

## ELECTROLUMINESCENCE\*

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THE following description can be given at present of the mechanism of the electroluminescence of Cu-activated zinc sulfide powder in an alternating electric field. The applied external field is concentrated in a small region of the crystal, in which a positive space charge appears. However, this region also contains localized electrons trapped in deep energy levels. These levels are so deep that the electrons cannot be liberated by thermal excitation, but only by the electric field. The freed electrons immediately pass into the region of the strong field, are dispersed, and some of them act to bring about ionization of the ZnS crystal structure. Some of the holes thus produced are captured by luminescence centers, and thus a certain concentration of ionized centers accumulates. After passing through the strong-field region, the electrons finally come to the opposite end of the crystal. Here, there exists an increased concentration of ionized luminescence centers which had been formed during the previous half-cycle. Thus, the electrons combine with the ionized centers there. As a result, a flash of light occurs. In the next half-cycle, the entire process is repeated, the ends of the crystal exchanging roles.

In a study of oscillograms of the electroluminescence intensity, Georgobiani and Fock<sup>1</sup> found that the greatest depth of the electron traps participating in electroluminescence is about 0.7 eV. The liberation of the electrons from these traps occurs by collision ionization at low temperatures, and by the tunnel effect at high temperatures. At 240° K, both processes have approximately the same probability. In studying the relation of the mean intensity to the electric field intensity and the temperature, the same authors<sup>2</sup> found that the total number of electrons, stored in the traps or migrating through the crystal, is determined by the tunnel effect at all temperatures. This means that the source governing the total number of these electrons cannot be any of the traps within the interior of the crystal. Apparently, this source can only be an accessory phase, e.g., Cu<sub>2</sub>S, occurring on the surfaces of the crystallites, or else the ZnS structure itself. As has been shown by Georgobiani,<sup>3</sup> the probability of a tunneling transition from the valence band to the conduction band of ZnS under the customarily-applied

fields is sufficient for this process to provide the necessary number of electrons for electroluminescence.

A strong electric field can liberate not only electrons, but also holes from traps. This has an effect on the electroluminescence yield and the recombination interaction of the blue and green luminescence centers in zinc sulfide. M. V. Fock<sup>4</sup> has shown that the frequency dependence of the ratio of intensities of the blue and green bands may be explained precisely by the effect of the electric field on the recombination interaction (i.e., on the exchange of holes between the two types of centers). Here it turns out that in the electric-field effect the probability ratio for liberation of holes from the blue and green luminescence centers is about unity. On the other hand, the probabilities for thermal liberation at room temperature differ by at least one or two orders of magnitude. Since the electric field cannot hinder the liberation of holes from ionized centers, such a change in the probability ratios for their liberation can be due only to unequal increases in the probabilities. However, an increase in the probabilities of liberation of holes from the ionized centers leads to an increase in the surface quenching. This is apparently the reason for the small energy yield of electroluminescence. It also follows from this that we may increase the yield not only by reducing the number of centers for radiationless recombination, but also by increasing the probability of capture of the holes by the luminescence centers.

We should note another phenomenon related not only to electroluminescence but also to the luminescence mechanism of zinc sulfide in general. A. M. Bonch-Bruевич<sup>5</sup> has studied the intensity oscillations in the blue and green luminescence bands separately under excitation by square pulses. The observations were performed under the microscope, thus permitting the recording of the emission from one end of the crystal alone. It turned out, as was to be expected, that each end of the crystal flashes not twice, but once per cycle. When the exciting pulse here was so brief that it was over before the luminescence could decay, the intensity of the green band dropped sharply as soon as the exciting pulse ceased. The explanation of this fact is obvious: as soon as the external electric field vanishes, the liberation of electrons from the traps ceases. Thereupon, the flow of electrons into the region having a high concentration of ionized luminescence centers also ceases. However, we do not observe this behavior in the blue band: the course of decay of the flash is independent of whether the exciting pulse has ceased or not. This difference in be-

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havior between the blue and green bands cannot be explained by the recombination interaction between the luminescence centers. This is because the electrons which recombine with the ionized centers are common to the centers of both types. Then, if their number changes sharply, the intensity of both bands will be affected, regardless of how the holes may migrate in this process.

This difference in behavior of the blue and green bands is observed for exciting pulses of duration shorter than 30  $\mu$ sec. Apparently, it may be explained on the basis of the diffusion theory developed by V. V. Antonov-Romanovskii.<sup>6</sup> This theory takes into account the fact that the ionized luminescence centers attract the electrons, since they have an excess positive charge. Even at relatively great distances, the potential energy of an electron in the field of an ionized center is greater than the energy of thermal motion of the electron. Thus, it cannot escape from the ionized center, and gradually approaches it until it recombines. Thus, if an appreciable fraction of the electrons are located within the capture spheres of the ionized centers, the luminescence will follow a quasi-monomolecular law, rather than a bimolecular law. The electric field due to an ionized center is very great. A simple estimate shows that it amounts to  $10^6 - 10^7$  v/cm at a distance of several lattice constants from the center, that is to say, it exceeds the applied external field. Hence, if an electron is situated in the capture sphere of an ionized center, the external field can have no great effect on its motion. The time during which the electron remains in the captured state depends only on the structure of the luminescence center. If this time is of the order of 10  $\mu$ sec for blue luminescence centers, but considerably shorter for green centers, then in the microsecond time range, the green luminescence will react immediately to the concentration of free electrons, while the blue luminescence will react only after a delay. Within this period of time, the intensity of the blue band will have decayed by several-fold. Thus, it will seem experimentally that the blue band does not react at all to the external field affecting the concentration of free electrons.

It is of interest that such anomalies in the behavior of the blue band are observed not only in the electric excitation of zinc sulfide phosphors. T. P. Belikova and M. D. Galanin<sup>7</sup> have observed a difference in the

rates of decay of the blue and green bands during the same time interval, both upon excitation by the light of very brief sparks and upon excitation by  $\alpha$  particles. After a brief excitation pulse, not only ionized centers and electrons ejected from them remain in the phosphor, but also a certain number of ionized centers having electrons within their capture spheres. These electrons will proceed to recombine. If enough of these pairs have been generated during the excitation period, then they will determine the intensity of the corresponding band at the beginning of the afterglow. Decay will proceed at a rate determined by the recombination probability of such pairs, until the formation of new pairs begins to have an effect. These new pairs originate as electrons approach the ionized luminescence centers in their chaotic motion and are captured. Here the decay will be slower, and will now obey the ordinary kinetics of luminescence of crystal phosphors. If the time which electrons spend in the capture spheres of the ionized blue centers is considerably greater than that of the green centers, within a certain time range the intensity of the blue band will be determined by the number of electrons captured by ionized blue centers, while the intensity of the green band will be determined by the number of free electrons. This time range turned out to be the same in the experiments with spark photoexcitation as with electric excitation. Under excitation by  $\alpha$  particles, the range turned out to be shorter. This may be explained by the greater density of excitation attained, and the correspondingly smaller dimensions of the capture spheres of the blue centers.

<sup>1</sup>A. N. Georgobiani and M. V. Fock, *Optika i Spektroskopiya* 9, 775 (1960).

<sup>2</sup>A. N. Georgobiani and M. V. Fock, *ibid.* 10, 188 (1961).

<sup>3</sup>A. N. Georgobiani, *Optika i Spektroskopiya* (in press).

<sup>4</sup>M. V. Fock, *Optika i Spektroskopiya* 11, 98 (1961).

<sup>5</sup>Bonch-Bruevich, Kariss, and Molchanov, *ibid.* 11, 87 (1961).

<sup>6</sup>V. V. Antonov-Romanovskii, *Trudy FIAN* 2, No. 2-3, 157 (1943).

<sup>7</sup>T. P. Belikova and M. D. Galanin, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 25, 364 (1961).

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