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1960

SovietRxiv

Abstract

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PHYSICS

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PHOTOLUMINESCENCE IN THE REGION OF THE FUNDAMENTAL ABSORPTION EDGE OF MIXED CdSe–CdS CRYSTALS

In a number of crystals (CdS, CdSe, HgJ_2, ZnS, and others ([1])), in the region of the long-wavelength edge of intrinsic absorption at low temperatures, a complex structure of emission and absorption is observed. The spectrum of this edge emission is usually divided into two parts: an equidistant group of narrow bands and a more short-wavelength group of narrow lines*. Despite numerous studies, the nature of the emission remains unclear. In some earlier works ([3,4]) it is assumed that the banded edge emission belongs to the pure lattice of the crystals; in others ([5–7]) it is attributed to emission of one or two "specific" centers. The situation is similar for the line-like edge emission: some authors ([7–10]) assume an excitonic origin of this luminescence, others ([5,6]) an "impurity" origin. In a number of works, on the basis of the dependence of the emission of CdS crystals on exciting ultraviolet light ([6,7]), infrared light ([6]), X-ray irradiation ([11]), irradiation by high-energy electrons ([12]), and thermal quenching ([13]), a bulk origin is ascribed to the banded edge emission, while for the line-like emission some authors ([5,6]) ascribe a surface origin, others ([12,7]) a bulk origin. A characteristic feature of the banded edge emission is the equidistance of the emission bands, the distinctness of which in the spectrum depends both on temperature and on the kind of crystal. In some crystals an even finer structure (doublet character) of the equidistant bands is observed (fine-crystalline ZnO and ZnS powders ([2–4]) and CdS single crystals ([5])). It is interesting to note that the doublet character of CdS emission is observed only with very deep cooling of single crystals (down to $T = 20.4^\circ$ K), whereas for detecting the doublet character of the emission of ZnO and ZnS powders, cooling to $T = 77.3^\circ$ K proved sufficient.

In connection with the great diversity of the complex emission structures of crystals and the difficulties encountered in interpreting their nature, studies of isomorphous crystals and their solid solutions are of great interest. In works ([14]) it was established that, when the composition of the CdSe–CdS solid solution is changed, a monotonic change is observed in the width of the forbidden band, the lattice constant, and the maximum of the spectral distribution of photoconductivity. Kroger ([2]) found, in the emission of certain CdS–ZnS solid solutions at $T = 93^\circ$ K (ZnS content less than 50%), bands analogous to the known bands of the "green" (banded edge) and blue (line-like edge) luminescence of

CdS, monotonically shifting into the short-wavelength region of the spectrum with increasing percentage content of ZnS in CdS—ZnS.

* An example of edge emission is the well-known "green" luminescence of CdS crystals, first discovered by Kroger ([2]), and the line-like "blue" emission of the same crystal, widely studied in recent times ([7,12,18]). In what follows, for a clearer distinction between these two parts of the edge emission, which apparently have different nature, we shall call the first part banded edge emission, and the second line-like edge emission.

The present work is devoted to the study of photoluminescence in large-crystalline solid solutions of CdSe—CdS of seven compositions, as well as of CdSe single crystals and large-crystalline layers of CdSe and CdS in the region of their intrinsic absorption edge.* All the samples studied had a hexagonal structure. The spectra were recorded at 77.3 and 4.2° K on spectrographs with dispersions of 50 and 13 Å/mm in the region of 7000 Å.

I. **Cadmium selenide single crystals.** Both the emission spectra and the absorption spectra[^15] of CdSe single crystals are very similar to the spectra of CdS single crystals[^16]: their line edge emission consists of a large number of lines, the shortest-wavelength of which coincide with absorption lines, while the band edge emission of both crystals forms two systems of equidistant vibrational bands with spacings between the intensity maxima of the bands in each system of 213 cm^{-1} for CdSe and 300 cm^{-1} for CdS. These two systems of bands, which constitute the main, as it were coarse, structure of the band edge luminescence, are shifted in the spectrum relative to one another by a certain distance. In the CdSe single crystals studied by us this distance varies from crystal to crystal within the limits of 80–100 cm^{-1}. Further studies showed that the picture of the phenomenon in CdSe proved to be much more complex than in other crystals (as regards the band edge emission). A careful study of spectrograms obtained on approximately 80 cadmium selenide single crystals at $T = 4.2°$ K led us to the conclusion that, apparently, the individual maxima of the equidistant structure are themselves complex and have a fine structure consisting of several lines, the spacing between which is approximately the same: $\bar{H} = 26\ \text{cm}^{-1}$.** From crystal to crystal the intensity ratio between the bands changes very strongly, which in some crystals sometimes makes it impossible to reveal clearly the details of the fine structure.

When CdSe single crystals are heated from $T = 4.2°$ K to $T = 77.3°$ K, a complex redistribution of intensities occurs among the members of the equidistant groups of bands, with enhancement of the longer-wavelength bands in each group of bands and with enhancement of the intensity maxima of the shorter-wavelength system of equidistant bands relative to the second system of bands.*** At the same time the luminescence intensity falls sharply, the bands broaden, and at $T = 77.3°$ K only one group of broad equidistant bands is observed instead of the two groups appearing at $T = 4.2°$ K.****

II. **Large-crystalline pure layers of cadmium selenide and cadmium**

sulfide. The line edge emission of CdS layers studied by us at $T = 4.2^\circ$ K consists of a large number of lines, of which the short-wavelength lines 4804; 4809; 4813; 4826; 4850; 4856; 4858; 4865; 4888 Å, etc., coincide with the absorption lines of CdS single crystals[^17]. The band edge emission of CdS layers at $T = 4.2^\circ$ K has a triplet structure in each of the equidistant bands, with a spacing of $\simeq 90$ cm^{-1} between the components of the structure, in contrast to CdS single crystals, which, as is known, have a doublet structure.

Like CdS layers, the line edge emission of CdSe layers at $T = 4.2^\circ$ K consists of lines, of which the short-wavelength lines 6660; 6700; 6750; 6807 Å coincide with the absorption lines of CdSe single crystals[^16]. In the pure large-crystalline CdSe layers studied by us it has so far been found that at 4.2° K the band edge emission of CdSe has a triplet structure of equidistant bands, with a spacing between the components of $\simeq 26$ cm^{-1}.

* For kindly providing the samples, the authors express their gratitude to Professor S. M. Ryvkin, L. P. Bogomazov, and R. Yu. Khansevarov.

** At present we have undertaken experiments under new conditions in order to reveal the fine structure of the emission maxima with greater certainty.

*** An analogous temperature dependence has been found in CdS single crystals[^18].

**** A detailed account of the emission spectra of CdSe single crystals will be given elsewhere.

At $T = 77.3^\circ$K, the banded edge emission of pure CdS layers that we studied consists of broad structureless bands, as in CdS single crystals, while that of pure CdSe layers consists of equidistant bands with a doublet structure (the spacing between the components of the doublets is $\simeq 70$ cm^{-1}).

III. **Coarse-crystalline layers of mixed crystals CdSe–CdS.** We studied 7 different compositions of coarse-crystalline mixed CdSe–CdS layers, more than 20 samples in all. At $T = 4.2^\circ$K, the photoluminescence of all mixed layers has a structure similar to that of the photoluminescence of pure CdSe and CdS layers: its spectrum can likewise be divided into two parts—line and banded edge luminescence. The line emission of the mixed layers

Fig. 3. Change in the spacing between equidistant bands $\Delta\nu_n$ (1), the position of the main band of the equidistant group ν_n (2), and the position of the short-wavelength line ν_ℓ of the short-wavelength emission group (3), as a function of the percentage composition of the mixed CdSe–CdS crystals at $T = 4.2^\circ$K.

at 4.2°K is very weak (relative to the banded emission) and consists, as a rule, of several lines. The intensity and number of lines in the line emission decrease sharply on going from layers with a higher CdSe content to layers with a higher CdS content. The banded edge emission of mixed CdSe–CdS layers has, for

Fig. 3. Change in the spacing between equidistant bands $\Delta\nu_n$ (1), the position of the main band of the equidistant group ν_n (2), and the position of the short-wavelength line ν_ℓ of the short-wavelength emission group (3), as a function of the percentage composition of the mixed CdSe–CdS crystals at $T = 4.2$°K.

Figure 1: Fig. 3. Change in the spacing between equidistant bands $\Delta\nu_n$ (1), the position of the main band of the equidistant group ν_n (2), and the position of the short-wavelength line ν_ℓ of the short-wavelength emission group (3), as a function of the percentage composition of the mixed CdSe–CdS crystals at $T = 4.2$°K.

Fig. 1

Figure 2: Fig. 1

some layer compositions (for example, 50% CdSe—50% CdS), a distinct triplet structure of equidistant bands (Fig. 2), while in other layers (for example, 33% CdSe—67% CdS, 17% CdSe—83% CdS) it has a doublet structure. It should be noted that the doublet and triplet character of the structure of the equidistant bands of mixed CdSe–CdS layers is expressed much more clearly than in pure CdSe and CdS single crystals. From Fig. 3 it is seen that, when the composition of the CdSe–CdS solid solution is changed, there is a monotonic shift of the vibrational structure of the banded edge emission (curve 2) and a change in the spacing between the members of the groups of equidistant bands (curve 1) from 200 cm^{-1} (pure CdSe) to 310 cm^{-1} (pure CdS), and also a monotonic change is observed in the position of the lines in the spectrum of the line edge emission (curve 3).

When the mixed layers are heated from $T = 4.2$°K to $T = 77.3$°K, the following changes occur in the emission spectra: 1) the emission intensity decreases; 2) the definition of the complex structure of the banded emission decreases strongly (at 77.3°K, in many mixed layers the banded emission is a single very broad band; only in the composition 96% CdSe—4% CdS is a well-pronounced equidistant structure with a doublet band structure preserved (Fig. 1)); 3) the intensity of the shortest-wavelength lines of the line edge emission drops sharply; 4) a temperature redistribution of intensity is observed between the components of the complex doublet and triplet structure of each member of the equidistant

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Fig. 1. Emission spectrum of
96% CdSe –4% CdS at
$T = 77.3$°K

Fig. 2. Emission spectrum of
50% CdSe –50% CdS at
$T = 4.2$°K

Fig. 2

Figure 3: Fig. 2

Fig. 1

Figure 4: Fig. 1

For the article by L. A. Kochanova, E. D. Shchukina, V. I. Likhtman, and P. A. Rebinder, p. 71

Fig. 1. Microphotographs of longitudinal polished sections of amalgamated zinc single crystals with initial orientation $\chi_0 = 21^\circ$ at various stages of stretching. Numerous cracks located in the basal plane are visible. 40×. The values of the relative elongations ε and shear stresses τ are:
$a - \varepsilon = 1.2\%$, $\tau = 59$ G/mm^2; $b - \varepsilon = 2.2\%$, $\tau = 84$ G/mm^2; $v - \varepsilon = 9.6\%$, $\tau = 145$ G/mm^2; $g - \varepsilon = 22\%$, $\tau = 216$ G/mm^2.

radiation, as in CdSe and CdS single crystals: when the temperature of the samples is raised from 4.2 to 77.3° K, the short-wavelength component of the doublet or triplet structure is strengthened, while the long-wavelength component is weakened*.

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Received
28 III 1960

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* It would, of course, be important and interesting to compare the luminescence spectra of the mixed layers described above with their absorption spectra. Unfortunately, because of the large thickness of the layers available to us ($d \approx 0.2$ mm), we have not yet succeeded in observing the structure of the absorption edge. In the layers studied, it was possible to observe only the sharp edges of fundamental absorption, which were located at the point in the spectrum where the short-wavelength part of the band-like edge emission was observed. This indicates that the luminescence of the mixed layers that we detected was indeed edge luminescence.

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