Photoluminescence and tunnel relaxation of localized excitons in A_2B_6 solid solutions with anionic replacement.

A. G. Abdukadyrov, S. D. Baranovskiĭ, S. Yu. Verbin, E. L. Ivchenko, A. Yu. Naumov, and A. N. Reznitskiĭ

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR

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The energy distribution of excitons, localized by composition fluctuations, in semiconducting A_2B_6 solid solutions has been studied. A kinetic theory of steady-state population by excitons of the tail of the energy density of states in the model of a highly localized hole has been constructed. The theory takes into account how the probability of the tunnel jump of an exciton depends on the distance between the localization centers, and allows for partial filling of states. The low-temperature spectra of luminescence and absorption of $CdS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ solid solutions of different compositions were measured experimentally. A relationship was established between the location of the emission band maximum and a quantity characterizing the decrease of the density of hole states with the depth of the mobility gap. It was found that as the pumping intensity increases, starting with a certain critical value, the luminescence band maximum shifts appreciably to the short-wavelength side, reflecting the process of filling of the tail of localized states. The characteristic radius of hole localization on composition fluctuations and the total number of localized states per unit volume were determined by comparing theory with experiment.

1. INTRODUCTION

Solid solutions constitute a special class of disordered solids which preserve the crystalline long-range order in the arrangement of the points of the space lattice, the disorder being due to the random arrangement of the atoms of the substituent components at the points of at least one of the sublattices. As in the case of amorphous or vitreous compounds, the presence of disorder in a semiconducting solid solution causes localized states for electrons and holes to appear in the forbidden gap. These states are eigenstates; they arise from a fluctuational deviation of the composition of the solid solution in a given region of space from average composition.

The possibility of localizing excitons in potential wells produced by large-scale fluctuations of composition was put forward in Ref. 1. The electron and hole in an exciton were treated as a single whole, and it was assumed that the Bohr radius a_B of the exciton was small compared to the radius of its localization on the fluctuation potential. This type of exciton localization was apparently observed in Ref. 2. In an analysis of the photoluminescence spectra of $CdS_{1-x}Se_x$ solid solutions, Ref. 3 proposed a different model of exciton localization, according to which an exciton is a hole that is highly localized on fluctuations of the composition and has bound an electron by its Coulomb field. The inequality $a \ll a_B$, where a is the hole localization radius, serves as the criterion for the applicability of this model. The latter has found confirmation in experiments on selective resonance excitation of localized exciton states and in the study of their latent anisotropy in $CdS_{1-x}Se_x$ (Ref. 4), and was also used to analyze experimental data obtained for the $ZnSe_{1-x}Te_x$ system (Ref. 5), which is still another solid solution with replacement in the anionic sublattice of the crystal.

In the present work, we construct a theory of tunnel energy relaxation of excitons with respect to localized states in the model of a deeply localized hole and calculate the spectrum of exciton photoluminescence, study experimentally the dependence of the location of the luminescence band maximum in A_2B_6 solid solutions with anionic replacement as a function of solution composition and intensity of exciting light, and compare the theoretical and experimental results obtained.

2. THEORY

In the model under consideration, the excitation energy of a localized exciton is

$$E=E_0-\varepsilon-\varepsilon_B, \qquad (1)$$

where E_0 is the forbidden gap width (width of the mobility gap), ε is the binding energy of the hole on the localization center, measured from the hole mobility boundary, $\varepsilon_B = e^2/(2\varkappa a_B)$ is the Bohr binding energy of the electron on the hole, and $\varkappa$ is the static permittivity. Thus for $a \ll a_B$, the dependence of ε_B (and a_B) on ε can be neglected, and the photoluminescence spectrum $J(\hbar\omega)$ is determined by the energy function of the hole distribution $p(\varepsilon)$:

$$J(\hbar\omega) \propto p(E_0-\hbar\omega-\varepsilon_B). \qquad (2)$$

The distribution $p(\varepsilon)$ is formed as a result of the competition of two processes, namely, radiative exciton recombination, characterized by a lifetime τ_0, and tunnel relaxation of the hole with respect to the tail of the state density (a hole, while moving from one center of localization to another, drags behind it the electron bound to it). The nonradiative recombination channels are neglected. The time of the tunnel jump $\tau_d(r)$ depends exponentially on the distance r between the localization centers

$$\tau_d(r)=\omega_0^{-1} \exp(2r/a), \qquad (3)$$

where the quantity a, with allowance for the inequality $a \ll a_B$, is close to the hole localization radius, and $\omega_0 \sim 10^{13}$ sec^{-1}. At low temperature it suffices to take into account only the transitions of the hole $\varepsilon \to \varepsilon'$ to deeper states ($\varepsilon' > \varepsilon$).

The quantities τ_0, ω_0, and a are treated as the parameters of the theory, and their possible dependence on ε is neglected. As for the energy density of the localized states of the hole $g(\varepsilon)$, it is assumed to decrease fairly rapidly with the depth of the forbidden zone, i.e., as ε increases. In specific calculations and estimates, we approximate $g(\varepsilon)$ by the exponential

$$g(\varepsilon)=g_0\exp(-\varepsilon/\varepsilon_0), \tag{4}$$

thereby introducing into the theory two more parameters, g_0 and ε_0. To find the distribution function $p(\varepsilon)$, we use the theory developed in Ref. 6 for describing interpair recombination in amorphous semiconductors, having modified this theory for application to localized excitons.

Note that similarly formulated problems have been solved in several studies.$^{7-10}$ However, in Ref. 7 the energy dependence of the electron-phonon interaction coefficient was considered to be the main factor determining the energy relaxation of a particle, and Refs. 8 and 9 used dependences of the jump time on the jump length different from Eq. (3). Reference 10 is the closest to our ideas, but it considers only the photoluminescence kinetics at short times and allows only for the first jump in the process of energy relaxation, whereas the present study deals with the energy distribution of localized excitons under steady-state illumination conditions.

Before presenting the quantitative theory, we shall make certain estimates. First, we estimate the energy location of the maximum of the luminescence spectrum. Obviously, the maximum should correspond to the binding energy ε_m at which the time of the next jump becomes equal to τ_0: From shallower states ($\varepsilon<\varepsilon_m$), holes relax rapidly into the tail of localized states, and they are unable to reach the deeper states ($\varepsilon>\varepsilon_m$) during the lifetime τ_0. We introduce the concentration of localized states with a binding energy greater than ε:

$$\rho(\varepsilon)=\int_{\varepsilon}^{\infty} g(\varepsilon')d\varepsilon'=g_0\varepsilon_0\exp(-\varepsilon/\varepsilon_0). \tag{5}$$

The average length $R(\varepsilon)$ of a jump of a hole from the ε state is related to $\rho(\varepsilon)$ as follows:

$$R(\varepsilon)=\left[\frac{4\pi}{3}\rho(\varepsilon)\right]^{-1/3}. \tag{6}$$

Equating τ_0 and $\tau_d(R(\varepsilon_m))$, we obtain for ε_m the estimate

$$\varepsilon_m=\varepsilon_0\ln\left[\frac{\pi}{6}g_0\varepsilon_0a^3\ln^3(\omega_0\tau_0)\right]. \tag{7}$$

This estimate applies at moderate rates G of electron-hole pair production when steady-state filling of the state density tail does not play any appreciable role in the process of relaxation of localized excitons.

To estimate the threshold rate of production G_c, at which the filling of the states begins to become appreciable, we equate the energy ε_m determined in accordance with Eq. (7) to the energy ε_f, which satisfies the equation

$$\rho(\varepsilon_f)=G\tau_0.$$

We thus obtain

$$G_c\tau_0a^3=\frac{6}{\pi}\ln^{-3}(\omega_0\tau_0). \tag{8}$$

For $G>G_c$, the location of the band maximum begins to shift appreciably to the short-wavelength side as G increases.

Turning to the discussion of a more rigorous theory, we note that the state of the localized exciton is characterized by the hole-binding energy ε and by the distance r to the nearest unfilled state of high binding energy $\varepsilon'>\varepsilon$. The degree of population f of the (ε, r) state satisfies the kinetic equation

$$\frac{f(\varepsilon,r)}{\tau(r)}=\Gamma(\varepsilon)[1-f(\varepsilon,r)] \tag{9}$$

or

$$f(\varepsilon,r)=\frac{\Gamma(\varepsilon)\tau(r)}{1+\Gamma(\varepsilon)\tau(r)}.$$

Here the lifetime is $\tau(r)=\tau_0\tau_d(r)/(\tau_0+\tau_d(r))$, and the function $\Gamma(\varepsilon)$ is conveniently represented in the form

$$\Gamma(\varepsilon)=G(\varepsilon)/\tilde{g}(\varepsilon), \tag{10}$$

where $\tilde{g}(\varepsilon)=g(\varepsilon)-p(\varepsilon)$, $G(\varepsilon)d\varepsilon$ is the rate of influx into the states $(\varepsilon, \varepsilon+d\varepsilon)$ from delocalized states or states of lower binding energy. The hole energy distribution function is related to $f(\varepsilon,r)$ by the integral equation

$$p(\varepsilon)=g(\varepsilon)\int_0^{\infty} f(\varepsilon,r)P_\varepsilon(r)dr, \tag{11}$$

where $P_\varepsilon(r)dr$ is the probability that a hole reaching the state ε will, at a distance from r to $r+dr$, find an unfilled state with binding energy $\varepsilon'>\varepsilon$. On the assumption of a random distribution in the space of the localization centers

$$P_\varepsilon(r)=4\pi r^2\tilde{\rho}(\varepsilon)\exp(-V(r)\tilde{\rho}(\varepsilon)), \tag{12}$$

where $V(r)=4\pi r^3/3$

$$\tilde{\rho}(\varepsilon)=\rho(\varepsilon)-\int_{\varepsilon}^{\infty} p(\varepsilon')d\varepsilon'. \tag{13}$$

We introduce the probabilities $w_j(\varepsilon)$ and $w_{\rm rec}(\varepsilon)$ that an exciton in the ε state will, respectively, execute a tunnel jump or recombine radiatively. Obviously, $w_j(\varepsilon)+w_{\rm rec}(\varepsilon)=1$. From Eqs. (9) and (10) it follows that

$$w_j(\varepsilon)=\int_0^{\infty}\frac{f(\varepsilon,r)}{\tau_d(r)G(\varepsilon)}g(\varepsilon)P_\varepsilon(r)dr$$

$$=\int_0^{\infty}\frac{\tau_0}{\tau_0+\tau_d(r)}\frac{g(\varepsilon)}{\tilde{g}(\varepsilon)}[1-f(\varepsilon,r)]P_\varepsilon(r)dr. \tag{14}$$

The energy production rate $G(\varepsilon)$, the distribution function $p(\varepsilon)$, and the probability $w_j(\varepsilon)$ are related by the additional integral equation (see Ref. 6)

$$G(\varepsilon)=G\frac{\tilde{g}(\varepsilon)}{\tilde{\rho}(0)}\exp\left[\int_0^{\varepsilon}d\varepsilon'\,w_j(\varepsilon')\frac{\tilde{g}(\varepsilon')}{\tilde{\rho}(\varepsilon')}\right]. \tag{15}$$

Equations (10)–(15) form a closed system of integral equations which was solved numerically by iterating for specific values of the parameters τ_0, ω_0, a, g_0, ε_0 and of the variable G. The accuracy of the calculation could be checked by comparing the total concentration $N=\int d\varepsilon p(\varepsilon)$, calculated by means of the procedure (10)–(15), with its exact value $N=G\tau_0$. The luminescence spectra, calculated in accordance with the expression (2), are compared with the experimental data of Sec. 4.

The time $\tau(r)$ can be written with exponential accuracy in the form

$$\tau(r)=\begin{cases}\tau_0, & r>\tilde{r},\\ \tau_d(r), & r<\tilde{r},\end{cases} \tag{16}$$

where the distance $\tilde{r}$ satisfies the condition $\tau_0 = \tau_d(\tilde{r})$, i.e.,

$$\tilde{r}=(a/2)\ln(\omega_0\tau_0).$$

In the approximation (16), the expressions for $w_j(\varepsilon)$ and $p(\varepsilon)$ are simplified:

$$w_j(\varepsilon)=\frac{g(\varepsilon)w_j{}^0(\varepsilon)-p_<(\varepsilon)}{g(\varepsilon)-p(\varepsilon)}, \tag{17}$$

$$p(\varepsilon)=p_<(\varepsilon)+p_>(\varepsilon), \tag{18}$$

where

$$w_j(\varepsilon)=\int_0^{\tilde{r}} P_\varepsilon(r)\,dr=1-\exp[-V(\tilde{r})\tilde{\rho}(\varepsilon)], \tag{19}$$

$$p_>(\varepsilon)=g(\varepsilon)\exp[-V(\tilde{r})\tilde{\rho}(\varepsilon)]\frac{\Gamma(\varepsilon)\tau_0}{1+\Gamma(\varepsilon)\tau_0}. \tag{20a}$$

$$p_<(\varepsilon)=g(\varepsilon)\int_0^{\tilde{r}} P_\varepsilon(r)f(\varepsilon,r)\,dr. \tag{20b}$$

When the intensity of the exciting light is low, $G<G_c$, the population of the states can be neglected, and for $G(\varepsilon)$ an explicit expression is obtained which for $V(\tilde{r})\rho(0)\gg 1$ has the form

$$G(\varepsilon)=\frac{G}{\varepsilon_0}\exp[Ei(-X)], \tag{21}$$

where $Ei(-X)$ is the exponential integral function, $X=V(\tilde{r})\rho(\varepsilon)$. Thus, for $G<G_c$

$$p_>(\varepsilon)=\frac{G}{\varepsilon_0}\tau_0\exp[-X+\mathrm{Ei}(-X)], \tag{22a}$$

$$p_<(\varepsilon)=\frac{G}{\varepsilon_0\omega_0}\int_0^{\tilde{r}} 4\pi r^2\rho(\varepsilon)\exp[-V(r)\rho(\varepsilon)]\exp(2r/a)\,dr. \tag{22b}$$

For $\varepsilon \sim \varepsilon_m$, the main contribution to $p(\varepsilon)$ is due to states with $r>\tilde{r}$, i.e., $p(\varepsilon_m)\approx p>(\varepsilon)$. The function $[-X+Ei(-X)]$ reaches a maximum for $X_m \equiv \ln(1/X_m) \approx 0.567$, and a more accurate values of ε_m exceeds the approximate value (7) by an amount $X_m\varepsilon_0$:

$$\varepsilon_m=\varepsilon_0\ln\left[\frac{\pi}{6X_m}g_0\varepsilon_0a^3\ln^3(\omega_0\tau_0)\right]. \tag{23}$$

For this reason, a more accurate estimate of the critical rate production G_c [see Eq. (8)] has the form

$$G_c\tau_0a^3=\frac{6X_m}{\pi}\ln^{-3}(\omega_0\tau_0). \tag{24}$$

The results obtained in this section are applicable on the assumption that the hole binds an electron while either in a delocalized state or in a state of low binding energy ε, at which $G(\varepsilon)\approx G/\varepsilon_0$. This made it possible in calculating $p(\varepsilon)$ to exclude from consideration the processes of binding of electron-hole pairs into excitons.

3. CHARACTERISTICS OF THE SAMPLES

The $CdS_{1-x}Se_x$ samples $(0.05\leqslant x\leqslant 0.6)$ used in this work consisted of plane-parallel wafers 5–20 μm thick, grown from the gaseous phase. For quantitative measurements, samples possessing a bright luminescence and distinct structure in the exciton reflection spectrum were selected. Particular attention was paid to the uniformity of the composition both at the surface and in the interior of the sample. In all cases, the absolute composition x at opposite points of the sample differed by $\leqslant 0.005$, and the inhomogeneity along the surface of the face was also less than the indicated value.

The $ZnSe_{1-x}Te_x$ $(0.1\leqslant x\leqslant 0.6)$ solid solutions were obtained from the melt. Single-crystal blocks possessing bright luminescence were cleaved from the initial samples, then, plane-parallel wafers ~ 1.5 μm thick were cut out of the blocks. The wafer thickness was reduced mechanically, and in the last stage, also by chemical-mechanical polishing, to 60–100 μm. In the last stage of the treatment, the samples were etched in a polishing etchant. The final thickness of the samples was determined by optical methods to be 5–40 μm. The samples thus obtained had a homogeneity equal to that of $CdS_{1-x}Se_x$. To reduce the influence of possible inhomogeneity of the solid solution composition, all the spectra of the sample were obtained from the same region, whose characteristic size was of the order of 0.1×0.0 mm^2.

4. EXPERIMENTAL RESULTS AND DISCUSSION

The form of the long-wavelength exciton-absorption wing of the samples was exponential:

$$K=K_0\exp[-(\hbar\omega-E_{n=1})/\varepsilon_0]. \tag{25}$$

The value of ε_0 was determined from the transmission spectrum, and this was the value used in the calculation as the parameter ε_0 characterizing the drop in the density of localized exciton states [see Eq. (4)].

Figure 1a shows the reflection spectrum of a $CdS_{0.8}Se_{0.2}$ sample; this spectrum made it possible to determine the location of the resonance frequency of the exciton $E_{n=1}$, i.e., also the binding energy corresponding to states radiating at frequency ω [see Eqs. (1) and (2)]. Note that, as was shown by a combined study of the transmission and reflection spectra of fairly thin samples of this type, in the relevant range of compositions the maximum of the exciton absorption line coincides with the minimum in the exciton reflection spectrum.[11]

In the case of $ZnSe_{1-x}Te_x$, determination of the energy corresponding to the bottom of the exciton band is a separate problem. Figure 1b shows the absorption spectrum of a $ZnSe_{0.85}Te_{0.15}$. The absence of fine structure in the absorption spectrum, characteristic of all the samples in the composition range studied, is due to the fact that the line width of the transition to the ground state and the exciton binding energy are of the same order.[11] For this reason, the fine structure is absent from the reflection spectra as well. In this case, for sufficiently thick samples, the only source of information on the location of the bottom of the exciton band remains the low-temperature luminescence spectrum.

Note that for both $CdS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$, the maximum of the exciton absorption line coincides quite well with the origin of the portion of rapid increase of the lumi-

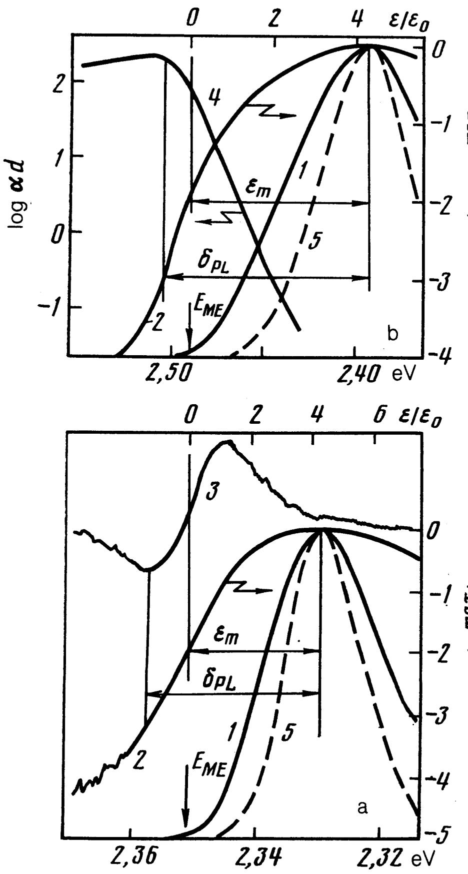

FIG. 1. Optical spectra of $CdS_{0.8}Se_{0.2}$ (a) and $ZnSe_{0.85}Te_{0.15}$ (b). 1, 2—luminescence spectra for interband excitation on a linear and a semilog scale, respectively; 3—reflection spectrum; 4—spectral dependence of the absorption coefficient on a semilog scale; 5—calculation using Eqs. (10)–(15). Values of the parameters of the theory are indicated in the text. In Fig. 1b the label of the vertical axis is ln αd instead of log αd.

nescence intensity. In the spectrum of the majority of the samples studied, this frequency is associated with an intensity amounting to 10^{-3} of the intensity at the luminescence band maximum. We used both of these results to determine the location of the bottom of the exciton band of the state $n = 1$ in an analysis of the luminescence spectra of comparatively thick $ZnSe_{1-x}Se_x$ samples. In the case of a discrepancy between the energy values obtained on the basis of these two characteristics, we took the average value for $E_{n=1}$, and used the difference to estimate the uncertainty of the value of $E_{n=1}$.

A study of the absorption spectra of the $CdS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ solid solutions showed[11] that the maximum magnitude of the disorder effects, which is manifested in the maximum length of the tail of localized states, is reached in the concentration range $x = 0.1$–0.2, while the maximum value of the parameter ε_0 in the case of the $ZnSe_{1-x}Te_x$ solid solution is almost five times the corresponding value in the $CdS_{1-x}Se_x$ solid solution. The large length of the tail of localized states accounts for a considerably greater role of the electron-phonon interaction in the formation of the luminescence spectrum. This causes the shape of the luminescence spectra over a wide range of compositions of the $ZnSe_{1-x}Te_x$ solid solution[5] to differ markedly from the shape of the spectra of the $CdS_{1-x}Se_x$ solid solution.[3,7] Nevertheless, as will be shown below, many of the characteristics of the luminescence spectra of these two solid solutions are very similar.

The luminescence spectrum of both types of samples of solid solutions in the composition range $0.02 \leqslant x \leqslant 0.6$ at liquid helium temperature contains a single band corresponding to the recombination of localized excitons. The luminescence spectra of $CdS_{1-x}Se_x$ at $x = 0.2$ and of $ZnSe_{1-x}Te_x$ at $x = 0.15$ are shown in Fig. 1 on a linear and a semilog scale, respectively. On excitation above a certain frequency, which may be related to the exciton mobility threshold,[3] the shape of the spectrum is practically independent of the wavelength of the exciting radiation and its intensity over a fairly wide range of their variation. This makes it possible to compare and analyze the luminescence spectra of samples of different compositions without being concerned about the absolute identity of the excitation conditions. The results given below were obtained by excitation with the light of an He–Cd or Ar^+ laser with a power density of the order of 1–10 W/cm^2, unless otherwise specified.

An important characteristic of the luminescence spectrum of localized excitons is the location of the band maximum relative to the mobility threshold. Note that in the optical spectra themselves the exciton mobility threshold, i.e., the boundary separating the free states from the states localized by fluctuations of the solid solution composition, is not manifest. At the same time, results of a polarized-luminescence study of the latent anisotropy of localized states indicate that the region of transition from localized states to zone-type states corresponds to the start of a sharp short-wavelength rise of the intensity in the luminescence spectrum.[12] In all the samples possessing a sufficiently bright luminescence, this region coincides closely in energy with the portion of the luminescence spectrum where the radiation intensity amounts to $\sim 10^{-2}$ of the value at the emission band maximum.

We used this result to characterize the location of the mobility boundary in the spectrum of all the samples studied (arrow E_{ME} in Fig. 1). The location of the luminescence band maximum relative to the mobility threshold determined in this manner—the quantity ε_m in the notation of Fig. 1—changes in regular fashion with the composition of the solid solution, reaching its highest value in the same range of compositions as $\varepsilon_0(x)$. This makes it possible to expect the presence of a functional relationship between ε_m and ε_0. In Fig. 2, the dependence $\varepsilon_m(\varepsilon_0)$ is plotted on a log-log scale. It is obvious that ε_m is accurately proportional to ε_0 with a single proportionality coefficient of 4.3 for the compositions of both solid-solution systems. Comparison of this coefficient with Eq. (23) makes it possible to draw certain conclusions regarding the parameters of the problem. Thus, if we take the reasonable values $\omega_0 = 10^{13}$ sec^{-1} and $\tau_0 = 3 \times 10^{-9}$ sec as an estimate, then for $g_0 \varepsilon_0 a^3 = 0.077$, the ratio $\varepsilon_m / \varepsilon_0$, calculated from formula (23), is practically equal to the experimental value 4.3.

Note that the shift of the emission maximum relative to $E_{n=1}$ (the quantity δ_{PL} in the notation of Fig. 1) is also proportional to ε_0, and we have $\delta_{PL}/\varepsilon_0 = 5.3 \pm 0.8$. This means, in particular, that the exciton mobility threshold is shifted relative to $E_{n=1}$ to the long-wavelength side by an amount $\sim \varepsilon_0$.

An important experimental result is the weak depen-

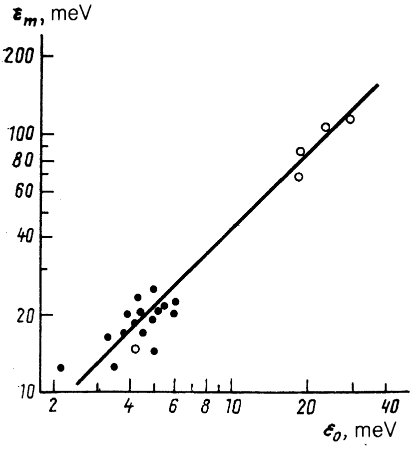

FIG. 2. Relative location of the emission band maximum as a function of ε_0 [see Eq. (25)] for different samples of the solid solutions $ZnSe_{1-x}Te_x$ (open circles) and $CdS_{1-x}Se_x$ (closed circles). Straight line—the dependence $\varepsilon_m = 4.3\varepsilon_0$.

dence of the location of the maximum in the luminescence of localized excitons on the intensity of the exciting light. Figure 3 shows the corresponding dependence for the luminescence of the $CdS_{0.8}Se_{0.2}$ sample during excitation to the exciton spectral region. Up to excitation levels of 10 W/cm^2 (this corresponds to a photon flux of the order of 10^{19} cm^{-2} sec^{-1}), the luminescence was excited continuously by the 5145-Å Ar^+ laser line; for excitation at a level exceeding 10^{20} cm^{-2} sec^{-1}, use was made of the radiation of a pulsed Cu-vapor laser (exciting wavelength, 5106 Å; pulse width, 15 nsec; repetition rate, 10 kHz), and the luminescence in this case was recorded at the excitation pulse maximum. During pulsed excitation and recording at the instant corresponding to the highest intensity, the location of the luminescence maximum at the lowest excitation levels accessible to experimental study was shifted by ~ 2 meV to the short-wavelength side relative to the location corresponding to continuous excitation. This shift evidently reflects the difference between the conditions of excitation and recording, and it is not shown in Fig. 3.

As is evident from the data of Fig. 3, up to an excitation density of $(2\text{–}3)\cdot 10^{21}$ cm^{-2} sec^{-1}, the location of the luminescence band maximum is independent of the excitation level. A further increase in pumping intensity causes the location of the band maximum to shift in the short-wavelength direction, and this increases with the excitation.

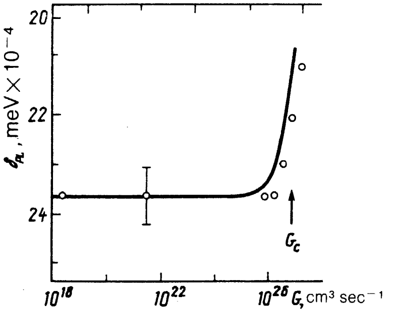

FIG. 3. Shift of the luminescence band maximum of the solid solution $CdS_{0.8}Se_{0.2}$ as the excitation intensity increases. Points—experiment ($T = 2$ K), solid curve—results of calculations (the parameter values are indicated in the text). The arrow shows the critical value of the production rate G_c, calculated from the approximate formula (24). The intensity of the exciting light I_0 (upper scale) and production G (lower scale) are related by the relation $G = I_0 K^{-1}$, where the absorption coefficient at the excitation frequency is $K = 10^5$ cm^{-1}.

Such behavior of the luminescence spectrum as the pumping intensity increases finds a natural explanation in terms of the theory developed above. Comparison of the measured critical excitation level with the estimate based on Eq. (24) makes it possible to determine the radius a of the bound state of the hole. In Fig. 3, the continuous curve represents the result of a calculation using the same values $\omega_0 = 10^{13}$ sec^{-1} and $\tau_0 = 3\cdot 10^{-9}$ sec that were used in estimating ε_m. Satisfactory agreement with experiment is reached for $a = 7$ Å. Interestingly, the value obtained for the radius a differs from $a = \hbar/(2m\varepsilon_m)^{1/2}$ by a factor <2. From the values obtained, $g_0\varepsilon_0 a^3 = 0.077$, and $a = 7$ Å, one can find the total number of states below the mobility threshold $N_t = g_0\varepsilon_0 = 2.3\cdot 10^{20}$ cm^{-3}. Since in specially undoped A_2B_6 samples, the background concentration of impurities and defects is usually less than 10^{16} cm^{-3}, the present estimate of N_t explains why at sufficiently low temperatures in these systems of solid solutions, fluctuational localized states are the main channel of recombination of nonequilibrium carriers.[13]

To conclude this section, we discuss the shape of the luminescence spectrum. In Fig. 1, dashes represent the emission spectra, calculated from Eqs. (10)–(15) for the parameter values indicated above. Given a correct description of the location of the emission band maximum, the model employed leads to an appreciable difference in the spectrum at both the short-wavelength and long-wavelength edges. According to this model, the excitons, tunnelling with respect to the tail of localized states, jump too quickly over the region of shallow states. Obviously, this process will slow down if one allows for the dependence of the exciton-phonon interaction probability on the difference between the energies of the initial and final localized exciton states. Correct inclusion of the electron-phonon interaction should also improve the agreement between the calculated and experimental spectra at the long-wavelength luminescence edge. In the theory developed above, this portion, starting with energies where the population factor may be considered equal to unity, reflects the appearance of the density of states. Actually, the emission at this frequency also includes the contribution of shallower states, recombination from which is accompanied by a simultaneous emission of acoustic and optical phonons. Obviously, the role of such pumping of the transition oscillator strength from the zero-phonon line to phonon repetitions increases with the localization energy.

5. CONCLUSION

We have studied the characteristics of the low-temperature luminescence spectra of $CdS_{1-x}Se_x$ and $ZnSe_{1-x}Te_x$ solid solutions with compositions for which the main recombination channel of nonequilibrium carriers is their capture in localized states caused by fluctuations of the solid solution concentration. We also discussed the problem of finding a steady-state distribution of holes with respect to the tail of localized states when the recombination proceeds only through exciton states. On the assumption of an exponential form of the density of localized states, the theory makes it possible to explain the universality of the basic properties of the spectrum, expressed in units of ε_0, where ε_0 is a parameter characterizing the scale of the energy dependence of the state density. The theory also makes it possible to describe such experimental results as the location of the maximum in the spectrum of the emission band and the existence of a region of excitation intensities where the location of the maximum in the spectrum is independent of intensity, and also gives a correct estimate of the excitation level, at which the effects of filling of the tail of localized states begin to be observed. The parameter values obtained in such a description are consistent with the corresponding estimates for other classes of disordered substances. A certain discrepancy between theory and experiment in the luminescence band halfwidth can, in particular, be decreased by allowing for the dependence of the localization radius a of the probability of exciton radiation, and of the matrix elements of the exciton-phonon interaction on the localization energy of the hole.

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