

## ELECTROLUMINESCENCE

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LUMINESCENCE is, as is well known, the excess over the thermal radiation of a body if it possesses a wavelength which exceeds considerably the wavelength of light. The first part of this definition, proposed by Wiedemann, separates luminescence from the equilibrium thermal radiation, and the second part, introduced by Vavilov, separates it from the various forms of dispersion and also from induced radiation and the Cerenkov radiation. From the very definition it is clear that the idea of luminescence refers not to single radiating atoms or molecules but to their aggregates — to bodies, since the elementary acts of the excitation of molecules and the emission of light quanta can be the same as in luminescence, and the difference consists merely in the relative numbers of the various energy transitions from which the temperature of the body is intrinsically determined. Naturally, all these statements are valid only for bodies which have a defined temperature. If, however, the energy does not have a Maxwell-Boltzmann distribution over the degrees of freedom, then there is also no sense in speaking of thermal radiation or luminescence.

The extent of the deviation from thermal radiation is determined by the energy transfer within the radiating bodies from the place of its absorption to the radiative centers. In studying luminescence one must, therefore, not limit oneself to a consideration of transitions leading to the emission of light, and it is essential to investigate the process as a whole, beginning from the moment of the energy absorption. The study of luminescence allows not only to explain the mechanism of the formations responsible for the radiation, but also to study how the energy is transported in the luminescent body, and how it is stored in it. The resonance migration of energy from one oscillator to another, and also the electron traps in solids, for example, were discovered in this manner.

Depending on the form in which the energy is fed to the luminescent body, we differentiate between photo-, cathode, x-ray, electro- and other types of luminescence.

In electroluminescence the radiating body draws the energy from an electric field. Naturally, the electric field can release its energy only when charges move in it. Therefore, electroluminescence is closely connected with the various forms of electric discharge and breakdown. On the other hand, it is essential that the body be able to transform the absorbed energy into radiation. Since the emission of

quanta is the last stage of any luminescence, one may think that there is a connection between photo-, cathode, x-ray, and electroluminescence. This connection can be seen in the fact that zinc-sulfide luminophors are not only the most intense electroluminophors, but also luminesce excellently under other forms of excitation. This connection, however, is not completely unambiguous; thus, for instance, zinc sulfide powder, which has good photoluminescence, possesses weak electroluminescence, and vice versa.

For a long time the only electroluminescence known was that of gases — the glow of a gas discharge. In the Twenties the Soviet scientist O. V. Losev discovered the glow of silicon carbide near a rectifying contact, but little attention was paid to his work. In the Thirties Destriau<sup>2</sup> in France observed the glow of zinc sulfide activated by copper, mixed with a liquid dielectric, and placed between the plates of a capacitor to which alternating voltage was applied. His work also received for a long time no attention. This can be explained to a large extent by the fact that the luminophors which he prepared glowed weakly. For a long time it was not certain whether this radiation is photoluminescence excited by the ultraviolet light of the corona discharge appearing when the voltage is applied. In the Forties the number of works refuting the existence of the Destriau effect was comparable with the number of works proving its existence. Only in the Fifties, when it became possible to synthesize sufficiently strong electroluminophors, doubts concerning the existence of the very phenomenon disappeared. There appeared the possibility of its practical application, and the study of the luminescence of crystalline substances progressed at a fast rate.

Generally speaking, liquids can also glow under the action of an electric field, although this phenomenon has thus far not been reliably established.

In the following we shall consider only the electroluminescence of crystalline substances.

In considering the mechanism of the electroluminescence of crystals, there appear three fundamental questions:

1. What is the source of the free charges that are accelerated in the electric field?

2. How and where do these charges draw the energy from the electric field and transfer it to the luminescence centers?

3. Where and at which instant does the de-excitation of the energized luminescence centers take place, and how is it regulated?

The answers to these questions can differ for each specific case.

To answer these questions, it is necessary to make use of the theory of semiconductors and of solid-state theory in general. At the same time, however, the investigation of electroluminescence presents in itself a new method for the study of the electric discharge and the pre-breakdown state in crystals. It is a feature of the electroluminescence method that we can determine directly, from the brightness of the radiation, the number of acts of recombination of the charge carriers at centers of a given kind. If the crystal has several kinds of recombination centers, then it is possible to observe the recombination at the centers of each kind separately, since each yields radiation of a different spectral composition. In a number of cases it turns out that it is also possible to determine the locations where the recombination takes place. At present many crystalline substances are known which can become electroluminescent, such as SiC,<sup>1,3,4</sup> Ge,<sup>5</sup> Si,<sup>6</sup> ZnO,<sup>7</sup> CdS,<sup>8</sup> AlN,<sup>9</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>10</sup> diamond, and others.

To observe electroluminescence, two methods are usually employed, proposed at the time by Losev (Fig. 1) and Destriau (Fig. 2).

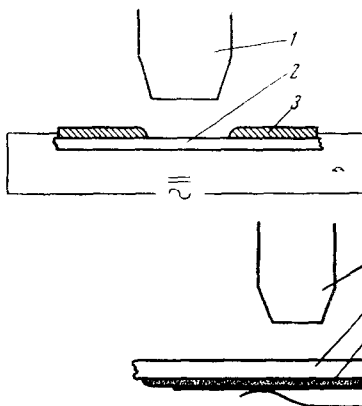


FIG. 1. Electroluminescence excitation with direct contact with the electrodes: 1 - radiation detector, 2 - crystal, 3 - electrodes.

FIG. 2. Electroluminescence excitation without direct contact with the electrodes: 1 - radiation detector, 2 - glass, 3 - transparent conducting layer on the glass, 4 - layer of electroluminescent material in the dielectric, 5 - second electrode.

We shall first consider the radiation on direct contact with the electrodes. In exciting electroluminescence by this method it was observed<sup>11</sup> that when current flows in the forward direction in a crystal with a p-n junction the light originates precisely in the vicinity of this junction.\* In this instance the electrons and holes move towards each other and penetrate through the p-n junction. Thus, holes appear in a region where the majority carriers

\*A p-n junction is the boundary between the parts of a crystal with predominantly electron (n region) and hole (p region) conductivity. Such a junction has a small resistance for current passing in one (the "forward") direction, and a large resistance for current passing in the opposite ("backward") direction.

are the electrons, and electrons appear in a region where the majority carriers are the holes. Such a process is called "injection" of minority carriers. The minority carriers recombine with the majority carriers on both sides of the p-n junction. The spectrum of the accompanying radiation is rather complex, and differs for various samples.<sup>12</sup> Apparently this is connected with the fact that we have here direct recombination of free electrons and holes, along with recombination at the various recombination centers - impurities, vacancies, and other defects of the crystal lattice. All these types of centers can in different cases be present in various concentrations, each having its own radiation spectrum.

In germanium electroluminescence can also be observed when an electric field is applied in the backward direction. However, in this instance the glow occurs only at some sufficiently large voltage, close to the breakdown voltage. The electrons and holes in the region of the p-n junction move in opposite directions, leaving behind a space charge precisely in the vicinity of the p-n junction, whereby a positive charge is produced on one side and a negative one on the other. The production of such a double layer leads to a concentration of the field in the p-n junction. When the magnitude of this field reaches a given value, impact ionization begins. This means that some of the electrons which appear in the region of the strong field on account of the thermal fluctuations are accelerated and acquire enough energy to knock out new electrons as they collide with the atoms of the lattice or of the activator. The glow is caused by the recombination of the resultant holes with the electrons. The radiation spectrum in this case differs somewhat from the spectrum when the current passes in the forward direction. This difference is apparently due to the fact that more energetic electrons and holes recombine,<sup>13</sup> and also to the Stark effect in the luminescence centers.<sup>14</sup> A similar mechanism of electroluminescence occurs, for instance, in Ge and Si (infrared radiation), and in SiC (visible radiation).

Electroluminescence may also occur if the rectifying junction is not within the crystal, but at the point of contact with the electrodes. In such a case the minority carriers are injected not from one half of the crystal to the other, but from the material of the electrode. The glow is observed in this case near the electrode.

Electroluminescence can also occur without the participation of the rectifying junction. This was observed in crystals of cadmium sulfide.<sup>8</sup> At some sufficiently large voltage, the current through the crystal begins to grow very quickly with increasing voltage. This process is reversible, and the current can be kept at an arbitrary level for a long time with the aid of a limiting resistance. The radiation is concentrated between the electrodes in discrete small

regions that move through the crystal. The crystal is thereby considerably heated, and the whole process is apparently analogous to the arc discharge in a gas: the conductivity is kept high by heating, and the system has a drooping volt-ampere characteristic.

In the cases considered till now the electroluminescence was produced by the passage of the current through the crystal. The study of electroluminescence under these conditions is most promising for solid-state theory, since it is possible here to study all the electrical and optical characteristics simultaneously. At present, however, the fastest progress is in the study of electroluminescence excited by Destriau's method, analogous to the electrodeless discharge in gases. This is apparently connected with the fact that it is possible to obtain bright and steadily glowing light sources from a powder mixed with a dielectric. The largest number of papers in this field is devoted to the study of zinc sulfide activated by copper and other activators.

A unique feature of electroluminescence without direct contact with the electrodes is the fact that it is a self-regulating process. This means that the absorption of energy by the electroluminophor is determined not so much by the power of the source of this energy as by the processes in the electroluminophor itself. Whereas in photo-, cathode, x-ray, etc. luminescence the extent of the energy absorbed by the luminophor is largely determined by the power of the source, independently of the properties of the luminophor, in electroluminescence everything is determined by the motion of the charges in the luminophor itself. If, for example, there are no free charges in the strong-field region, the luminophor will simply not absorb the energy fed to it. At the same time, the number of free charges is determined by the excitation state of the luminophor, which is in turn determined by the absorption of energy.

It is obvious that in the electroluminescence of isolated crystallites the electrons can move only within the limits of one small granule of the electroluminophor. Therefore, on the sides of the granules which face the electrodes there appear charges of opposite sign, which produce a field opposing the applied external field. As a result the observations have to be conducted in an alternating electrical field, and a stationary state in the strict sense of the word cannot be achieved. Even if the mean brightness remains constant, its instantaneous value pulsates within certain limits at twice the frequency of the applied voltage. Figure 3 shows schematically typical brightness oscillograms — "brightness waves," as they are commonly called. It is seen that the brightness never falls to zero. The magnitude of this constant component increases with increasing frequency of the applied field. Different phosphors have somewhat differing brightness waves. However, almost always two maxima of brightness

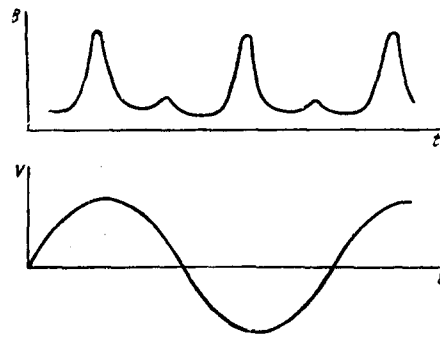


FIG. 3. Brightness oscillograms of electroluminescence  $B$  and the excitation voltage  $V$ .

are observed during a half cycle — one large (main) and one much smaller (additional) maximum. The position of the second maximum within the brightness wave is strongly temperature and frequency dependent. The mean brightness of electroluminescence increases rapidly with increasing applied voltage, approximately following the  $B = B_0 \exp(-b/\sqrt{V})$  law, where  $B$  is the brightness  $B_0$  and  $b$  are constants, and  $V$  is the voltage. At high voltages a formula with  $\sqrt{V}$  replaced by  $V$  is sometimes more precise. The increase of brightness with frequency is approximately linear up to 5 to 10 Kc/sec, and at higher frequencies it slows down. If a luminophor contains two kinds of luminescence centers, then both the brightness waves, as well as the dependence of the average luminosity on the voltage and frequency are somewhat different for these centers.

The mechanism of electroluminescence in an alternating field can apparently be essentially the same as in a constant field. This means merely that in principle the answers to the questions raised at the beginning of this article can be the same as in the case of direct contact with the electrodes. However, as we have already noted, in each specific case these questions have to be answered anew.

Studies of the electroluminescence of zinc sulfide have been going on for five years at the S. I. Vavilov luminescence laboratory of the P. N. Lebedev Physics Institute of the U.S.S.R. Academy of Sciences, directed by V. V. Antonov-Romanovskii. During this time T. I. Voznesenskaya, R. M. Medvedeva, E. I. Panasyuk, and Z. A. Trapeznikova have synthesized a whole series of zinc sulfide electroluminophors, both in the form of powders and in the form of single crystals. The studies carried out on these electroluminophors permitted us to clarify many peculiarities in the mechanism of their electroluminescence.

The first question was that of the electroluminescence centers. According to the presently accepted point of view, the centers that radiate light in photoluminescence are more or less uniformly distributed within the volume of the crystalline phosphor, and are not connected with large defects of the crystal lattice — internal fractures, dislocations, etc. It was not

clear heretofore whether one can also say the same about the centers of electroluminescence, since all these special locations, and also simply the outer surface of the crystal, may turn out to be favorable for the acceleration of electrons at least because an electric field can be concentrated on them. To clarify this problem V. E. Oranovskii and Z. A. Trapeznikova<sup>15</sup> investigated the electroluminophor ZnS-Cu, Nd. As is well known, trivalent ions of rare-earth elements used as an activator for a crystalline phosphor produce a line spectrum; the relative intensities and the positions of these lines depend strongly on the structure of the nearest vicinity of the activator ion. Comparison of the electro- and photoluminescence spectra of this luminophor has shown that the positions and the relative intensities of the neodymium lines do not depend on the form of the excitation, and consequently the main group of centers participating in the electroluminescence is located in the unaffected portion of the crystal.

The distribution of the electric field in the small crystals was investigated next. According to the estimates of the average voltage of the field applied to the electroluminophor made by numerous workers, it is insufficient to enable the electrons to acquire the several eV necessary for ionization, or at least for the excitation of the luminescence centers. On the other hand, as is well known, the presence of a space charge leads to a non-uniform distribution of the field over the crystal. In the region of the space charge the field is proportional to  $\sqrt{V}$ , while outside this region it is practically equal to zero. At high voltages the region of the space charge should extend over the whole crystallite, and then the field acting within it becomes proportional to the applied voltage. This apparently causes the aforementioned change of the dependence of the average brightness of electroluminescence on the applied voltage. V. Trofimov<sup>16</sup> investigated this charge further for a layer of a ZnS-Cu electroluminophor one crystallite thick. In this case one can assume that the entire voltage is actually applied to the crystals of the electroluminophor. Trofimov found that the field intensity at which the space charge spreads over the whole of the crystal amounts to about  $1.4 \times 10^5$  v/cm. Considerable electroluminescence is observed at an average field intensity smaller by one order of magnitude. This means that generally the region of the space charge amounts to some tenths of the volume of the whole crystallite. This region can be located near the p-n junction if it exists, or most probably at the boundary of the crystallite. The dimensions of this region are approximately proportional to the square root of the donor concentration, so that for different luminophors they may vary by as much as one order of magnitude.

V. E. Oranovskii and Z. A. Trapeznikova,<sup>15</sup> in investigating the luminophor ZnS-Cu, Er, Mn, found that the relation between the manganese band and the er-

bium lines in its luminescence spectrum depends on the density of excitation. Choosing the intensities of the photo- and electro-excitations such as to make this ratio the same for photo- and electroluminescence, they found that under these conditions the luminophor luminescence in electro-excitation is weaker by a factor of 14 than in photo-excitation. Inasmuch as the average density of excitation is the same under these conditions, this indicates that the effective luminescent volume in electroluminescence amounts to about 7% of the entire volume of the crystal. The region of the space charge ought to be a few times larger, since electrons are accelerated and ionize the luminescence centers only where the field is sufficiently large. One can, therefore, say that this result is in good agreement with the data of Trofimov.

The estimate of the glowing volume is, naturally, approximate. Actually the brilliantly bright portion of the crystallite is even smaller. The fact is that a weak glow occurs also in that portion of the crystallite where there is no field, and where there are no fast electrons able to ionize the crystal lattice or the luminescence centers. The excitation penetrates into this region because the holes which appear in the ionization of the crystalline lattice diffuse from the strong-field region, or are thermally released from the ionized luminescence centers. The radiation from this region produces a constant component in the brightness wave, since it is dependent to a lesser extent on the phase of the applied field. The varying component appears in the region where space charge and a strong field exist during a half-cycle of the applied voltage and give rise to a high concentration of ionized centers. We shall return to the varying component later.

A. N. Georgobiani and M. V. Fock,<sup>17</sup> in an investigation of the luminophor ZnS-Cu, Al, found that after the excitation is turned on the amplitude of the varying component builds up within the first few cycles of the voltage, while the constant component builds up approximately ten times more slowly. For the constant component to build up it is obviously essential that a sufficient number of holes diffuse from the region where they are produced into the remaining portion of the crystal, a process that requires a considerable time. The authors have also found that infrared light extinguishes the constant component, and barely affects the varying component. This is also usually explained from the above point of view, since it is known that the extinguishing action of infrared light increases with a decrease in the concentration of the ionized centers, and the constant component appears in the region where this concentration is small. The following fact, observed by E. E. Bukke, L. A. Vinokurov, and M. V. Fock,<sup>18</sup> also indicates that the glow is present throughout the volume of the crystallites. These authors investigated the attenuation of the luminescence of ZnS-Cu, Al and chose the

intensities of electro- and photo-excitations such as to make the average brightnesses of the photo- and electroluminescence equal during the time of excitation. It turned out that immediately after the excitation was discontinued the brightness of the electroluminescence fell considerably faster than that of the photoluminescence. However, subsequently the decrease of the brightness of electroluminescence slowed down, and became even slower than the decrease of the photoluminescence. Finally the curves merged. As is well known, in the later stages of the afterglow the luminescence of the luminophor is independent of the intensity of excitation. Therefore, the merging of the brightness curves at the late stages indicates equality of the luminous volumes, and consequently, also the fact that in electro-excitation the ionized centers have a considerable concentration throughout the volume.

We shall now consider the varying component of the brightness. It arises, apparently, during that half cycle when there is no field in the region with high concentration of ionized centers, and the electrons from the other end of the crystal return to it. The free electrons are the first to return. Their contribution to the glow, however, is insignificant, since their total number is small. These are followed by electrons which had fallen into electron traps. The rate of their return is determined by the probability of their thermal release from traps, and is therefore strongly temperature dependent. According to the data of a number of authors,<sup>19,20</sup> the return of these electrons is accompanied by an additional maximum in the brightness waves. Georgobiani and Fock<sup>21</sup> investigated the mechanism of the formation of the main maxima of the brightness waves. They found if the amplitude of the applied voltage is sufficiently large the position of the main maximum is determined by the instant when the voltage reaches a given critical value. A further increase in the voltage is accompanied by a decrease in brightness. The brightness obviously stops increasing because of the depletion of the source of the electrons that have recombined with the ionized centers, since an increase of voltage cannot decrease the number of ionized centers. The critical voltage increases with temperature up to 240° K, and then decreases again. Investigating this dependence in more detail, Georgobiani and Fock reached the conclusion that the main maximum is due to the return of electrons liberated from the deep traps of the strong-field region by the action of this field. The liberation is due to the tunnel effect, at higher temperatures (above 240° K) and to the impact ionization of the traps at low temperatures. It was also established that the depth of these electron traps amounts to about 0.71 eV and the energy of the optical phonons, the collisions with which hinder the acceleration of the electrons, is 0.038 eV. These data

are in agreement with results obtained from other considerations.

We now return to the average (over the cycle) brightness of electroluminescence. Bukke, Vinokurov, and Fock<sup>22</sup> showed that in spite of the magnitude of the applied external electric field the brightness of electroluminescence is determined by the number of electrons that are able to participate in the process of electroluminescence. Thus, after the beginning of the excitation the average brightness of electroluminescence builds up much faster if the electroluminophor was previously excited by an electric field or by ultraviolet light. From these experiments it was found that each stored electron produces a new electron before it disappears as a result of recombination, and this process may repeat itself tens of times. Thus an increase in the stored supply of localized electrons increases the brightness of electroluminescence. At a low temperature (80° K) some electroluminophors store so many localized electrons that these begin to prevent the free electrons from accelerating sufficiently to ionize the luminescence centers. In this case the average brightness of electroluminescence increases rapidly after the start of the excitation, reaches a maximum, and then begins to fall after a few seconds. The stationary value of the average brightness turns out to be 10 to 20% less than the maximum. Illumination with infrared light decreases the number of stored electrons and leads to an increase of the brightness of electroluminescence. At the same time illumination by ultraviolet light seems to increase the number of localized electrons. This leads to a prolonged decrease in the brightness of electroluminescence.

The brightness of luminescence under the simultaneous action of photo- and electro-excitation is practically never equal to the sum of the brightnesses of photo- and electroluminescence taken separately, and is always either larger (positive non additivity), or smaller (negative non additivity) than this sum. As the experiments of Vinokurov and Fock<sup>23</sup> have shown, one can go over from negative to positive nonadditivity on increasing the applied voltage. Increasing the intensity of photo excitation does not always lead to such a result. To the contrary, in some luminophors positive nonadditivity is observed at low photo-excitation intensity and negative non-additivity at higher intensities. These same authors, together with Antonov-Romanovskii,<sup>24,25</sup> proposed a qualitative explanation of these phenomena, accounting not only for the effect of the stored electrons on the electroluminescence, but also for the effect of the electric field on the photoluminescence. We shall, however, not dwell on this.

The described phenomena show clearly that electroluminescence is indeed a self-regulating process, and that this regulation is achieved by means of a

change in the number of electrons that participate in the electroluminescence. All these experiments bring to mind that the sharp increase in the brightness with increasing applied voltage is caused not so much by the improved conditions for electron acceleration, as by the increase of the number of electrons participating in this acceleration. Such an increase may be due both to the increase in the number of ionized radiation centers, or donors, and to the drawing of electrons by the electric field from the  $\text{Cu}_2\text{S}$  layer which is usually located on the surface of the crystal-lites of the  $\text{ZnS-Cu}$  electroluminophor.

The question of what determines the brightness of electroluminescence (the conditions for electron acceleration or the number of electrons) is of considerable practical significance. The fact is that present-day electroluminophors have a low yield of glow energy: almost all the absorbed energy is transformed into heat, and only a small fraction into light. It is still unknown whether this is an inalienable property of electroluminescent crystals, or whether it is possible to produce electroluminophors with a larger yield. If the former is correct, then the energy yield cannot be large. In this case the energy of the electric field is absorbed by numerous electrons, but only those which have acquired velocities sufficient to ionize luminescence centers transfer this energy to the luminescence centers. The remaining electrons transfer their energy to the thermal vibrations of the crystal lattice. In the second case, on the contrary, only a small number of electrons is accelerated and can consequently absorb energy, but each of these ionizes a luminescence center. Therefore, almost all the absorbed electric energy can be transformed into light. In this case the energy yield of electroluminescence can be large, and it is reasonable to seek such electroluminophors in which no additional processes cause useless energy loss.

Georgobiani and Fock<sup>25</sup> showed that the second hypothesis is apparently correct. They started from the fact that the temperature dependence of the constant  $b$  in the formula for the brightness should be different in these two cases. The value of  $b$  increases with the temperature in the first case and decreases in the second. The experiment which they conducted showed that  $b$  decreases with increasing temperature, thus supporting the second hypothesis.

Microscopic investigations of the glow of single crystals of zinc sulfide are also conducted at the Physics Institute of the Academy of Sciences. It is known that such crystals excited by the Destriau method do not radiate uniformly, but at discrete points located on long bright lines. V. E. Oranovskii, E. I. Panasyuk, and B. T. Fedyushin<sup>26</sup> have established that the radiation of discrete points obeys the same dependence of the brightness on the voltage as the radiation of powder-like electroluminophors. It turns out that only the component of the field parallel to the

principal direction of crystal growth is active. A similar anisotropy is also indicated in the literature with respect to the photoconductivity. All this speaks for a sharp anisotropy in the electric properties of similar zinc sulfide crystals. The brightness waves of the points differ in that they all have one main maximum per cycle and not two. V. E. Oranovskii and V. A. Khmelinin<sup>27</sup> investigated also the glow of lines. They observed that even those lines which appear perfectly continuous under the microscope actually consist of discrete portions which have one brightness maximum per cycle. The maxima of the neighboring portions are shifted in phase relative to each other. The fact that the brightness maximum of a portion of a line does not coincide in time with the brightness maximum of a point proves that they are different glowing objects in spite of the fact that the brightness of lines and of points has a similar dependence on the magnitude and direction of the applied field.

The following very interesting fact was also observed by Oranovskii and Khmelinin. If a narrow beam of ultraviolet light strikes the line, a change in brightness occurs even in some portions of the line not touched by the beam. The brightness increases when the narrow beam strikes one end of the line portion and decreases when it strikes the other.

These two properties of electroluminescent crystals of zinc sulfide are apparently connected with the presence of regions with different conductivity which are divided by rather sharp boundaries. At present, however, it is still not clear what these boundaries are: are they p-n junctions, or n-n' junctions, or boundaries between cubic and hexagonal phases, or some other boundary. In general the investigation of discrete crystals is still at the stage when experimental facts are being collected.

It must be said that our knowledge of the electroluminescence of powder-like electroluminophors is still also far from complete. It is not known, for instance, how general the above mechanism is. In particular, certain electroluminophors may turn out to have not an external but an internal source of electrons. If this source consists of not too deep donors, then they will become completely empty during each half cycle, and the total number of electrons participating in the electroluminescence will be approximately constant. In this instance the dependence of the brightness on the voltage will be determined by the dependence of the conditions for electron acceleration on the voltage. On the other hand, it may turn out that the electrons originate in the luminescence centers themselves. This means that the ionization of the luminescence centers will be accompanied by a substantial change in the concentration of the field, since the space charge produced by them will play an important part. In this case the total number of electrons participating in the electroluminescence will also not be

constant, but the dependence of the brightness on the voltage will be determined not only by the number of these electrons, but also by the conditions of their acceleration in that region of the crystal in which there exist non-ionized luminescence centers.

It is not clear what processes determine the frequency dependence of the electroluminescence brightness. Obviously, the slowing down of the increase in the brightness with increasing frequency above 10 kc/sec is due to the fact that some process has no time to develop. One may assume this process to be the concentration of the field by the transport of both free electrons and the electrons localized in small traps. If this is so, then the frequency dependence of the brightness should change strongly with temperature. However, from this point of view it is difficult to explain why, for instance, the brightness of the blue band of ZnS-Cu increases longer with frequency than the brightness of the green band of the same luminophor. The difference in the frequency dependence of bands belonging to various activators is usually attributed to the inertia of these bands. With the exception of the activator manganese and certain rare-earth elements, the excited states of most activators are so short that the inertia connected with them cannot appear at these frequencies. It is therefore more probable that the delay in the increase of the brightness of the blue and green bands of ZnS-Cu is connected with an accumulation not of excited but of ionized centers of luminescence in the region where there exists a strong electric field. If all centers turn out to be ionized in this region, then the increase of the brightness will slow down considerably.

The mechanism of the "electric memory" of the electroluminophor<sup>28</sup> remains unexplained. The brightness wave of an electroluminophor under the action of a single voltage pulse depends on whether another pulse was applied to the electroluminophor before; the memory of a large pulse is retained even if followed by several small pulses. These properties are connected apparently with the distribution of electrons not only in the traps, but also over the volume of the crystal.

We have already mentioned the ZnS-Mn electroluminophors, which were investigated by many authors,<sup>29-31</sup> and possess many interesting properties. In particular, some glow brightly under the action of a direct voltage, even if they are mixed with a dielectric, when the ZnS-Cu luminophors glow only under the action of an alternating voltage. It is, however, thus far not known wherein the mechanisms of the electroluminescence of these luminophors differ.

A very important problem, particularly for applications, is the explanation of the nature of the "aging" of electroluminophors. It is known that powder-like electroluminophors lose their brightness with time. This process is irreversible, and is apparently con-

nected with some chemical changes; however, their nature is not clear.

Finally, as has already been mentioned, the study of electroluminescence of various crystals can yield a wealth of material for solid-state theory, and in particular for the theory of the electric breakdown. In this connection, it is especially interesting to study thin-film electroluminophors obtained by sublimation.<sup>34-35</sup> On these it is easy to combine luminescence measurements with absorption and electrical measurements.

Practical applications of electroluminescence are still in the project stage. The simplest application is the use of electroluminescence for illumination. True, thus far the efficiency of electroluminescent sources of light is not high, it is somewhat lower than that of incandescent bulbs. However, even now it is possible to make electroluminescent coatings for instrument scales, for purposes of signaling, etc. A series of other applications is possible. So called image transformers and "amplifiers" are described in the literature. Their operation is based on the sharp voltage dependence of the brightness of electroluminescence. If an additional layer of photosensitive semiconductor is placed above the electroluminophor layer in an electroluminescent capacitor excited by the Destriau method, then the applied voltage will be divided between these two layers. If we now project an image on the semiconductor layer, then it will become more conducting in the illuminated portions, a larger portion of the voltage will fall on the layer of the electroluminophor, and the latter will light up more brightly. On this principle one can also construct devices that remember the image projected on them. For this purpose, it is necessary to make the semiconducting layer sensitive to the light of the electroluminophor. After illumination with an external source, the semiconductor will remain conducting because of the electroluminescence light of the electroluminophor.

There are attempts to replace television tubes by an electroluminescent screen where the glow is the result of the potential difference between crossed wires. Such a screen will have the advantage that it can be made as large as desired, for instance as large as a cinema screen.

Thus, the investigation of electroluminescence is of both theoretical and practical interest.

**Editor's note.** In the April number of *Usp. Fiz. Nauk* [70, 621-677 (1960)], we published a translation of a review by Piper and Williams under the same title [*Solid State Phys.* 6, 95 (1958)]. This review was written some three years ago. At that time, only very general assumptions could be expressed regarding the mechanism of electroluminescence of one of the most widely utilized electroluminophors - powder-like zinc sulfide. During the past years there appeared a large number of new papers, mainly Soviet, which made it possible to explain better the mechanism of electroluminescence

of these luminophors. It is now possible to consider electroluminescence from a certain general point of view, and also to raise a number of specific physical questions regarding electroluminescence which must be answered in the first place.

The article by M. V. Fock supplements the article of Piper and Williams and is already based on up-to-date material. However, the author did not attempt a complete survey of the literature, and employed only those works, chiefly Soviet, which were essential for the presentation of the present state of the problem on the mechanism of electroluminescence.

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