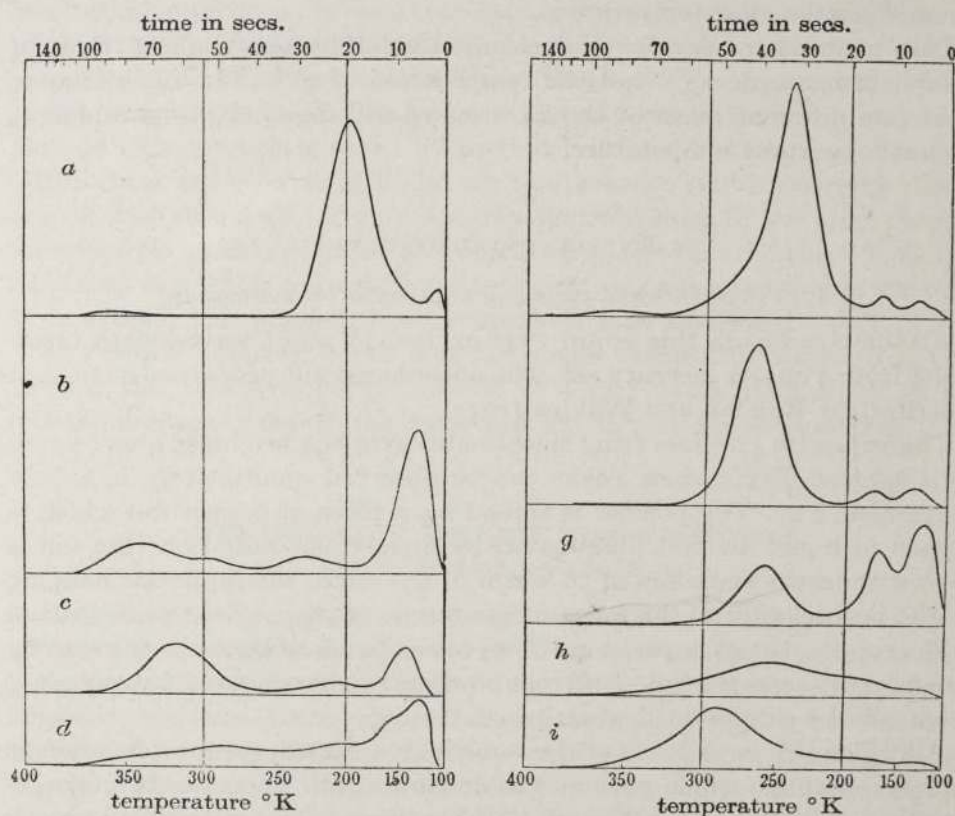


FIGURE 6. Thermal glow curves for phosphors activated by manganese. *a*, Cadmium borate. *b*, Cadmium chlorophosphate. *c*, Zinc mesodisilicate. *d*, Cadmium silicate. *e*, Green zinc silicate 0.5% Mn. *f*, Zinc silicate 1% Mn. *g*, Zinc silicate 0.1% Mn. *h*, Zinc beryllium silicate Mn. *i*, Zinc beryllium silicate 2% Mn.

Cadmium borate (figure 6*a*) has practically no room temperature phosphorescence, as there are no traps of the depth required to produce such phosphorescence. The peak near liquid air temperature gives rise to strong phosphorescence at liquid air temperature. Cadmium chlorophosphate, zinc mesodisilicate, and cadmium silicate (figure 6), all have slight room temperature phosphorescence. None of the powders in this group have more than a trace of a phosphorescence tail of period ~ 0.1 sec.

No general similarity is apparent in the glow spectra of the various phosphors activated by manganese; and these experiments give no indication that the traps are associated with the manganese impurity.

When studying the photoconductivity of these phosphors (Randall and Wilkins 1945), it was found that space charges were produced in the phosphor after the photoconductivity current had flowed for a time. This space charge decayed away slowly in the dark when there was no applied field. The most probable explanation is that the space charge is produced by electrons which travel through the crystal some distance and are then trapped. In the dark the electrons are slowly released from the traps, this process corresponding to phosphorescence, and the space charge is dispersed. The magnitude of the space charge shows that, at the lowest limit, there are 10^{12} electrons trapped per c.c. of phosphor. The space charge can be stored in both pure zinc silicate and zinc silicate activated by manganese; this indicates that the traps in this phosphor are a property of the crystal matrix and not of the manganese impurity. Infra-red light has little effect in dispersing the space charge in the phosphors of the group we are considering; and this agrees with the observation referred to in the section on the optical properties of trapped electrons—that infra-red has little effect in releasing the glow from these phosphors.

An important observation has been made by Herman and Hofstadter (1940). A zinc silicate-Mn was exposed at liquid air temperature to ultra-violet light and then warmed in the dark. A sudden increase in the dark current was observed at 213° K. This temperature corresponds to that of the large glow peak observed in our experiments, and it is almost certain that the electrons which contribute to the dark current are the same electrons which produce the thermal glow. Thus the observation shows that the electrons do pass through the conduction band during the phosphorescence process. Another indication of this is in the observation that a glow is produced in phosphorescent zinc silicate when an electric field is applied to the phosphor in the dark. The electric field apparently assists the electrons to leave the traps (cf. Frenkel 1938).

The observation made on the dark current of zinc silicate suggests a new kind of experiment in which the variation of dark current with temperature is measured during the glow experiment. In this way trap distributions could be studied in non-fluorescent solids. The experiment could also be used to distinguish between semi-conductors which contain equal numbers of electrons and semi-conduction levels and those which contain less electrons than levels. In the second type of semi-conductor the trap distribution could be found by the method, and this would supplement the

knowledge already gained from experiments in which the semi-conduction current is measured under equilibrium conditions at different temperatures. The experiments which are described in this paper, on trap distributions in phosphors, indicate that most impurity levels in solids are distributed in depth. The trap levels in phosphors resemble in many ways semi-conduction levels; it is, therefore, reasonable to suppose that the apparent variation with temperature of the activation energy in semi-conductors is to be attributed to a distribution with depth of the semi-conduction levels.

2. *The phosphorescence and thermal glow of potassium chloride activated with thallium*

The phosphorescence of KCl-Tl has been studied with great thoroughness by Büniger and Flechsig (1931 *a* and *b*), and an interpretation has been given by Seitz (1938) and Hilsch (1937). The study of the glow, however, enables some further information about the phosphorescence to be obtained. Also KCl is of special interest in that specimens can be obtained with a single trap depth E , while in all other phosphors we have examined there is a wide distribution of E values in any one specimen. The single value of E should give rise to a glow peak of the type calculated above (figure 5); and hence, by using Büniger and Flechsig's values for E and s , it is possible to check the theory we have given of the glow curve, or alternatively to assume the theory and check Büniger and Flechsig's values.

Büniger and Flechsig found that in some specimens of KCl-Tl the phosphorescence (which is almost entirely in the ultra-violet) decays near room temperature almost exactly according to an exponential law. The rate of decay changed rapidly with temperature and the decay law fitted the formula:

$$I = I_0 \exp(-se^{-E/kT}),$$

where I is the intensity of phosphorescence, E is an activation energy equal to 0.67 eV and s is a constant $2.9 \times 10^9 \text{ sec.}^{-1}$

The specimen of KCl-Tl (kindly given us by Prof. Pohl) which we have used was not a specimen with a single E value; but it was found that the value of E was distributed only over a narrow range, the E values differing by less than 1%. This small distribution of E values, however, causes the phosphorescence decay law to differ considerably from an exponential form. It must be pointed out that it is not impossible that the constant s will vary as well as E , but experimentally it is difficult to distinguish between trap distributions in which E varies slightly and s is constant and those in which E is constant and s varies slightly. This distinction is not of much physical

importance, and for convenience of discussion we will assume s is constant and E varying.

Figure 7 shows the decay curves plotted on a logarithmic scale for KCl-Tl at various temperatures: a slice of crystal was excited by a mercury arc and the phosphorescence curve recorded by the multiplier and rotating drum.

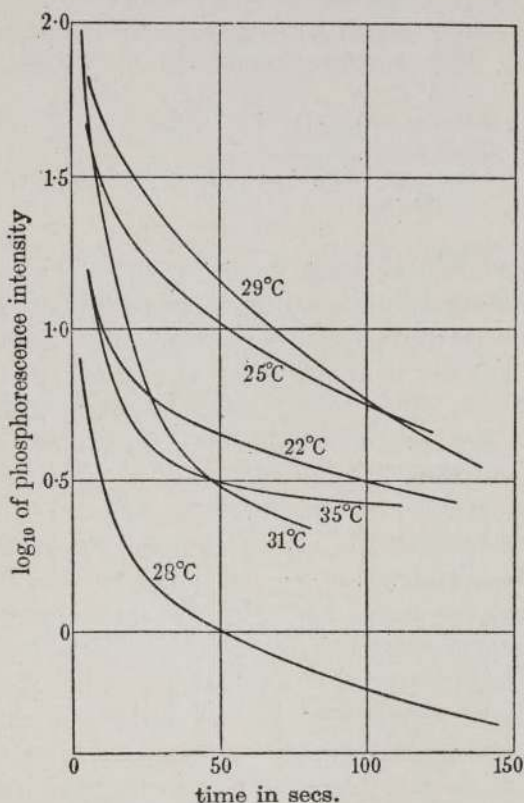


FIGURE 7. Phosphorescence decay curves of KCl-Tl at different temperatures. The exciting light used for the 28° C curve was $\frac{1}{30}$ normal intensity.

We will now consider what distribution of E values will give rise to the phosphorescence observed. The E value will not be expressed in electron volts, but as the corresponding glow temperature.

For the rate of warming used (1.3° per sec.) equation (6) gives the following connexion between period t of phosphorescent decay at temperature T and the glow temperature:

$$\log_{10} t = 9.5 (T_G \times 1.08 - T)/T,$$

taking s as $10^{9.5}$ sec.⁻¹

The results of figure 7 may be stated in the following way, the temperature of glow corresponding to the period of decay being calculated from the formula above.

Temperature of phosphorescence	Characteristics of the decay	Glow temperature corresponding to period of phosphorescence decay
295° K	Predominant period of decay is ~100 sec. With a lesser proportion of period ~15 sec.	336° K 310° K
302° K	Predominant period is ~30 sec.	328° K
308° K	Predominant period is ~10 sec. With a lesser proportion of period ~200 sec.	316° K 358° K

The glow peak should be built up from component glow peaks which have maxima at different temperatures corresponding to different E values. The mean temperature of the predominant period is, from the table, 327° K. Hence the predominant component of the glow peak should have its maximum at 327°; in other words, the maximum of the E distribution should be at 327°. The E distribution should on this scale of corresponding temperatures extend from 310° to 358°.

To test the correctness of these ideas the glow curve has been studied. Powdered KCl was used on the glow apparatus (type 1). The powder was excited at room temperature, a drop of liquid air was then placed in the funnel and warming was begun from below room temperature. The powder phosphoresces at an appreciable rate while at room temperature, and if this phosphorescence is allowed to proceed for some time before the glow curve is recorded, the resulting glow peak will be much smaller than the undecayed peak. Figure 8 shows the glow curve after different times of phosphorescence at room temperature. If the peak corresponded to a single value of E , the peak would decay as a whole and its maximum would remain at a fixed temperature. In fact the maximum moves to higher temperatures as the peak decays; which means that the components of the peak with maxima at lower temperatures decay more rapidly than the higher temperature components. From the data of figure 8 the E distribution can be deduced. For, roughly, the height of the E distribution curve at a certain temperature is proportional to the height of the decayed peak which has its maximum at that temperature. The dotted curve in figure 8 shows the approximate E distribution curve deduced in this way. The curve agrees with the rough estimates obtained from the phosphorescence data.

In the above we have shown that the phosphorescence decay curve may be correlated with the glow curve by assuming the value of s given by Büniger and Flechsig. This amounts in fact to a confirmation of that value of s . It is possible to make a more precise check of the E and s values given by Büniger and Flechsig (and alternatively to test the correctness of the theory given above of thermal glow) by comparing the experimental glow curve of figure 8 with that of figure 5 which has been calculated by assuming the E and s values of Büniger and Flechsig. When the different rates of warming for figures 8 and 5 are taken into account, the position of the maxima of the peaks is found to agree to 2%; and the width and shape of the peak also agrees well.

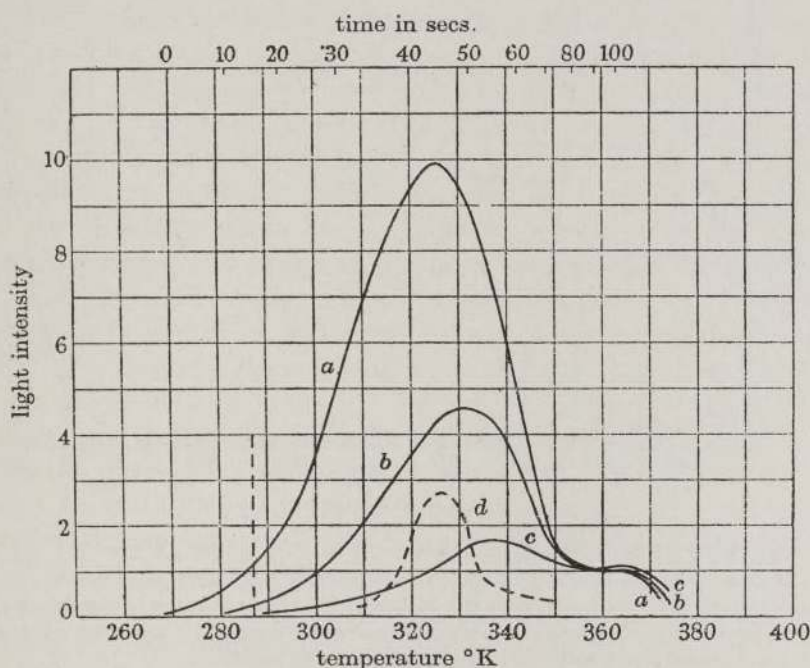


FIGURE 8. Glow peak of KCl-Tl after decay at 287° K. Time of decay: (a) 10 sec., (b) 7 min., (c) 33 min. Curve d shows the probable distribution of traps at different depths.

The discussion so far has referred only to one part of the E distribution, in the region of 0.7 eV or 330° K. The curves in figure 8 show that there are also traps in the region of 370° K. It is not possible to tell from the glow curve alone whether there is a sharply defined E level at 370°, or whether the E values are spread over a region several degrees wide; to use an optical analogy, the resolving power of the glow experiment is not

sufficiently great. To analyse the peak at 370° it would be necessary to measure the phosphorescence decay curve at a suitable temperature such as 340° , or to measure the peak after various times of decay at that temperature.

The whole glow spectrum from 90° K upwards is shown in the lower curves of figure 9. In all there are four peaks in the spectrum. The peak near 200° K would correspond at room temperature to a decay period of

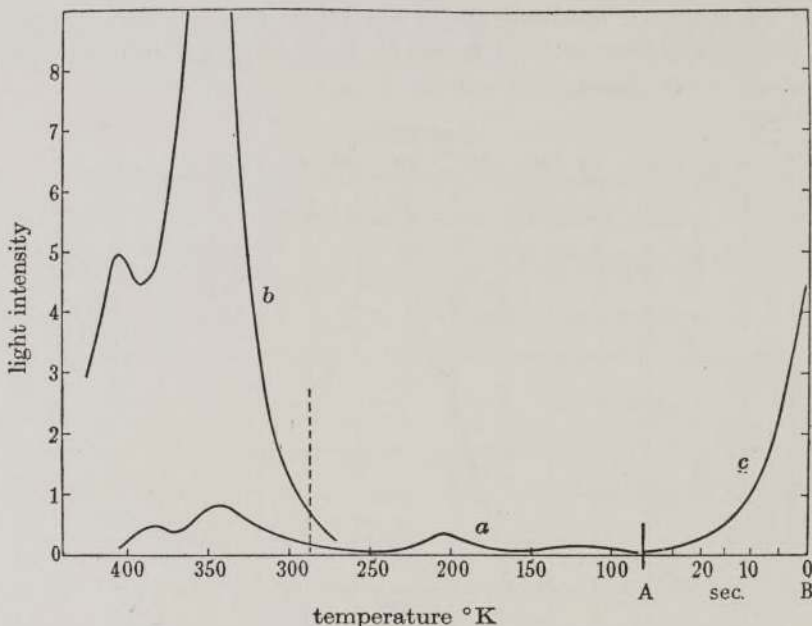


FIGURE 9. Glow of KCl-Tl when excited (*a*) at 90° K, (*b*) at 286° K. (*c*) is the phosphorescence curve at 90° K which is continuous with the glow curve (*a*). Thus the temperature is kept constant at 90° K from *A* to *B* and starts to rise at the point *A*. The mean rate of warming is about 3° per sec., hence the position of the high temperature peaks is slightly different from those in figure 8.

$\sim 10^{-3}$ sec. Bunger and Flechsig have, in fact, observed a very short decay period which they suggested was 0.5×10^{-4} sec. It may well be that this quick decay is due to release of electrons from the 200° K traps. There is also a glow peak near 100° K which causes intense phosphorescence at 90° K. The decay curve of this phosphorescence is almost exponential (see figure 9*c*), hence the *E* level is sharply defined.

The two curves, (*a*) and (*b*), in figure 9 illustrate a phenomenon which has not been observed in any phosphor other than KCl-Tl. When the phosphor

is strongly excited at 90° K, very little energy is subsequently released in the glow peaks between 300° and 400° . If excited at room temperature, about ten times as much energy is released from these peaks. To explain this phenomenon it must be remembered that KCl-Tl is an exceptional phosphor in that it does not photoconduct (Hilsch 1937), while all the other phosphors we have used are known to photoconduct (e.g. Randall and Wilkins 1945). Also the trap levels in KCl are much more sharply defined than those in other phosphors. In any ordinary phosphor the traps are almost certainly separate from the luminescence centres, and the electron wanders about the crystal from the fluorescence centre to the trap. In KCl-Tl, Seitz (1938) suggests that the trap consists of a metastable level in diatomic thallium molecules which are also the luminescence centres. The excited electrons do not at any time pass outside their particular centre. The different trap depths we have observed probably correspond to different levels in the thallium molecules. The coexistence of these various levels in one centre is also indicated by the structure in the infra-red quenching spectrum (Bünger and Flechsig 1931 *b*). In an ordinary phosphor which photoconducts there are, apparently, always more luminescence centres than traps; and hence at whatever temperature the phosphor is excited, all the traps corresponding to higher temperatures are filled and the phosphor is said to be saturated; this is shown by the fact that the saturated glow curve is the same height at whatever temperature excitation takes place. In KCl-Tl, however, for low temperature excitation each excited electron enters the shallower trap level in its particular thallium molecule and the deeper trap levels are not all filled. When excited at higher temperatures the electrons are not stable in the shallower traps, and the electrons all fill the deeper traps. This idea is supported by the observation that the total light energy which can be stored (in phosphorescence and glow) at 90° K is about equal to that which can be stored when excitation takes place at room temperature. This total of energy corresponds to the total number of thallium molecules in the phosphor.

*The determination of the value of the constant s by
measuring the decay of the glow curve*

As has been said before, the emission of energy during phosphorescence corresponds to a diminution in the amount of energy stored in the phosphor and to a diminution in the height of the glow curve. If the phosphor is kept at a fixed temperature T during phosphorescence, the various parts

of the glow curve, corresponding to different trap depths, decay at rates given by equation (6),

$$\log t = \log s \frac{T_G \{1 + f(s, \beta)\} - T}{T},$$

where T_G is the glow temperature and t is the period of decay of that part of the glow curve.

These decay periods can be found by measuring the glow curve in various stages of diminution after phosphorescence has taken place for various times. Such measurements provide a method for finding a value for the constant s in phosphors which contain a wide distribution of trap depths. It must be noted that equation (6) is only approximate, as in its derivation it is implicitly assumed that each part of the glow curve corresponds to a single E value and to a single period of exponential decay. In fact, the glow curve is built up from component glow peaks of finite width, each peak corresponding to a single value of E . Hence, during phosphorescence, each temperature of the glow peak corresponds to a range of decay periods the mean of which is given by equation (6). It has been found that the most convenient way of finding s —and the way which seems least affected by the approximation contained in equation (6)—is to allow the glow curve to decay for various times, and to find the glow temperature at which the glow curve has fallen to half its undecayed value, and to plot these temperatures against the logarithm of the time of decay.

From equation (6) it is seen that the graph T_G against $\log t$ will be very nearly a straight line which makes an intercept on the $\log t$ axis, when T_G is zero, which is equal to $\log s$. Also, the line should cut the temperature axis, at a point T_1 , below the temperature at which decay took place. At this temperature T_1 , $\log t$ is zero; hence from (6)

$$f(s, \beta) = \frac{T - T_1}{T_1}.$$

Figure 10 shows the experimental results for a ZnS-Cu phosphor (no. 2). The decay took place at room temperature and the apparatus was cooled slightly before the glow curve was recorded. At high temperatures (near 440° K) the glow curve is not appreciably decayed, and the various glow curves overlap accurately. The undecayed glow curve was obtained by exciting the powder at a temperature well below room temperature. The amount of stored energy (the area under the glow curve) decreases rapidly with time; hence the phosphorescence decay of this type of phosphor is rather rapid.

Figure 11 shows representative decayed glow curves for a SrS-Bi phosphor (no. 1).

The decay of the glow curve of the SrS-Bi phosphor (no. 1) while phosphorescing at liquid air temperature is shown in figure 12. Frosting up of the powder while the decay took place was avoided by placing the powder (on apparatus 1) in a box with a cellophane window warmed by an air blast at about 100°C . Figure 12 shows that for long times of decay the glow curve decays in all temperature regions; this effect being superimposed

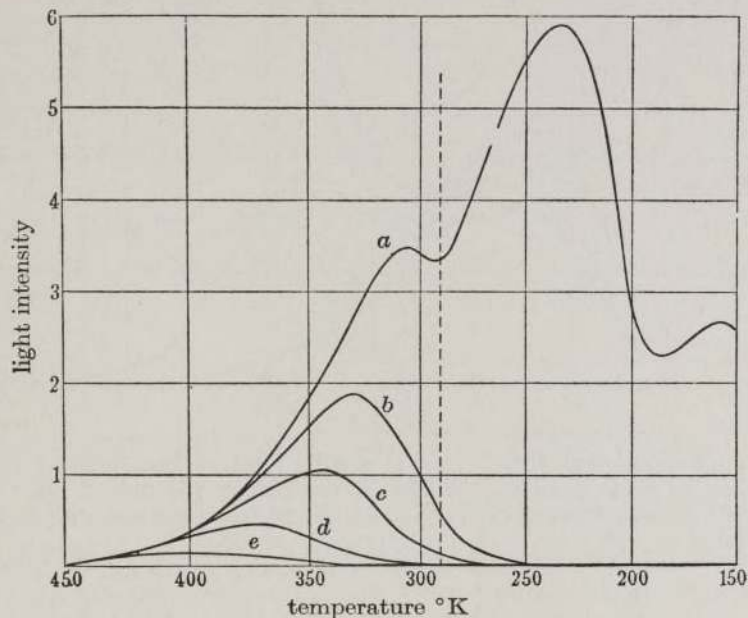


FIGURE 10. Glow curve for ZnS-Cu phosphor after various times of phosphorescence decay at room temperature 290°K marked by the dotted line. Rate of warming 2.2° per sec. Time of decay (a) zero, (b) 25 sec., (c) 140 sec., (d) 20 min., (e) 95 min.

on the decay of the curve on the low temperature side, as predicted by equation (6). This phenomenon is not general in phosphors and is probably caused by absorption of infra-red radiation of wave-length $2-3\mu$, which may be radiated from the box and the warm window. In order that the decay predicted by equation (6) may be separated from the general decay of the glow curve, the decayed glow curve has been multiplied in height by a factor such that the height of the curve at high temperatures is the same as the height of the undecayed curve. The temperature at which the glow curve has decayed to half its initial height is measured from the curve multiplied in this way.

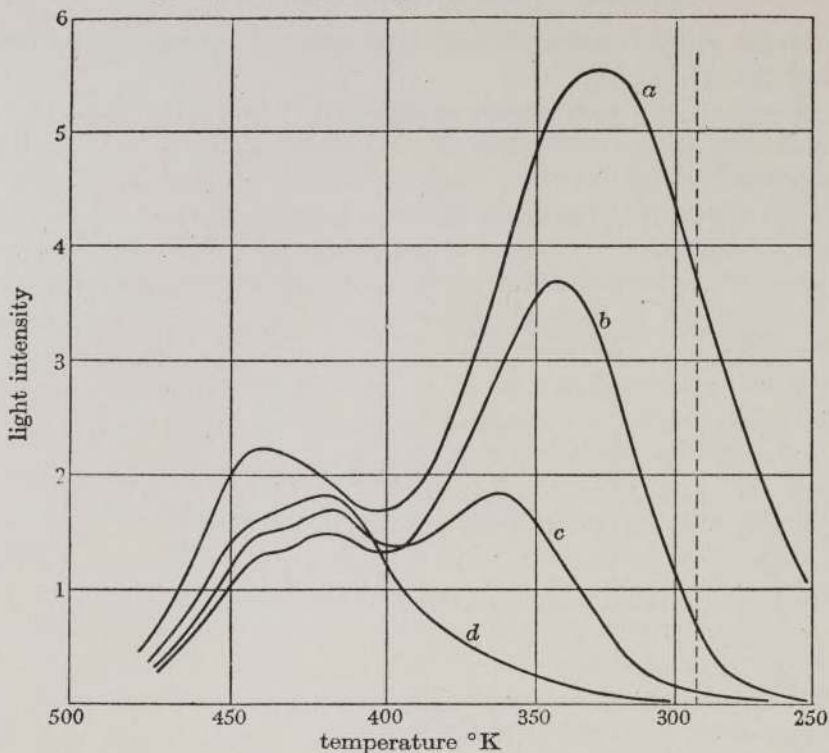


FIGURE 11. Glow curve for SrS-Bi (no. 1) powder after various times of phosphorescence decay at room temperature 293° K marked by the dotted line. Rate of warming 2.2° per sec. Time of decay (a) zero, (b) 35 sec., (c) 9 min., (d) 80 min.

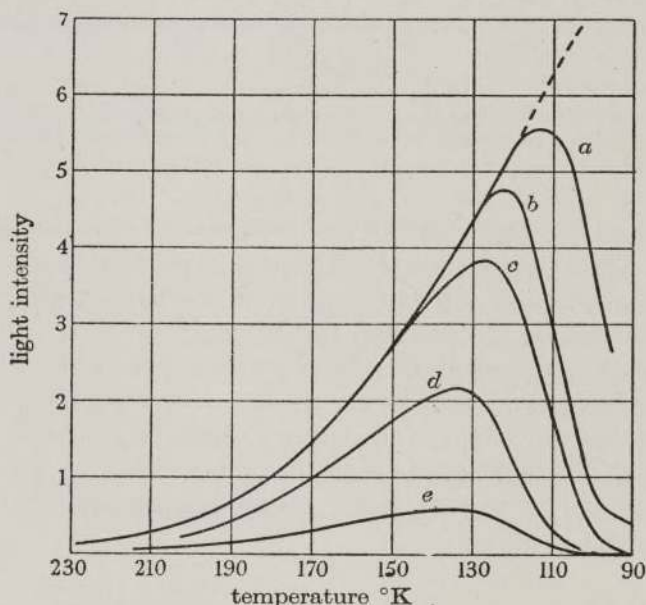


FIGURE 12. Glow curve of SrS after phosphorescence has proceeded for various times at liquid oxygen temperature 90° K. Rate of warming 5° per sec. Dotted curve shows probable form of undecayed peak. [The temperature scale is not quite correct; 10° on the scale correspond in fact to 11° .] Time of decay (a) 5 sec., (b) 25 sec., (c) 140 sec., (d) 10.5 min., (e) 30 min.

The results of figures 10, 11 and 12 are plotted graphically in figure 13 together with data obtained from other experiments. The results agree with theory; the points obtained by decay at 90 and 290° K both lie on

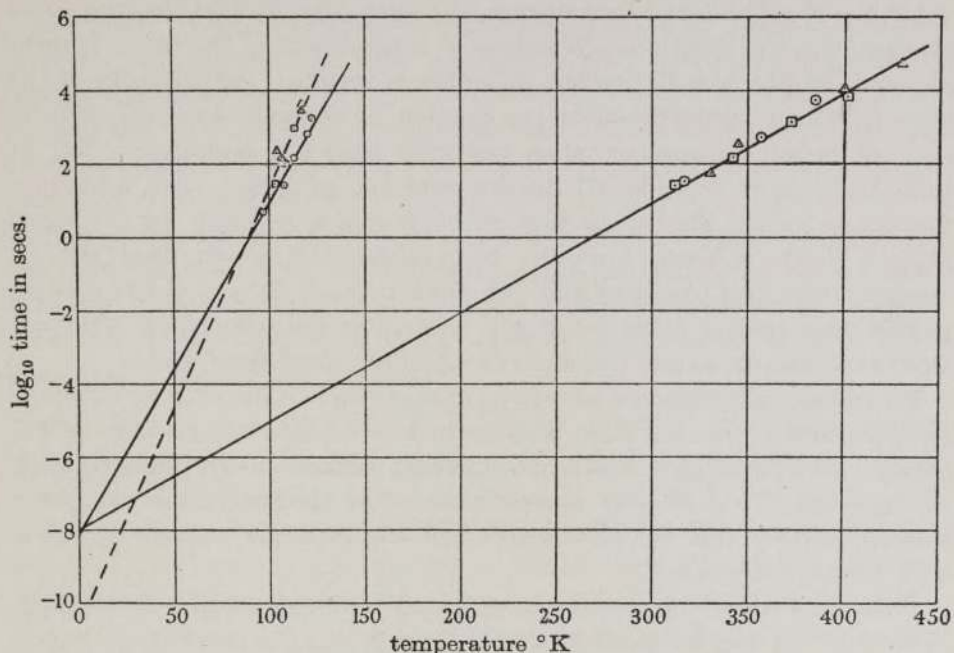


FIGURE 13. Decay of glow curve. The log of the time of phosphorescence decay is plotted against the temperature for which the glow curve has decayed to half its original value. The temperature at which decay took place was about 90 and 290° K. The straight lines drawn through the points cut the $\log t$ axis at the value $-\log s$.

Temp. at which decay took place ° K	Phosphor	Glow curves shown in
290	□ ZnS (no. 2)	Fig. 10
293	○ SrS (no. 1)	Fig. 11
293	△ SrS (no. 3)	—
90	⊙ SrS (no. 1)	Fig. 12
90	□ Cadmium borate Mn	—
90	△ Cadmium chlorophosphate Mn	—

straight lines which cut the time axis at the same point. s appears to be $\sim 10^{8\pm 1} \text{ sec.}^{-1}$ for both zinc and strontium sulphides. The results for the cadmium phosphors appear higher ($\sim 10^{11} \text{ sec.}^{-1}$), but the experiments in this case were not made so carefully.

OPTICAL PROPERTIES OF TRAPPED ELECTRONS

Electrons in traps in a phosphor should give rise to an absorption band which will not be present in the unexcited phosphor. Absorption of a quantum of radiation of frequency ν will cause the trapped electron to be ejected from the trap if $h\nu > E$, where E is the depth of the trap. If after absorption of such radiation the phosphor is warmed, the intensity of the glow (which is proportional to the number of trapped electrons) will be reduced below its normal value, provided that the radiation is not of sufficiently short wave-length to re-excite the phosphor. The minimum frequency which will cause this effect provides a value for E , since $h\nu_{\text{min.}} = E$. It is clear, however, from arguments which need not be repeated here (ref. de Boer and van Geel 1935, Mott and Gurney 1940, p. 160), that such a value for E will be greater than the value obtained from experiments on the thermal release of electrons from traps.

Preliminary experiments have been made to find values of E for different temperatures of thermal glow. The method used was a combination of the thermal glow experiment and a photographic method due to Dahms (1904). As expected, E was roughly proportional to the temperature of the glow; this applied for different glow peaks and within single peaks covering a wide temperature range.

Phosphors cooled by liquid air, or liquid hydrogen, might be useful in photographing the infra-red spectrum from 2–10 μ . A sheet of phosphor would be exposed to the infra-red, then placed over a photographic plate and warmed a few degrees.

TABLE 1. OPTICAL AND THERMAL ACTIVATION ENERGIES
FOR A CaSrS-Bi PHOSPHOR

Glow temperature ° K	λ maximum	E (optically) eV	E (thermally) eV
400	1.0 μ	1.2	0.75
250	1.4 μ	0.9	0.5
130	2.0 μ	0.6	0.3

Table 1 shows specimen results for a CaSrS-Bi phosphor. The temperatures shown correspond to the maxima of three large peaks in the glow spectrum. Near the maximum wave-length the effect of the radiation increases rapidly with decrease of wave-length. Several zinc sulphide phosphors gave similar effects. Zinc silicate, zinc mesodisilicate and cadmium silicate and borate were much less sensitive to the radiation.

There was in no case an indication that the effect ceased for short wave-lengths; hence it is reasonable to suppose that the radiation which excites

luminescence in a phosphor is active also (but in general to a lesser extent) in ejecting electrons from traps. Luminescence produced after trapping and ejection from the trap requires the absorption of two quanta to produce one luminescence quantum; hence the efficiency will be lower than usual.

Mott and Gurney (1938) have suggested that the decrease in apparent luminescence efficiency of some phosphors with decreasing temperature may be due to reduction in the absorption coefficient of the phosphor when most of the electrons from the luminescence centres are held in traps. This effect is observed for ZnS-Mn and CaS-Bi and SrS-Bi phosphors. If the explanation is correct, there should be a rapid rise in fluorescence at temperatures associated with well-defined peaks in the thermal glow spectrum; such an effect is, however, not apparent. It may be significant that the phosphors which show decrease in luminescence at low temperatures are those which seem to have empty luminescence centres in the unexcited phosphor (see Paper II).

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