Induced Conductivity and Light Emission in Different Luminescent Type Powders*†

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The currents induced in various (Zn:Cd)S luminescent-type powders by ultraviolet radiation have been investigated as well as the quenching and stimulating effects due to infrared radiation. Similar experiments on the fluorescent emission have also been carried out. Currents induced in these powders by high energy particle radiation is also described. A model is proposed which contains two types of electron traps, deep traps and shallower traps (which are associated with the emission levels at the activator), and a coupling between the deep traps and the emission levels is assumed. Theoretical calculations based on this model are compared to the experimental results for stationary and nonstationary behavior. This comparison shows that in all (Zn:Cd)S powders investigated, traps exist from which so-called "direct transitions" to the activators occur with negligible contribution to the conductivity. These transitions may not be radiative, and they also occur in materials which exhibit no noticeable light-stimulation by infrared radiation.

I. INTRODUCTION

IN the last few years an increased interest has developed in the light or high energy particle induced conductivity in ZnS or [Zn:Cd]S phosphors. The earliest paper of Pohl and his co-workers has already described basic experiments in this field.[1] The situation became more interesting when Frerichs[2] found that in single CdS crystals tremendous currents can be produced, that one single alpha-particle or gamma-photon can induce a charge transport of about 10^{10} or more electrons. Such experiments have been described in more detail by Frerichs,[3] by Kallmann and Warminsky,[4] and Kallmann.[5] Another type of experiment dealing with fluorescent powders has been described by Hardy,[6] who also describes the influence of infrared light on these induced currents. Other papers in this field were also published by Bube[7] and Gildart and Ewald.[8] We will discuss these papers later.

The present paper deals with the conductivity of different [Zn:Cd]S powders. The experimental arrangement is similar to that of Hardy. The main difference is that in the present paper the investigation is also carried through for high energy radiation as an exciting agent; that our experiments cover a much larger range of current than those of Hardy; and that the infrared stimulation and quenching was investigated as a function of simultaneous ultraviolet intensity and infrared wavelength.

We will first present the results obtained with seven different luminescent powders and several nonluminescent samples and will then describe a theory which seems to cover some of the most important and general features of these measurements. In these measurements it was found that the ultraviolet induced current exceeds the number of electrons excited per second in the sample by a large factor. In the experiments with single CdS crystals[3-5] the current was 10^6 times larger than the number of excited electrons per second, while in the present experiments with different powders the current is only about 100 to 1000 times larger than the number of excited electrons per second, probably as a consequence of the contact resistance and nonuniform illumination of the powders.

II. EXPERIMENTAL APPARATUS

A. Current Measuring System

Figure 1 shows the electrical circuit used to measure the induced currents. Since a range of currents from 10^{-11} ampere to 10^{-2} ampere was covered, the circuit actually consisted of two separate units, each of which served only for a part of the range. For currents below 10^{-9} ampere an electrometer tube with a grid resistor of 10^{10} ohms was used in series with the powder being
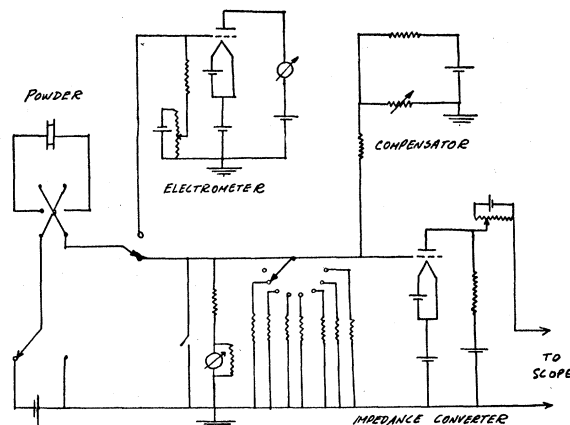
[1] B. Gudden and R. W. Pohl, Z. Physik. 3, 98 (1920); see also L. Bergmann and F. Ronge, Physik. Z. 41, 349 (1940).

[2] R. Frerichs, Phys. Rev. 72, 594 (1947).

[3] R. Frerichs, Phys. Rev. 76, 1869 (1949).

[4] H. Kallmann and R. Warminsky, Ann. Physik 4, 69 (1948) and 4, 57 (1948).

[5] H. Kallmann, Signal Corps Engineering Report E-1036 (Fort Monmouth, New Jersey).

[6] A. E. Hardy, Trans. Electrochem. Soc. 87, 355 (1945).

[7] R. H. Bube, Phys. Rev. 83, 393 (1951).

[8] L. Gildart and A. W. Ewald, Phys. Rev. 83, 359 (1951).

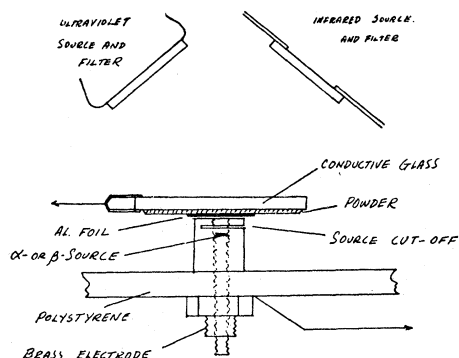FIG. 1. Schematic diagram of current measuring apparatus.

FIG. 2. Diagram illustrating radiation and electrode arrangement.

investigated, and the voltage drop across the resistor was determined. To extend the range of the electrometer circuit to higher currents, a variable voltage (up to 45 volts) was placed in series with the grid resistor so that the tube could be brought back to its original grid bias by varying this voltage.

For current ranges above 10^{-9} ampere a high sensitivity galvanometer was used with a protecting resistance of 10^7 ohm in series. Suitable shunting resistances could be placed across this combination so that currents up to 10^{-2} ampere could be measured. A resistance of 25,000 ohms was placed directly across the galvanometer's terminals so that it was critically damped at all current ranges. To permit observation of relatively fast changes a dc oscilloscope, connected directly across the galvanometer and its protecting resistance so that both instruments would simultaneously follow the current range as the shunt resistors were thrown in was desirable. It was necessary, therefore, to introduce an impedance converter (electrometer tube) between the galvanometer and oscilloscope so that the oscilloscope could be used in parallel with resistances up to 10^{12} ohm. The oscilloscope was connected between ground and the high side of the plate resistor and a variable voltage inserted between the letter and the high terminal of the oscilloscope. This voltage could shift the zero current line of the oscilloscope and adjust for the constant plate voltage otherwise acting on the input of the oscilloscope. To eliminate pick-up a 60-cycle filter was also inserted before the oscilloscope.

In order to measure small current changes super-imposed upon steady dc currents, a compensating circuit as shown in Fig. 1 was used. This supplied an additional current through the resistor network. The "powder noise" was the limiting factor to the amount of compensation that could be applied; thus only a change of 1 percent of the steady current through the powder could be detected.

B. Radiation Arrangement

The radiation arrangement allowing simultaneous exposure by ultraviolet, infrared, and high energy particle radiation is shown in Fig. 2.

The ultraviolet source was of the mercury discharge type with the most intense radiation at 3660A. This wavelength is not low enough to excite electrons from the valence band to the conductivity band of ZnS phosphors, but with ZnCdS phosphors this wavelength is close to the absorption edge of the lattice or even below this value. About 5 to 10 microwatts per cm^2 was incident upon the powder during measurements. The infrared source was an ordinary 250-watt heating lamp enclosed in a light tight container with a 1-inch aperature. Using the most common type of infrared filter (Corning 7-56) about 1 milliwatt per cm^2 (about 25 percent between 0.8 and 1.2μ) was incident upon the powder. Both lamps had appropriate provision for mounting several 2-inch square filters directly in front of the light source.

The alpha- and beta-sources were directed at the side of the powders (away from the ultraviolet and infrared illumination) through a thin aluminum electrode (see below). They were placed within 0.5 centimeter of the powder's surface. The gamma-source was placed on top or at the side of the conductive glass. The alpha-particles were supplied by a 3-millicurie polonium source, the beta-particles by a 10-millicurie strontium 90 source, and the gamma-radiation by a 1-millicurie radium source.

The ultraviolet and infrared intensities were measured by a calibrated thermopile. These measurements were made several times during the investigation and showed that the sources stayed comparatively constant.

To measure the light emission of the excited powder a more elaborate method was required. For this purpose a Photovolt Meter (512M) with a 1P28 multiplier was used, and Corning Glass Filters were interposed

TABLE I. Composition, electrical and optical characteristics of some luminescent powders investigated.

Powder	Composition	Activators	Luminescent color	Visual persistence	I_{uv} (max) amp	Time to decay to $1/50 I_{uv}$ for strongest excitation	I_{ir} amp	Q (%)	I_{uv} amp
K	(Zn:Cd)S	Pb; Cu; Ni	Yellow	Short	10^{-3}	15	2×10^{-6}	54	1.3×10^{-5}
L	(Zn:Cd)S	Pb; Cu	Yellow	Long	3×10^{-5}	60	0	72	2.5×10^{-7}
M	ZnS	Mg; Cu	Green	Long	2×10^{-4}	120	7×10^{-9}	99	6×10^{-7}
N	ZnS	Ag	Blue	Long	2×10^{-6}	10	5×10^{-8}	26	2×10^{-6}
O	(Zn:Cd)S	Ag	Red	Short	10^{-5}	15	$\cdots$	$\cdots$	$\cdots$
D[a]	ZnS	Pb; Cu	Blue-green	Short	2×10^{-6}	10	2×10^{-7}	65	2.6×10^{-6}
P	ZnS	Cu; Co	Green	Long	2×10^{-6}	18	$\cdots$	82	10^{-6}

[a] This powder was supplied by Dr. Dropkin of the Polytechnic Institute of Brooklyn.

between the sources and powder and between the powder and photomultiplier so that only the luminescent wavelengths were effective. The sources were placed at the same positions with respect to the powders to be measured for light emission as they were when the powder's conductivity was to be investigated. The small amount of direct radiation was measured and subtracted from our readings.

C. Powder and Electrode Arrangement

Most conductivity measurements on powders are made using metal plates pressing the powder together and simultaneously acting as electrodes. Such an arrangement was not feasible in our experiments since alpha- and beta-particles were to be used in some investigations. On the other hand, a transparent electrode was required so that the powder in the electrical field could be exposed to ultraviolet and infrared radiation. The following method of preparing the powder and electrodes has proven satisfactory. A thin film of amyl acetate in which a small amount of Duco cement had been dissolved was spread on a glass plate which had been obtained with a transparent conductive layer.[6,9] The powder was scattered onto the solution until the required thickness (5-30 milligrams per cm²) was obtained, and left to dry for several hours. In this way a thin, rather homogenous layer of powder making good contact with one electrode was obtained. The ultraviolet and infrared radiation was directed at the powder through this glass electrode, and losses in intensity due to passage through the glass were less than 15 percent.

The other electrode was a thin aluminum foil which was transparent to alpha- and beta-particles. This foil was placed on top of a hollow brass cylinder, the high energy source screwing into the cavity. The sample was placed over the aluminum foil with the exposed powder surface resting on the aluminum, and the potential between the conductive glass and the brass cylinder slowly raised. The field drew the foil tightly against the powder making electrical contact with the surface grains. The powder and electrode arrangement are shown in Fig. 2.

III. EXPERIMENTAL RESULTS

Table I lists some of the luminescent powders used together with a summary of their optical and electrical characteristics.

A. Voltage Dependence of Ultraviolet Induced Currents

Figure 3 shows the voltage dependence of the current induced in powder K by ultraviolet radiation. This curve is typical of all powders measured and shows an almost exponential dependence at low field strengths

[9] Now available from Corning Glass Works or Pittsburgh Plate Glass Company.
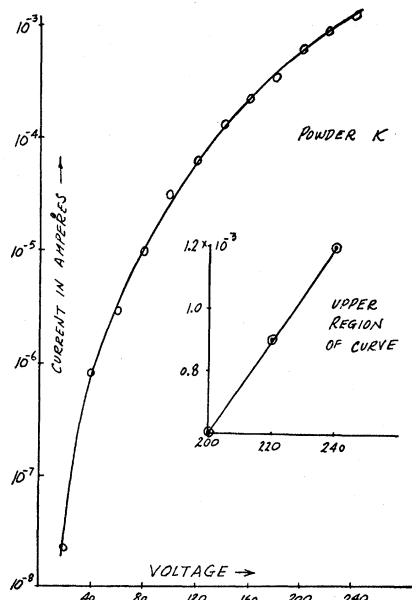

FIG. 3. Dependence of ultraviolet induced current as a function of potential across powder.

changing to an almost linear dependence at higher field strengths contrary to the results obtained[4,5] with single CdS activated crystals which showed an ohmic relation over the entire voltage range measured. Although no other powder shows as high an induced current as powder K, all show the same tendency toward linearity at higher field strengths indicating that there was negligible breakdown even at these higher fields. The magnitude of the fields used in our measurements may be roughly given by noting that the powders ranged from about 0.1 to 0.2 mm in thickness, and potentials of several hundred volts were applied, giving fields of about 10,000 volts per centimeter.

Since Duco cement was used as a binder, measurements were made to determine if there was any effect on the induced current by the binder. A thin film of Duco was deposited on the conductive glass surface, which then was placed in our apparatus. This layer was about 5 milligrams per cm² and showed approximately constant resistance, 10^9 ohms up to 600 volts, the largest potential applied. There were no changes in this current when the layer was exposed to ultraviolet or infrared radiation. Since a powder which had been excited by ultraviolet until its effective resistance was 10^5 ohms could be "quenched" until its effective resistance was greater than 10^{13} ohms, it can be seen that the binder has negligible effect upon our measurements. It is to be noted that the amount of binder used to fix the powders is much smaller than the layer measured.

Figure 4 shows the dependence of current on field strength for two thicknesses of the same powder. It can be seen that in this case this relationship is not a function of the sample's thickness, the ratio of the thick-
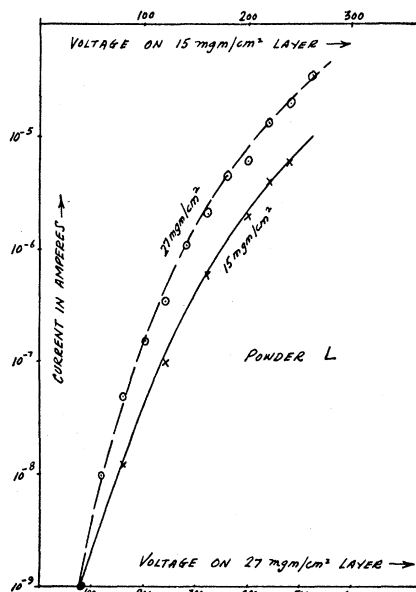
FIG. 4. Dependence of ultraviolet induced current as a function of potential across powder for two different thicknesses of the same powder.

nesses being approximately equal to the ratio of the applied potentials to obtain the same induced current. There may be some such dependence if much wider ranges of thicknesses are used, but this was not investigated.

B. Intensity Dependence of Ultraviolet Induced Currents

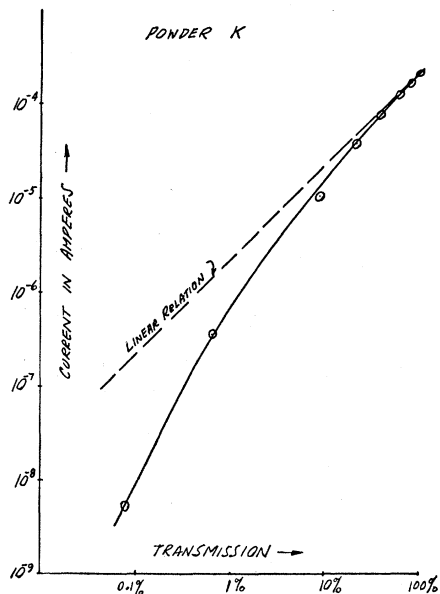To measure the dependence of the ultraviolet induced current as a function of the exciting radiation,

FIG. 5. Dependence of ultraviolet induced current as a function of the exciting intensity for powder K. The abscissa refers to the transmission rating of the Wratten filter placed in front of the ultraviolet source.

a series of neutral filters were inserted directly in front of the ultraviolet source. In this way the effective intensity could be varied down to 0.1 percent of the original value. The magnitude of the current induced by ultraviolet radiation without any neutral filters before the source (about 5 to 10 microwatts per cm² intensity) is given in column 5 of Table I. When unexcited the dark current exhibited by these powders was less than 10^{-10} ampere if the powder was dry and thoroughly quenched by infrared radiation.

All powders showed a tendency toward a linear dependence of the currents on the intensity at higher intensities, the current dropping off from the linear relation at lower intensities; this is very pronounced for powder M. Figures 5, 6, and 7 show current *versus*
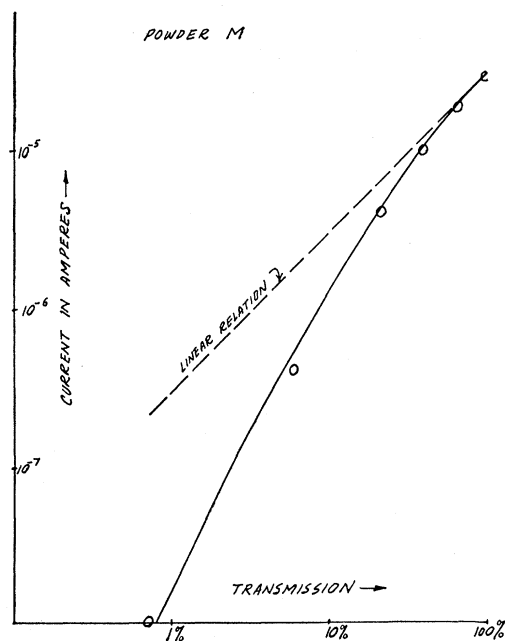

FIG. 6. Dependence of ultraviolet induced current as a function of the exciting intensity for powder M.

intensity curves for several powders measured. Some discrepancy was noted when measurements made with decreasing intensity were checked against measurements made while the intensity was increased. It was found, however, that this lack of consistency could be eliminated if enough time was given (up to several hours) so that the current could come to an equilibrium value. This effect can be explained by the assumption that the probability for the electrons in the conductivity band to fall into empty traps is greater than that of their recombination with the ionized activators (see Sec. IV B).

An explanation of these current-intensity curves will be given in the theoretical section of this article. Since the current-voltage curves show that the resistance of the samples depends strongly on the applied voltage it might be suspected that the resistance also depends

on the current, and that, for instance, the drop in current from linearity at low intensities stems from a certain change in the contacts of the individual grains of the powder. To investigate this point we have made current-intensity runs at various voltages. The curves obtained (Fig. 8) show similar current-intensity relations for different voltages, and since at different voltages the current changes greatly, these results seem to indicate that the observed deviation from linearity is an intrinsic effect of the powder and is not appreciably affected by grain contact.

C. Decay of Ultraviolet Induced Currents

After an equilibrium current value had been established under steady ultraviolet excitation, the ultra-
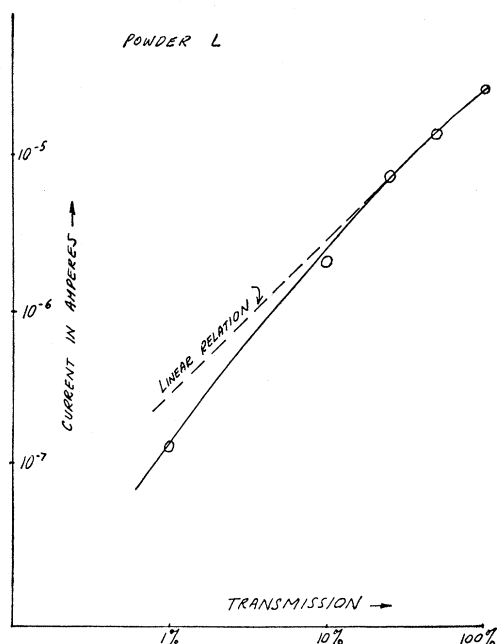

FIG. 7. Dependence of ultraviolet induced current as a function of the exciting intensity for powder L.

violet radiation was interrupted and the decay of the current was measured. Column 6 of Table I shows the time required (in seconds) for the current to decay to 1/50 of its original value. Figures 9 and 10 show decay curves for powders K and L for various values of initial exciting intensities. Although the initial currents vary by large amounts it can be seen that all curves merge after a given time, that is, the magnitude and rate of decay of the currents is independent of the initial intensity if we are far enough along the decay curve. Thus the large induced currents show a very fast initial drop, while the smaller currents decay initially at a much slower rate. Although some powders (L, M) had "long persistence" light emission while others
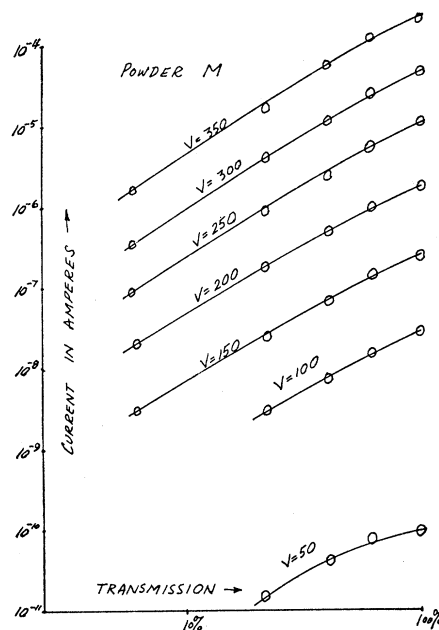
FIG. 8. Current versus intensity curves for various potentials across the powders.

(K, O) showed no persistence at all, the current decay times were all of similar magnitude.

A dependence of the decay curve on temperature was noted. A hot air blower directed at the sample under investigation increased the rate of decay (Fig. 11). However, this dependence was not investigated in detail.

FIG. 9. Current decay for different values of initial ultraviolet excitation for powder K.

FIG. 10. Current decay for different values of initial ultraviolet excitation for powder L.

D. Effects of Infrared Irradiation on Ultraviolet Induced Currents
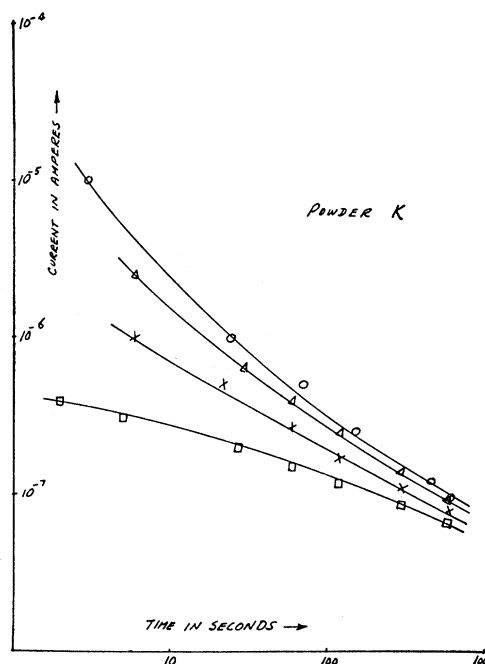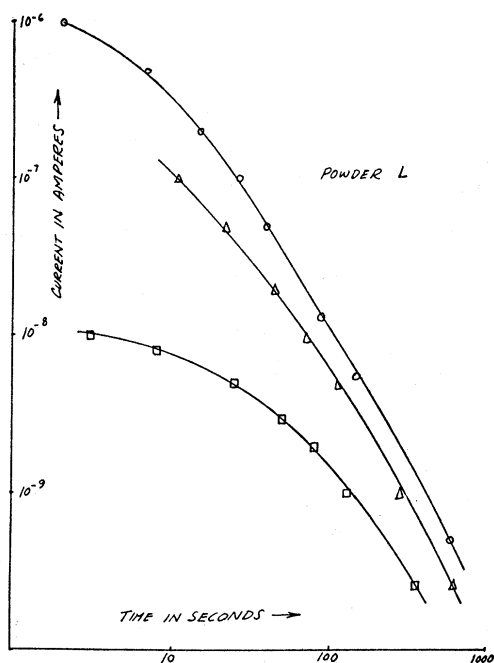
1. Simultaneous Irradiation

Simultaneous irradiation of the powder by ultraviolet and infrared light resulted in general (after the current induced by ultraviolet radiation had come to a stationary value) first, in a stimulation, then in a quenching of the current. For some powders (K, D)
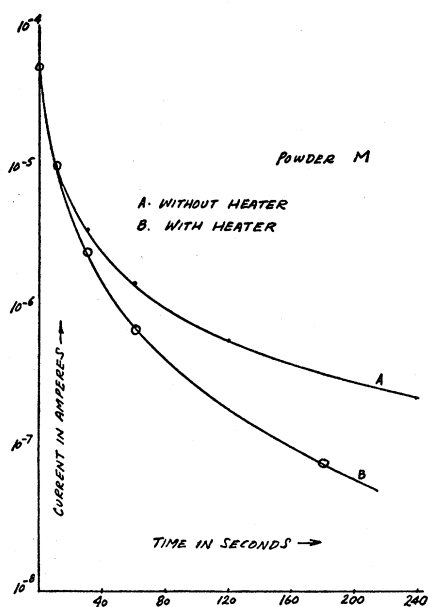

FIG. 11. Heating effect on the current decay of powder M.

the stimulation could be observed at large currents (greater than 10^{-6} ampere), but for others (L, M) the stimulation effect could be noted only at much lower currents.

The stimulation effect was readily noted by using the compensating circuit to buck out the steady ultraviolet current through the galvanometer. The sensitivity of the entire detecting system could then be increased, and if there was any stimulated current pulse, it could be easily observed. Column 7 in Table I gives the absolute magnitude of these peaks (ΔI_{ir}). Since these values depend on the simultaneous ultraviolet intensity, column 9 gives the steady ultraviolet induced current which is indicative of the ultraviolet intensity at which these readings were taken.

The magnitude of ΔI_{ir} showed definite saturation effects with increasing ultraviolet intensity. For large intensity, ΔI_{ir} approached a constant, while it became proportional to the intensities at lower values of the latter. This is seen in Fig. 12 in which ΔI_{ir} is plotted as a function of I_{uv} for powder K.[10]
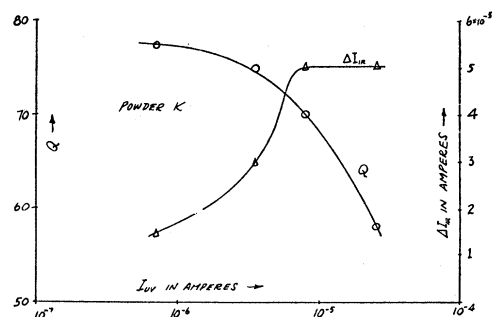

FIG. 12. Dotted line: infrared current stimulation as a function of original ultraviolet induced current; full line: infrared quenching of current as a function of original ultraviolet induced current.

The quenching of the initial currents by the infrared radiation is given in column 8. Q is defined as $[(I_{uv} - I_{uv+ir})/I_{uv}] \times 100$ percent, where I_{uv+ir} is the equilibrium current obtained when infrared radiation is added to ultraviolet radiation. The quenching Q was observed for all luminescent powders measured, and showed a definite dependence on the ultraviolet intensity. This dependence is shown for powder K in Fig. 12 where the abscissa again describes I_{uv} which is indicative of the uv intensity in this range. In contrast, other powders show Q's greater than 90 percent at lower ultraviolet intensities.

When I_{uv+ir} had reached an equilibrium value, the infrared radiation was interrupted and the current began to increase to its original values. If a stimulated peak had been observed before quenching occurred, then a drop in current $(\Delta I_{ir}')$ of the same order of magnitude as the peak was usually observed when the infrared radiation was cut off. A similar increase,

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[10] Powders N and D show similar saturation effects.

quenching, dip, and recovery had previously been noted.[6]

For low values of I_{uv} this increase after quenching by infrared radiation was extremely slow and sometimes hours were required before the current reached its original value. At higher values of I_{uv} this recovery was much faster but was still relatively slow when compared to the recovery if the ultraviolet radiation had been interrupted for the same period as the infrared had been turned on. This indicates the existence of a limited number of deep traps and will be discussed more fully below.

By using Corning filters some idea of the stimulation and quenching effects as functions of the wavelength of infrared radiation could be obtained, and a brief summary is given in Table II. An ultraviolet intensity was chosen to give noticeable stimulation and quenching effects, but it should be noted that for each powder ΔI_{ir} and Q varied with the ultraviolet intensity. With filter 7-69 passing wavelengths between 0.70 and 1.1 microns, the stimulation and quenching effects are of the same order of magnitude as the effects noted when using a 7-56 filter which passes from 0.8 to 4 microns

TABLE II. Infrared stimulation and quenching effect (at various infrared wavelength regions) on induced currents.

Powder	I_{uv}	ΔI_{ir} 7-56	7-69	7-56 4-72	Q 7-56	7-69	7-56 4-72
K	1.3×10^{-5}	2×10^{-6}	10^{-6}	0	54	43	5
D	2.6×10^{-6}	2×10^{-7}	2×10^{-7}	5×10^{-8}	65	75	20
M	6×10^{-7}	7×10^{-9}	10^{-8}	2×10^{-9}	99	99	94
L	2.5×10^{-7}	0	0	$\cdots$	72	94	$\cdots$
N	2×10^{-6}	5×10^{-8}	5×10^{-8}	0	26	40	10

and passes an over-all light intensity greater than 7-69 by a factor of 10. It is thus evident that the transitions giving rise to stimulation and quenching are mainly in the energy range defined by the 7-69 filter. Although this effect is pronounced, a second effect—the production of stimulation and quenching by radiation further in the infrared has been noted. With a combination of a 7-56 and 4-72 filter the intensity is about the same as for the 7-69 filter, but no wavelengths below 1.3 microns are effectively passed. Stimulation could be detected in some powders, and at low uv intensities Q values even greater than 90 percent were obtained (powder M).

2. Infrared Irradiation without Simultaneous Ultraviolet Excitation

A curve for powder K showing the effect of infrared irradiation applied at different times along the decay curve is given in Fig. 13. Along the earlier parts of the decay curve a noticeable quenching may be observed, while the quenching at very low currents (long after excitation has ceased) becomes smaller. At these low intensities, the infrared radiation stimulates the current
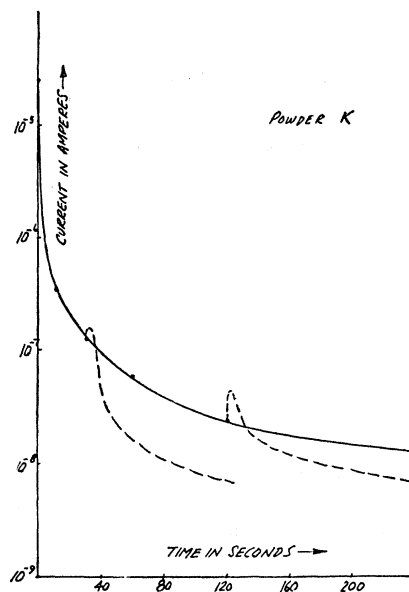
FIG. 13. Infrared current stimulation and quenching after ultraviolet excitation had been interrupted. Dotted lines indicate current when infrared is turned on.

for a long interval (up to several minutes) before the current is driven below the original decay curve (not shown in Fig. 13). Thus, in general, it can be said that on the decay curve the stimulation effect gains dominance over the quenching effect as the current drops in magnitude.

If the infrared radiation is shut off when the current has been driven below the usual decay curve, a further

FIG. 14. Fluorescent intensity as a function of ultraviolet intensity for powders L and K.

TABLE III. Infrared stimulation and quenching effects on light emission of two luminescent powders.

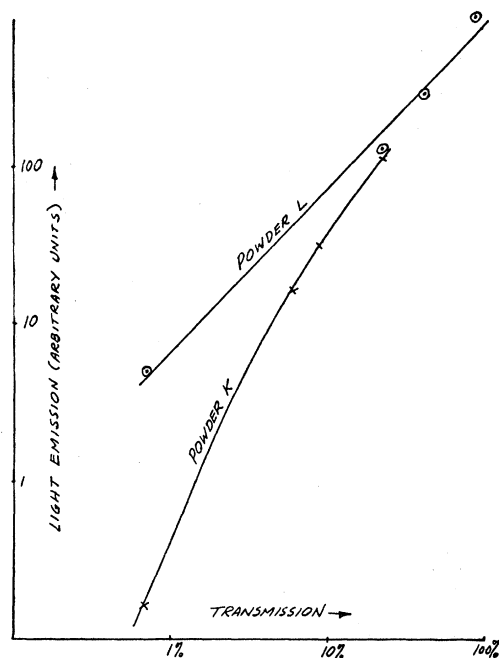| Powder	E_{uv}	ΔE_{ir}	$\Delta E_{ir}'$	Q_E
L	1000	0	0	6
	310	0	0	10
	135	0	0	10
	7	3	3	40
K	320	0	0	25
	170	0	0	35
	42	20	2	33

drop is noticeable, indicating that a stimulating effect was still in process, although the over-all effect was of quenching. These stimulation and quenching effects following ultraviolet radiation were similar for other powders measured, with differences appearing in the magnitude of the stimulation and quenching.

E. Light Emission Measurements

Using the apparatus described in Sec. II, the light emission of powders L and K were measured as functions of the incident ultraviolet intensity, the latter being varied by means of neutral filters. The results obtained are shown in Fig. 14. For powder L, linearity of light emission with the existing intensity is obtained down to 1 percent of the original intensity, but for powder K the emission drops off gradually from linearity beginning at 10 percent. The latter result was carefully checked by removing the source rather than inserting the filter and the same results were obtained.

When the infrared radiation (using a 7–56 filter) was directed at the powder during ultraviolet radiation, quenching and stimulating effects in light emission were noted and are given in Table III. Although the intensities of radiation were about the same as in the conductivity measurements, it can be seen that the quenching effects are less pronounced and that stimulation appeared only at the very low intensity ranges. In the table E_{uv}, ΔE_{ir}, $\Delta E_{ir}'$, and Q_E are used instead of the corresponding current terms defined in Sec. D above. Figure 15 shows the stimulation and quenching of both the current and light emission of powder L at low ultraviolet intensities, and shows the sharp drop in light emission when the infrared radiation was turned off.

Quite generally, the light curves lie above the corresponding current curves under additional infrared irradiation and the reduction of the light emission seems to be smaller than the corresponding current reduction.

F. High Energy Particle Measurements

Using the electrode arrangements described above, the powders were bombarded by high energy alpha-particles and electrons.

With alpha-particles induced currents up to 5×10^{-6} ampere were detected with powders K, M; currents up to 10^{-6} noted with L, while other powders gave

smaller induced currents. It was found that the polarity of the voltage applied to the powder could cause the induced current to change by a factor of 10. The larger currents were induced when the bombarded side was at a negative potential. Thus a definite rectifying effect is produced, probably due to the thin surface layer actually ionized by the incident particles. Similar effects were noted with pure CdS crystals.[4,5] If ultraviolet and alpha-particle radiation were applied simultaneously, it was found that $I_{\alpha+uv}$ was greater than $I_{uv}+I_\alpha$. This may be understood by assuming that without uv illumination most of the powder is in a relatively nonconducting state except for the surface exposed to alpha-particles, and that the additional ultraviolet excitation makes the unbombarded grains more conducting, thus allowing the alpha-induced conductivity to be measured.

The current to be expected from alpha-particle bombardment can be roughly calculated as follows: assuming an effective 3-millicurie source, a loss due to geometric factors by about 80 percent, and an energy of about 10 electron volts required to ionize an activator, we have, for 5-Mev alpha-particles,

$$i = 1 \times 10^{13} \text{ el/sec} = 1.6 \times 10^{-6} \text{ amp.}$$

When infrared radiation was added to the alpha-particle radiation, effects similar to the results outlined in Sec. III D were obtained. Table IV gives the alpha-induced current (I_α), the stimulated peak (ΔI_{ir}), and the quenching (Q). These results (using the 7–56 filter) for powders K and M are compared with the results obtained when ultraviolet instead of alpha-particle radiation was used. It can be seen that, in general, the
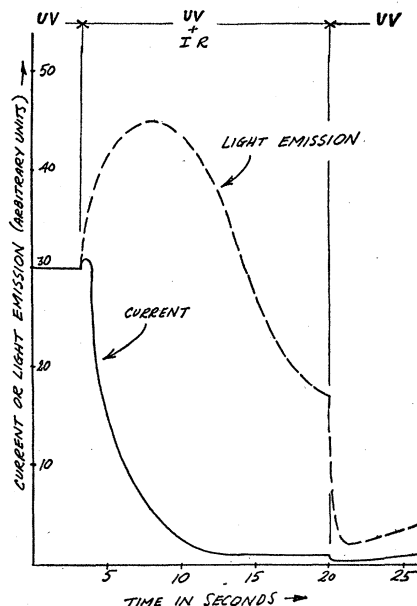

FIG. 15. Effect of infrared irradiation added to ultraviolet excitation on the induced current and the fluorescent emission of powder L.

results are similar, but quantitative differences exist; it is not yet clear whether these are caused by the experimental arrangement, or are inherent in the mechanism of current production.

Electrons were used as ionizing particles with only powder M. A current of about 10^{-8} ampere was induced in the sample, and this equilibrium value was reached after 5 minutes. Stimulation and quenching was noticed when the sample was simultaneously irradiated by infrared. The effects were small and may have been due to the action of the infrared on the zero current which was not completely quenched.

A calculation to determine the current to be expected for electron bombardment (assuming 10 percent of the electrons are absorbed in the powder) gives (with an average energy of $\frac{1}{2}$ Mev and a geometry loss of 80 percent)

$$i = 3 \times 10^{11} \text{ el/sec} = 5 \times 10^{-8} \text{ amp.}$$

The reasons why the currents obtained under alpha- and electron bombardment are relatively small compared to the light induced current (when reduced to the same absorbed energy) may be due to the quite generally observed drop in current intensity from a linear relationship, since the absorbed energies in the case of electrons are only of the order of one erg, compared to 100 ergs with the maximum light intensities.

Many experiments were made to detect the current induced by weak gamma-radiation, but none was successful. A gamma-irradiation of 10 r/hour was apparently not strong enough to be detected in this arrangement.

G. Miscellaneous Powders

For purposes of comparison the currents induced by ultraviolet and infrared radiation in pure anthracene (scintillation grade), pure, nonactivated, and nonluminescent ZnS and CdS, ZnO, and a special experimental powder supplied by the courtesy of du Pont were measured using the same technique described above (Sec. C).

Using anthracene flakes in layer form (8 mg/cm²) an induced current of 2×10^{-7} ampere was observed when the sample was exposed to ultraviolet radiation using a potential of 500 volts. About 30 seconds were required for the currents to build up to this value, and a rather long decay was observed and is shown in Fig. 16. No effects on the induced current were noted when the layer was exposed to infrared radiation.

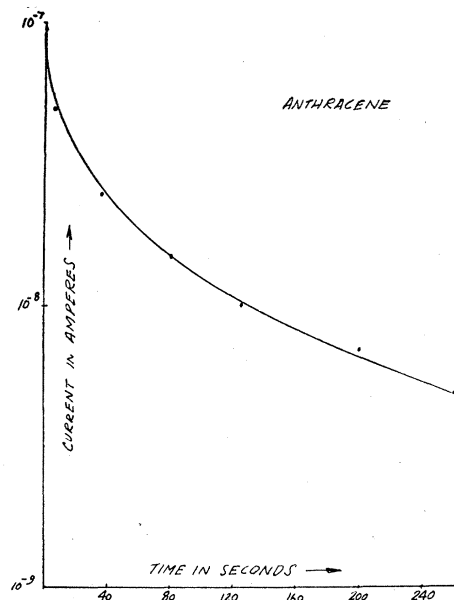Pure ZnS and CdS were supplied by the New Jersey Zinc Company and were prepared in powdered layers.

FIG. 16. Current decay in anthracene.

The ZnS showed no measureable induced currents by either ultraviolet of infrared radiation. The CdS, however, showed a small response to ultraviolet and infrared radiation. Both types of radiation caused induced currents of 10^{-8} ampere, either separately or additively. Measurements on both of these powders were difficult because of a rather large zero current which did not remain constant and could not be quenched.

ZnO crystals with unknown impurities (provided by the American Zinc Company of Illinois) were ground to a fine powder and prepared in the usual manner. At a potential of only 10 volts, a dark current of 2×10^{-6} ampere was observed. Ultraviolet radiation induced an additional current of about 10^{-6} ampere. The build-up and decay of the ultraviolet current was quite slow compared to that of the luminescent powders measured.

A specially activated CdS powder was provided by the du Pont Company (their identification Q59–2427). This powder exhibited unusually large ultraviolet and infrared induced currents superposed on a very large dark current, thus behaving like an ordinary semiconductor. Figure 17 shows the dark current, ultraviolet induced current, and infrared induced currents as functions of the applied voltage.

IV. THEORETICAL CONSIDERATIONS

A. General Description of the Model

The foregoing described experiments demonstrate that the induced current exceeds the number of electrons excited per second considerably. This is not only true for excitation by light but also in the case of excitation by alpha-particles when the current-voltage curves are compared to the ionization current in an air chamber. This excess of the induced currents over the

TABLE IV. Comparison of infrared quenching and stimulating effects on ultraviolet and alpha-particle induced current.

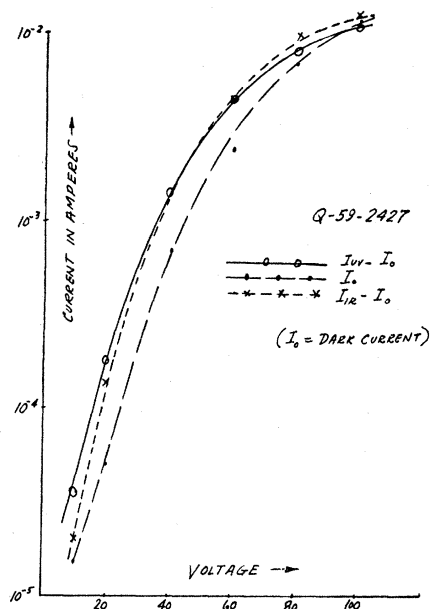| Powder	I_{uv}	ΔI_{ir}	Q_I	I_α	ΔI_{ir}	Q_I
M	6×10^{-7}	7.5×10^{-9}	99	5×10^{-7}	5×10^{-9}	97
K	1.4×10^{-6}	1.5×10^{-7}	43	1.2×10^{-6}	3×10^{-7}	56

FIG. 17. Ultraviolet induced current, infrared induced current, and dark current for CdS activated powder.

number of electrons excited per second may be interpreted as a real conductivity phenomenon in which the electrons in the conductivity band are the carriers. The current density j may then be described by the following formula:

$$j = e n_c w E, \tag{1}$$

where n_c is the number of electrons in the conductivity band per unit volume, w their mobility, e the electron charge, and E the applied field strength. The experiments show that Ohm's law is not fulfilled since there is a strong, nearly exponential increase of the current with voltage at low field strength. At high field strengths the relationship in some cases approaches $\Delta j/\Delta E$ = constant. There may be several reasons for such deviations from Ohm's law; they may be partly attributed to the inhomogenity of the powder and the fact that the contact between the grains may depend on the field strength. It may also be due to the fact that the density of electrons is so low that the potential layer near the boundary may be extended considerably into the interior of the grains; and finally, since at least some of these powders are not excited uniformly through the whole thickness, a layer of small resistance may be followed by a layer of high resistance. This high resistance layer may essentially determine the current through the powder, and only some of the electrons in the layer of low resistance may diffuse or may be drawn by the field strength through the high resistance layer. Similar effects were observed previously[4,5] with single crystals and light and high energy excitation where these particles only excited a small boundary layer. A more detailed investigation of this voltage-current relationship in powders is underway.

With these results in mind it may appear doubtful as to whether the observed current-light intensity relationship is an intrinsic one or is influenced by the dependence of the resistivity on the applied field strength. The measurements shown in Fig. 8 seem to indicate that our current-light intensity curve represents, at least to some extent, the true relationship between current and light since nearly the same current-light intensity curves were found where the current was varied by a factor of 10^4 as a result of a change in the applied voltage. From Figs. 5, 6, and 7 it can be seen that powders exhibit a tendency toward a linear relationship between current and light intensity at higher values of the latter, and that in all powders a dropping off from linearity occurs for low illumination. In the literature current-light intensity relationships of the form $j = cI^a$ are found where a varies between $\frac{1}{2}$ and 1; Kallmann and Warminsky find $a = 1$, Frerichs gives the value a as $\frac{1}{2}$, and Bube finds that a lies between $\frac{1}{2}$ and 1 depending on temperature.

In this section we shall present a description of a simplified model which can account for these different types of current-light intensity relationships. It is most important that such a model explain not only the relationship between induced current and the intensity of the exciting radiation but also the relationship between the induced current and the intensity of the emitted fluorescent and phosphorescent light. The above described experiments show that current and emitted light intensity are neither concomitant with each other when additional infrared radiation is applied to the excited powder, nor when the decay of the current and of the intensity of the emitted light is observed after the removal of the excitation.

One special point may be recalled here. In the [Zn:Cd]S phosphors there exist "storage" and "quenching" types. In the first type, light is stimulated by irradiation with infrared light of two ranges of wavelengths (about 8000 and 13,000A). In the second type, similar wavelengths produce a quenching of the emitted light in fluorescence as well as in phosphorescence. The above described experiments as well as the experiments of Hardy, however, indicate that the same wavelength range has both a stimulating as well as a quenching effect in one and the same phosphor. But the stimulating and quenching effects on current are different from those on light. We shall not try to assign the observed stimulating and quenching wavelength to a definite specific elementary process. We shall, however, develop a general picture which may lead to an understanding of the underlying processes.

We assume that a relatively small number of traps (about 10^{16} per unit volume) exist, with an energy depth of about 0.7 volt or larger, and that the electrons bound in these traps, or at least a certain portion of them, have the possibility of "recombining directly" with the positive charge without passing through the conductivity band at all or that they may pass through it

for only a very short time so that, at most, they give only a very small contribution to the electron density in the conductivity band. The removal of the electrons from the traps is mostly induced by thermal impacts or by infrared radiation. One can visualize such "direct recombination" by assuming either that these traps, or at least a certain portion of these traps, are associated with the activator atoms[11] in such a way that the electrons in these traps can be raised "directly" to the emission level of the activator atom when the latter is ionized (transition δ_1' in Fig. 18), or that electrons in these traps "recombine directly" (δ_2') with the ionized activators or the free positive holes in the valence band created by thermal impacts or infrated radiation. The first process is accompanied by light emission (if the activator is not a "quencher"), and the second one is not, so that it would represent a light quenching process. We assume further that these traps also exist if the activator atoms are not ionized. This is necessary in order to account for the observation that there is only a slow recovery of the current after the traps have been emptied by infrared irradiation. Apparently after such infrared illumination a considerable number of empty traps exist, which have to be filled before n_c regains its equilibrium value. It may be that the above assumptions are much too simplified to apply to all cases (see Sec. V A).

From the above assumption the described experiments on the influence of simultaneous infrared irradiation on light emission and current can be understood. Under exciting radiation, but with no infrared light present, a certain number of the traps are filled; and for our range of investigation the density of trapped electrons under stationary conditions is always larger than the density of electrons in the conductivity band, as will be seen from the equations below. There are two starting points for light emission: one, mainly from the conductivity band or from shallow traps affiliated with this band, and a second, from the above described deep traps mostly induced by thermal impacts or infrared radiation. If such radiation is additionally applied, more trapped electrons are brought to emit light per unit time, and the empty traps are refilled by electrons from the conductivity band. Thus a drain of electrons from the conductivity band sets in, its electron density is decreased, and the current decreases too. If no special quenching process is present, the same total number of excited electrons recombine to give radiative transitions when the equilibrium state is reached, and the infrared irradiation does not change the intensity of the emitted light, but only decreases the time lapse between excitation and recombination. Besides these "direct recombinations" (δ_1' and δ_2'), transitions of the trapped electrons to the conductivity band (δ_0) can also occur under the action of infrared irradiation.

<hr>

[11] This association between traps and activator atoms can perhaps be more easily visualized, by assuming that the activator or quenching atoms are localized near the traps.

These two transitions ("direct recombinations" and conductivity band jumps) could also be covered by an alternate assumption: that two different types of traps exist, each of which is responsible for only one type of transition. (The calculations below do not explicitly include this last possibility.) From such transitions to the conductivity band, an increase in current results immediately after the turning on of the infrared irradiation. This increase in current will fade away as soon as the refilling of the emptied traps from the conductivity band is established as can be seen from the equations developed below. The intensity of this increase in current depends on the number of trapped electrons and depends further on the way in which the electrons are removed from the traps by infrared irradiation.

On the other hand, the further decrease in current observed after infrared light is removed results from the fact that after this removal many traps are unoccupied by electrons and are refilled from the conductivity band while electrons are no longer transferred from traps to the conductivity band by infrared radiation. The steady current under additional infrared radiation is the resulting effect of two competing processes: the infrared radiation moving some electrons from the traps to the conductivity band, and other electrons going from the conductivity band to the traps to replace the electrons removed by ir from the traps by the δ_1' transitions. When the infrared irradiation is turned off, the transfer of electrons from traps to the conductivity band stops immediately, but the refilling of the traps by electrons from the conductivity band goes on, and this causes a dip in the current after the removal of the infrared irradiation. This current dip is thus closely correlated to the current increase at the beginning of the infrared irradiation. Both are caused by the transfer of electrons from traps to the conductivity band by infrared light.

The fact that all [Zn:Cd]S powders investigated up to now show a quenching of the current under simultaneous excitation and infrared irradiation proves that a removal of electrons by infrared light occurs from the traps which makes the electron recombine with the positive charge without bringing them to the conductivity band, and the probability of this process exceeds that of electron transfer from traps to the conductivity band by infrared irradiation. The relation between the light curves and the current curves essentially depends on the way in which the infrared light acts on the trapped electrons. If all infrared induced transitions of trapped electrons are accompanied by light emission (δ_1'), the current is quenched but the light is not. Only in the moment when the infrared irradiation is turned off is the light emission interrupted, since the electrons now tend to fall from the conductivity band into the unoccupied traps from which light emission no longer occurs without infrared irradiation. If the infrared radiation causes some of the trapped electrons to re-

combine without emitting light (δ_2' transition), the light emission is also quenched, that is, the steady light emission under ultraviolet and infrared irradiation is less than under ultraviolet irradiation alone. (The question of whether the δ_2' transitions end up at positive charges at the activator level or at positive holes in the valence band is left open; it is not essential to the calculations described below.) In this way the proposed model gives a consistent description of the observed processes, and it will be seen from the explicit formulas that the behavior of light and current during the phosphorescence can be explained as well.

B. Quantitative Formulations

The quantitative formulation of these ideas provides for two different starting points of the electrons for light emission: (1) light emission from the conductivity band which is described by a term $\beta n_c n_H$, where n_H is the density of positive holes (this is the normal light emission); (2) light emission from a deep trap, which may be described by a term $\delta' n_t$ where n_t is the density of trapped electrons. It might be assumed that there are also different processes of emission corresponding to these different starting points. Since, however, no noticeable change in the emission spectrum under uv excitation and infrared stimulation was observed, the possibility must be considered that these different starting points lead to the same emission process. There is, however, also another possibility which must be examined, namely, that the light emission from the conductivity band also occurs by way of traps, but of very shallow traps connected to the emission level. Such an assumption seems to be supported by the short emission time observed with single alpha-particle light flashes. It is very difficult to understand time constants as short as a microsecond due to electrons directly emitted from the conductivity band. The assumption of shallow traps could account for these short lifetimes. The following equations already include this assumption. The first equation, (2), deals with the formation and removal of the electrons from the conductivity band. The first term at the right side gives the number of electrons transferred

$$\dot{n}_c = \alpha I_{uv} - \beta' n_c (n_0 - n_t) + \delta_0 n_t - \bar{\beta}' n_c (n_H - \bar{n}_t) + \bar{\delta}_0 \bar{n}_t \quad (2)$$

into the conductivity band per second and per unit volume by the exciting radiation of intensity I_{uv}; α is a constant inherent to the substance; the second term scribes the number of electrons going over per second from the conductivity band to the traps where n_0 is the number of unoccupied traps in the unexcited powder and β' is the constant of this reaction; the third term gives the number of electrons per second moved from the traps to the conductivity band either by thermal impact or by infrared irradiation; in the latter case δ_0 would also depend on the infrared irradiation; the fourth and fifth term have the same meaning as the second and third term, only they refer to the shallow

traps.[12] It is hereby assumed that the total number of available shallow traps is practically given by the number of positive charges n_H. $\bar{n}_t$ is the number of electrons occupying these traps.

$$\dot{n}_t = \beta' n_c (n_0 - n_t) - \delta_0 n_t - \delta' n_t. \quad (3)$$

$$n_H = n_t + \bar{n}_t + n_c. \quad (4)$$

$$d\bar{n}_t/dt = \bar{\beta}' n_c (n_H - \bar{n}_t) - \bar{\delta}_0 \bar{n}_t - \bar{\delta}' \bar{n}_t. \quad (5)$$

Equation (3) deals with the electrons moved into or from the deep traps. The first term on the right gives the number of electrons moved from the conductivity band into the deep traps and the second term gives just the reverse process. Both terms are the negative of the second and third term in Eq. (2). The third term of (3) describes the number of electrons moved from the traps to the valence band without passing through the conductivity band. This may occur by thermal impacts or by infrared radiation. In the latter case the constant δ' would be proportional to the infrared intensity. This term may also describe the removal of the electrons from the traps by thermal agitation. It thus describes any leakage of the electrons from the traps which does not pass through the conductivity band. This term is a most critical one and can change the whole light and current behavior of the powder. Equation (4) describes the balance between the positive and negative charges. In this model the traps also exist when no excitation takes place; thus the number n_0 is independent of the excitation. The general form of these equations is not altered when the electrons in the traps cannot undergo "direct recombinations" with the positive holes. However, the value of δ' would be thereby decreased. The strong decrease in current under infrared irradiation seems to indicate the existence of "direct recombinations." Equation (5) describes the filling and emptying of the shallow traps close to the conductivity band. $\bar{\delta}'$ describes the recombination of
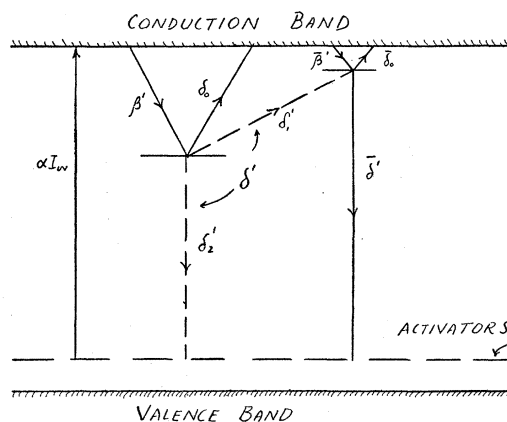

Fig. 18. Assumed model of fluorescent crystal showing allowed transitions.

[12] These transitions are shown in Fig. 18 which is a simplified drawing of the proposed model.

the electrons from the shallow traps with the positive charge, mostly accompanied by light emission. It is this term which is responsible for the normal light emission.

The constants introduced in the above described equations are not independent of each other. In the case of no infrared irradiation there is the following well-known statistical formula for β' and δ_0:

$$\delta_0/\beta' = (2\pi m KT/h^2)^{\frac{3}{2}} e^{-E/KT}, \qquad (6)$$

where m is the effective mass of the electron and T is the absolute temperature.[13] A similar equation holds for $\bar{\beta}'$ and $\bar{\delta}_0$. Equations of the type (2) to (6) are well known and have been previously discussed.[14-17] However, the δ' has not been taken into account accordingly. A consideration of these equations leads to the idea that there are different ranges of intensity where n_c (and thus the current) behaves quite differently.

Equations (2) through (5) are similar in some respects to the equations used by Broser and Warminsky. This similarity, however, is only formal. The essential differences are the following. We assume that electrons bound in traps do not contribute to the conductivity as long as they are in the traps. This seems to be brought out by our experiment in which powders filled with trapped electrons give practically no contribution to the conductivity. For instance, powder L shows very large infrared induced light stimulation after the uv excitation. The current remains very small. We assume further that the occupation of the traps takes place only from the conductivity band and is thus determined by the β' transition of Eq. (3). We further introduce three transition probabilities (which are affected by infrared radiation) from these traps which are necessary to describe the experimental data, especially the relation between current and light intensity under the same conditions. The effect of the positive charge is implicitly contained in our equation by the δ_2' part of δ'. Since the contribution of the positive holes to the conductivity is small as long as the number of activators is large compared to the number of traps, we see no reason to introduce equations dealing with the time change of the positive charge. This is only true without infrared irradiation; if such radiation is applied, it may be that enough positive holes are set free to give a noticeable contribution to the stimulated current. For this special case the contribution of the positive holes may not be negligible.

The order of magnitude of the constants occurring in these equations are as follows: α is proportional to the quantum yield of the exciting light and, since all relations refer to unit volume, αI_{uv} is of the order of

[13] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 156 ff.
[14] M. Schon, Z. Physik **119**, 470 (1942) and Ann. Physik **3**, 333 (1948).
[15] H. A. Klasens, Nature **158**, 306 (1946).
[16] I. Broser and R. Warminsky, Ann. Physik **7**, 19 (1950).
[17] A. Rose, RCA Rev. **12**, 402 (1951).

10^{15} electron/sec for an exciting radiation of 10 μwatt/cm^2 (calculated for a thickness of $\frac{1}{10}$ mm and quantum yield one). β' and $\bar{\beta}'$ are both assumed to be of the order of 10^{-7} cm^3 sec^{-1}. δ_0 and $\bar{\delta}_0$ are then given by (6). This gives 10^{-5} sec^{-1} for a trap depth of one electron volt. $\bar{\delta}'$, the normal light emission term, is of the order of 10^{+8} sec^{-1}, and δ' will be discussed later. The constant β^* which occurs below in Eq. (7) is of the order of 10^{-11} cm^3/sec. These equations are now solved for the steady state by making the left side of the equation equal to zero. n_H, n_t, and $\bar{n}_t$ can easily be eliminated from three of these equations. The fourth equation then gives a cubic equation for n_c which may be conveniently written in terms of n_c/n_0 and $\delta = \delta_0 + \delta'$:

$$(n_c/n_0)^3 + (n_c/n_0)^2(1 + \delta/\beta' n_0)$$
$$+ n_c/n_0(-\alpha I_{uv}/\beta^* n_0^2 + \delta'/\beta^* n_0) = \frac{\delta \alpha I_{uv}}{\beta^* \beta' n_0^3} \qquad (7)$$

where

$$\beta^* = \bar{\beta}' \bar{\delta}'/(\bar{\delta}_0 + \bar{\delta}').$$

The solution of (7) can be divided into two different ranges:

$$\alpha I_{uv}/\beta^* n_0^2 > 1, \qquad (8)$$

$$\alpha I_{uv}/\beta^* n_0^2 < 1. \qquad (9)$$

The cubic term of (7) is important only when $n_c/n_0 > 1$; that is, when $\alpha I_{uv}/\beta^* n_0^2 > 1$, since $\delta/\beta' n_0 \ll 1$ for the traps considered in this paper [see Eq. (6)]. But this solution cannot be applied since for all practical cases αI_{uv} is much smaller than $\beta^* n_0^2$ if we assume 10^{16} traps per unit volume (n_0) and β^* of the order of 10^{-11} cm^3/sec. The latter assumption is required to account for the relatively short duration of the light flashes produced by alpha-particles. If the cubic term in Eq. (7) is canceled, a quadratic equation is obtained to which, if necessary, the cubic term can be added as a correction factor. The following solution is obtained:

$$\frac{n_c}{n_0} = \frac{1}{2}\left\{ \left(\frac{\alpha I_{uv}}{\beta^* n_0^2} - \frac{\delta' n_0}{\beta^* n_0^2}\right) + \left[\left(\frac{\alpha I_{uv}}{\beta^* n_0^2} - \frac{\delta' n_0}{\beta^* n_0^2}\right)^2 \right.\right.$$
$$\left.\left. + \frac{4\alpha I_{uv}}{\beta^* n_0^2}\frac{\delta}{\beta' n_0}\right]^{\frac{1}{2}}\right\}. \qquad (10)$$

Here again it is convenient to discriminate between two ranges:

$$\alpha I_{uv}/\delta' n_0 > 1, \qquad (11)$$

$$\alpha I_{uv}/\delta' n_0 < 1. \qquad (12)$$

In the first range we get the following approximate solution:

$$n_c/n_0 = \alpha I_{uv}/\beta^* n_0^2, \qquad (13)$$

if (14) and (9) are fulfilled. n_c/n_0 depends linearly on the light intensity.

$$\alpha I_{uv}/\beta^* n_0^2 > \delta/\beta' n_0. \qquad (14)$$

In this range one finds $n_t \sim n_0$ and $\bar{n}_t \sim \bar{\beta}'n_0n_c/\bar{\delta}$ where $\bar{\delta} = \bar{\delta}_0 + \delta'$ and if δ' is small $\bar{n}_t$ can be easily determined using the equivalent of Eq. (6) for $\bar{\beta}'$ and $\bar{\delta}_0$.

Deviation from this linear dependency occurs when $\alpha I_{uv}\beta'/\delta n_0\beta^*$ approaches or becomes less than 1; for very small I_{uv} the linear curve goes over to a relationship of the following type: $n_c/n_0 = \mathrm{const} I_{uv}{}^a$, where a is less than one and approaches $\frac{1}{2}$.

In the latter case

$$n_c/n_0 = [(\alpha I_{uv}/\beta^* n_0{}^2)(\delta/\beta' n_0)]^{\frac{1}{2}}, \qquad (15)$$

$$\alpha I_{uv}/\beta^* n_0{}^2 \ll \delta/\beta' n_0, \qquad (16)$$

where δ_0/β' is again known from the statistical consideration. It should be noted that δ' appears in this equation mainly by the factor $\delta = \delta_0 + \delta'$.

If, however, $\alpha I_{uv}/\delta' n_0$ becomes <1, n_c/n_0 drops below the curves calculated from (13) and (15) and the following relationship is obtained:

$$n_c/n_0 = (\alpha I_{uv}/\beta^* n_0{}^2)(\delta\beta^*/\delta'\beta'), \qquad (17a)$$

$$\delta'\beta'/\delta\beta^* \gg 4\alpha I_{uv}/\delta' n_0. \qquad (17b)$$

Equation (17a) holds when Eq. (17b) is fulfilled, which is true in most cases. The drop to curve (17) can become noticeable either in the linear part [Eq. (13)] or in the lower part of the curve [see Eq. (15) and Fig. 19]. Equation (17) also shows a linear dependence on I. This linear dependence, however, may not be a real one, since up to now we have neglected the fact that δ' may itself depend on n_H. Such a dependency can be taken into account by describing δ' in terms of δ_0:

$$\delta' = \epsilon \delta_0, \qquad (18a)$$

$$\delta' = \epsilon \delta_0 n_t/n_a, \qquad (18b)$$

where ϵ is smaller than one. Assuming that all trapped electrons n_t are located near ionized activators leads
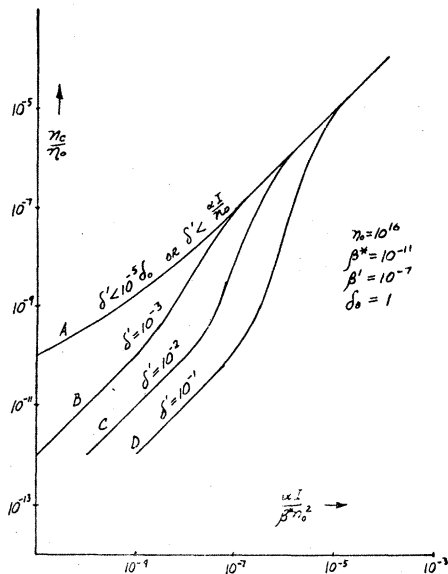

FIG. 19. Theoretical curves showing electron density in conductivity band as a function of exciting intensity for various values of δ'.

to (18a). If only n_H of the n_a activator atoms are ionized only a portion (n_H/n_a) of the trapped electrons may have an opportunity of recombining with a positive charge and since n_H is practically equal to n_t in all our approximations, one obtains (18b). Now according to (3) for the stationary state $n_c = \delta n_t/\beta' n_0$, if one realizes that for all cases where deviations of (13) occur n_t is no longer $\sim n_0$. If this relationship is used for n_t in (18b) and the value for δ' in (17) substituted in (18b), Eq. (19) is obtained.

$$n_c/n_0 = [(\alpha I_{uv}/\beta^* n_0{}^2)(\beta^* \delta_0 n_a/\epsilon\beta'^2 n_0{}^2)]^{\frac{1}{2}}. \qquad (19)$$

Thus one gets a square root dependency again between n_c and the exciting intensity. The first term in the square root is equal to that of Eq. (13); the second one gives the effect of the recombination of the trapped electrons with the positive charge. Equation (19) is only valid under condition (12) and (17b), otherwise Eq. (14) or (15) holds. With β^*/β' of the order of 10^{-4} and with $n_a/n_0 \sim 100$, Eq. (19) yields much smaller n_c values than (14) and (15).

Curve 19A gives the plot of the solution of Eq. (10) under condition (11). Curves 19B, C, D give the shape of the curves with various values of δ'. The main result of these calculations is that they show how a relatively small leakage factor from the traps (δ') changes the character of the curves completely (from shape A in Fig. 19 to B to D) and may account for a drop in the light and current curves below the linearity (see the experimental curve 14) and a quenching factor of 90 percent for small excitation intensities. It may be noted that the electron density values n_c give the current intensity directly and that the emitted light intensity can be determined from n_c with the help of the relationship between n_c and $\bar{n}_t$ and the third term in (5). If the leakage from the traps is accompanied by radiation, the term $\delta' n_t$ in (3) also gives a contribution to the light emission.

Up to now, we have described δ' without any special assumption about the elementary processes. It may be that such a leakage occurs just by thermal impacts in traps which are associated with ionized activators or that the positive charge localized at the activators is removed to the valence band and while passing a trapped electron recombines with this electron. All these possibilities are included in our calculation.

For the special case of the infrared radiation used, δ' can be evaluated more exactly by assuming that 10^{16} trapped electrons (associated with ionized activators) covering unit area have approximately the absorption coefficient one for the infrared light. Under this assumption one obtains the following value for δ' similar to (18b).

$$\delta' = 10^{-2} n_t/n_a. \qquad (20)$$

In Fig. 20 the resulting curve is drawn for a range of uv intensities. It is seen that for large uv intensities the effect of the infrared light is very small, whereas for a small uv intensity a large quenching is obtained.

Again no specific assumption has been made as to how the infrared radiation releases the trapped electron. If the released electron is brought by infrared irradiation directly to an emission level, then a decrease in current intensity without a decrease in light intensity would be observed. If the infrared irradiation brings about a recombination of the trapped electrons with a positive charge without light emission, for instance by releasing the positive charge from the localization at the activators into the valence band, then the positive charges may collide with the trapped electron without light emission. Again the electric current is decreased below the values of (13) and (15), but in this case the decrease in current would be accompanied by a similar decrease in light intensity.

V. COMPARISON BETWEEN EXPERIMENTS AND THEORY

A. Stationary Conditions

As already indicated, the above derived formulas can account for our experimental results and those described in literature.[4,5] Such a varying relationship as is there described is obtained if a considerable number of traps are present and the constant δ_0 of the traps is relatively small (14) (deep traps). If the number of traps is small enough, a relationship of $a=\frac{1}{2}$ is always found [conditions (8) and (16)]. The linear range is obtained when the traps are already practically filled, but the number of electrons in the conductivity band is still small. The moment this number (n_c) approaches or exceeds n_0, the square root relationship again occurs as can be seen from (7). But with only a very small number of traps ($n_0 \sim 10^{13}$) this region would be reached with light intensities of 10 μwatt/cm^2. In such a case range with a linear relationship between current and light intensities would exist. The separation between the linear and the square root range is determined by the constant δ_0. For larger δ_0, the region where the square root law prevails is extended to higher exciting intensities. Since δ_0 increases with increasing temperature, it should be expected that at low temperature the linear relationship holds, whereas at high enough temperatures the square root relationship must prevail within the same ranges of light intensities. This is just what was found in the experiments of Bube. This relationship holds only as long as practically no direct combination of the traps with the positive charges occurs. With δ' very small compared to δ_0 ($<10^{-5}\delta_0$) curve A of Fig. 19 is obtained. The different values given for a in literature indicates that these authors have worked on different ranges of curve A. Curves B, C, and D are drawn for δ' larger than the above mentioned value. Their upper portions ($n_c/n_0 > 10^{-10}$) are similar to the curves we have found in our current experiments, but this interpretation of our curves remains uncertain as long as it is not completely established that the current-intensity relaitonship is not essentially distorted by the contacts or non-uniform
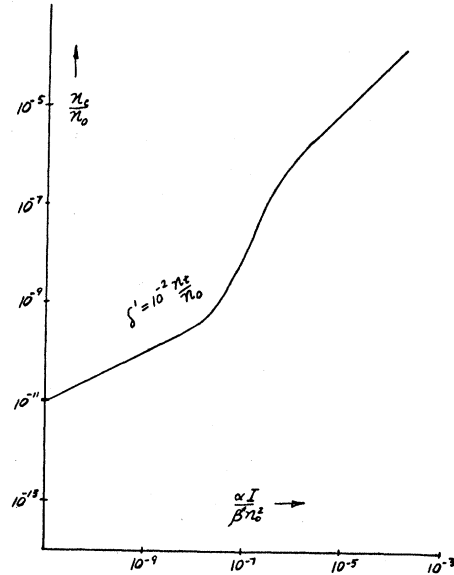

FIG. 20. Theoretical curve showing electron density in conductivity band as a function of exciting intensity assuming that δ' is proportional to n_H when $n_H \sim n_t$.

excitation within the powder (see Sec. IV A and Fig. 8). There is, however, another reason which seems to favor the introduction of a recombination between the electrons in the traps and the positive charges without the electrons passing through the conductivity band. This is the observation that in some powders the light efficiency decreases with decreasing exciting intensity (see Fig. 14). As already stated, the light efficiency is constant along the whole curve A of Fig. 18 and also along the curve B, C, and D, if the third term in (3) describes radiative transitions. If some of these transitions are nonradiative, the light efficiency goes down the moment the curve for n_c/n_0 deviates considerably below the curve A of Fig. 19. The observed decrease in light efficiency seems to be a confirmation of the proposed type of reaction with δ' only partly radiative. The same mechanism gives an understanding for the influence of infrared light on the current and light emission. The curves of Fig. 19 shows what happens when δ' is considerably enlarged by the additional infrared irradiation. There then occurs a shift from a curve with smaller δ' to one with larger δ'. At very large uv intensities the number of electrons brought from the traps to the positive charge by infrared light is small compared to the number of electrons excited by the uv light and, therefore, at high exciting intensities ($\alpha I_{uv} \gg \delta' n_0$) the quenching effect is relatively small (as observed with all powders). With decreasing uv light intensity the reaction in question becomes considerable, and the n_c/n_0 curves drop below the values of the curves with smaller δ' giving a very high quenching factor at low intensities. The fact that in the steady state the current-intensity curves drop considerably with all powders is another support for

the assumption that in all these powders the infrared light induces a recombination of the trapped electrons with the positive charge without contributing to the current. It is very interesting to see that such transitions occur in practically all powders.

If now the light emission curves are considered, their shape depends again upon the extent to which the factor δ' in (3) describes radiative or nonradiative transitions.

In some powders the effect of the additional infrared irradiation is to decrease the steady light emission, but this decrease is smaller than the relative decrease in current by the same additional infrared irradiation. This indicates again that the δ' transition leads partly to radiative recombinations. The process which is responsible for the light emission decrease could be that in which the infrared light transfers the positive charge from the localized activator to the valence band (one electron is raised from this band to the ionized activator) so that the positive charge recombines with the trapped electron transferring the available energy to the lattice. It would be reasonable to assume that these two processes (radiative and nonradiative) are induced by different wavelengths, but up to now we have not yet observed such an influence of different wavelengths. It also seems that for longer wavelengths around 1.3 microns the same effects occur. More experiments on these points are underway.

In the calculations we have assumed that at least a certain portion of the n_0 traps are associated with activators. Some of these traps associated with activators may be associated with non-ionized activators and some with ionized activators, and only those latter ones are effective for recombination. It may seem strange to assume that these traps already exist as traps when the activators are not yet ionized. It is possible to modify this consideration by assuming that the traps associated with activators only exist if the activators are ionized, but the light and current curves cannot be explained with this assumption alone as will be shown in the section dealing with nonstationary processes. We have made the above assumption of associated traps already existing without ionization to explain the nonstationary effects. It may be that this assumption is still an over-simplification and that the true processes are better represented by a model containing at least two different types of traps, some of which are associated with activators and which are sensitive to infrared light, and others which are much less sensitive to infrared light and which, when emptied, give only a relatively small amount of light emission. A quite different method has been developed to detect such traps, and such experiments seem to support the idea of two different types of traps.

B. Nonstationary Conditions

Still more information about the prevailing processes can be obtained by considering the nonstationary effects

which occur immediately after the turning on or removal of the infrared irradiation during and after uv excitation. If infrared irradiation is added during uv excitation, at the very beginning an increase in current intensity is observed which is followed within seconds by the strong quenching effect of the infrared light (see Figs. 13 and 15). Such a behavior follows immediately from Eq. (3), if it is assumed that the infrared irradiation also increases the factor δ_0. This would mean that the infrared radiation also brings some of the trapped electrons directly into the conductivity band (see Sec. IV A). This increase in δ_0 constitutes an increase in the number of electrons in the conductivity band, but at the same time the number n_t decreases since a large amount of electrons recombine under the influence of infrared irradiation with a positive charge without giving a contribution to the conductivity (δ'). If the increase of δ' by the infrared irradiation is large enough, the decrease in n_t more than compensates the increase of δ_0 by the infrared light and as a consequence a strong drop of the current below its original value occurs after a certain interval. In the steady state the number n_t is thus decreased for two reasons: an increase in δ' and an increase in δ_0. This means that during the steady state an additional transfer of electrons from the traps to the conductivity band takes place constantly but is overshadowed by the additional transfer of electrons from the traps to the positive charge without contribution to the conductivity (Sec. IV A). The fact that in all these powders quenching prevails indicates that the increase in δ_0 is only small. It may be that the increase in δ_0 which is indicated by the initial rise of the current is not so much a transfer of electrons from the traps directly to the conductivity band under the influence of infrared radiation but may be a thermal transfer to the conductivity band of electrons, from the emission level of the activators to which they had been brought by the infrared light. It may also be as already mentioned, that two different types of traps exist: one from which the electrons are transferred to the conductivity level by infrared light and another type from which the infrared light removes the electron without bringing them into the conductivity band.

If the infrared light is switched off, the effect is a strong decrease in δ' and a certain decrease in δ_0. The latter means that now less electrons are transferred from the traps to the conductivity band (directly or by way of the emission levels), thus the first effect of the removal of the infrared light is a further dip in the current. This drop will be more pronounced the larger the initial peak in the current curve is since both the peak at the beginning of the infrared irradiation and the dip at the end of the infrared irradiation depends upon the change of δ_0 by the infrared light. But very soon the number n_t increases since no additional drain is exerted on the trapped electrons, and, therefore, the current intensity slowly rises to its

original value before the turning on of the infrared light. The time of this rise mainly depends on the number of n_0 of the traps to be filled and on the exciting radiation, if we are on the linear part of the curves of Fig. 19. Therefore, $n_0/\alpha I$ gives the order of magnitude of this rise time. From the measured rise time we estimate the number of empty traps to be of the order of $10^{16}/cm^3$.

In the same way the dependence of the emitted light on the infrared irradiation can be evaluated. The initial effect of infrared light is mainly an additional transfer of electrons from the traps to the emission level of the activators which induces an additional increase in light intensity until the number of trapped electrons are reduced to the stationary value under combined ultraviolet and infrared irradiation. This explains the large increase in light intensity immediately following the turning on of the infrared light in our experiments, especially at low intensities (Table III and Fig. 15). This rise in intensity has nothing to do with the rise in the current curve since the current peak is due to an increase in δ_0, whereas the light peak is due to an increase in δ'. The difference between the light and the current curves are thus evidence for a transfer of electrons to the emission level without passing through the conductivity band. The steady value of the light emission depends on the extent to which the δ' processes are accompanied by light emission (see Sec. IV A).

The moment the infrared light is removed, the additional light emission accompanying the removal of the electrons from the traps disappears and the light emission only takes place from the conductivity band or the shallow traps of Eq. (5). Since n_c is very low immediately after the removal of the infrared radiation, a strong decrease in light emission should occur in all powders. In fact our experiment with low exciting intensities show such decrease in light emission even with a powder of very high stimulability. After this drop in intensity, n_c/n_0 increases and thus makes the light intensity increase in a similar way to the increase of conductivity. This is just what was found in our experiments.

The behavior of the light and current curves is, however, quite different if such measurements were carried through during the decay and not during uv excitation. The current decay curves differ considerably from the light decay curves which may again be attributed to the existence of traps associated to the activator atoms as well as nonassociated traps. If the electrons in the associated traps also undergo a direct transition from the traps to the emission level by thermal agitation, powders with many associated traps may show an extended light decay curve without having a similar current decay curve. A detailed knowledge of the character of the different traps is necessary to understand these curves in detail, but there are two other striking effects which yield interesting information on these processes. The current decay curves for different exciting intensities tend to merge to one single curve for longer decay times (see curves 9 and 10). This can be understood if the real decay process is of the hyperbolic type and yields a formula of the following form:

$$n_c=(n_c)_0/(1+\kappa t); \quad \kappa=\beta^*(n_c)_0. \tag{21}$$

For a time large compared to $1/\kappa$ these curves are always of the form of

$$n_c=1/\beta^* t, \tag{22}$$

independent of $(n_c)_0$. The time at which this merging occurs should depend on the initial values of $(n_c)_0$. In the case of the powder K the current decay curves seem to follow such a relationship, but in the case of the powder L the behavior is different. The shape of the curves of Fig. 10 can perhaps be understood from the assumption that traps of different depths and character exist.

If now the influence of infrared light along the decay curve is studied it is found as shown in Fig. 13 (see Sec. III, D2) that the initial peak in the curve becomes more pronounced compared to the quenching effect of the infrared light. This is just what can be derived from our equations. The peak in the curves is given by the increase in δ_0 and by the number of electrons in the traps at the beginning of the infrared irradiation. The number of trapped electrons at any point of the decay curve has not yet decreased as much as the number of electrons in the conductivity band. Since the peak depends on $\Delta\delta_0 \times n_t$ and since the quenching effect depends on n_c the quenching effect is less pronounced the further we go along the decay curve. For very large decay times the quenching effect may even completely disappear since the number of electrons in the conductivity band before infrared irradiation is much smaller than the increase in this number due to the increase in δ_0 by infrared light. This is exactly what was observed with most of the powders. The longer the decay time the less pronounced becomes the quenching effect.

The proposed theory is supposed to be essentially a first guide to the understanding of the observed effects. We have the feeling that the basic ideas of the presented model gives an adequate over-all explanation of the observations. There are, however, major results which require further considerations; in particular the dependence of the induced current on voltage and the influence of this dependence on the current vs light intensity curves, and the failure to detect weak gamma-radiations by noting changes in the current. One reason for the inability of detection is, without doubt, connected to the fact that our picture deals only with one or two types of traps, whereas in reality more types of traps must be considered. Further experiments have already provided evidence that traps exist, which behave quite differently from each other under infrared irradiation and with respect to their light emission.