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V. M. FRIDKIN

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**Abstract**

**Full Text**

## **Reports of the Academy of Sciences of the USSR**

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**PHYSICS**

**V. M. FRIDKIN**

### **SOME EFFECTS OBSERVED IN THE STUDY OF THE LUMINESCENCE OF ELECTRETS MADE OF ZnS**

*(Presented by Academician A. V. Shubnikov on 20 XI 1959)*

In a number of previous works <sup>(1,2)</sup> it was shown that, for the formation of dark polarization in electroluminescent zinc sulfide, localization of electrons at the least deep trapping levels is essential, whereas the photoelectret state in ZnS is characterized by localization of electrons at the deepest levels, in particular at activator levels. From this point of view, in work <sup>(2)</sup> the question of depolarization of photoelectrets made of ZnS under the action of an alternating electric field was considered.

In studying electrets made of electroluminescent ZnS, we observed a number of effects, a qualitative description of which is given below. The experiments were carried out with ZnS activated by copper in accordance with the method described in work <sup>(3)</sup>. The electroluminophor was dispersed in an alcoholic solution of polyvinyl butyral in a weight ratio of 10 : 1. Polycrystalline layers were prepared by applying the emulsion to semiconducting glass or paper. Polarization of the resulting layers was carried out in a flat capacitor in strong electric fields. Between the ZnS layer and one of the capacitor plates a dielectric layer (getinax) approximately 1 mm thick was placed. In the course of polarization of the electroluminophor, discharge occurred in the pores of the getinax and adsorption of ions on the surface of the electroluminophor took place. In the present work we did not set ourselves the task of separating the effects caused by the internal polarization of the electroluminophor layer (heterocharge) and by adsorption of ions from the discharge gap onto the surface of the electret (homocharge). Here it is important only to emphasize that the observed effects are fundamentally due to the presence of a large homocharge in electrets made of ZnS.

1. We observed intense luminescence of electrets made of ZnS under the action of a constant electric field. The intensity of this luminescence consider-

ably exceeded the intensity of luminescence of uncharged ZnS layers under the action of a constant electric field of the same strength. The luminescence intensity of electrets made of ZnS depended on the direction of the applied field. The intensity and duration of the luminescence were greatest in the case when the direction of the field applied to the electret was opposite to the direction of the field during polarization of the ZnS. The field strength applied to the electret and necessary to obtain sufficiently intense luminescence could be much smaller than the field strength used during polarization. In all cases the observed luminescence of the electret was green. With an increase in the density of the homocharge of the electret, the luminescence intensity increased. Our observations showed that the duration of the luminescence could amount to several seconds. When the field was switched on again, luminescence of the electret appeared once more, but it was considerably weakened. After several switchings-on

the field, the glow of the specimen disappears. Observation of this effect was conveniently carried out by creating a latent electrophotographic image on the surface of a ZnS electret. For this purpose a ZnS layer was polarized in a flat capacitor, after which it was irradiated with ultraviolet light through some slide. As a result of such exposure the irradiated portions of the electret were discharged, while the unirradiated portions retained the initial charge. Reapplying the field to the layer caused intense luminescence of its charged portions, as a result of which the latent electrophotographic image became visible. Since the electret state in ZnS is stable <sup>(2)</sup>, the latent image could be observed several tens of hours after its formation. Apparently, the effect described is directly connected with a phenomenon previously observed by I. N. Orlov and I. Ya. Lyamichev and later by some other authors, which consisted in the fact that the character of the luminescence of certain electroluminophores under the action of electrical pulses depends on the frequency of their repetition <sup>(4-6)</sup>. In the experiments of I. Ya. Lyamichev and I. N. Orlov, the polarization of ZnS under the action of electrical pulses was apparently unstable, since at pulse repetition periods exceeding 10 sec the phenomenon they had discovered was no longer observed.

2. We found that the electret state in the investigated specimens of electroluminescent zinc sulfide leads to an enhancement of their fluorescence. Observation of this effect was conveniently carried out by the method described above. A latent electrophotographic image was created in the electret layer, after which the electret was irradiated with a mercury-quartz lamp through a light filter isolating the mercury line  $\lambda = 313 \text{ m} \mu$ . At the moment of irradiation of the electret (it was carried out through a photographic shutter), a bright flash (green luminescence) of the portions of the layer that had retained polarization was observed on its uniformly fluorescing surface, as a result of which the latent electrophotographic image became visible. In contrast to the preceding effect, visual observation of this picture can be carried out for a very short time (fractions of a second), after which the picture disappears against the general background

Fig. 1. On the tunneling mechanism of depolarization of ZnS electrets

Figure 1: Fig. 1. On the tunneling mechanism of depolarization of ZnS electrets

of fluorescent luminescence. The effect described is close in its character to the Destriau effect <sup>(7)</sup>, which was observed for electroluminophores in the range of X-ray radiation. It was important for us to establish that an analogous effect occurs upon excitation of ZnS by ultraviolet radiation and that both these effects are undoubtedly due to the electret state in ZnS.

3. In studying ZnS electrets we observed still another effect, which is a kind of analogue of thermoluminescence. It was found that heating the electret leads to its intense luminescence (green luminescence), and, as the electret is depolarized, the luminescence weakens. The duration and intensity of the luminescence depend on the temperature and on the rate of its change in the course of depolarization of the electret. As in the two preceding cases, observation of this effect was conveniently carried out by creating a latent electrophotographic image in the electret. When the layer was placed in a heated thermostat, the latent image became visible owing to the intense luminescence of the portions of the layer that had retained polarization.

All the effects observed by us and enumerated above are due to the presence in the ZnS thermoelectret of a sufficiently strong internal field. It seems to us that, for their explanation, one could use the scheme proposed by F. F. Volkenstein for the interpretation of electroluminescence phenomena <sup>(3)</sup>. According to this scheme (Fig. 1), when a field is applied to a crystal the conduction band is tilted, as a result of which an electron localized at a relatively deep activator level  $I$  can, owing to the tunnel effect, pass into the conduction band (transition 1) and recombine with a hole at the activator level. The application

the application of an alternating field to the crystal leads to “rocking” of the conduction band, continuous recombination of conduction electrons with holes at activator levels, as a result of which continuous electroluminescent glow of the crystal occurs. In an electret made of ZnS there is a nonuniform spatial distribution of holes and electrons localized at certain trapping levels  $II$ , the depths of which may be different. The presence in the electret of an internal field, caused by the nonuniform distribution of holes and localized electrons, leads to a tilt of the conduction band.

**Fig. 1.** On the tunneling mechanism of depolarization of electrets made of ZnS

If the trapping levels  $II$ , on which the electrons responsible for the polarization are localized, are sufficiently deep and, as a consequence, the probability of the tunneling transition 4 is small, then the electret state in the crystal may be preserved for an indefinitely long time (it is assumed here that the probability of the thermal transition 3 may also be neglected). Obviously, under these conditions

the electret state can be destroyed only in two ways. The first method consists in applying to the electret an electric field that produces an additional tilt of the conduction band. As a result, the probability of tunneling transition 4 of electrons localized on the trapping levels  $II$  into the conduction band increases; from there these electrons recombine with holes at the activator levels  $I$ , which is accompanied by luminescence of the electret. This scheme explains, in particular, why noticeable luminescence of the electret occurs when a field is applied to it whose strength is many times smaller than the strength of the field used in forming the electret. The second method of depolarizing the electret consists in using transition 3, which occurs when additional energy is imparted to the localized electron. This additional energy may be imparted to the electron both by irradiating the electret and by heating it. In the first case we observe an enhancement of fluorescence, and in the second—luminescence upon heating of the electret. In our opinion, the latter phenomenon is of special interest, since, being an analogue of thermoluminescence, it makes it possible simultaneously to study the glow curves and depolarization curves for the corresponding crystal.

It is also important to emphasize the circumstance that the effects discovered make it possible to visualize a latent electrophotographic image without using the developers ordinarily employed in electrophotography. At present a detailed quantitative study of the effects listed above is being carried out.

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