

# Exciton localization by a potential well formed by a solid solution in the surface region of a semiconductor

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New striking features were observed in low-temperature ( $T=2-77$  K) optical excitonic spectra of CdS crystals. These features are caused by the trapping of excitons in a potential well formed by the solid solution  $\text{CdS}_{1-x}\text{Se}_x$  ( $x\sim 0.01$ ) in the surface region of a semiconductor.  
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The optical excitonic spectra of semiconductor crystals can contain features which are due to the trapping of excitons in the surface region of a semiconductor.<sup>1</sup> As a rule, such features appear as a result of external surface-sensitive actions.<sup>2</sup> They can also be observed in crystals which have not undergone special treatment.<sup>3,4</sup> Analysis of these features yields important information about the mechanism of localization of excitons in the surface region and the properties of this region. In the present letter we report the results of an experimental study of the nature of the striking anomalies which we observed in the optical excitonic spectra of a number of CdS crystals. We show that the observed structure of the spectra is due to a localizing surface exciton potential (SEP) produced by a thin layer of the solid solution CdS/SdSe in the surface region of the semiconductor.

The photoluminescence and the optical reflection and absorption spectra of CdS crystals in the region of the A excitonic state were investigated in the temperature range  $T=2-77$  K. The crystals consisted of single-crystalline wafers grown from the gas phase. The hexagonal C axis was parallel to the surface plane of the sample. In the batch of experimental crystals we observed a group of crystals with pronounced anomalies in the contours of excitonic reflection of light (CERL) (“anomalous” crystals).

The experimental CERL of an “anomalous” CdS sample in the region of the excitonic resonance  $A_{n=1}$  at  $T=2$  K is shown in Fig. 1a. The CERL was recorded in the  $p$  component of the polarization ( $E\perp C$ ) with normal incidence of light on the surface of the sample. As one can see from Fig. 1, the CERL of the “anomalous” sample has a complicated structure which sharply distinguishes it from the ordinarily observed dispersion contour by the fact that an intense and narrow reflection peak, a so-called spike, is

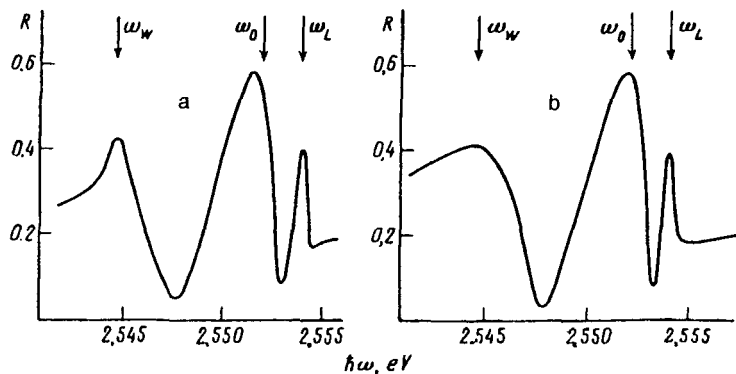


FIG. 1. a — Experimental CERE of a CdS/CdSe—CdS sample in the region of the excitonic state  $A_{n=1}$  at  $T=2$  K,  $E \perp C$ ,  $k \perp C$ ; b — CERE computed with the surface potential shown in Fig. 2b. The  $\omega_w$  arrow indicates the position of the bottom of the potential well.

observed at the frequency  $\omega_L$  of the longitudinal state of the exciton and an additional structure in the form of a wide and deep minimum is observed in the spectral region immediately below the resonance frequency  $\omega_0$ . The CERE is widely extended along the frequency scale: The energy difference between the extreme reflection maxima is approximately 10 meV, while in CdS crystals the width of the CERE is usually of the order of the longitudinal-transverse splitting,  $\omega_{LT} = 2$  meV.

Contours of excitonic reflection of light with similar anomalies were observed previously in solid solutions CdS/CdSe, whose composition was close to that of CdSe.<sup>4</sup> It was assumed that the anomalies are associated with a one-dimensional large-scale surface fluctuation of the composition, which leads to the formation of a potential well (PW) for excitons at the surface. This suggests that the “anomalous” samples which we investigated consist of a bulk solid solution CdS/CdSe whose composition is close to that of CdSe. However, measurements of the absorption spectra in the forbidden polarization  $E \parallel C$  showed that the absorption line, which characterizes the bulk properties of a material, of a longitudinal exciton in these samples occupies a position corresponding to a “pure” CdS crystal.

On the basis of this circumstance and taking into account the results of Ref. 4, we assumed that a thin layer of the solid solution CdS/CdSe, which forms a unique SEP that contains a well because of the difference in the values of the band gap  $E_g$  in the surface layer and in the volume of the crystal ( $E_g^{\text{CdS/CdSe}} < E_g^{\text{CdS}}$ ), is present in the surface region of “anomalous” crystals. Proceeding from this assumption, we performed numerical calculations of the  $A_{n=1}$  CERE with different model SEPs in order to obtain the best agreement between the computed and experimental CERLS.<sup>2)</sup>

The theoretical  $A_{n=1}$  CERE, calculated using a complicated SEP consisting of a square well with a linear “tail” extending into the bulk of the crystal is shown in Fig. 1b (Fig. 2b); the parameters of the SEP are given in the caption). A 7-nm-thick surface exciton-free, surface (“dead”) layer of intrinsic nature was also taken into account in the calculation.<sup>5</sup> It is evident from Fig. 1 that the computed CERE reproduces in detail the

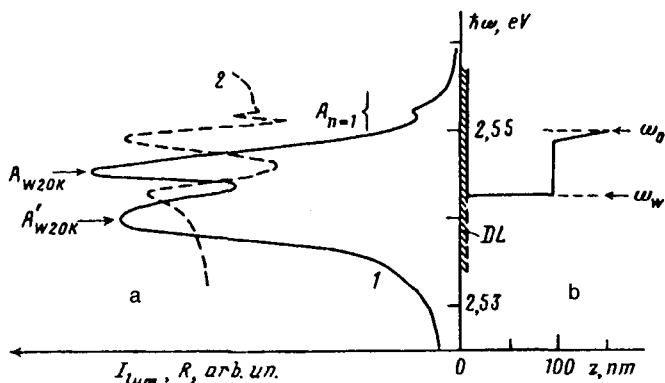


FIG. 2. a — Photoluminescence spectrum (curve 1) and light reflection spectrum (curve 2) of a CdS/CdSe–CdS sample at  $T=20$  K, E1C,  $k\perp C$ ; b — surface excitonic potential used to calculate the CERL in Fig. 1b. The potential is 7.5 meV deep and 88 nm wide; the “tail” is 50 nm long and 1 meV deep. The hatched section represents the “dead” surface layer (DL).

basic features of the experimental CERL. Varying the parameters of the SEP in the calculations of the CERL shows that the long-wavelength structure observed in the experimental spectrum in the region of the main reflection maximum, as well as the long tail of the spectrum on the frequency scale, are due to the presence of a deep well in the surface exciton potential. At the same time, the form of the CERL near the frequency  $\omega_L$  is determined by the parameters of the “tail” of the SEP (see also Refs. 1 and 4).

To determine the composition of the surface layer, the “anomalous” crystal, whose spectrum is shown in Fig. 1a, was subjected to x-ray microprobe spectral analysis by the electron microprobe method. These investigations confirm that selenium is present in the surface region of the “anomalous” CdS crystals. In accordance with these data, selenium with a concentration of  $\sim 10^{20}$  atoms/cm<sup>-3</sup> is present in the surface layer of these crystals. This gives us a basis to focus on the solid solution CdS<sub>1-x</sub>Se<sub>x</sub> with a concentration of the narrow-band gap component (CdSe)  $\sim 1\%$  ( $x\sim 0.01$ ). In light of these data, there is a natural physical explanation for the structure of the SEP, as determined from the form of the CERL.

The bottom of the deep surface potential well with sharp edges is formed by a region of constant composition of the surface layer of the solid solution. The tail of the SEP is determined by the region of the surface layer of the solid solution where the content of the narrow band gap component decreases in the direction of the main volume of the crystal. Such a region with a smooth transition from a three-component solid solution in the surface layer to a binary compound in the volume of the crystal probably arises at the crystal-growth stage as a result of diffusion of Se atoms, which smears the CdS/CdSe–CdS heteroboundary. The existence of a transitional region is confirmed by data from x-ray microprobe spectral analysis, which indicate that the selenium content decreases in a direction away from the surface into the volume of the sample.

Unfortunately, the technology of gas-phase growth of II–VI crystals does not permit sufficiently reliable monitoring of the growth process. The appearance of anomalous

crystals is therefore an accidental event to a certain extent (see also Ref. 6). Our method of excitonic spectroscopic diagnostics of the surface structure of a transitional layer of crystals could be an important, if not the only, method for perfecting the technology of preparation of crystal samples with prescribed properties.

The SEP which forms the complicated structure of the CERL observed experimentally also determines the mechanism of the formation of the resonance excitonic photoluminescence spectra of the experimental crystals CdS/CdSe–CdS. This result follows from a comparison of the photoluminescence spectra with the corresponding CERLs, and therefore with the structure of the SEP. It also follows from an analysis of their temperature dependence.

The photoluminescence spectrum in the region of the excitonic resonance  $A_{n=1}$  and the corresponding CERLs measured at  $T=20$  K (the curves 1 and 2, respectively) are shown in Fig. 2a. From this figure it can be concluded that the intense line  $A_{w20K}$  observed in the photoluminescence spectrum in the region of the dip in the CERL should be attributed to the radiative annihilation of an exciton localized, as a whole, in a surface potential well. We attribute the  $A'_{w20K}$  line observed at frequencies below  $\omega_w$ , corresponding to the bottom of the well (see Fig. 2b), to the localization of an exciton on fluctuations of the composition of the solid solution in the spatial region at the bottom of the potential well. We note that in the bulk solid solutions CdS/CdSe exciton localization on composition fluctuations and its manifestation in the photoluminescence spectra have been studied. It has been established that the strongest manifestation of the effect is in compositions which are similar to CdS.<sup>7,8</sup>

Investigation of the temperature dependence of the resonance excitonic photoluminescence spectra confirms the proposed interpretation of the lines  $A_w$  and  $A'_w$ . As one can see from Fig. 3 and 2a, the relatively wide line  $A'_w$ , which predominates in the photoluminescence spectrum at liquid-helium temperatures, is rapidly quenched as the temperature of the sample is raised. At the same time, the line  $A_w$  flares up in the short-wavelength region of the spectrum, and the volume-polariton  $A_{n=1}$  radiation also becomes more intense. At liquid-nitrogen temperatures the emission line  $A_w$ , on whose short-wavelength shoulder the volume radiation of a free exciton  $A_{n=1}$  is observed, predominates in the photoluminescence spectrum.

The transformation of the photoluminescence spectra which is observed as the temperature changes is a result of the effective, thermally activated delocalization of excitons from the localized states in the region of a potential well into the state of free motion inside and outside the potential well. The quenching of the line  $A'_w$  and the excitation of the emission line  $A_w$  are associated with the delocalization of excitons from states which are determined by the fluctuation part of the potential at the bottom of the well into a state of free motion within the potential well. The intensification of the  $A_{n=1}$  volume-polariton luminescence with increasing temperature is due to the thermally activated delocalization of excitons from the localized states  $A'_w$  and  $A_w$  in the region of the potential well into a state of free motion of the exciton outside the potential well.

We note that the changes which are essentially similar to those described above and which appear in the photoluminescence spectra as a result of thermally activated delo-

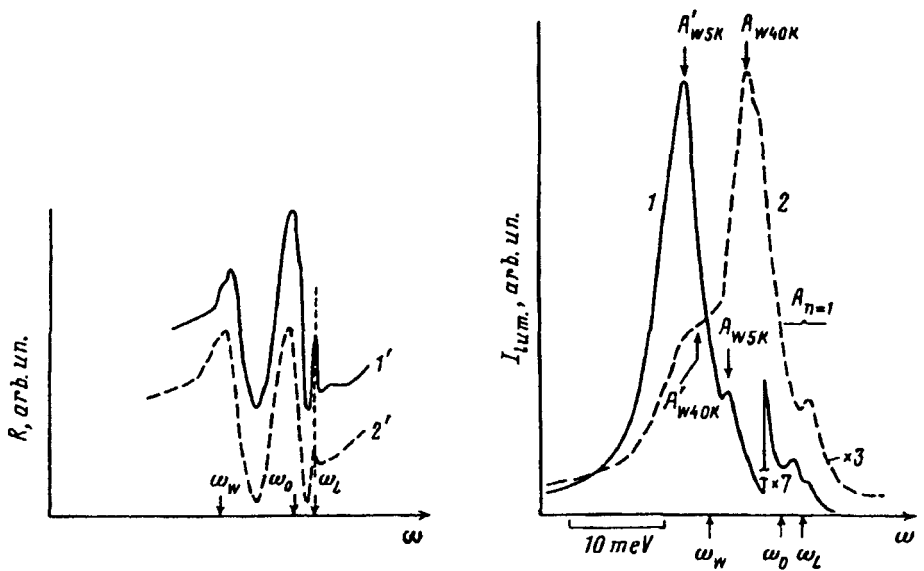


FIG. 3. Photoluminescence spectra (curves 1 and 2) and the corresponding  $A_{n=1}$  CERL (curves 1', 2') of a CdS/CdSe-CdS sample at  $T=5$  K (curves 1, 1') and  $T=40$  K (curves 2, 2'), E.L.C, k.L.C.

calization of excitons have been observed previously in a number of bulk II-VI solutions.<sup>9</sup>

In conclusion, we note that the mechanism of surface localization of excitons which we investigated is not reflected among the mechanisms discussed in the literature (they are reviewed in Ref. 1).

In summary, we have studied the mechanism for surface localization of excitons which is governed by the presence of a solid substitution solution in the surface region of a semiconductor. We showed that in the presence of a sufficiently deep surface potential well formed by the solid solution the resonance excitonic luminescence is determined largely by the contribution to the emission of excitons localized in the well. A surface potential well can also strongly influence the formation of volume polariton luminescence spectra.

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<sup>2</sup>) The method for calculating the CERL is based on a step approximation of the SEP corresponding to the model

of a multilayer medium with spatial dispersion.<sup>1</sup>

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