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ANISOTROPY OF BLUE-COPPER LUMINESCENCE CENTERS ZnS:Cu(Al) CRYSTALS

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Results concerning the polarization of the blue-copper luminescence in ZnS:Cu(Al) crystals are presented in this paper. The experimental diagrams of polarization fit the calculated results well. The centers of absorption and emission are composed of linear oscillators of the type π and circular oscillators of the type σ. The population of the luminescence centers depends on the temperature of the crystal.

1. Introduction

The optical spectra of Cu^{+2} ions in ZnS were carefully studied by Brosner et al. [1–3]. The absorption spectrum consists of two parts: one in the 1.4 μm region due to the $d-d$ transition which takes place within a Cu^{+2} ion, and the other in the 0.5—0.9 μm region due to the electron transition from the valence band to the Cu^{+2} level.

Shionoya and coworkers [4] found that an infrared absorption in 3—14 μm region appears simultaneously with the G-Cu luminescence in a ZnS:Cu(Al) single crystal when excited with UV. This absorption is attributed to the electron transitions from the aluminium donor levels to the conductivity band.

The mechanism of the G-Cu luminescence in ZnS:Cu(Al) crystals and polarization characteristics are described in the paper [5]. The results [5] show that the G-Cu luminescence in ZnS:Cu(Al) is produced by the radiative recombination of electrons trapped at aluminium donors with holes trapped at copper acceptors. The wavefunction of the *s*-electrons of aluminium donors is widely spread while that of the *d*-holes of copper acceptors is localized very strongly.

According to the results given in [5] the G-Cu liminescence is preferentially polarized perpendicularly to the [111] axis of the regular crystal. It is well known [6, 13] that the ZnS:Cu(Al) crystals show B-Cu luminescence in addition to the G-Cu one. In this work some information about the orientation and anisotropy of the B-Cu luminescence centers in the ZnS:Cu(Al) crystals are presented.

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2. Polarization diagrams of the B-Cu luminescence in ZnS:Cu(Al) crystals

For polarization studies of the ZnS single crystals activated with Cu and coactivated with Al (concentration of Al, Cu – 10^5 g/g) were grown by the vapour phase method. To obtain the experimental polarization diagrams for the emission band at 2.70 eV the equipment used was similar to that described in [10, 11]. The crystals have been ground

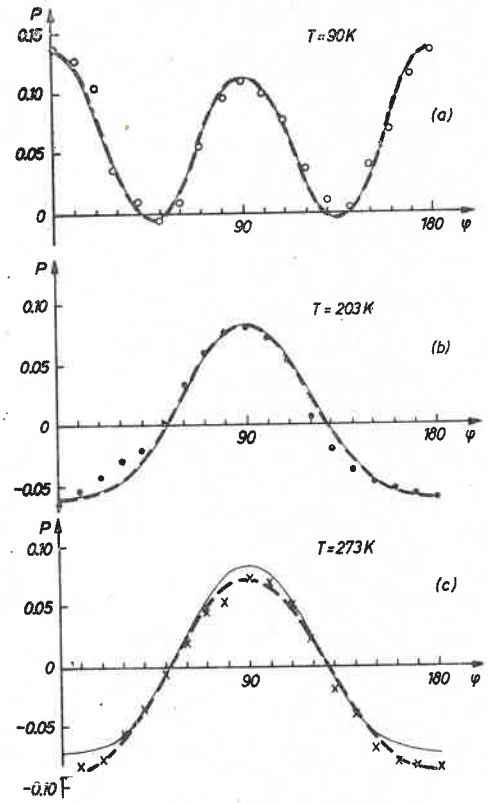

Fig. 1. Polarization diagrams of the blue-copper luminescence in ZnS : Cu(Al) crystals for three temperatures: 93 K, 203 K, 273 K. Experimental values of polarization are denoted by ●, ○, ×, the calculated curves are shown by solid lines for three-fold symmetry and dashed lines for two-fold symmetry. Parameters β and $\varkappa$ for three-fold and two-fold symmetries take the following values:

(a) 93 K $\beta = 0.358$, $\varkappa = 1.019$; $\beta = 0.4284$, $\varkappa = 1.0404$
(b) 203 K $\beta = 0.620$, $\varkappa = 0.158$; $\beta = 0.8824$, $\varkappa = 0.6893$
(c) 273 K $\beta = 0.650$, $\varkappa = 0.050$; $\beta = 1.0287$, $\varkappa = 0.6649$

and polished along the $(11\bar{2}0)$ planes (the cleavage surface). Luminescence in the slab was excited by linearly polarized UV light (365 nm) directed perpendicularly to the optical axis of the crystal (electric vector is parallel to the $(11\bar{2}0)$ plane). Measurements of glow were carried out along the excitation direction from the opposite side of the crystal. The two components of the glow intensity, parallel $I_{\parallel}(\varphi)$ and perpendicular $I_{\perp}(\varphi)$, were measured for the two positions of the analyzer with respect to the excitation vector.

In Fig. 1 we can see the polarization diagrams of the B-Cu luminescence in ZnS:Cu(Al) crystals for three different temperatures 93°, 203°, 273°K. Points ●, ○, × denote the experimental values of polarization. Solid and dashed lines represent the theoretical diagrams for the three-fold and the two-fold symmetry axes, respectively. In the papers [11–13] it was assumed that the role of the absorption and emission centers was played by a system consisting of a linear π oscillator with a fixed axis and circular oscillator σ spinning about this axis. To characterize the contribution of the rotator in the distribution of excitation and emission energies a parameter β is introduced. For information about the statistical weight of the π oscillators oriented along the optical axis of the crystal, we have introduced a parameter κ.

Values of the parameters κ serve as a measure of the population of the dipoles π. Values of the polarization and shape of the luminescence curves depend on the birefringence of the crystals and parameters β, κ [13]. Birefringence of the crystals ZnS:Cu(Al) for blue band emission $\delta l = 265°$. By comparing, at points $P(0°)$ and $P(90°)$, the theoretical and experimental results, we can determine β and κ (the values of the parameters β, κ are given in the figure captions). The calculated polarization diagrams presented in Fig. 1 for three-fold and two-fold symmetry axes fit the experimental results well. As is seen in Fig. 1 there is satisfactory agreement between the experimental and theoretical results for the three different temperatures.

It is possible that the orientation of luminescence centers responsible for the B-Cu luminescence in the ZnS:Cu(Al) crystals coincides with the three-fold and two-fold

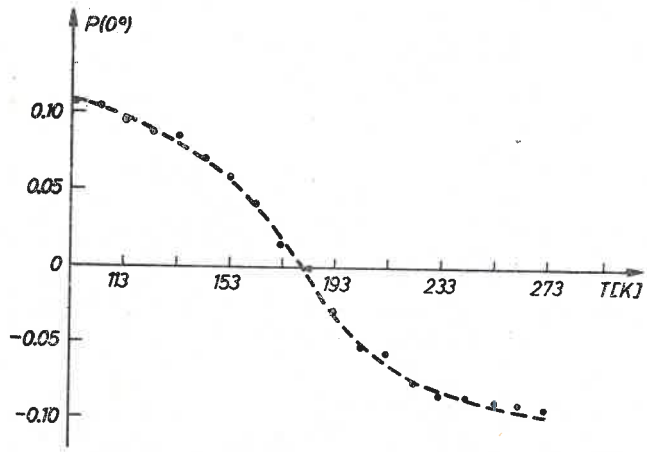

Fig. 2. Temperature dependence of the polarization luminescence $P(0°)$ in ZnS:Cu(Al) crystals

symmetry axes. The population of the centers in crystals depends on the temperature of the crystal. The contribution of the oscillators π of statistical weight κ increases when the temperature of the crystal is decreasing, and at the same time the contribution of the rotators β decreases.

The change in contribution of the oscillators π oriented along the optical axis (oscillator population depends on the temperature of the specimen) determines the sign and the

value of $P(\varphi)$ for $\varphi = 0°$. The values of P(90°), however, depend on the contribution of the rotators σ. When the crystal temperature is decreasing the values of the β parameter decrease too, and we observe an increase in the values of $P(\varphi)$ for $\varphi = 90°$.

Fig. 2 presents the temperature dependence of $P(0°)$ for the B-Cu luminescence in a ZnS:Cu(Al) crystal. The decrease in values of $P(0°)$ is not caused by the thermal depolarization effect. It is possible that a change in the κ parameter causes a change in the $P(0°)$ value.

3. *Final remarks*

The nature of the B-Cu and G-Cu luminescence centers in ZnS:Cu crystals has been studied by many authors [5–9, 14]. The temperature dependence of the stationary photoluminescence of the ZnS:Cu(Al) crystal (Fig. 3) shows that at low temperatures

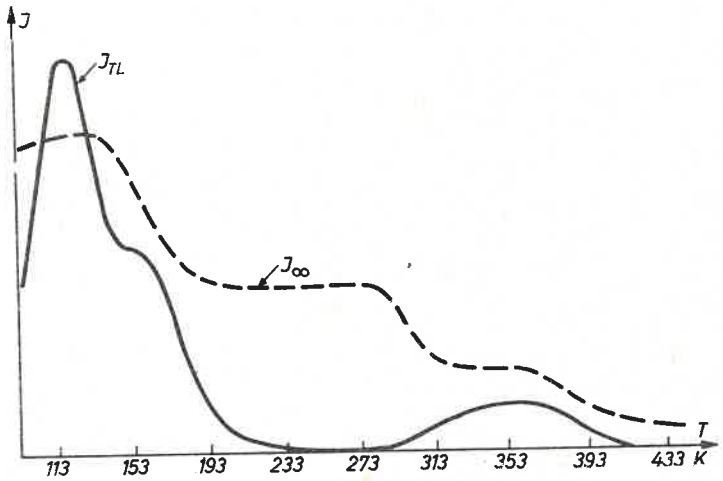

Fig. 3. Glow curve I_{TL} and curve for stationary luminescence I_α of a ZnS : Cu(Al) crystal. The values of thermoluminescence for each temperature T divided by the corresponding values of stationary luminescence intensity under UV excitation

(below 170°K) high efficiency of luminescence appears in the crystal. At temperatures lower than 170°K there are probably some radiative recombinations which influence the shape of the polarization diagrams. It is possible that the radiative recombinations responsible for thermoluminescence occur along the three-fold and two-fold symmetry axes of the regular crystals. This conclusion is suggested by the polarization diagrams for lower temperatures, where stationary luminescence is relatively large and where the thermoluminescence appears. At low temperatures the polarization diagrams change shape, but the values of $P(0°)$ are always positive. The model of luminescence centers in the form of a spatial oscillator, as discussed here, can be formed by the two-point defects of the crystalline lattice.

The direction of radiative recombinations is determined by the direction of the spatial oscillator moments. The luminescence centers in ZnS:Cu(Al) crystals are donor-acceptor emission pairs made of the Cu^+ ions located in the substitutional and interstitial sites, and pairs of the $[V_{Zn}, Al_{Zn}]$ and $[Cu_{Zn}, Al_{Zn}]$ type. The population of the centers depends on temperature, and their symmetry is conditioned by the polytypism of the structure of ZnS:Cu(Al) crystals.

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