

Number of Traps and Behavior of Excited Electrons in Luminescent Materials*†

HARTMUT KALLMANN AND GRACE MARMOR SPRUCH

Department of Physics, New York University, Washington Square, New York, New York

(Received December 20, 1955)

The number of traps per unit volume in different types of luminescent materials, and the prolonged lifetimes of excited electrons due to trapping, were studied by means of curves of the rise of fluorescence with time under constant high-energy electron and alpha-particle excitation. These rise curves were taken after various dark decay periods and after different infrared irradiation conditions. They were found to be different in shape for different types of phosphors. Lifetimes longer than one week were found to occur in most of the zinc cadmium sulfides. The number of traps per unit volume responsible for lifetimes longer than about a minute was found to be of the order of 10^{15} (10^{-7} mole fraction) in the zinc cadmium sulfides, and the number responsible for lifetimes longer than a week was of the same order of magnitude. There is no direct correlation between infrared stimulability and the number of traps in which electrons remain for some time.

Substances with extremely high stimulability (Fonda type) and those with extremely low stimulability both contained about the same number of these traps per unit volume. Materials with large concentrations of Ni exhibited no more such traps than those with smaller concentrations. Lack of phosphorescence is caused either by the preponderance of excited electrons of very long lifetime or by the radiationless recombination of electrons of short lifetime. Examples of each are given. It was found further that most of the electrons which remain in traps for long periods could be ejected by infrared radiation of wavelength greater than 1.25μ , indicating that retrapping of both electrons and positive holes is of major importance. The different effects of alpha particle excitation and electron excitation on the filling of the traps is discussed.

1. INTRODUCTION

TRAPPED electrons in solids manifest themselves in phosphorescence and photoconductivity after excitation, in glow emission,¹ and in light² and photoconductive³ stimulation by infrared radiation. From observations of each of these phenomena information on the number and nature of the traps may be obtained. The most significant progress in this field was made by Hoogenstraaten and Klasens,⁴⁻⁶ since they succeeded in relating the traps to the chemical composition of the phosphors. Some of the information on traps, particularly that concerning energy levels and lifetimes, obtained by the means mentioned above is subject to some question, however, because of the light quenching induced by temperature changes^{4,7} and infrared radiation,⁴ and because of the large change that the state of excitation of the phosphor undergoes during decay. As a consequence of the latter, the ratio of retrapping to recombination changes with time, and this, in turn, has a considerable effect upon the length of time excited electrons remain in traps, and upon the ratio of radiative to radiationless recombinations.

Relatively little information on the length of time

excited electrons remain in traps is available, in spite of the great deal of study devoted to traps. It is the purpose of this paper to augment such information by presenting the results of an investigation of the rise of fluorescence under constant high energy particle excitation. (The reason for using high-energy particle excitation will be discussed below.) This method, which detects the existence of traps,^{4,5,8} does not suffer as much as the others from the indeterminate influences mentioned above, and has the advantage of being operable even in cases where other methods cannot be applied, i.e., where little or no phosphorescence or stimulation is observed. In addition, it permits the measurement of the length of time excited electrons exist in traps.

A curve of fluorescent light intensity *versus* time under constant exciting intensity is plotted after the traps in the substance have been emptied (de-excitation). From the "deficiency" area above the curve and below the line through the stationary value, it is possible to determine the number of excited electrons which have been trapped without having emitted light. If a second curve is plotted after the substance either remained in darkness for a given period of time following the first run, or was subjected to various de-excitation processes, the second curve may exhibit a shape different from the first. This comes about because prior to the second excitation some traps are already occupied as a result of the first excitation, and therefore fewer excited electrons are consumed in the nonradiative trapping process in the second run than in the first. Thus the second curve will rise more rapidly than the first in all cases in which complete exhaustion of the

* This work was supported by the Signal Corps Engineering Laboratories, Evans Signal Laboratory, Belmar, New Jersey.

† Part of a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree (G.M.S.) at New York University.

¹ J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 366 (1945); G. F. J. Garlick and A. F. Gibson, *Proc. Phys. Soc. (London)* **60**, 574 (1948), and other papers by these authors.

² H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950).

³ Kallmann, Kramer, and Perlmutter, *Phys. Rev.* **99**, 391 (1955).

⁴ W. Hoogenstraaten, *J. Electrochem. Soc.* **100**, 356 (1953).

⁵ W. Hoogenstraaten and H. A. Klasens, *J. Electrochem. Soc.* **100**, 366 (1953). See also R. H. Bube, *J. Phys. Chem.* **57**, 785 (1953).

⁶ H. A. Klasens, *J. Electrochem. Soc.* **100**, 72 (1953).

⁷ C. Bull and D. E. Mason, *J. Opt. Soc. Am.* **41**, 718 (1951).

⁸ I. Broser and R. Warminsky, *Z. Physik* **133**, 340 (1952); A. Levisaldi and V. Luzzati, *J. phys. radium* **8**, 306, 341 (1948); J. T. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **184A**, 390 (1945); and G. F. J. Garlick and M. H. F. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 408 (1945).

traps has not been effected before excitation commences, whether by decay in darkness or by infrared irradiation. From the area between the curves it is possible to determine the number of excited electrons which remain in the traps for a length of time greater than the period in darkness, or, one can determine the effectiveness of de-excitation by different infrared wavelengths. The method is especially useful in detecting the electrons trapped for very long periods of time, which were found to be quite numerous in many types of phosphors whether stimuable or not.

2. EXPERIMENTAL PROCEDURE

The phosphors were excited by electrons from a 20-millicurie Sr^{90} — Y^{90} source with an intensity of 3000 r/hour at the sample, unless stated otherwise, or by alpha particles from a 20-millicurie polonium source, unless stated otherwise. Both sources were situated about 15 millimeters from the phosphor which was in a light-tight chamber also containing a 1P21 photomultiplier. The exciting particles entered the chamber through a thin aluminum window (3.6 mg/cm² for electrons and 0.2 mg/cm² for alpha particles) which prevented any light excited in air by the alpha particles from reaching the photomultiplier. Powdered phosphors were mounted on a Lucite backing by means of a dilute solution of Duco cement, the Lucite preventing the exciting electrons from reaching the photomultiplier. Lucite was selected because it exhibits little fluorescence under electron excitation and negligible fluorescence under alpha-particle excitation. The former had to be determined separately and subtracted from the intensity of powdered phosphors. The contribution of the Lucite was only of importance with those phosphors which emit in the yellow-orange region of the spectrum where the photomultiplier is much less sensitive. The intensities were measured with a conventional circuit which permitted a range of four orders of magnitude to be covered.

All the points on the rise of fluorescence curves except the first, that at 2500 microseconds, were obtained under constant excitation. For the first point the excitation was pulsed with the aid of a rotating wheel, which allowed a burst of high-energy particles to impinge upon the phosphor, within an interval of 2500 microseconds. To fit the point obtained at 2500 microseconds onto the curve obtained with constant excitation, the integrated intensity to which a given pulse height corresponded was determined. Since anthracene has negligible long-time emission, the ratio of the pulse height to the integrated intensity for anthracene was taken to be the factor by which the pulse height readings could be converted to intensity readings.

Observation of the rise of fluorescence was preceded by de-exciting the sample by strong infrared irradiation. The intensity and duration of the irradiation necessary to completely de-excite the samples were determined from the height of the 2500- μsec pulse as a function of

the irradiation. This pulse height decreases with increasing irradiation, becoming constant when all the traps have been emptied. In addition, rise curves were taken after different de-excitation conditions, the lowest of these indicating the proper conditions for complete de-excitation. The infrared transmitting Corning 7-56 filter ($\lambda_{\text{trans}} > 0.77\mu$) was used for most substances. KBr(Tl) and CsBr(Tl) were irradiated through a Corning 2-64 filter ($\lambda_{\text{trans}} > 0.66\mu$), and NaCl(AgCl 5%) was de-excited with radiation in the near ultraviolet.

A series of rise curves were taken after various lengths of time in darkness following excitation to a stationary intensity, and after de-excitation with different wavelengths and for different lengths of time.

3. PROBABILITY OF RECOMBINATION

The intrinsic lifetime, τ , of a trap is usually given by the relationship

$$1/\tau = \gamma e^{-E/kT}. \quad (1)$$

We prefer to discuss instead another quantity, namely the probability that an electron localized in a particular trap level will recombine with a positive charge either radiatively or nonradiatively. This probability, $1/\tau'$, is given by

$$1/\tau' = \gamma' [p_f / (p_f + p_t)] e^{-E/kT} + p_r, \quad (2)$$

where γ' is a constant with the dimensions of a lattice vibration [as is γ in (1)]; E is the energy depth of the trap measured from the bottom of the conduction band; k is Boltzmann's constant; T is the absolute temperature; p_f is the probability per unit time of a recombination by an electron in the conduction band, which may or may not lead to light emission; p_t is the probability per unit time of retrapping; and p_r is the probability per unit time of a radiationless transition in which the electron does not pass through the conduction band. p_r may depend upon the temperature in a manner similar to that of the first term with E' instead of E in the exponential, or in a completely different fashion, depending upon the nature of the processes assumed for such radiationless transitions. The traps may be distributed over a range of energy levels; then expressions similar to (2) hold for each trap level and the sum of these expressions gives the probability for recombination for a particular state of excitation of the phosphor. It is this latter recombination probability which affects the size of the deficiency area above the rise of fluorescence curve.

Although this paper deals mainly with the length of time for which electrons are trapped, it can also be stated that experiments with different de-excitation wavelengths have shown that very often all, or almost all, of the electrons which remain excited for very long periods (days) can be de-excited by rather long wavelengths, much greater than 1.25μ . This could be explained either by the assumption that even those electrons with long excitation lifetimes are bound in

TABLE I. Some properties of the materials investigated.

A. ZnS phosphors													
Letter name	Composition in percent ^a										Fluorescence	Persistence of phosphorescence	Stimulation
	Cd	Cu	Ag	Au	Mg	Ni	Pb	Si	Ti	Fe	Co		
LG ^b	<0.005	0.0031	<0.0001	<0.001	0.040	0.010	<0.001	green	very long
A ^c	...	yes	green	medium
R	0.18	0.007	<0.001	<0.001	<0.0005	<0.001	<0.001	green	very long
M	0.006	0.0035	0.0003	...	0.593	0.002	0.0008	...	green	extremely long
D	<0.005	<0.0001	0.0030	<0.001	<0.0005	0.001	<0.001	blue	medium short
N	0.005	0.001	0.040	...	0.007	0.003	...	0.002	...	blue	medium
70 ^d	<0.005	0.070	<0.001	<0.001	<0.0005	<0.001	<0.001	green	medium short
B. ZnCdS phosphors													
Letter name	Composition in percent ^a										Fluorescence	Persistence of phosphorescence	Stimulation
	Zn	Cd	Cu	Ag	Au	Mg	Ni	Pb	Si	Ti	Fe	Co	
L	55.69	13.19	0.01	0.0036	0.0024	0.028	yellow-orange
O	38.40	31.97	0.008	0.0005	...	0.276	0.002	0.003	0.003	...	orange-red
K	31.74	40.97	0.010	0.0030	0.0025	...	0.0005	0.015	yellow-orange
U ^b	29.89	42.58	<0.0001	0.040	<0.001	0.001	<0.001	<0.001	yellow
C. Miscellaneous phosphors													
Substance		Activator		Fluorescence		Persistence of phosphorescence							
Anthracene		...		blue		short							
Diphenyl acetylene		...		blue		short							
Naphthalene		...		ultraviolet		short							
Stilbene		...		blue		short							
CaWO ₄		...		ultraviolet + blue		short							
CsI ^e		...		ultraviolet + blue		short							
CsI ^e		Ti		blue + green		short							
CsBr ^e		Ti		ultraviolet + visible		medium short							
KBr ^e		Ti Br ½% ^f		ultraviolet		medium short							
NaCl ^e		AgCl 5% ^f		ultraviolet + blue		long							
Potassium uranyl sulfate		...		green		short							
Uranyl acetate		...		green		short							
ZnO		...		green		short							
SrS (Standard 7)		Eu, Sm		blue + green		long							

^a Obtained through spectral analysis.^b Supplied through the courtesy of the New Jersey Zinc Company.^c Supplied through the courtesy of N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands.^d Supplied through the courtesy of the Sylvania Electric Company.^e Supplied through the courtesy of the Harshaw Chemical Company.^f This is the amount of activator added to the melt. The amount retained in the crystal is much less.

levels of comparatively small energy depth but that the probability of recombination via the activators or via holes liberated thermally is extremely small compared to retrapping (the fact that photoconductivity is observed even after long periods in darkness may support this idea), or by the assumption that the thermal emission of electrons from traps may occur with an activation energy which is greater than the energy depth of the trap, so that the energy required to empty the trap thermally is greater than that required to empty it with infrared radiation.⁹

4. RESULTS

A list of the phosphors investigated is given in Table I. The first column gives our letter name for the phosphor, and the second the composition. The next columns give the color of the fluorescence and the persistence of phosphorescence. The final column gives the stimulability qualitatively. Quantitative results, determined in this laboratory by M. Sidran, will be published at a later date. The zinc sulfides, zinc cadmium sulfides, zinc oxide, strontium sulfide, and the uranyl salts were used in powder form. The various materials were selected in an effort to learn the differences in behavior of different types of phosphors (alkali halides, alkaline earth sulfides,

zinc cadmium sulfides, zinc oxide, etc.). The several zinc cadmium sulfides were studied in order to learn how much the number of traps per unit volume varied from one to the other of these phosphors which differed widely in their composition, activation, and such properties as phosphorescence, fluorescence, stimulation, and polarization.

Curves showing the rise of fluorescence for several different types of phosphors are given in Figs. 1 through 4. The discontinuity in each curve is caused by a change in the time scale after five minutes, which was introduced in order to facilitate study of the initial rise. A stationary value is reached after a time of about one hour, the time being essentially determined by the intensity of excitation (see Sec. 5). Curves for a single substance were adjusted to the same stationary value to eliminate differences due to geometry. If a straight line is drawn through the stationary value, parallel to the time axis, the area between the curve and this line, the deficiency area, represents the energy consumed in traps, and gives the number of electrons which remain excited if the energy necessary to excite an electron is known. It is a measure of the relative number of traps, even in phosphors with different light efficiencies, when the rise curves for different phosphors are normalized to the same stationary intensity. The assumption which

⁹ R. Kubo, Phys. Rev. **81**, 929 (1952).

is made is that the electrons which are trapped ultimately recombine with positive charges in processes equivalent to those undergone by the electrons which were not trapped.

Traps which give rise to a relatively wide range of lifetimes were found to be present simultaneously in most phosphors, but it will be made clear in the next section that the deficiency areas are essentially a measure of those traps responsible for the long lifetimes of excited electrons.

Figures 1 through 4 give examples of the characteristic differences in shape of the rise of fluorescence curves for various materials. In Fig. 1 curve *A* is the rise curve of a completely de-excited zinc sulfide. Curve *C* shows the rise of fluorescence after the phosphor had remained in darkness for 24 hours following excitation to a stationary value. This curve shows that a

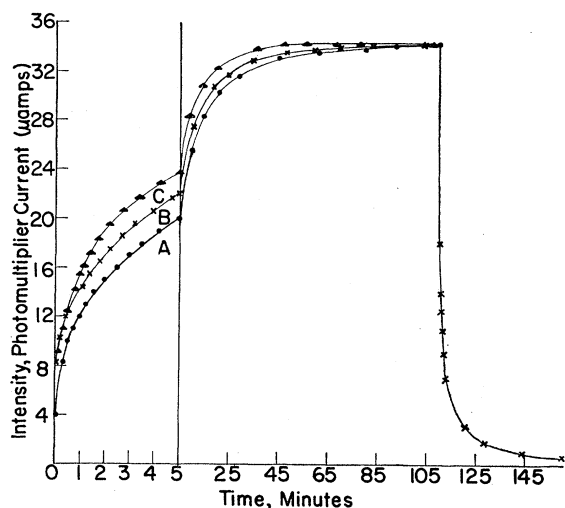


FIG. 1. Rise of fluorescence and decay of phosphorescence in ZnS R. Curve *A* was obtained after de-excitation with infrared radiation with $\lambda > 0.77\mu$, curve *C* after a 24-hour dark decay period following excitation to a stationary value, and curve *B* after de-excitation with infrared radiation with $\lambda > 1.25\mu$.

considerable number of excited electrons had recombined with positive charges, while the difference between curves *C* and *A* shows that a noticeable number of excited electrons remain in the phosphor after this length of time. A curve taken after a dark period of several minutes fell much higher than *C*.

To investigate the effect of de-excitation with different infrared wavelengths, additional rise curves were taken after irradiation through a combination consisting of a Corning 7-56 and a 4-97 filter, which transmits only wavelengths greater than 1.25 microns, corresponding to energies less than 0.8 eV. Curve *B* was taken after 1.5 hours of infrared irradiation. It shows that even wavelengths as long as 1.25 microns induce recombinations with positive charges of electrons which would normally remain excited for more than 24 hours.

Figure 2 gives the rise curves for a ZnCdS phosphor

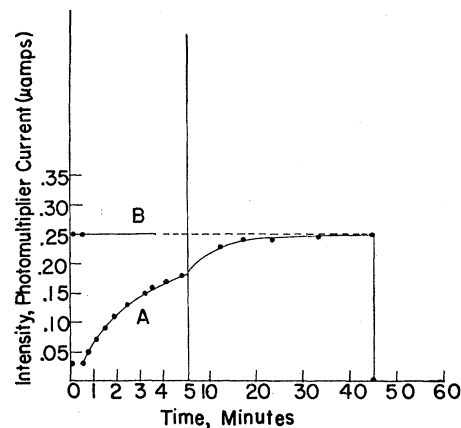


FIG. 2. Rise of fluorescence and decay of phosphorescence in ZnCdS U. Curve *A* was obtained after de-excitation with infrared radiation ($\lambda > 0.77\mu$), *B* after a 12-minute dark decay period following excitation to a stationary value.

which exhibited a very rapid decay. Curve *A* was taken after complete de-excitation, and *B* after a dark period of 12 minutes following excitation to a stationary intensity. The latter curve indicates that practically no recombination had taken place in this interval of time. Thus in this phosphor only a small number of excited electrons recombine with positive charges during a time which is of the order of the total rise time. The rapid decay can be explained by the fact that the rate of recombination of the stored excited electrons is very low. (See Sec. 5.) It may be further noted that the rise time for this phosphor is decidedly less than those of phosphors with a larger number of traps per unit volume.

Rise curves for ZnO are given in Fig. 3. ZnO behaves quite differently from the zinc cadmium sulfides in that the rise of fluorescence curve starts at a value which is about 65% of the stationary value even for a time as low as 2500 microseconds. The zinc cadmium

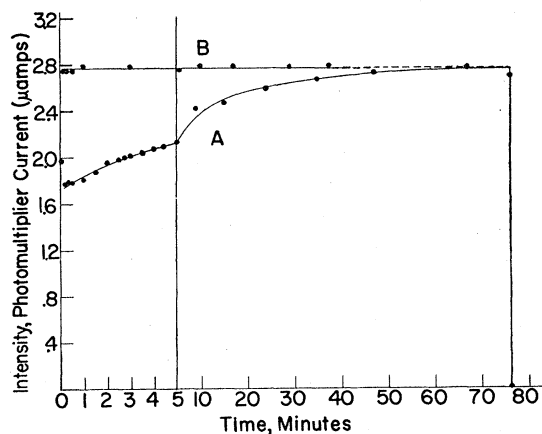


FIG. 3. Rise of fluorescence and decay of phosphorescence in ZnO. Curve *A* was obtained after de-excitation with infrared radiation ($\lambda > 0.77\mu$), curve *B* after a one hour dark decay period following excitation to a stationary value.

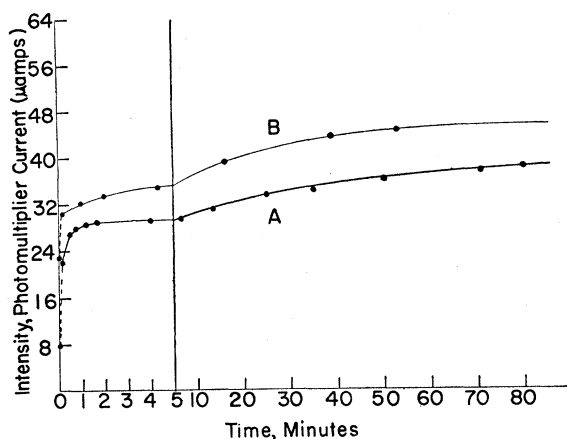


FIG. 4. Rise of fluorescence in two alkali halides. Curve A, for NaCl(AgCl 5%) was obtained after de-excitation with ultraviolet light. Curve B, for KBr(Tl), was obtained after de-excitation with infrared radiation ($\lambda > 0.66\mu$).

sulfide curves have much lower initial values. This means that only a relatively small number of the excited electrons produced by the exciting particle are trapped in ZnO as contrasted with the zinc sulfides in which a large fraction of the excited electrons are trapped immediately. It is similar to the ZnCdS in Fig. 2 in that it possesses practically only those traps in which electrons remain excited for long periods. The total number of traps per unit volume is less than for most of the zinc cadmium sulfides.

Figure 4 gives the rise curves for two phosphors quite different from those discussed above, the alkali halides KBr(Tl) and NaCl(AgCl 5%). The characteristics of the two curves are similar, with NaCl exhibiting more traps. A stationary value is not reached for hours. The steep rise of both curves in the first few seconds indicates the presence of traps in which electrons exist for only a short time. The slow rise which continues for many hours indicates that a very large number of electrons are trapped for long periods of time. The presence of these electrons was confirmed by stimulation measurements in which large quantities of stimulated light was obtained from these substances even after dark periods of several months. Curves for CsBr(Tl) are not shown. They exhibited the same general shape, but indicated fewer traps than in either of the two other alkali halides.

Curves for the Standard 7 phosphor are not shown. They exhibited still another feature in that they showed a slow rise similar to that of the alkali halides, but there was no steep rise for small values of the time. Standard 7 was found to contain a tremendous number of traps. The value of the integrated intensity doubled in 19 hours, indicating that many exciting particles must traverse the same area before all the traps can be filled. In spite of this the initial intensity is a considerable portion of the final intensity (about 50% of the value at 19 hours). This means that the mechanism

for emission is not the same as in zinc sulfide. Here the probability that an excited electron will return to the ground state almost immediately is about the same as the probability of being trapped, even though there is such a large number of traps.

Results for all the phosphors studied are summarized in Tables II and III. The first column in each gives the phosphor, the second the stationary intensity. The values of the stationary intensity for different phosphors are not to be compared with one another. They are merely the observed values, and have not been corrected for thickness of the sample, stopping power, or spectral sensitivity of the photomultiplier. In all cases in which the intensities in the second column of Table II are not large compared to the value for the Lucite backing, only the difference between the measured value and that of Lucite is given. A value of 0.31 was assumed for Lucite in that case, to account for the fact that its intensity was somewhat diminished by the absorption of some of the excitation energy by the thin phosphor layer which covered it. The third column gives the value of the intensity at 2500 microseconds as a fraction of the stationary intensity. This number is a measure of how much energy is emitted as light and not consumed in traps when a high-energy particle hits a completely de-excited sample. For the organic

TABLE II. Fluorescent intensities under electron excitation and the relative number of traps computed from the rise of fluorescence curves.

Substance	Stationary intensity ^a microamperes	Ratio of intensity at 2500 μ sec to stationary value	Relative number of traps
Anthracene	59.7	0.90	0
Diphenylacetylene	47.2	1.01	0
Naphthalene	16.0	0.95	0
Stilbene	7.75	0.98	0
CaWO ₄	20.0	0.97	0
CsI (nonactivated)	26.5	0.99	0
CsI(Tl)	78.8	0.91	0
CsBr(Tl)	149	0.79	0.076
KBr(Tl)	49.8	0.45	0.44 ^b
NaCl(AgCl 5%)	40.6	0.2	0.83 ^b
Potassium uranyl sulfate	2.04	1.08	0
Uranyl acetate	0.70	1.28	0
ZnS <i>D</i>	24.1	0.079	0.23
ZnS <i>R</i>	31.4	...	0.81
ZnS <i>N</i>	18.6	0.18	0.17
ZnS <i>M</i>	30.6	0.029	0.70
ZnS <i>A</i>	9.70	0.031	1.9
ZnS 70	3.46	0.32	0.93
ZnS <i>LG</i>	15.9	0.18	1.0
ZnCdS <i>L</i>	3.92	0.084	0.40
ZnCdS <i>K</i>	5.21	0.12	0.48
ZnCdS <i>O</i>	0.88	0.045	0.61
ZnCdS <i>U</i>	0.26	0.12	0.42
ZnO	2.70	0.67	0.44
SrS (Std. 7)	2.10	0.43	0.70 ^b
Lucite	0.33	1.03	0
Nothing	0.66	small	0

^a Values of the stationary intensity are not to be compared with one another for they are merely observed values which have not been corrected for thickness and stopping power of the samples and sensitivity of the photomultiplier.

^b The figures given represent the relative number of traps occupied after two hours of excitation. A stationary intensity had not yet been attained.

substances this fraction should be very close to 1; deviations in the table are probably due to experimental error. Those substances which evidenced a slow rise of fluorescence, the zinc sulfides and alkali halides for example, exhibit ratios of the 2500 microsecond intensity to the stationary value which are much less than unity. It can be seen also that substances which have a low ratio under electron excitation have a ratio much closer to unity under alpha particle excitation.

In the fourth column of Table II the size of the deficiency area is given as a fraction of the area below the line through the stationary value for a given time of excitation, sufficiently long to ensure that the stationary state had been attained in most substances. The value for phosphor *LG* obtained in this manner has arbitrarily been set equal to unity. The values in this fourth column are a measure of the number of electrons trapped for times at least of the order of minutes, which is of the order of 10^{15} per unit volume, with the exception of Standard 7 and the alkali halide phosphors. These substances had not attained a stationary state in the length of time normally used for observation of a stationary value of the fluorescent intensity. In these cases the figures in the table give the relative number of traps occupied after two hours of excitation. The number of electrons trapped by the time the intensity becomes stationary is considerably larger.

In those substances for which a zero is given in the last column, CsI, CaWO_4 , the uranyl salts, and the organic phosphors; the number of electrons trapped was very much smaller than for the other substances (see next section). The intensity was the same at very short excitation times as that observed after hours.

For alpha-particle excitation no figures are given for

the relative number of traps, since it was found that in most cases the rise of fluorescence under alpha-particle bombardment was instantaneous. Thus the ratio of the intensity at 2500 microseconds to the stationary intensity was nearly always found to be close to unity. For only four substances was this ratio less than unity, NaCl(AgCl 5%), ZnS *LG*, ZnCdS *L*, and Standard 7. The lower value indicates that at the very beginning of excitation a noticeable number of excited electrons are trapped. Most are trapped for less than one minute, for within one minute a practically stationary value of the intensity is observed. The difference in the behavior of the fluorescence under alpha-particle and electron excitation will be discussed in the next section.

5. CONCLUSIONS

Excitation by high-energy particles, unlike light excitation, is not uniformly distributed over the phosphor, but instead occurs in discrete regions, or channels. This can be described accurately by an integral equation, the solution of which is somewhat involved if there exists more than one trap level. It will be discussed in a future publication. As a sort of first approximation a simplified model will be presented here, which incorporates many of the essential features of the problem. The following assumptions are made. An exciting particle, in traversing the thickness of the phosphor, produces a channel containing a definite number p of excited secondary electrons. These electrons fall to the lowest excitation level from higher ones, and a fraction κ of them are trapped in states close to the lowest excitation level and in which they do not move freely. The remaining fraction, $(1-\kappa)$, of the excited electrons move close to the lower edge of the conduction band from which they recombine with positive charges according to the mechanism appropriate to the particular substance. The recombination can be either radiative or nonradiative. If the number of excited electrons in a channel is smaller than the number of available traps, almost all the electrons will tend to occupy traps. This assumption seems to hold for most of the zinc sulfides and related phosphors, since their light emission at the beginning of excitation is only a fraction of the light ultimately emitted.

Subsequent exciting particles will act in the same manner until an exciting particle produces a channel which fully or partially overlaps some previous channel or channels. When overlap occurs fewer traps are available to the excited electrons than with an unexcited area, because some of the traps are occupied due to prior excitation. Thus fewer excited electrons are consumed in traps, and more light will be emitted immediately. There will, of course, be more overlap, and hence more immediate recombination, the longer excitation continues. The probability of light emission may also increase with prolonged excitation because of the increased number of positive activators. In the zinc sulfides this does not seem to be important. As a

TABLE III. Fluorescent intensities under alpha-particle excitation.

Substance	Stationary intensity ^a microamperes	Ratio of intensity at 2500 μsec to stationary value
Anthracene	2.78	1.06
Diphenylacetylene	1.58	1.04
Naphthalene	0.49	0.94
Stilbene	2.60	1.06
CaWO_4	2.03	1.15
CsI (nonactivated)	1.00	1.15
CsI(Tl)	22.0	1.03
CsBr(Tl)	21.5	0.97
KBr(Tl)	4.00	0.95
NaCl(AgCl 5%)	6.30	0.57
Potassium uranyl sulfate	0.82	1.19
Uranyl acetate	0.22	1.00
ZnS <i>D</i>	138 ^b	0.96
ZnS <i>LG</i>	39.8 ^b	0.88
ZnCdS <i>L</i>	20.8 ^b	0.77
ZnCdS <i>K</i>	50.3 ^b	1.10
SrS (Std. 7)	8.74 ^b	0.77
Lucite	0.025 ^b	small
Nothing	0.35 ^b	small

^a Values of the stationary intensity are not to be compared with one another, for they are merely observed values which have not been corrected for the sensitivity of the photomultiplier.

^b These measurements were taken with a weaker alpha-particle source. The values given are the results obtained with the weaker source multiplied by 25, in order to permit comparison with the other substances in the table.

further simplification it is assumed that only traps of a single energy depth are present. Then one obtains the following equation for the filling of the traps:

$$dn_t/dt = r\kappa p(1 - n_t/n_{0t}) - \delta_t n_t, \quad (3)$$

where n_t is the number of traps per unit volume which are occupied; κp is the number of traps filled per unit depth by a single exciting particle when its channel does not overlap any previously excited area; n_{0t} is the number of traps per unit volume available in the unexcited sample; δ_t is the probability per unit time that an electron will leave a trap and not be retrapped [it corresponds to $1/\tau'$, in Eq. (2)]; and r is the rate at which exciting particles impinge upon unit area of the phosphor. δ_t represents a kind of average of the probabilities of release from traps with subsequent recombination, which is, of course, an oversimplified representation of the recombination mechanism in phosphors of the zinc sulfide type, since the number of electrons which are released from traps and not retrapped, but recombine, depends upon the state of excitation. There is a major point in favor of the simplified picture. When high-energy particles are used for excitation, the state of excitation for different channels is always the same, at least as long as no considerable overlap occurs, and the probability that an electron will recombine with a positive charge is the same for each excited region.

The term $-r\kappa p n_t/n_{0t}$ in Eq. (3) represents the overlap of the channels. It is that fraction of the total volume in which the traps are occupied.

If δ_t is very small, then the trapped electrons have a long lifetime; the fluorescent intensity reaches an almost stationary value when the first term in (3) becomes very small ($n_t \approx n_{0t}$ corresponding to saturation of the traps). In the other limit δ_t is so large that the right side of Eq. (3) approaches zero even for values of n_t considerably smaller than n_{0t} . The traps are filled to equilibrium.

The solution to Eq. (3) is

$$n_t(t) = \frac{r\kappa p}{(\delta_t + r\kappa p/n_{0t})} [1 - e^{-(\delta_t + r\kappa p/n_{0t})t}]. \quad (4)$$

Since $r\kappa p(1 - n_t(t)/n_{0t})$ is the number of electrons trapped per unit time at the time t , $\epsilon(t)$, the number of electrons which recombine per second without being trapped, is given by the following equation:

$$\epsilon(t) + r\kappa p[1 - n_t(t)/n_{0t}] = r\kappa p. \quad (5)$$

If all recombinations are radiative, then the number of fluorescent quanta emitted per second will be given by

$$I(t) = \epsilon(t) + \delta_t n_t(t) = r\kappa p[1 - \kappa e^{-(\delta_t + r\kappa p/n_{0t})t}]. \quad (6)$$

$I(\infty)$ equals $r\kappa p$ because of the assumption that there are no radiationless recombinations. This stationary state is reached when $t \gg (\delta_t + r\kappa p/n_{0t})^{-1}$. When δ_t is small compared to $r\kappa p/n_{0t}$ the lifetime of the electrons in the traps is long, and the time required to approach a stationary state is $n_{0t}/r\kappa p$, which is inversely propor-

tional to the intensity of excitation represented by r . For δ_t large compared to $r\kappa p/n_{0t}$ the stationary state is reached in a time of the order of $1/\delta_t$, which does not depend on the intensity of excitation.

One would expect that Eq. (6) would give a rather good approximation to the observed rise of fluorescence if the lifetime of the electrons in the traps is of the order of one hour or longer, for then the most questionable part of the equation, δ_t , gives only a small contribution.

Theoretical curves, plotted from Eq. (6) are given in Fig. 5. The values of the parameters κ and n_{0t} were selected to approximate the experimental conditions as closely as possible. The number of exciting electrons was $3 \times 10^7/\text{cm}^2 \text{ sec}$ at the position of the sample. The quantity $p = 0.5 \times 10^5$ is the number of excited electrons per high-energy electron in unit thickness of zinc sulfide.¹⁰ The number of traps per unit volume, n_{0t} , was chosen to be 1.5×10^{15} in order to make the theoretical curves reach stationary values at about the same time as the experimental curves, namely, one hour. κ was assumed to be 0.8. These values roughly correspond to phosphor LG. If κ is smaller, corresponding to a greater initial emission, then n_{0t} is also smaller by the same factor, for a given time to reach equilibrium. The uppermost curve in Fig. 5 was plotted assuming κ equal to 0.4 and n_{0t} equal to 0.75×10^{15} . The experimental rise curves taken after different dark periods show that there is little recombination of stored electrons during the rise time. With phosphors of the type given in Figs. 2 and 3 this condition is fulfilled accu-

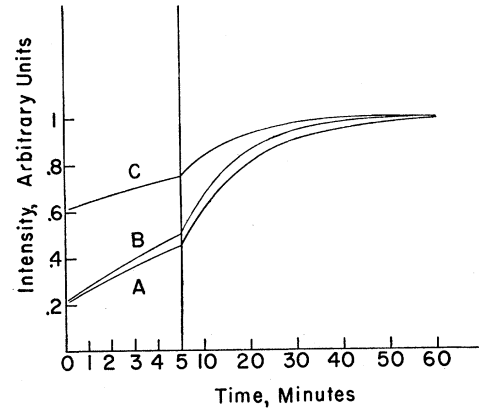


FIG. 5. Theoretical curves of the rise of fluorescence plotted from $I(t) = r\kappa p\{1 - \kappa \exp[-(\delta_t + r\kappa p/n_{0t})t]\}$, where $r = 3 \times 10^7$ exciting particles per cm^2 per second, $p = 0.5 \times 10^5$ excited electrons per high energy electron in unit thickness of ZnS, n_{0t} is the number of traps per unit volume, κ is the fraction of the excited electrons which are trapped in a de-excited sample, and δ_t is the probability per unit time that an electron will leave a trap without being retrapped. Curve A: $n_{0t} = 1.5 \times 10^{15}$, $\delta_t = 0$, $\kappa = 0.8$. Curve B: $n_{0t} = 1.5 \times 10^{15}$, $\delta_t = 1/3600$, $\kappa = 0.8$. Curve C: $n_{0t} = 0.75 \times 10^{15}$, $\delta_t = 1/3600$, $\kappa = 0.4$.

¹⁰ This number was obtained by assuming that a 1-Mev electron is stopped in one centimeter of ZnS, and that the efficiency of conversion from high energy to light is about twenty percent. See Furst, Kallmann, and Kramer, Phys. Rev. **89**, 416 (1953).

ately. Therefore it must be assumed that the stationary intensity in these experiments corresponds to saturation of the deeper traps. Direct evidence that this is the case was provided by measurements on the infrared stimulation as a function of the duration and intensity of excitation. The stimulated intensity obtained after one hour of excitation was not exceeded by that obtained after increased intensity and duration of excitation. It can be seen that there is very little difference between the curve plotted assuming that the electrons are trapped for an infinitely long time and that plotted assuming that the electrons are trapped for one hour. Only for very much shorter trapping times would a pronounced difference become evident. Deviations of the experimental curves from the shape of the theoretical curves occur because of the presence of various trap levels and because of the change in re-trapping with continued excitation. The deviations occur mostly at the very beginning of the curves where the intensity increases faster than according to Eq. (6), indicating that they are due to electrons which are trapped for only a short time. If the first minute or so of some of the experimental curves were to be eliminated, the agreement with the theoretical curves would be good. The experimental curve for ZnO, in which electrons are trapped only for long periods of time, shows good agreement with the uppermost theoretical curve. The curve for phosphor *U* can be approximated by a theoretical curve with κ equal to 1 and n_{0t} equal to 0.3×10^{15} .

No assumption has been made thus far concerning the radius of the channel of excited electrons. The size of the channel appears only indirectly in the factor κ and the number of traps available. For a given radius, if there is only a small number of traps available, κ can only be small. Now it was observed that in most of the zinc sulfides κ is close to 1, the rise curves having set in at low values, even in those substances which have a relatively small number of traps, such as phosphor *D*. This may indicate that the radius of the channel is to some extent determined by the number of available traps. That is, the excited electrons diffuse out until they are stopped by traps. An experimental observation which lends credence to this hypothesis is that in substances with relatively small trap densities the stationary state is reached earlier. With phosphor *U* the intensity reaches $1/e$ of the final value in 3.5 minutes, while with phosphor *LG* the intensity reaches that value in 7.5 minutes. The relative number of traps, calculated from the deficiency areas, is 0.4 to 1 for *U* compared to *LG*. This would not be compatible with the assumption of a definite channel radius, because, in that case, a stationary state should not be reached until overlap of the channels has occurred at least once, and the time required for that would be completely determined by the radius of the channel, for a given excitation intensity. The material presented here is not sufficient to warrant drawing a definite

conclusion, the number of electrons trapped with long lifetimes being not very different in the different phosphors. Experiments conducted with other substances which contained far fewer traps than those reported on here, however, indicate that when the lifetime of the electrons in the traps is long a stationary state is indeed reached in far less time than one hour with the same intensity of excitation.

The difference between the results of electron excitation and those of alpha-particle excitation stems from the large difference in their densities of excitation. With alpha-particle excitation there is no question but that the excited electrons do not diffuse far enough for them to be consumed in traps to any great extent. In most of the cases studied, under alpha-particle excitation κ is a very small number, as can be derived from the fluorescent intensity at 2500 microseconds. The explanation is the following: the alpha particle, in passing through the sample, produces a line of positive charge which diffuses only slightly, because the positive charges are localized at activator atoms, which are far more numerous than traps. The channel of excitation therefore consists of an interior core of positive charge surrounded by a cylinder of excited electrons. Because the charge of the core is so much greater in the case of alpha-particle excitation than for electron excitation the excited electrons will not diffuse beyond a certain distance ρ . Thus in the case of alpha-particle excitation the radius of the channel is essentially determined by the strength of the positive charge, whereas with electron excitation the positive core very likely does not interfere with the diffusion of the excited electrons. Only those traps in the area up to which electrons are able to diffuse can be filled, and their number is much smaller than the number of excited electrons produced by an alpha particle. The radius of the channel due to a 3-Mev alpha particle in ZnS can be calculated to be approximately 3×10^{-5} cm by assuming that a difference of potential of 10 volts between the outer radius and the radius of the cylindrical positive core is sufficient to stop the diffusion of electrons, and that the charge of the core is 2×10^{-11} coulomb/cm. With a channel of this size the number of traps is less than 1% of the number of excited electrons (assuming 1.5×10^{15} traps/cm³). The radius of the channel will very likely be somewhat smaller in actuality, for the higher energy electrons which originate from the center of the positive core will not travel in a direction perpendicular to the path of the alpha particle, but will be scattered. With a potential difference of 1 volt between the channel and core radii, the former is only about 10% larger than the latter, which is about 6×10^{-6} cm. The core radius was obtained by assuming that the positive holes created migrate to activators, of which there are 10^{18} /cm³.

From the results presented here, several conclusions can be drawn: The number of traps per unit volume responsible for the long lifetimes of excited electrons is

rather small, at most one part in 10^7 of the molecules of the base material and does not vary considerably among the different ZnCdS phosphors. Therefore it seems unlikely that these traps are due to the impurities Ni, Co, or Fe, which are present in larger concentrations and vary considerably from phosphor to phosphor (Table I). Phosphor *M*, with a mole fraction of 10^{-5} of Ni, has no more traps than samples containing much less Ni. These findings may indicate that those traps in which electrons remain for long periods of time are due to imperfections other than the impurities indicated.¹¹

Another consequence of the investigation is that for the ZnCdS phosphors stimulability is not related to the number of traps available in a sample, and the high stimulability of the Fonda type phosphors is not due to a large number of traps. Phosphors with a comparable number of traps showed huge differences in stimulability, that property being characteristic of only those phosphors in which suitable activators are present, as in phosphor *LG*, for example. Phosphor *A*, with twice as many traps as *LG*, shows one-sixth the stimulability of *LG*.

Phosphorescence is related to the number of traps in the following way: If there are no traps from which electrons recombine radiatively with positive charges after a relatively short time, there will be no phosphorescence, because very few electrons recombine per unit time from the deeper traps. This is the case with phosphors *U*, *O*, and ZnO. Phosphor *K* also has a rapid decay, and yet it possesses a considerable number of traps in which electrons remain only for several minutes. Here the short persistence is due to a strong quenching of the radiation. Comparison of the deficiency areas above rise curves for different dark periods with areas under the phosphorescence decay curves for the same lengths of time as the dark periods provides an independent means for determining the radiation quenching.

Another point which should be discussed is the factor $(1-\kappa)$, which represents the fraction of the excited electrons which give rise to light emission without having been trapped. $(1-\kappa)$ is practically given by the ratio of the intensity at 2500 microseconds to the stationary value. $(1-\kappa)$ is small for most of the zinc sulfides with the exception of *N*, *LG*, and 70. This smallness of $(1-\kappa)$ is consistent with the bimolecular recombination process assumed for zinc sulfide. The number of ionized activators is roughly equal to the number of trapped electrons, and since the cross section for recombination accompanied by radiation is much smaller than that for trapping, it is not unreasonable that $(1-\kappa)$ is small. What is surprising is that there are some zinc cadmium sulfides for which this factor is considerable. With the *LG* powder this may be due to the presence of the special activators which are also

responsible for the strong stimulability of the phosphor and which increase the probability of recombination, as was shown by photoconductivity measurements.³ The fact that $(1-\kappa)=0.6$ in ZnO is also remarkable, and seems to point to another mechanism for emission and trapping, since for about the same number of traps per unit volume as the zinc sulfides the initial emission is greater by almost a factor of ten.

Though it is true that the organic phosphors have fewer traps than the zinc sulfides, the number is not so small that a zinc sulfide with this number would not exhibit a measurable rise of fluorescence. Because the mechanism for emission is different in the organic phosphors, $(1-\kappa)$ is very large, and the initial value of the rise curve is very close to the maximum. There is a slight increase in intensity which continues for a long period of time, which is difficult to detect. This may also be true of other substances where no traps were found.

For the alkali halide phosphors and Standard 7 the situation is quite different from that of the zinc cadmium sulfides. These phosphors contain a very large number of traps per unit volume, most of which are those in which electrons remain for long periods of time. In spite of this, the factor $(1-\kappa)$ is of the order of $\frac{1}{2}$ in some cases. One must conclude, therefore, that the light-emitting process is not at all related to the trapping process in these phosphors, and there is equal likelihood for an electron to recombine with a positive charge radiatively as for it to be trapped, regardless of the number of empty traps available.

The foregoing considerations pertain to excited electrons with long lifetimes due to the presence of relatively deep traps. There are certainly many shallow traps, however, as is evident from the initial steep rise in the alkali halide curves and from the low ratio of the intensity at 2500 microseconds to the stationary value under alpha particle excitation in some substances. The fact that the fluorescent intensity increases only slightly from 2500 microseconds to 1 second in most substances under electron excitation, showing that there is not much radiative recombination in this interval, does not mean that there are not many shallow traps, but that electrons released from them are retrapped in deeper traps, preventing their immediate radiative recombination.

The fact that the ratio of intensity at 2500 microseconds to the stationary value is at all smaller than unity for the zinc cadmium sulfides with alpha particle excitation may be somewhat surprising, since the rise of fluorescence is rather rapid in those substances. This probably means that all the deep traps in the limited region excited by an alpha particle are occupied by electrons immediately, and, in addition, a considerable number of very shallow traps in which electrons remain for only very short periods of time are also occupied, and electrons leaving them are not retrapped in deeper traps as is the case with electron excitation, since these are already occupied.

¹¹ In reference 4 curves are presented which show a change in the traps per unit volume with Ni content. Neither these results nor those in reference 5 can be compared with ours because the intensity of illumination and the lifetimes of the excited electrons are not given.