PHOTOLUMINESCENCE OF THIN FILMS BASED ON Cadmium Fluoride

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The photoluminescence (PL) spectrum of thin films of cadmium fluoride (CdF₂), activated by manganese chloride (MnCl₂), consists of a band with \( \lambda_{\text{max}} = 520 \) nm, characteristic of the Mn²⁺ ion in this compound, and bands with maxima 685 and 780 nm, which depend on the energy of the exciting radiation [1, 2]. The excitation spectrum of Mn²⁺ ions in CdF₂ films consists of an intense band with \( \lambda_{\text{max}} = 241 \) nm and a number of weak bands in the region of 273-445 nm [1-4]. In the x-ray and cathode luminescence spectra, bands with maxima 375, 530 and 530 nm, respectively, are observed [3-7], and in the electroluminescence spectrum a band with \( \lambda_{\text{max}} = 530 \) nm [3, 8].

To reveal the mechanism of the excitation of PL and the nature of the emission bands in CdF₂-Mn, Cl films, we investigated the emission spectra at various temperatures, activator concentrations, and energies of exciting radiation. The activator concentration was varied from 0.5 to 4% by weight. Films were produced by thermal evaporation under a vacuum of \( 5 \times 10^{-3} \) Pa.

Figure 1 presents the PL spectra of thin films of CdF₂-Mn, Cl at various temperatures and wavelengths of the exciting radiation. The PL spectrum can be seen to depend on \( \lambda_{\text{excit}} \). Thus, in the case of exciting radiation with \( \lambda_{\text{excit}} = 310 \) nm, bands are observed at \( \lambda_{\text{max}} = 520 \) and 685 nm (Fig. 1a), and bands with \( \lambda_{\text{max}} = 520 \) and 780 nm are observed in the case of excitation by radiation with \( \lambda_{\text{excit}} = 415 \) and 450 nm (Fig. 1b,c). When the temperature is increased from 85 to 240 K, an appreciable decrease in the intensity of the bands with \( \lambda_{\text{max}} = 520, 658, \) and 780 nm is observed.

It is characteristic that for the PL spectra in the case of excitation by radiation with \( \lambda_{\text{excit}} = 310 \) nm, the steepness of the decrease in the intensity of the band with \( \lambda_{\text{max}} = 520 \) nm is higher than for the band with \( \lambda_{\text{max}} = 685 \) nm (Fig. 1a). For the PL spectra with \( \lambda_{\text{excit}} = 415 \) and 450 nm, the rate of decrease in the intensity of the band with \( \lambda_{\text{max}} = 520 \) nm is lower than for the band with \( \lambda_{\text{max}} = 780 \) nm (Fig. 1b,c). Moreover, it was found that the intensity ratio of the PL bands with \( \lambda_{\text{max}} = 520 \) nm and \( \lambda_{\text{max}} = 685 \) and 780 nm depends on the concentration of the activator MnCl₂. With increasing MnCl₂ concentration the relative intensity of the bands with \( \lambda_{\text{max}} = 685 \) and 780 nm increases [1]. The band with \( \lambda_{\text{max}} = 520 \) nm is characteristic of the emission of Mn²⁺ ions in CdF₂. the emission of Mn²⁺ ions is evidently associated with the absorption of energy in the surroundings of the Mn²⁺ ions, induced by the presence of Cl⁻ ions close to the emitting site. This is supported by the characteristic shape of the excitation spectra of Mn²⁺ ions in CdF₂-Mn, Cl films and the dependence of the intensity of the bands of these spectra and the PL spectra on the activator concentration [2-4].

It is of interest to determine the nature of the long-wave bands with \( \lambda_{\text{max}} = 685 \) and 780 nm. It may be associated with transitions in the Mn²⁺ ions as a result of the action of chloride ions (Cl⁻) on the energetics of transitions of the emitting ion or may be due to the presence of defects in CdF₂ [9]. In connection with this, we investigated the PL spectra of films of cadmium chloride (CdCl₂), activated by Mn²⁺ ions, i.e., when the Mn²⁺ ion is surrounded by Cl⁻ ions. In this case a band with \( \lambda_{\text{max}} = 630 \) nm is observed in the PL spectrum. Thus, we can conclude that the long-wave bands observed in the PL spectra of CdF₂-Mn, Cl films evidently are not associated with transitions in the Mn²⁺ ions under the action of Cl⁻ ions. These bands may be associated with the presence of complexes of Mn²⁺ ions in the presence of oxygen ions and associative sites of Mn²⁺ ions [3, 4, 10-12].

The question of the position of the energy levels of the Mn²⁺ ion relative to the energy zones of the basic substance of the luminophore is fundamental and debatable. In connection with this, the position of the levels of the Mn²⁺ ion relative to the energy zones of CdF₂ is of interest [1]. The excitation and emission spectra do not permit a determination of the posi-
tion of the levels of the Mn$^{2+}$ ion in CdF$_2$ but give information on the energy state of the Mn$^+$ ion or the emitting complexes [1, 3, 4]. It was found that when CdF$_2$-Mn, Cl films are irradiated at $\lambda_{\text{excit}} = 445$ nm, thermostimulated photoluminescence with maxima in the region of 105-345 K is observed in the excitation band of the Mn$^{2+}$ ion [2, 13, 14]. In this case the accumulation of the photosum may occur as a result of energy transfer from the excited Mn$^{2+}$ ion to its closest surroundings or by transfer of an electron from the Mn$^{2+}$ ion to the conduction zone, followed by capture at adhesion levels. Cadmium fluoride is a broad-zone compound with a 6-8 eV zone [3, 7]; it has electron traps at a depth of 0.1-0.8 eV from the bottom of the conduction zone and autolocalized p-type centers in the form of the molecular ion F$_{1}$ with activation energy of temperature quenching equal to 0.072-0.075 eV [4, 7, 14].

Considering what has been stated above, as well as the nature of the thermostimulated photo- and x-ray luminescence, associated with the capture and subsequent thermal release of electrons from the adhesion levels [1, 2, 4, 13, 14], it can be concluded that the emission energies of the Mn$^{2+}$ ion are insufficient for filling the adhesion levels. Transfer of an electron from the Mn$^{2+}$ ion to the conduction zone of CdF$_2$ under the action of external radiation, followed by capture at adhesion levels, is more probable. The thermal release of these levels leads to the appearance of thermostimulated PL maxima [2, 13, 14].

On the basis of this we can suggest that the ground level of the ion evidently lies above the ceiling of the valence zone. However, a final clarification of this question will require further experiments.

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REFERENCES

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