

directions introduced solely by scattering in the target should be accompanied by a deviation from the secant law for the exit face. With the present arrangement in which the foils are identical, the departure from the secant law for the surface in the forward direction (Fig. 1, face 2) should be twice that for the entrance face. Since this is not precisely verified experimentally, some of the other factors mentioned above undoubtedly influence the measurements at large angles to some extent.

It should be emphasized that the situation is much more complicated when the bombarding energies are

low. In that case, the range of the primary electrons is not large compared with the range of the secondaries, and the rate of production, $N(l)$, is a very sensitive function of l . Under these circumstances, the theoretical problem becomes much more difficult and the yield should certainly not be expected to follow a simple secant law.

V. ACKNOWLEDGMENTS

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Field-Induced Color Shift in Electroluminescent Zinc Sulfide*

JOHN F. WAYMOUTH, *Sylvania Electric Products Incorporated, Salem, Massachusetts*

AND

FRANCIS BITTER,† *Massachusetts Institute of Technology, Cambridge, Massachusetts*

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In a previous paper it was shown that the application of an electric field to certain electroluminescent phosphors in an equilibrium condition produced little light, but that luminescent centers were activated in some way, and radiated upon removal of the field. It is here shown that while the luminescent centers are held in the activated state, changes are taking place which are observed as a color shift in the light radiated as a function of time held in the activated state. For certain green and blue phosphors, prompt removal of the field after activation produces green and blue bands which are also observed in operation at 60 cps. If the field is maintained for some seconds, and then removed, these bands are suppressed and a "yellow band" appears in their place at a rate determined by a temperature dependent time constant of the order of a second at room temperature. Possible explanations of this result are discussed.

IN an article¹ recently published in this journal experiments are described concerning the response of electroluminescent cells to the application and removal of dc fields. The purpose of this paper is to report on additional experiments which reveal additional detail concerning the mechanisms involved.

The procedure previously¹ adopted, and elaborated here, begins with the phosphor sample in a condition which may be referred to as "zero-field equilibrium." This condition is arrived at either by allowing the sample, a thin sheet of plastic in which the phosphor is imbedded, to remain in zero applied field in the dark for some hours, or by irradiating the sample for some seconds with infrared light in zero applied field. If a dc field is applied, and then removed a few seconds later, it is observed that the integrated light output on charging the sample condenser (ILO_c) is of the order of one percent of the integrated light output on discharging the sample condenser (ILO_d).

* This material was first presented at the Centennial Symposium on Electroluminescence and Photoconduction in Inorganic Phosphors at the Polytechnic Institute of Brooklyn, September 9 and 10, 1955.

† This work was done at the Sylvania Electric Products, Inc., plant in Salem, Massachusetts.

¹ J. F. Waymouth and F. Bitter, *Phys. Rev.* **95**, 941 (1954).

The light output on discharging (ILO_d) decreases with increasing time t during which the sample condenser was charged. The light output observed on recharging the sample condenser (ILO_c) which has been charged for a length of time t depends upon both the charging time t and the time t' between discharging and recharging. For fixed t' , ILO_c increases with increasing t toward a saturation value approximately equal to ILO_d for t very small. For a fixed value of t , ILO_c decreases with increasing discharged time t' toward its zero-field equilibrium value. These observations have all been qualitatively explained by the hypothesis that when the electric field is applied, a "frozen" polarization develops, which eventually reduces the actual field in the phosphor to zero.¹ The time constants of these effects are of the order of fifty to one hundred seconds.

The new experiments to be described below relate to the emission spectrum of these ILO 's. It had been noted that ILO_c was "bluer" than ILO_d but that ILO_c had approximately the same emission spectrum as the 60-cps luminescence.² Moreover, the emission

² J. F. Waymouth, *J. Electrochem. Soc.* **100**, 81 (1953).

spectrum of ILO_d was a function of charging time t in the 0–30 second range.

Therefore measurements were made of ILO_d as a function of charging time using the following filters: (1) 4585 Å interference filter, 50 Å band pass; (2) 4960 Å interference filter, 50 Å band pass; (3) Corning No. 3482 yellow filter, cut off about 5600 Å; (4) Corning No. 3307 “signal yellow” filter. For a blue phosphor, the response through the 4585 Å filter should be due almost entirely to the blue band, while the response through the 4960 Å filter should be due to both green and blue bands. For a green phosphor, response through the 4960 Å filter should be due to the green band, while response through the 4585 Å filter should be due to both green and blue bands. The Corning No. 3307 filter together with a phototube with an S-4 response has a spectral response characteristic similar to that of the human eye.³

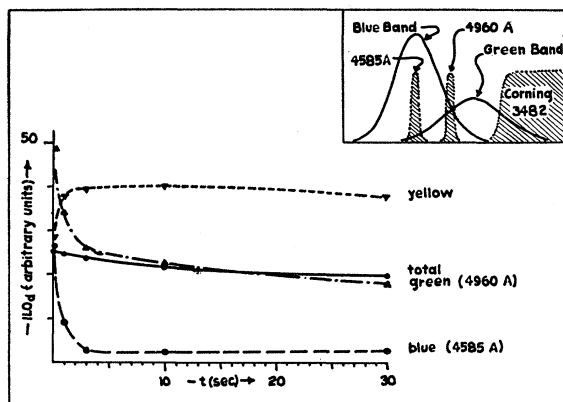


FIG. 1. ILO_d (green, blue, yellow, and total) vs charging time t for a blue electroluminescent phosphor. Inset shows approximate locations of filter pass bands relative to emission bands observed under 60-cps excitation.

The results obtained for a blue phosphor are shown in Fig. 1. The inset at the upper right shows approximately the filter pass bands and the amplitudes of the emission bands under 60-cps excitation. Note first of all that “total” ILO_d , measured through the No. 3307 filter shows a slow decay due to the frozen polarization mechanism already described. On this time scale this decay is relatively slight. Blue-band ILO_d decreases with approximately a one-second time constant to a small fraction of its value for short charging time. ILO_d measured through the 4960 Å filter shows a rapid decrease with the same time constant as that of the blue-band ILO_d followed by an additional decrease with a longer time constant. The ILO_d measured through the 3482 yellow filter *increases* to a maximum with a time constant of the order of one second, and then decays at approximately the same rate as the total ILO_d .

³ This combination was erroneously reported at the Symposium to have a constant quantum efficiency response.

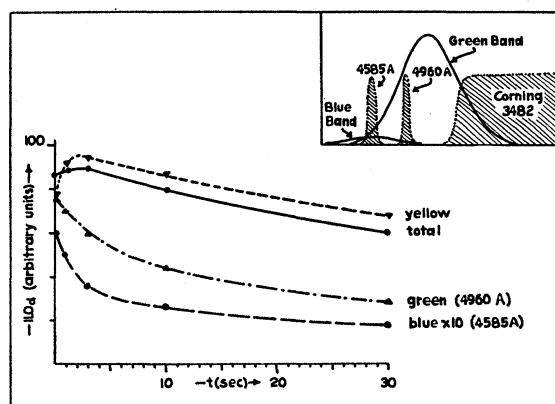


FIG. 2. ILO_d (green, blue, yellow, and total) vs charging time t for a green electroluminescent phosphor. Inset shows approximate locations of filter pass bands relative to emission bands observed under 60-cps excitation.

It is evident that during the charging interval, the blue and green emission bands are suppressed. The blue centers are not being converted into green centers. If they were, the ILO_d measured through the 4960 Å interference filter would not decrease as the blue-band ILO_d decreases. From the increase in yellow ILO_d , however, we can conclude that an additional emission band appears to the “yellow” side of the green band, and that after about 30 seconds of charging the emission spectrum of ILO_d consists largely of this emission band.

This conclusion is corroborated by the data shown in Fig. 2, which shows the results of similar measurements on a green phosphor. In this case there is evidence for an initial decrease in green-band ILO_d which is

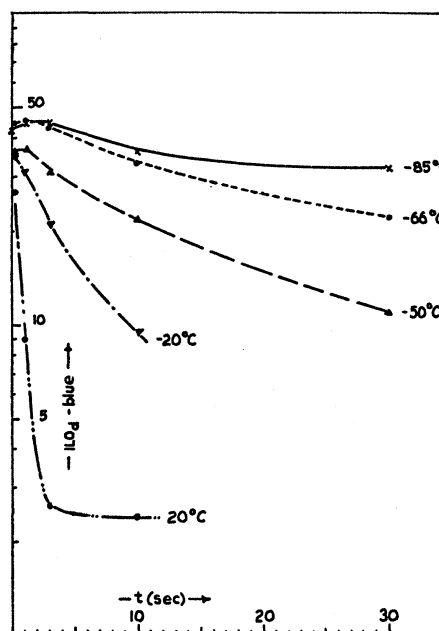
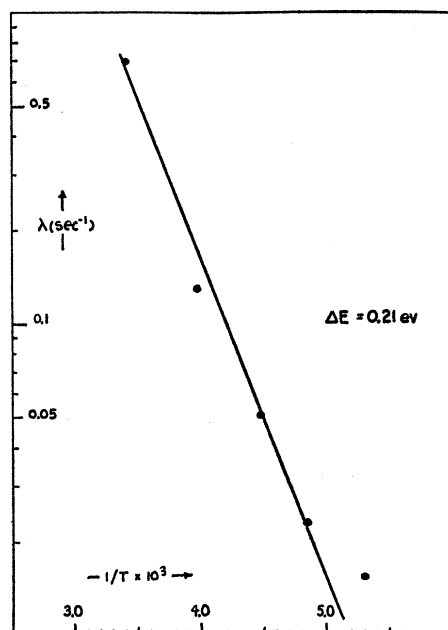


FIG. 3. ILO_d (blue) vs charging time t for a blue electroluminescent phosphor. Sample temperature is the parameter.

FIG. 4. Log decay constant for ILO_d (blue) vs $1/T$.

more rapid than that of the total, together with a corresponding increase in yellow ILO_d . This shows that "green" centers are likewise converted into yellow centers while the field is applied. It must be pointed out, however, that there is no evidence one way or another to indicate whether the "yellow" emission band⁴ is the same in the case of both the green and the blue phosphors.

In order to learn more about the mechanism for this effect, the rates of decay of the green and blue bands were studied as a function of temperature. Figure 3 shows blue-band ILO_d as a function of charging time t for various temperatures. Decay constants were estimated from these slopes and are plotted as a function of reciprocal temperature in Fig. 4. The points fall reasonably well on a straight line for which the slope is 0.21 eV. Similar data for the green phosphor are shown in Figs. 5 and 6. The application of infrared light during the charging period accelerates the color shift. The rate of color shift is independent of applied field between 5×10^4 and 7.5×10^4 v/cm. These facts indicate that the rate-limiting process is thermal in nature, and that the mechanism is probably electronic rather than due to migration of ionized activators into different types of sites.

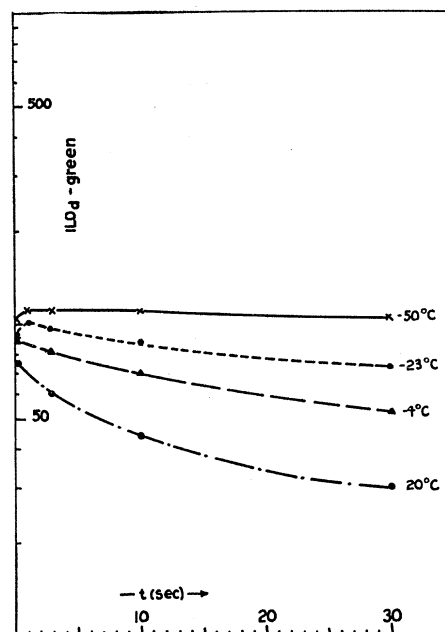
The main features of the phenomenon can be accounted for within the framework of the Schön-Klasens theory⁵ concerning the temperature quenching

⁴ These experiments are incomplete in that the location and extent of the "yellow" band have not been determined. We are reporting on our results in this state as we do not expect to undertake further work in this respect.

⁵ M. Schön, Z. Physik 119, 463 (1942); H. A. Klasens, Nature 158, 306 (1946); H. A. Klasens, J. Electrochem. Soc. 100, 72 (1953).

of luminescence in zinc sulfide. Figure 7 shows schematically the processes which are thought to take place. The upper half of the illustration, (a), shows the cycle as it might occur in a zinc sulfide excited by ultraviolet radiation, while the lower half (b) illustrates the electroluminescent case.

In the case of Fig. 7 (a), electrons are excited by ultraviolet photons from the filled luminescent levels to the conduction band. This is represented by transition (1). This process results in a "free" electron in the conduction band and a vacant luminescent level. The vacant luminescent level may be filled by either of two processes: an electron excited thermally from the filled band, leaving behind a "hole," as represented by transition (2), or the free electron in the conduction

FIG. 5. ILO_d (green) vs charging time t for a green electroluminescent phosphor. Sample temperature is the parameter.

band may recombine with the vacant luminescent state, with the emission of fluorescence radiation, as in transition (5). If transition (2) occurs, the free electron and free hole may recombine elsewhere, as at the quenching center. Since the rate of transition (2) is dominated by an exponential ($-eV/kT$) factor, at low temperatures, most of the vacant luminescent levels are filled by means of transitions of type (5), and efficient fluorescence results. At elevated temperatures, the rate of transition (2) will exceed that of transition (5); the fluorescence is quenched and recombination of electrons and holes takes place at the quenching centers. This recombination is presumably nonradiative. Hence, at high temperatures, the fluorescence is quenched.

To apply this model to the case of the electrolumines-

cent phosphor, we note that the assumption that the luminescent centers become ionized in the high field (by whatever mechanism) affords a simple explanation of the fact that ILO_c is very much smaller than ILO_d . When the field is applied and the centers are ionized, all the electrons released to the conduction band are swept over to the positive side of the crystal. They are held there until the field is removed, whereupon they return to their parent centers and recombine with the emission of radiation. However, during the interval that the field is on and the electrons are held at the positive side of the crystal, the thermal filling of the vacant activator states can proceed without competition, liberating free holes into the filled band. If the

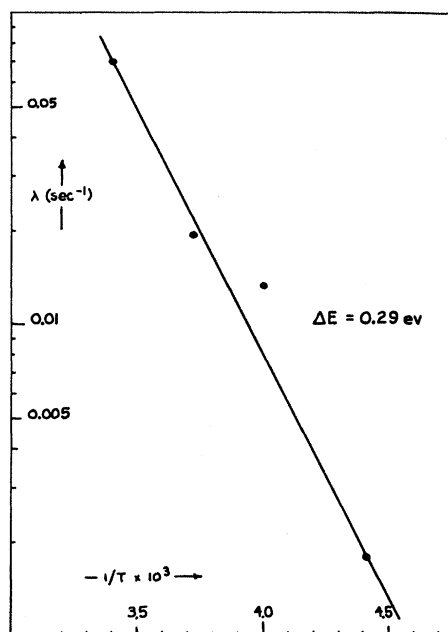


FIG. 6. Log decay constant for ILO_d (green) vs $1/T$.

field is maintained for a sufficiently long time, all the vacant activator states will be filled.

When the field is removed and the electrons return, they must recombine with the holes, presumably at the quenching centers instead of at the activators. To account for the fact that luminescence of a different color is observed when the field is removed after some seconds, instead of no luminescence at all, requires the hypothesis that this recombination is radiative at room temperature.

The assumption that a transition within a single center might be radiative at room temperature though not so at elevated temperature does not require too

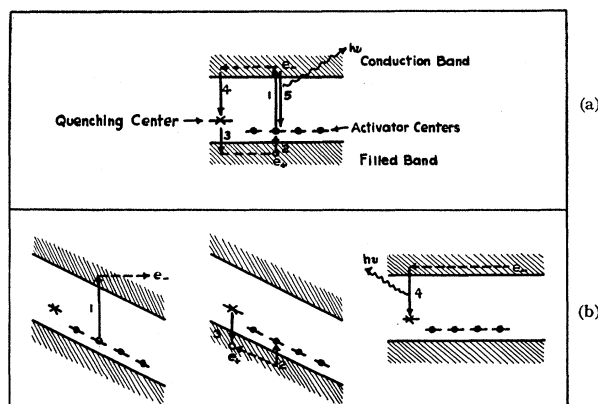


FIG. 7. (a) Schematic representation of Schön-Klasens model applied to temperature quenching of fluorescence. See text for details. (b) Schematic representation of Schön-Klasens model applied to electroluminescence under the conditions of these experiments. See text for details.

great a stretch of the imagination, since it is qualitatively explained by the configuration-coordinate model.

It is of course possible that the hole in the valence band created by transition (2) is removed to the crystal surface by the electric field and that after removal of the field transitions (3) and (4) are in competition with a radiationless recombination of holes and electrons. The illustration is drawn as it is because a very low mobility would permit holes to be readily captured by hole traps or the like. Such trapping, thermal detrapping, drift in the direction of the field, and retrapping would lead to the development of an internal polarization with a long time constant. A polarization of this kind was found in our earlier work.

On the basis of this model for the field-induced color shift, the activation energies for the decay of the green and blue bands, 0.29 and 0.21 eV respectively, would be associated with the energy gap between the vacant luminescent levels and the filled band. The relative values are in the same direction but do not agree with the values 0.95 eV and 0.55 eV obtained by Garlick and Gibson⁶ for ZnS:Cu and ZnS from temperature quenching.

It must be pointed out that by interchanging the roles of holes and electrons and turning the picture upside down, the effects observed could also be accounted for by means of the Lambe-Klick model,⁷ which may be thought of as the inverse of the Schön-Klasens model. The observations reported in this paper do not establish a basis for preference of one model or the other.

⁶ G. F. J. Garlick and A. F. Gibson, *J. Opt. Soc. Am.* **39**, 935 (1949).

⁷ J. Lambe and C. C. Klick, *Phys. Rev.* **98**, 909 (1955).