SOME NONADDITIVE PROPERTIES OF THE LUMINESCENCE BRIGHTNESS OF THE ZnSe, CdS – Cu PHOSPHOR

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Negative nonadditivity of the luminescence brightnesses shows up in most powdery and sublimated electrophosphors [1], electroluminescent phosphors [1], as well as the ZnS – Cu single crystals, if they are acted upon simultaneously by a variable voltage and by ultraviolet light or x-radiation. This property is also exhibited by the powdery electroluminescent phosphor of type ZnSe, CdS – Cu, grade ÉL-650, which we investigated. This widespread phenomenon still eludes a proper explanation, but information on the phenomenon is needed not only to uncover the electroluminescence mechanism, but also for expediting practical applications of electroluminescent phosphors.

The procedure followed in preparing the specimens and conducting the experiment, as well as a list of the instruments used, are described elsewhere [2, 3]. The emission brightness of the phosphor was recorded by a FÉU-51 photomultiplier. The dependence of the luminescence brightness on the amplitude of the exciting voltage was investigated to begin with. This was found to be an exponent, characteristic for all electroluminescent phosphors, of the type

$$B_{el} = a \cdot \exp\left(-\frac{a_1}{\sqrt{V}}\right),$$

where B_{el} is the electroluminescence (EL) brightness; V is the amplitude of the exciting voltage, and the constants a and a_1 are quantities which are dependent upon the frequency of the exciting voltage.

Figure 1 shows how the variation of the frequency of the variable voltage affects the negative nonadditivity when the specimen is acted upon simultaneously by ultraviolet radiation, the intensity of which is kept constant throughout all the experiments. Here and in what follows variables proportional to the number of photons emitted per unit wavelength interval will be plotted as ordinates. The photoluminescence (PhL) spectrum consists of a red band peaking at 660 nm, and the position of the band in the spectrum is independent of the intensity of the ultraviolet light. The EL spectrum also consists of a red band, but the position of the band maximum depends on the frequency of the exciting voltage in this case. At frequency 5 kHz, we find the EL spectrum and PhL spectrum coinciding (Fig. 1b). If we start our calculations from the unshifted maximum of the PhL band in the spectrum, then lowering the frequency of the exciting voltage will shift the maximum of the EL spectral curve toward longer wavelengths, while the negative nonadditivity will become enhanced (Fig. 1a). But raising the frequency tends to shift the maximum to the shortward range, and the negative nonadditivity decreases (Fig. 1c). The spectral curves of the sum of the EL and PhL brightnesses (curves 5) have one maximum each, at all of the frequencies which we investigated from 250 Hz to 100 kHz, and this is accounted for by the fact that the positions of the peaks in the EL and PhL spectral bands are close to one another. Positive nonadditivity was not found under any of the conditions tested. No coexistence of positive and negative nonadditivity in the same spectrum was detected either.

The effect of x-radiation and variable voltage on the emission of a given phosphor acted upon by those factors simultaneously or separately can be seen in Fig. 2. The x-ray luminescence (XL) spectrum features a band peaking at 570 nm. The distances separating the peaks in the EL and XL spectral bands are great, amounting to 110 nm at frequency 250 Hz, and about 80 nm at frequency 100 kHz. The spectrum of nonadditivity (curve 1) consists of two distinct portions, over the entire range of frequencies of the exciting voltage: an extended portion (negative nonadditivity) located at the shortward end of the spectrum with a clearly defined

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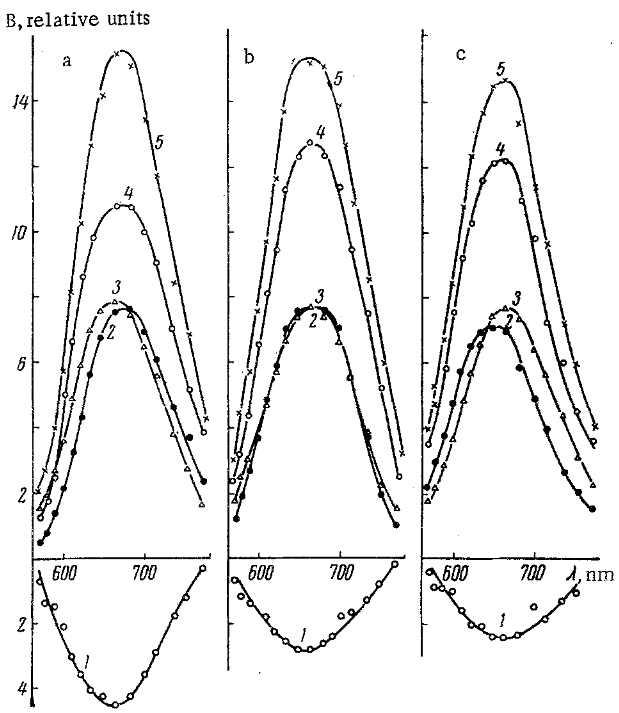

Fig. 1. Effect of ultraviolet emission and variable voltage on phosphor luminescence: 1) nonadditivity of phosphor emission brightnesses; 2) photoluminescence brightness; 3) electroluminescence brightness; 4) combined luminescence brightness of the phosphor; 5) sum of electroluminescence brightness and photoluminescence brightness; a) voltage amplitude 300 V, frequency 250 Hz; b) voltage amplitude 120 V, frequency 5 Hz; c) voltage amplitude 90 V, frequency 50 Hz. Intensity of ultraviolet emission: 140 relative units in all the experiments.

maximum at 570 nm, and a less extended portion (positive nonadditivity) at the longward end, with the maximum blurred. When the frequency is raised to 100 kHz, the area under the spectral curve for negative nonadditivity decreases. The spectral curve for combined brightness (curve 4), obtained in simultaneous action exerted by x-radiation and variable voltage, has the same shape as the EL curve. Its dependence on the amplitude of the voltage is similar to the EL dependence, and can be represented by an exponent of the form

$$B_{\text{exl}} = b \cdot \exp\left(-\frac{b_1}{\sqrt{V}}\right),$$

where B_{exl} is the combined luminescence brightness of the phosphor; V is the amplitude of the exciting voltage; and b and b_1 are constants which depend on the frequency of that voltage and on the x-radiation intensity.

The data plotted in Fig. 2 argue compellingly that the spectral curves for negative nonadditivity and XL (curves 1 and 2) are "antipodal" curves. Accordingly, XL quenching occurs in response to variable voltage and x-radiation acting upon the phosphor simultaneously. But this is accompanied by stimulation of electroluminescence, as confirmed by the mutual position of the EL spectral curve and the combined brightness curve (curves 3 and 4) and their identical dependence on the amplitude of the voltage. In the case in point, the integral nonadditivity is negative, so that the effect of XL quenching predominates over the effect of EL stimulation.

Comparison of the data presented in this paper and data found in [2-4] allows us to infer that the sign and magnitude of the nonadditivity depends primarily, for all the phosphors we studied, on the mutual arrangement of the spectral bands excited by the variable voltage and by the incident radiation.

If the phosphor exhibits the special feature that the maxima of the EL and PhL spectral bands lie close to one another or even coincide, then the nonadditivity of the phosphor luminescence brightnesses will be negative. It will acquire particularly high values when the maximum of the EL spectral band becomes shifted to longer wavelengths relative to the maximum of the PhL spectral band. In the case of some phosphors where the indicated spectral bands coincide, we witness additivity of the luminescence brightnesses; this is the case for the ÉL-510 phosphor. But if the maxima of the EL and PhL spectral bands are separated some appreciable distance from one another in the spectrum, with the EL spectral band located toward the shortward end of the spectrum relative to the PhL spectral band, then the nonadditivity will be positive. The integrated value will be dependent upon the distance separating the maxima, but also on the excitation conditions of the phosphor. The nonadditivity spectrum obtained in the case of simultaneous action of variable voltage and incident ultraviolet radiation will consist of nonadditivity of one sign, either positive or negative.

When the phosphor is acted upon simultaneously by sinusoidal voltage and x-radiation, the most interesting such cases are where the maxima of the EL and XL spectral bands are separated at some appreciable distance from each other in the spectrum, or where the maxima of these bands coincide. In the first instance, the nonadditivity spectrum is made up of two intervals: the interval of negative nonadditivity in the short-wavelength portion of the spectrum, and the interval of positive nonadditivity in the long-wavelength portion of the spectrum. The relationship between the extents of those intervals depends on the distance separating the maxima of the EL and XL bands, and also on the intensity of the x-radiation and on the amplitude of the exciting voltage, while the nonadditivity is positive in the second instance. The phenomenon of XL quenching

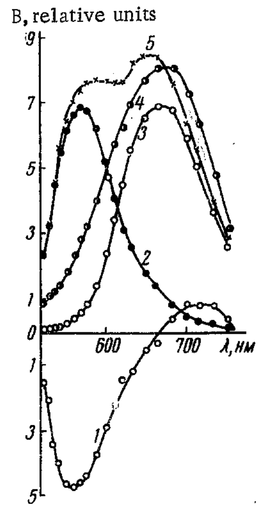

Fig. 2. Effect of x-radiation (current flowing through x-ray tube 10 mA, tube voltage 50 kV) and of variable voltage (voltage amplitude 160 V, frequency 250 Hz) on phosphor luminescence: 1) nonadditivity of luminescence brightnesses; 2) x-ray luminescence brightness; 3) electroluminescence brightness; 4) combined luminescence brightness of phosphor; 5) sum of electroluminescence brightness and x-ray luminescence brightness.

and EL stimulation also occurs, but only in the case of positive nonadditivity do we find the EL stimulation effect prevailing over the XL quenching effect.

LITERATURE CITED

1. N. A. Vlasenko, Opt. i Spektr., 18, 461 (1965).
2. F. I. Kolomoitsev, G. M. Ivanii, and S. M. Sidorenko, Izv. Akad. Nauk SSSR, Ser. Fiz., 30, 1459 (1966).
3. F. I. Kolomoitsev and S. M. Sidorenko, Opt. i Spektr., 22, 270 (1967).
4. F. I. Kolomoitsev and S. M. Sidorenko, Zh. Prikl. Spektr., 8, 975 (1968).