

Electroluminescence of organic compounds

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The importance attached to the shape of brightness waveforms as intrinsic properties of phosphors is not justified, unless the harmonic content in the applied voltage is quite low. In some slides shown by Prof. Destriau for the same phosphor at different frequencies, there was a sort of random relationship between the heights of the adjacent brightness wave peaks and in some cases the tops of the curves were flattened as though by saturation of the oscilloscope amplifier.

In my slides were seen two brightness waves corresponding to emissions viewed from two sides of a symmetrical cell with two transparent electrodes. The two waves were in phase, i.e. smaller and greater peaks of the brightness waves were emitted simultaneously from both sides of the cell. For a second harmonic content of 6% the difference in height of neighbouring peaks was 40%, whereas for 0.3% content this difference was negligibly small. From my slides of green and blue emission waveforms of a green-blue phosphor it is possible to locate the part of the cycle where green centres are mainly excited as corresponding to decreasing applied voltage.

Author's reply: In reply to Dr. Zalm, if electroluminescence was a pure surface effect, the highest peak should always

occur for the same polarity, but this is not so. Even for the same sample this polarity changes when the applied voltage is increased. On the other hand, electroluminescent crystals show many luminous spots under the microscope, some near the surface but others in the body of the crystal.

In reply to Dr. Diemer, the secondary peak of the brightness wave, or the inflexion, may occur either on the increasing or the decreasing side according to the applied voltage. This change in position of the secondary peak is independent of the metal backing, for which we have used Cu, Ag, Au, Pb, W, Al, Fe, Pd and In.

With regard to Mr. Ince's comments, some experiments of D. Curie have shown that when electrodes are in contact with a crystal, the pure electroluminescence is complicated by secondary effects.

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Paper 9

Electroluminescence of organic compounds

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Electroluminescence has been produced in organic fluorescent compounds. Adsorbates of such materials on cellulose films have been prepared which when dry and free from oxygen show phosphorescence. The films are mounted as the dielectric of a condenser having one transparent electrode and an alternating potential is applied. After these dielectric cells have been exposed to sunlight they show an electrophotoluminescence which quickly disappears leaving the normal electroluminescence. New emission bands in addition to the normal bands of luminescence emission are observed. Compounds investigated include gonacrin, brilliant acridine orange E and carbazole.

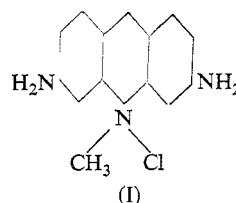
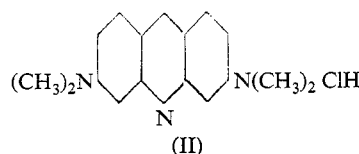
Since inorganic phosphors become luminescent under the sole action of intense alternating electric fields we have attempted to obtain the same phenomenon for adsorbates of organic molecules. When the latter are dispersed in a rigid medium they can exhibit phosphorescence. For dispersion in cellulose films the latter must be very dry and oxygen must be eliminated. After some preliminary difficulties we have succeeded in using this medium for the study of electroluminescence in organic compounds.

PREPARATION AND MOUNTING OF ELECTROLUMINESCENT CELLS

Earlier methods of making cells and the circuits used for measurement have been described elsewhere.⁽¹⁾ Films of cellophane are plunged into the fluorescent solution, dried, and finally placed with melted paraffin wax between a plate of aluminium and a sheet of mica. The whole is compressed to exclude air bubbles before cooling. The mica sheet is wetted on its exterior surface by a saline glycerine solution. The total thickness of dielectric in the cells is from 0.1 to 0.2 mm. The alternating applied potential was obtained from a mains transformer (50 c/s) and a potential difference of up to 2000 V could be used. The emission was measured

by a photomultiplier (either R.C.A. type 1P21 or a Lallemand 18 stage type) as previously described.⁽²⁾

Trials were made with acridine derivatives: gonacrin (I) and brilliant acridine orange E (II) at concentrations of 1/25 000 to 1/200 000, and also with carbazole.



From preliminary results it appears that other fluorescent compounds may show the effect provided that they do not

introduce appreciable electrical conductivity into the cellophane film.

STUDY OF EMISSION

Variation of brightness with applied potential. The prepared cells only show the electroluminescence effect proper after a certain time has elapsed. Initially two different phenomena occur: a lack of sensitivity due, in our opinion, to the presence of oxygen, and electrophotoluminescence due to release by the applied field of energy which was previously stored during exposure of the cells to daylight. After "aging" of the cells, which consists of exposure to sunlight, application of a field produces relatively strong emission which decays away leaving the normal electroluminescence emission after some hours. After such a procedure the cell shows stable performance. Increase of the applied field is ultimately limited by puncture of the mica and occurrence of discharges around the edges of the cell, the latter being evident from fluctuations in the recording galvanometer. Visual tests reveal that, below the field limit, the emission is due to luminescence in the body of the dielectric and not to spurious discharges.

For a given cell a potential V produces a surface brightness B which follows the relation:

$$B = aV^2 \exp(-b/V) \quad (1)$$

where a and b are constants. This relation is similar to that obtained by Destriau for ZnS phosphor cells.⁽³⁾

Oscillographic study of electroluminescence. Cells were prepared as described above and examined by Prof. Destriau and Mme. M. Destriau, using oscillographic methods available in Prof. Curie's laboratory, with field frequencies from 50 to 500 c/s. It was observed⁽⁴⁾ that the brightness waveform leads the voltage waveform. Destriau has shown⁽⁵⁾ that the real field in the dielectric ξ is related to the applied field E thus:

$$\xi = E / \left[1 + \left(\frac{4\pi}{\epsilon\rho\omega} \right) \right]^{\frac{1}{2}} \quad (2)$$

where ϵ is the dielectric constant of the medium, ρ the resistivity and ω the angular field frequency. The phase angle of the real field relative to the applied field is given by:

$$\tan \phi = 4\pi/\epsilon\rho\omega \quad (3)$$

We have calculated that for the two frequencies used, $\omega_1 = 100\pi$, $\omega_2 = 1000\pi$, $\tan \phi_1/\tan \phi_2 = 10$.

For our cells, as for ZnS type cells, it is found that the real field determines the electroluminescence as soon as the threshold potential, characteristic of a given cell, is reached. While the brightness follows the field variation at 50 c/s, a weak persistence is observed at 500 c/s between excitation regions. The same cells show a phosphorescence of several seconds duration after exposure to sunlight.

Dr. D. Curie: Although organic and inorganic materials show similar electroluminescence relations the necessary fields are much higher, and the mean acceleration paths are much smaller for the organic case and correspond to molecular size. The exponential brightness-field law for organic materials may thus be due to a Zener effect, in contrast to the inorganic case where the fields are not high enough.

Dr. P. Zalm: Regarding the experiments of Prof. Bernanose, attention should be directed to the so-called Reboul effect,

EMISSION SPECTRA

From preliminary trials on acridine orange⁽⁶⁾ the emission spectrum appears to be independent of the applied field. However, there was evidence for a new band in the blue region, but no explanation of this is yet available. These first measurements are only approximate being obtained by the use of interference filters.

ELECTROPHOTOLUMINESCENCE

The electrophotoluminescence which perturbs the initial observation of electroluminescence can be studied as follows. The cell is kept in the dark and then illuminated under known conditions, the subsequent variation of emission with time being measured for a given applied potential. Electrophotoluminescence was observed in all cases, but was most noticeable in the case of carbazole. For one of these cells the variation of emission B_1 with time t was determined and is given by:

$$B_1 = B + \alpha \exp(-\beta t) \quad (4)$$

where α and β are constants and B is the normal electroluminescence brightness. α and β depend on the conditions of previous illumination of the cell. For a particularly good cell, exposure to sunlight for several hours was followed by an emission of electrophotoluminescence some 20 times greater than the normal electroluminescence. This enhanced emission decreased to half its initial value in 3 min, normal brightness of electroluminescence being reached in about 20 min.

CONCLUSION

The two phenomena of electrophoto- and electroluminescence are experimentally distinguishable for these organic fluorescent compounds. The emission laws relating brightness to applied field appear to be similar to those found for inorganic phosphors.

ACKNOWLEDGEMENTS

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DISCUSSION

occurring at the anode side of insulating layers where soft cathode-rays or X-rays can be emitted. These rays can excite any normal non-electroluminescent phosphor.

Author's reply: In reply to Dr. Curie, it is possible that energy transfers occur between organic molecules, or that electrons move into organic crystals, but so far there is little experimental evidence.

Dr. Zalm's suggestion is a possible explanation, though the brightness waves suggest electroluminescence. No work has been done with d.c. fields.

[The following is a summary of a short lecture given during the session on Electroluminescence.]

Dr. G. Szigeti: The electroluminescence of silicon carbide crystals has been reported by several workers,⁽¹⁻⁵⁾ together with attempts to provide a theory of the effect. To provide more experimental data to distinguish between the theories we have measured the detailed characteristics of the emission spectrum and its temperature dependence. A microscope-spectrophotometer designed by G. Bauer of our laboratory was used. This gave an accuracy of 15% in intensity measurement and a resolution of approximately 20 Å in wavelength. The spectral distributions for the silicon carbide emission and absorption are given in Fig. 1 which also includes earlier

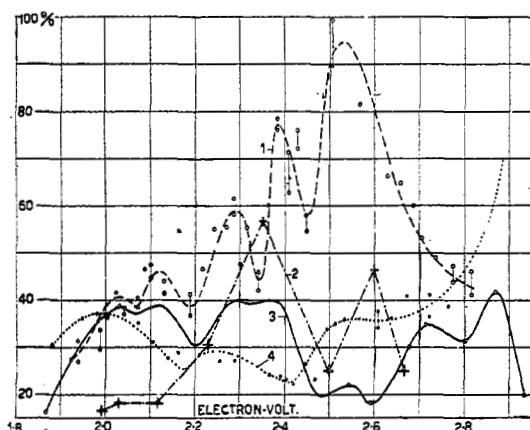


Fig. 1. Spectral distribution of emission and absorption

Curve 1, electroluminescence of silicon carbide.
Curve 2, electroluminescence of silicon carbide.⁽⁴⁾
Curve 3, cathodoluminescence of boron nitride.⁽⁵⁾
Curve 4, absorption of silicon carbide.

results by Lehovc and others.⁽⁴⁾ There is marked agreement of maxima with those given in Fig. 1, Curve 3, for the cathodoluminescence of boron nitride containing carbon impurity.⁽⁵⁾ The best agreement is for the peaks at 2.025, 2.125, 2.285 and 2.385 eV. From the measured spectra we can derive the energy level scheme of silicon carbide as shown in Fig. 2. It seems probable that excess of carbon in the carbide is

responsible for the emission centres since the spectra are not altered by impurities, except adversely in intensity. The activation energies for hole semi-conduction will be 0.15 and 0.25 eV from Fig. 2. Lehovc found 0.12 eV for the

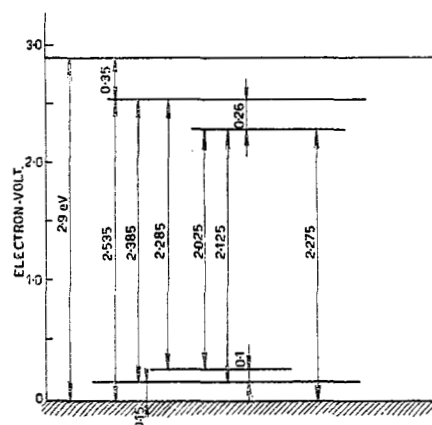


Fig. 2. Energy level scheme for silicon carbide

activation energy involved in the variation of emission with temperature (18–136°C), while Braun and Busch⁽⁶⁾ give 0.3 eV and 2.3 eV for the activation energy of semi-conduction at low and high temperatures respectively. Thus reasonable agreement is shown with results from spectral measurements.

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