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## Abstract

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## PHYSICS

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# ON THE NATURE OF THE GOODDEN-POHL EFFECT

**1.** The Goodden-Pohl effect (GPE)—a flash of light under the action of an electric field on a previously excited phosphor—was discovered in 1920. An explanation of the effect was proposed by L. Curie, who asserted that the effect consists in the emptying by the field of traps filled during the preliminary excitation (^1). This explanation was accepted by many authors. J. Destriau and H. Ivey cite it in their review of electroluminescent phenomena (^2). However, at the Paris Colloquium on the luminescence of inorganic crystals, Destriau, in discussion, put forward the hypothesis of the action of the electric field on special long-lived centers, the nature of which still remains to be clarified (^3). According to the latest data of Matossi, Gutjahr, and Siebert, at the moment of the flash a decrease in the number of conduction electrons in the bulk of the phosphor is observed (^4), whereas according to Curie' s hypothesis their concentration should increase. Curie' s theory accounted for only one feature of the effect—the appearance of an instantaneous flash; other essential features, which are considered below, were not taken into account by it. Under these conditions it is desirable to reconsider and analyze anew the principal features of the effect.

**2.** To obtain an intense Goodden-Pohl effect we used cells with a ZnS—Cu, Sn phosphor, described in detail earlier (^5). They were excited by irradiation from a PRK-4 mercury-quartz lamp through a UFS-3 ultraviolet filter. Long-wave irradiation was produced by a 40-watt incandescent lamp through an IKS-3 infrared filter. The flash was detected with an FEU-19M photomultiplier; the light sum of the flash was determined from the deflection of a ballistic galvanometer. To obtain flashes an alternating field with a frequency of 50 cps was applied.

The instantaneous character of the effect made it difficult to determine the spectral composition of the flash. Destriau and Ivey wrote that the spectral composition of the flash differs from the phosphorescence spectrum (^2). We determined the spectrum of the GPE flash of ZnS—Cu, Sn and found that it

Fig. 1

Figure 1: Fig. 1

coincides with the phosphorescence spectrum of the same specimen (ˆ5). This provided the starting point for analysis of GPE phenomena: the luminescence centers of the flash and the phosphorescence centers are identical at the moment when the field is applied and the flash arises. Before this moment these centers are in different conditions. The phosphorescence luminescence centers recombine with electrons from the conduction band as the latter are released from traps, and their luminescence ends practically after several tens of minutes. The flash luminescence centers do not recombine and retain for tens of hours the ability to give a flash at the moment the field is applied. This indicates that free electrons cannot penetrate to them. It is natural to suppose that the protection of the flash centers is provided by an electric barrier. One may think of a barrier that has arisen because, near the flash center, there is an electron bound at a lattice defect (ˆ6), or suppose the presence of electrons bound at surface levels, around which, in the near-surface layer of the phosphor, a region has arisen that is protected against electron penetration. Without excluding the first, more general possibility, we shall use the second variant of the hypothesis, which permits a simpler considera-

···Thus, we assume that, in the formation of the Gudden–Pohl effect, in addition to the short-wave excitation and the external field that produces the flash, there also acts an internal field, which exists for a long time and shields the centers from access to them by electrons, thereby converting phosphorescence centers into centers of the GPE flash. This internal field determines the number of possible GPE centers. The notion of the internal field as the principal element in the GPE is explained and refined with the aid of the experiments presented below.

3. If a phosphor specimen is kept for several days protected from the action of radiation, it acquires a state that we shall call the initial state. A similar state can also be obtained in a short time by subjecting the specimen to the action of long-wave radiation. In the experiments described below we started from the initial state, i.e., first subjected the phosphor to sufficiently strong and prolonged infrared irradiation. The first excitation of the phosphor from the initial state gives an effect considerably smaller than excitation under ordinary conditions.

**Fig. 1.** Buildup of the Gudden–Pohl effect from the initial state. $N$—ordinal numbers of excitations; $S$—light sums of the flash in relative units

Figure 1 shows how the GPE builds up. The phosphor specimen was first subjected to a 2-minute exposure to infrared rays. Then every 2 min the following sequence of operations was repeated: the specimen was irradiated for 10 sec with short-wave rays; after 60 sec an alternating voltage of 200 V was applied and the GPE was recorded; after 10 sec the field was switched off; and after another 40 sec the operations were begun again from the start. After the first excitation the light sum of the flash was 36 units; after the second excitation, switching on the field gave a flash of 63 units, i.e., a considerably more intense one; and with each subsequent excitation, switching on the field gave a larger effect than the preceding one. Thus, switching on the field after excitation not only produced a flash, but also strengthened in the specimen the conditions required for the next excitation to be able to accumulate more centers for the flash. The course of the increase gradually slows, and after a certain number of excitations and field switchings-on a practically constant value is reached, which we shall call stationary. Destriau used the procedure of successive excitations and field switchings-on to establish the "normal" effect (7), but he drew no further conclusions from this fact. We shall briefly call this procedure training of the phosphor. In our understanding, training is needed for the formation of a protective layer, in whose space the phosphorescence centers become centers of GPE emission. The described type of training can be replaced by a sufficiently long residence of the phosphor under voltage with constant excitation. During training the concentration of electrons on surface levels increases, which, for a given light sum of excitation and therefore for a constant concentration of ionized centers, will cause, together with thickening of the protective layer, an increase in the total reserve of GPE centers. The latter circumstance is clearly evident in the following experiment.

A ZnS—Cu, Sn specimen was first brought to the initial state (by 5-minute long-wave irradiation), then trained under a voltage of 50 V and after this excited for 10 sec; after 2 min a voltage was applied and the light sum of the flash was measured. In the second series all operations were the same, but training was carried out at 350 V (Fig. 2, 1 and 2). Although the excitations in both cases were identical, the course of the dependence of the flash light sum on the applied voltage was different.

On curve 1, the light sum of the flash increases with increasing voltage more and more slowly, evidently approaching a certain saturation. On curve 2, an almost linear increase of the light sum with voltage was obtained. At a voltage of 350 V the light sum of the flash on curve 2 is almost 3 times greater than on curve 1. Using the simplest model, we can extract some additional information from Fig. 1.

In a protective layer of 1 cm$^2$ and of thickness $\delta$, the positive charge, equal to $ne\delta$, can, in the best case, be equal to the surface density of negative charges $\sigma = Ne$, where $n$ is the number of centers in 1 cm$^3$ of the protective layer, and $N$ is the number of electrons per 1 cm$^2$ of surface. In this case the field at the surface is equal to $4\pi\sigma/\varepsilon = 4\pi n\delta e/\varepsilon$. The magnitude of the flash should acquire a certain limiting value when the external field $E_2$ eliminates the shielding throughout the entire thickness of the protective layer, i.e., $E_2 = 4\pi n\delta e/\varepsilon$, and in this case $n\delta e = \sigma = \varepsilon E_2/4\pi$. It is seen in Fig. 2, 1 that after conditioning at 50 V the magnitude of the flash upon application of a voltage of 350 V is close to

Fig. 2. Dependence of the light sum $S$ of the Gudden-Pohl effect on the applied voltage and on the voltage of preliminary conditioning. 1 –after conditioning at 50 V; 2 –after conditioning at 350 V.

Figure 2: Fig. 2. Dependence of the light sum $S$ of the Gudden-Pohl effect on the applied voltage and on the voltage of preliminary conditioning. 1 –after conditioning at 50 V; 2 –after conditioning at 350 V.

the saturation value. The thickness of the phosphor layer in the cell was of the order of 0.2 mm. Therefore $E_2 \approx 60$ CGSE units and $\sigma \approx \varepsilon \cdot 60/4\pi$, or $N \approx 10 \cdot 60/4\pi \cdot 4.8 \cdot 10^{-10} \approx 10^{11}$ cm$^{-2}$.

**Fig. 2.** Dependence of the light sum $S$ of the Gudden-Pohl effect on the applied voltage and on the voltage of preliminary conditioning. 1 –after conditioning at 50 V; 2 –after conditioning at 350 V.

Thus, this very rough calculation indicates that conditioning at 50 V brought the surface charge density up to a value of the order of $10^{11}$ electrons per 1 cm$^2$, while conditioning at 350 V increased the density by more than a factor of 3.

4. We present some data on the action of long-wavelength irradiation on the GPE. In these measurements the initial state was the stationary (i.e., post-conditioning) state of the phosphor, and before each measurement it was restored. A 10-second excitation produced, upon application of the field, a flash of 70 units. This effect was weakened by infrared irradiation, which was performed before the excitation. Depending on the duration $t$ of irradiation, the following flash magnitudes were obtained:

| $t$, sec. | 0 | 1 | 5 | 30 | 120 | 600 |
|---|---|---|---|---|---|---|
| GPE | 70 | 57 | 39 | 16 | 7 | 2 |

The weakening of the subsequent GPE flash by the preceding excitation with long-wavelength irradiation persists for an indefinitely long time. A phosphor that was in the stationary state gave, after 10-second excitation, a flash light sum of 64 units. It was irradiated for 10 sec with infrared rays; immediately afterward it was excited by 10-second ultraviolet irradiation; upon application of the field a flash of 47 units was obtained. The experiment was repeated, but each time with a longer pause between the infrared irradiation and the short-wavelength excitation. Finally, the pause lasted 22 hours. The flash proved to be equal to 45 units. Thus, for 22 hours the phosphor retained, almost without change, the result of the infrared irradiation to which it had been subjected. Similar experiments were described by F. Vigean ([8]). From our point of view, during long-wavelength irradiation the internal local shielding field is weakened, and with it the store of GPE luminescence centers. A different explanation of these facts was given by F. Vigean and D. Curie ([9]).

Let us also mention "memory" in the GPE. The ability, arising after excitation by short-wavelength irradiation, to give a flash is retained, slowly decreasing, for a long time ( "memory" ). It is extinguished by long-wavelength irradiation. The decrease of the effect after a pause of $t$ min. between the excitation and the application of the field is approximately expressed by the well-known for-

by the formula $S = At^{-n}$. This formula was confirmed in our measurements on many specimens. In one case, for example, $n$ was equal to 0.3. After 17 h 23 min after excitation, a flash was produced. Its light sum amounted to 15% of the light sum that the specimen gave when the pause between excitation and application of the field was equal to 1 min. Memory in this case means a slow decrease of the local protective field caused by training. This phenomenon is close to the phenomena in ZnS photoelectrets, in which, after 15 h of storage in the dark with short-circuited electrodes, 15% of the initial polarization was preserved ([10]).

5. Let us summarize:

1) At the instant of the flash, the luminescence centers of the EGP flash are identical with the phosphorescence luminescence centers of the same specimen.
2) Before the instant of the flash, the luminescence centers of the EGP flash differ from the phosphorescence centers in that they are protected by an internal electric field from recombination with free electrons.
3) The internal protective field is formed by electrons fixed at deep levels.
4) In phosphors with low conductivity (for example $10^{-7}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ and less), electrons at surface levels create near-surface protective bands, from which free electrons are driven away by the field. Phosphorescence luminescence centers located in such a band become centers of the EGP flash upon excitation.
5) A correspondingly directed external field removes the protection from part of the protective layer, and the stock of centers located in it recombines with free electrons, creating a flash.
6) During the flash the centers recombine, but the surface charge remains, determining the magnitude of the stored light sum at the next excitation.
7) By "training" the surface charge changes, increasing with an increase in the training voltage. As the training voltage increases, the dependence of the light sum of the EGP flash on the applied voltage approaches a linear one.
8) Long-wavelength irradiation removes the surface charge in ZnS—Cu, Sn, and along with it the protective layer and the EGP.

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## CITED LITERATURE

1. D. Curie, J. Phys. et Radium, **14**, 510 (1953).
2. G. Destriau, H. Ivey, Proc. I. R. E., **43**, 1911 (1955).
3. G. Destriau, J. Phys. et Radium, **17**, 740 (1956).
4. F. Matossi, A. Gutjahr, D. Siebert, Zs. Naturforsch., **16a**, 1391 (1961).
5. A. G. Goldman, A. I. Proskura, DAN, **149**, No. 3 (1963).
6. Ya. M. Zelikin, G. T. Paracheva, Opt. i spektroskopiya, **13**, 554 (1962).
7. G. Destriau, Phil. Mag., **38**, 887 (1947).
8. F. Vigean, C. R., **232**, 819 (1951).
9. F. Vigean, D. Curie, C. R., **232**, 955 (1951).
10. B. M. Golovin, N. T. Kashukeev et al., Fizika tverd. tela, **2**, 1006 (1960).

*Note: Figure translations are in progress. See original paper for figures.*