that the Cl_2^- molecule-ion reforms very close to its original neighborhood. Therefore, when a potassium chloride crystal is irradiated with x-rays at liquid nitrogen temperature, it seems likely that a positive hole which has been created moves only a very short distance before forming a Cl_2^- molecule-ion. Since the rate of formation of positive holes by x-ray irradiation should be the same in pure potassium chloride as in doped potassium chloride, Cl_2^- molecule-ions should be formed at the same rate in each of these crystals; yet it is observed that the net rate of formation of Cl_2^- centers is from 100 to 1000 times greater in the case of the doped crystals. It is believed that the added impurities act as very efficient electron traps,[12] decreasing the rate of recombination of electrons and positive holes, while in the pure crystals electron traps must be created slowly by the irradiation and consequently the recombination rate is much greater.

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Control of Luminescence by Charge Extraction*

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It has been discovered that the application of a potential of a few volts to phosphors of the ZnS group can quench the fluorescence. The effect has been observed in single-crystal and recrystallized wafers of the phosphors by illuminating one side with nonpenetrating light and applying a field, through suitable contacts, normal to the illuminated surface. With the illuminated surface negative, the fluorescence is reduced by an amount dependent on the voltage for as long as the voltage is maintained, and total extinction can often be obtained. The luminescent output follows variations in the applied voltage up to a maximum frequency which depends on the fluorescence time constant.

The effect is shown to be a fundamental property of phosphor materials possessing large differences in hole and electron mobilities or capture cross section. It is explained in terms of a decrease in the excess electron density due to the extraction of holes from the illuminated surface by the field. A simple mathematical theory is proposed which accounts in detail for the observed effects and which predicts current-voltage relationships which have been confirmed experimentally.

I. INTRODUCTION

IN the literature on phosphors there are many reports on effects of applying an electric field to photoluminescent materials. These include the Gudden-Pohl effect[1] (the transient stimulation of luminescence), Dechene's[2] experiment on the quenching of luminescence with a high field, and the Destriau[3] effect of stimulation of luminescence by an alternating field. Halsted[4] has observed modulation of fluorescence by an alternating field and explained the effect by assuming that the optically created hole-electron pairs are first separated and then brought back together under the influence of the field. These, and a number of less clearly defined effects have been reviewed recently in an article by Ivey.[5]

The purpose of this paper is to describe a new electrophotoluminescent effect and to propose an explanation for it. The effect is unusual in that dc as well as ac fields can be used, that these fields are very low, and that the effect produced can be very large, almost complete extinction or significant stimulation of fluorescence being obtained depending on the direction of the field.

In Sec. II the experimental arrangements are described. In Sec. III experiments are described which essentially repeat those of Halsted except that single-crystal phosphor material was used instead of a phosphor powder in a dielectric matrix. This allowed the field modulation effect to be studied in a more controlled manner. The results observed when a transparent conducting coating is placed in direct contact with the single crystals (and also with sintered layers of phosphor material) are described in Sec. IV and the interpretation of these results is discussed. A mathematical description of the observed effects is presented in an Appendix.

II. EXPERIMENTAL METHOD

In the majority of experiments, wafers of single-crystal cadmium sulfide were used. These were activated by heating in the presence of cupric chloride and

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[1] B. Gudden and R. W. Pohl, Z. Physik 2, 192 (1920).

[2] G. Dechene, Compt. rend. 201, 139 (1935).

[3] M. Destriau, Compt. rend. 238, 2298 (1954).

[4] R. E. Halsted, Phys. Rev. 99, 1897 (1955).

[5] H. F. Ivey, J. Electrochem. Soc. 104, 740 (1957).

emitted infrared fluorescent radiation in the 1.1-μ band when excited with blue or ultraviolet light.

The wafers, about half a centimeter square and one millimeter thick, were placed between two plates of conducting glass. Light from a microscope lamp, operated on direct current, was passed through a saturated solution of copper sulphate and focused on one side of the crystal, and a lead sulfide cell, with a silicon filter to exclude visible light and transmit the infrared, was placed close to the other side. This arrangement is shown in Fig. 1.

The experiments fell into two classes depending on whether the cadmium sulfide was insulated from the conducting glass or in electrical contact with it. The diagram applies to both cases since the liquid shown can be either a dielectric or a conductor.

III. INSULATED CASE

When the illuminated face of the cadmium sulfide was insulated from the conducting surface of the glass by a transparent dielectric, and an alternating field applied between the glass plates, a modulation of the infrared radiation at the frequency of the field could be detected. Halsted observed this effect, with a phosphor powder embedded in a dielectric matrix, and explained it on the assumption that the light creates hole-electron pairs at the surface and that with successive half cycles of the field the electrons were moved away from, and back to, the relatively immobile holes. The variation of the electron density in the vicinity of the holes, and the consequent variation in their rate of recombination, should therefore be dependent on the voltage applied and on the capacitance of the system. This was verified experimentally. It was assumed that the cadmium sulfide could be treated as a conductor and that the charge density at its surface, for constant applied voltage, should therefore depend on the dielectric constant of the insulating material and vary inversely with its thickness. The spacing between the glass plates was varied by attaching one to a micromanipulator and castor oil was used as the dielectric. It was then found that the modulation obtained was very nearly proportional to the reciprocal of the thickness of the dielectric, as would be expected.

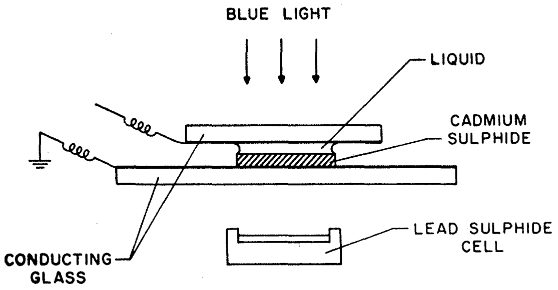

FIG. 1. Diagram of the apparatus.

It is easy to calculate that with a reasonable value of capacitance and applied voltage the maximum number of hole-electron pairs that can be separated, and therefore the maximum number of photons that can be created per cycle by their recombination, is very small when compared with the number arriving in a similar time in the exciting radiation from common light sources. Thus, with 300 v at 1000 cps applied, the alternating component of the fluorescence was very small and practically independent of the intensity of the blue excitation, above a low minimum. Thus the percentage modulation was only high (approaching 50%) when the excitation, and consequently the fluorescent radiation also, was of very low intensity.

IV. CONDUCTING CASE

An entirely different state of affairs prevailed when no dielectric was used and the cadmium sulfide was brought into intimate contact with the conducting surfaces of the glass by moistening it with a conducting liquid such as water or ethylene glycol. With only a few volts applied across the crystal a very strong modulation was obtained. In a typical case using a 300-cps field, the modulation increased with the voltage until about 15 volts when a modulation of about 80% had been reached. With a further increase in voltage little change in depth of modulation occurred, though the shape of the wave form altered somewhat. The modulation obtained decreased with increasing frequency, the time constant of the process being of the same order as the fluorescence time constant measured by chopping the exciting light.

Even at high frequencies, when the percentage modulation was greatly reduced, the depth of modulation remained independent of the field above the same saturating voltage as at low frequencies. Increasing the intensity of the excitation produced a proportional increase in both the ac and dc components of the fluorescence, but a higher voltage was required to reach saturation.

The effect is not limited to alternating fields. When a dc potential was applied, with the illuminated face negative, almost complete extinction of the fluorescence could be obtained for as long as the field was maintained. With the reverse polarity a stimulation of the fluorescence above the normal level was sometimes observed.

Liquid contacts are not essential for the occurrence of the phenomenon. Semitransparent gold films evaporated directly on to the opposite faces of a crystal were also used successfully.

Polycrystalline and sintered samples of cadmium sulfide behaved in a similar manner to single crystals. The effect was also observed with cadmium selenide and, in the visible region of the spectrum, with cadmium sulfide fluorescent in the red and with mixed zinc-cadmium sulfide phosphors excited with ultraviolet light.

Since the application of a dc bias in such a direction as to drive positive charge into the contact gives a steady state quenching of the output radiation, the hole-electron pairs generated by the light must be being removed in a field-dependent way other than by the radiative recombination mechanism. The one suggested is that the field enables some or all of the holes to be extracted through the conducting contact before they can fall into the recombination centers. The electrons move out through the other contact to meet the holes, giving continuity of current.

The fact that small photocurrents exist in the short circuit case implies that some extraction may even be taking place at zero bias. A reversal of the bias can then reduce this extraction and lead to a small stimulation.

First we would like to show that extraction will account for the essential features of the data, and then discuss how the extraction may be achieved by the field.

According to the concepts of Rose,[6] the excess concentrations of holes and electrons generated by the light may be characterized by essentially constant lifetimes, τ_p and τ_n, provided that these concentrations are small compared with the concentrations of empty and filled recombination centers. Since the number of recombination centers has been made deliberately large by doping the crystals used, this situation should prevail to rather high light levels. Thus if n and p are, respectively, the excess concentrations of electrons and holes in the steady state, then

$$f=n/\tau_n=p/\tau_p, \tag{1}$$

where f is the number of hole-electron pairs per unit volume generated per second by the light. The lifetimes, τ_p and τ_n, may differ greatly. Typical values quoted by Rose[7] for CdS, are 10^{-3} sec for electrons and 10^{-10} sec or less for holes. If it is assumed that these numbers apply to the situation above, most of the excess positive charge due to the light resides in the recombination centers near the illuminated surface. For example, if a diffusion constant of 1 cm^2/sec is assumed for the holes, the depth of penetration of this positive charge would be of the order of 10^{-5} cm. This is of the same order as the depth of penetration of the incident light. The output radiation is believed to occur when the electrons fall into the positively charged recombination centers, and is thus proportional to the density of excess free electrons in the neighborhood of the illuminated surface. Thus a steady state quenching of the output radiation implies a reduction in the electron concentration. Since the electrons offer the primary source of conduction, an increase in dynamic impedance should accompany the quenching as the voltage increases. If the hole-electron pairs are being extracted, the carriers excited by the incident light are removed nonradiatively as electrical current. Thus for voltages above that for which complete extinction of the radiation occurs, the current density should be given by

$$j_L=j_D+qfL. \tag{2}$$

Here j_L is the current density in the presence of the light, j_D is the current in the dark, q is the electronic charge and L is the average depth in the crystal in which the recombination centers are filled by optically produced holes in the absence of a bias. The product fL represents the number of hole-electron pairs generated per second per cm^2 of illuminated surface and is directly proportional to the incident light intensity. Thus for voltages above the extinction voltage, the current-voltage characteristics for varying light intensities should be a set of lines parallel to the dark current-voltage characteristic, and spaced above the dark curve in proportion to the light intensity.

In order to confirm this an attempt was made to measure the current, the voltage and the output radiation simultaneously for various intensities of light. At first it seemed prudent to study the current-voltage characteristics by displaying them on an oscilloscope about zero bias in order to avoid any polarization effects. While evidence of the anticipated results was present, the main features were masked by secondary effects which will not be gone into in detail at this time. On consideration it appeared that these effects were most likely associated with a charging of traps during the positive half of the cycle and a discharging of these traps, as the polarity was reversed and carriers could be extracted. By applying a bias so that only the negative half of the characteristics were being traced, the filling and emptying of traps was largely avoided and characteristics such as those shown in Fig. 2 were obtained. These curves were drawn from photographs of the oscilloscope traces and have been "improved"

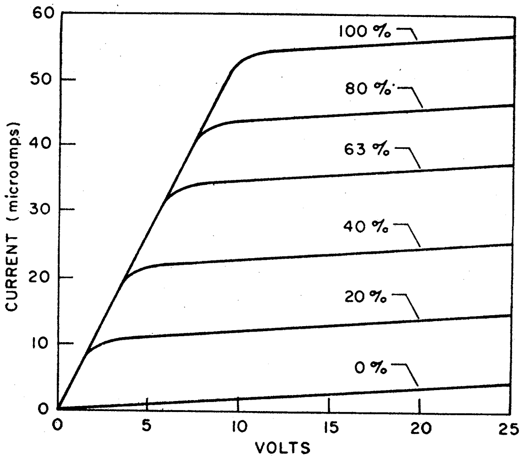

FIG. 2. Current-voltage characteristics for various percentages of the available incident light intensity.

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[6] A. Rose, Phys. Rev. **97**, 322 (1955).

[7] A. Rose, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (John Wiley and Sons, Inc., New York, 1956), p. 17.

to a small extent, as the originals showed a slight hysteresis due to this charging and to capacitive effects. This did not affect the slope or spacing of the curves above the extinction voltages, which were precisely as anticipated, but did obscure the exact form of the characteristics at lower voltages where the traces overlapped.[†]

Extraction also accounts for the essential features of the frequency response of the output radiation, when it is modulated by ac fields. This may be seen in the following way. If a large bias is suddenly applied, the hole-electron pairs generated by the incident light begin to be extracted. However, the positive charge already in the recombination centers cannot be removed since it is trapped there. Thus, for neutrality reasons, the electrons near the surface before the application of the bias are forced to remain there, and they continue to discharge through recombination. Therefore, the response time of the modulation should correspond approximately to the lifetime of the electrons. This would seem to be the case, since the fluorescence and the modulation have approximately the same cutoff frequency. A mathematical description of this situation is given in the Appendix.

There remains to be discussed the details of how the extraction may occur. Since the voltage necessary to complete the extraction increases with increasing light intensity, it would seem most likely that the modulation is produced by the external bias causing a variation in the internal potentials created by the incident light. Let us examine what these potentials might be in the open-circuit case.

Since most of the positive charge is trapped in a region near the surface, it can be assumed that, to a good approximation, the hole current is everywhere zero. Since the electron current must then also be zero to the same approximation internal fields must be set up which will oppose the diffusion of electrons both into the surface and into the bulk. These fields will be determined by the current equation and Poisson's equation, i.e.,

$$\mathbf{j}_n=q\mu_n(n+n_{eq})\mathbf{E}+kT\mu_n\nabla n=0, \tag{3}$$

and

$$\nabla\cdot\mathbf{E}=\frac{4\pi q}{K}(n-N_R{}^+). \tag{4}$$

Here **E** is the electric field, n_{eq} is the equilibrium concentration of electrons in the dark, k is Boltzmann's constant, T is the absolute temperature, $\mathbf{j}_n$ is the electron current density, K is the dielectric constant, μ_n is the electron mobility, and $N_R{}^+$ is the density of positively charged recombination centers due to the light. It is not difficult to show that qualitatively these equations lead to an electron potential energy diagram as shown in Fig. 3. The solid curve corresponds to one light intensity, the dotted curve to a stronger light intensity. The minimum occurs where the trapped positive charge is still appreciable and therefore occurs within 10^{-5} cm from the surface. The difference in the potential energy between the two conducting contacts should display itself as an open-circuit photovoltage. Only small photovoltages have been detected (of the order of 0.02 volts). Therefore it may be assumed that the end potentials are nearly equal while the depth of the potential well should be several tenths of a volt or more for the light levels used.

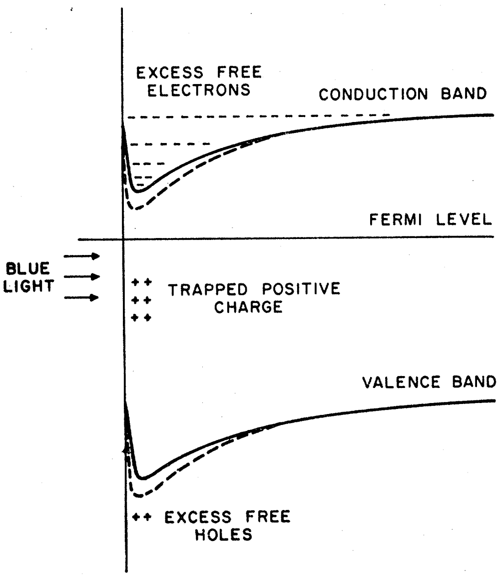

FIG. 3. Potential energy diagram, open-circuit case.

Much of the electronic charge is thus in a potential well, while an appreciable number of the few free holes which do exist, are behind a barrier which impedes their flow to the illuminated surface. The application of a negative bias to the illuminated surface will reduce the depth of the potential well and a sufficiently large bias will remove it completely. When sufficient bias is applied all holes are freed to move into the illuminated contact, and all electrons are freed to move out the opposite contact. Thus complete extraction can occur.

No mention has been made of the contact potential differences. These surely exist and may alter somewhat the detailed shape of the open-circuit potential energy diagram from one sample to the next. Since in all cases studied, the dark current curves are ohmic, these contact potential differences must be small.

APPENDIX

Let $\lambda(E)$ be the function which represents the ability of the field to extract holes. $\lambda(E)$ increases as the field increases in such a direction as to drive electrons away

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[†] *Note added in proof.*—Subsequent work verifies that the form of the characteristics at the low voltages are as shown. However the resistance of the cadmium sulfide in this low conductivity region was actually much smaller than that of the liquid contacts. The liquid contacts therefore controlled the current-voltage characteristics until the extinction voltage was reached.

from the illuminated surface. It need not necessarily be zero at zero external bias. Then the average concentration of excess holes in the neighborhood of the illuminated surface at any given time t is given by

$$f-p/\tau_p-p\lambda(E)=dp/dt. \tag{1-A}$$

Since for neutrality reasons, holes and electrons must be extracted at the same rate by the field, the average electron concentration in the neighborhood of the illuminated surface is given by

$$f-n/\tau_n-p\lambda(E)=dn/dt. \tag{2-A}$$

The steady state solutions are

$$p=\frac{f\tau_p}{\lambda(E)\tau_p+1} \quad \text{and} \quad n=\frac{f\tau_n}{\lambda(E)\tau_n+1}. \tag{3-A}$$

Thus n and p decrease with increasing $\lambda(E)$.

For $t<0$, let $E=E_0$, and for $t>0$, let $E=E_0+E_1$. Then the time-dependent solutions of (1-A) and (2-A) are

$$p=p_0-p_1(1-e^{-t/\alpha}), \tag{4-A}$$

and

$$n=n_0-n_1(1-Ae^{-t/\alpha}-Be^{-t/\tau_n}). \tag{5-A}$$

Here

$$p_0=\frac{f\tau_p}{\lambda(E_0)\tau_p+1}, \quad p_1=\frac{f(\tau_p)^2\lambda(E_1)}{[\lambda(E_0+E_1)\tau_p+1][\lambda(E_0)\tau_p+1]},$$

$$n_0=\frac{f\tau_n}{\lambda(E_0)\tau_p+1}, \quad n_1=\frac{f\tau_p\tau_n\lambda(E_1)}{[\lambda(E_0+E_1)\tau_p+1][\lambda(E_0)\tau_p+1]},$$

$$A=\frac{(\tau_p)^2\lambda(E_0+E_1)}{[\lambda(E_0+E_1)\tau_p+1]\left[\tau_n-\dfrac{\tau_p}{\lambda(E_0+E_1)\tau_p+1}\right]},$$

$$B=1-A,$$

and

$$\alpha=\frac{\tau_p}{\lambda(E_0+E_1)\tau_p+1}. \tag{6-A}$$

The equation for n determines the output radiation. For E_1 large, or 100% extinction of the output light, from (5-A) and (6-A), n reduces to

$$n=\frac{f\tau_n}{\lambda(E_0)\tau_p+1}\left[\frac{\tau_p}{\tau_n}e^{-t/\alpha}+\left(1-\frac{\tau_p}{\tau_n}\right)e^{-t/\tau_n}\right]. \tag{7-A}$$

Since $\tau_p/\tau_n \ll 1$ and $\alpha \ll \tau_n$, this further reduces to

$$n=\frac{f\tau_n}{\lambda(E_0)\tau_p+1}e^{-t/\tau_n}. \tag{8-A}$$

Thus, the modulation for large field strengths becomes independent of the field, and should be able to follow to frequencies which correspond to time constants of the order of τ_n.

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