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Abstract

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Determination of the Spectral Composition of the Flash of the Gudden-Pohl Effect in Zinc-Sulfide-Based Phosphors

1. The Gudden-Pohl effect (GPE)—a light flash of a previously excited phosphor when an electric field is applied to it—was discovered in 1920. Beginning in 1937, numerous works by J. Destriau and his co-workers were devoted to it. Destriau and Ivey reported (^{1}) that the spectral band emitted by the flash differs from the phosphorescence spectrum. Owing to the short duration of the flash, only rough experiments using optical filters were carried out. In some cases the discrepancy of the spectra proved sufficient for it to be perceived by the eye.

Contrary to these assertions, we have found that the spectrum of the Gudden-Pohl effect and the phosphorescence spectrum of the phosphors studied coincide, while the difference, visible to the naked eye, in the color of the flash and of the photoluminescence is caused by the presence in the latter of a short-lived short-wavelength component, absent in the long-lasting phosphorescence.

2. Measurements of the spectrum of the GPE flash proved possible when instruments with the most favorable parameters had been selected. We used a UM-2 monochromator with entrance and exit slit widths of 0.5 mm. The light from the exit slit fell on an FEU-19M photomultiplier with a dark current of $4 \cdot 10^{-8}$ A at a supply voltage of 1160 V and with an integral sensitivity of 100 A/lm. A galvanometer with a current constant of $0.41 \cdot 10^{-9}$ A/division had a full-oscillation period of 3.2 s. The phosphor was excited by radiation from an SVD-120A mercury lamp, filtered through UFS-3. Under these conditions the GPE flash gave, in the spectrum, deflections of the galvanometer pointer up to 50 divisions.

Intense GPE flashes were obtained from a phosphor prepared as follows (series No. 94): 5 g of zinc sulfide “for phosphors” was placed in 150 ml of distilled water, and 60 mg of chemically pure stannous chloride was dissolved. The whole was boiled for 15 min. The zinc-sulfide powder was dried and then fired for 20 min at 800° in an open quartz test tube. According to chemical analysis, the powder contained $6 \cdot 10^{-4}$ g of tin and $7 \cdot 10^{-5}$ g of copper per 1 g of zinc sulfide. A thin layer (about 0.1 mm) of the powder was clamped between a metal electrode and a glass plate with a transparent conducting layer of tin oxide.

Figure 1

Figure 1: Figure 1

3. Figure 1 presents the spectra of a cell with phosphor No. 94. Each point of curve I was obtained as follows: the specimen was excited for 10 s; after 30 s an alternating voltage (450 V, 50 cps) was switched on and the ballistic deflection on the galvanometer scale was read. All spectra were normalized; the largest value was taken as 100. The data were not reduced to an equal-energy spectrum. Curve II is the spectrum of the full photoluminescence of the same specimen under prolonged irradiation (through a UFS-3 filter).

The photoluminescence spectrum is shifted somewhat toward shorter wavelengths. At the maximum the shift is small (the GPE maximum is about $0.532\,\mu$, and the photoluminescence maximum about $525\,\mu$), but at shorter wavelengths the discrepancy becomes appreciable. At $0.468\,\mu$ the GPE light sum amounted to 6% of the maximum, whereas the photoluminescence brightness was 20.5%.

A greater proportion of short-wavelength rays in photoluminescence as compared with the EGP flash is also observed directly: if, while illuminating the specimen with ultraviolet rays, the voltage is switched on, then the flash against the background of photoluminescence appears greener than the latter.

Fig. 1. Emission spectra of phosphor No. 94. *I* –spectrum of the light sum of the Gudden-Pohl effect; *II* –brightness spectrum of total photoluminescence

4. It is clear that, for comparison with the EGP spectrum, one should not take those components of photoluminescence which have decayed by the moment when the EGP flash is produced by switching on the field; rather, the EGP spectrum should be compared with the phosphorescence spectrum determined approximately for the moment when the field is switched on.

The phosphorescence spectrum was determined by the following method: the specimen was excited by ultraviolet irradiation (for example, for 10 sec); the irradiation was stopped and, after, for example, 30 sec, a reading was taken on the galvanometer scale; the same procedure, beginning with irradiation, was repeated for each measurement of wavelength. In Fig. 2 are given the spectrum of total luminescence of specimen No. 94 (curve *I*) and the phosphorescence spectrum of the same specimen (curve *II*). The main difference between the phosphorescence spectrum and the spectrum of total photoluminescence consists in the absence of the blue band. Consequently, the processes producing this short-wavelength component had ceased before the moment at which the phosphorescence was measured, and also before the EGP flash was produced.

In Fig. 3 the spectrum of the EGP flash and the phosphorescence spectrum of specimen No. 94 are compared. They practically coincide.

Figure 2

Figure 2: Figure 2

Fig. 3 and Fig. 4: spectra of luminescence emission

Figure 3: Fig. 3 and Fig. 4: spectra of luminescence emission

Thus, in this case the difference in color between the EGP flash and photoluminescence is explained by the fact that in the spectrum of total photoluminescence there is a blue component absent both in phosphorescence and in the EGP flash.

Fig. 2. Emission spectra of phosphor No. 94. *I* —brightness spectrum of total photoluminescence; *II* —brightness spectrum of phosphorescence 30 sec after excitation

4. Measurements of the EGP spectra were also performed for a technical specimen—phosphor FK-106 (ZnS—Cu). The maxima of the spectra of the flash and of the phosphorescence are located at the wavelength 0.518 μ. The forms of the spectra

similar. Compared with the spectrum of specimens with a tin impurity, the spectra are shifted toward shorter wavelengths. The half-width of the GP-effect flash spectrum is approximately 0.052 μ; the half-width of the phosphorescence spectrum is somewhat greater, approximately 0.063 μ (Fig. 4).

5. The coincidence of the GP-effect flash spectrum and the phosphorescence spectrum indicates that, at the moment when the flash occurs under the action of the field, the emission of this flash and the phosphorescence take place at identical centers. However, this applies only to the moment of light emission; before it these centers are under substantially different conditions.

Fig. 3. Emission spectra of phosphor No. 94. *I*—spectrum of the light sum of the Gudden-Pohl effect; *II*—spectrum of the phosphorescence brightness 30 sec after excitation

Fig. 4. Emission spectra of phosphor FK-106. *I*—spectrum of the light sum of the Gudden-Pohl effect; *II*—spectrum of the phosphorescence brightness 30 sec after excitation

The centers of the Gudden-Pohl effect possess a definite orientation. If, by applying a constant field, the GP effect is exhausted in one direction, then an effect of approximately the initial magnitude is obtained if the field is applied in the opposite direction. If this effect too is exhausted, then, according to Destriau' s experiments, a strong effect can be obtained by applying the field in a direction perpendicular to the initial one (2). These facts can hardly be understood unless one assumes that the "GP centers" themselves are directed and variously oriented. The GP centers persist for a long time. Phosphorescence becomes imperceptible several minutes or tens of minutes after excitation. A noticeable GP flash can be obtained tens of hours after excitation. The lifetime of the GP centers exceeds the duration of phosphorescence by two orders of magnitude or more. Since the GP center does not emit light during phosphorescence, it is apparently protected against access by electrons from the conduction band. When an external electric field is applied, this protection is instantly removed, and the centers recombine with electrons. Hypothetically, the protection may be attributed to the presence, near the ionized centers, of trapped electrons forming dipoles with these centers.

Further experimental verification of the considerations set forth here is necessary.

Results. 1. The spectra of the flash of the Gudden-Pohl effect have been measured.

2. The spectrum of the flash of the Gudden–Pohl effect and the phosphorescence spectrum of the same specimen coincided. The normalized spectra compared were: (a) the light sum of the flash of the Gudden–Pohl effect and (b) the phosphorescence brightness of zinc sulfide activated with copper and tin.
3. The greener color of the GPE flash against the background of photoluminescence is due to the fact that the total photoluminescence includes a blue band with a maximum at about $0.470\,\mu$, which is absent in the long-duration phosphorescence.

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