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CALCULATION OF EXCITON LUMINESCENCE IN SOLID SOLUTIONS

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Abstract. The problem of developing theoretical methods for studying the energy distribution of localized photo-carriers in refractory materials in order to calculate photoconductivity and photoluminescence spectra is actual. A2B6 semiconductor compounds and their solid solutions, due to their optical, photoluminescent and photosensitive properties, are promising materials for science and technology, are widely used in optoelectronic technology as fluorescent screens, scintillation sensors, photodetectors, laser structural elements. These straight-band semiconductors, having high radiation efficiency, cover the entire spectrum range from the ultraviolet to the IR region [1]. In the constructed model, the function p(ε) determining the luminescence spectrum of a solid solution and the energy density of the generation rate G(ε) for different exciton lifetimes are calculated. For a more detailed comparison of theoretical calculations with experimental data [4,7], the density function of states was replaced by a three-parameter function that significantly affects the change in the half-width and the position of the maximum of the exciton luminescence spectrum, which is confirmed by the results of numerical calculations.

Keywords: lifetime, tunnel jump, spectrum, exciton, recombination.

1. Introduction

Structures based on A_2B_6 semiconductors are promising materials for use in various optoelectronic devices. The wide use of A_2B_6 compounds is due to both the high efficiency of optical processes in these materials and the large range of variation of their properties. Spectral capabilities, high probability of radiative transitions and relatively good mobility of current carriers of wide-bandgap A_2B_6 semiconductors were the basis for further practical application of these compounds. Compounds based on A_2B_6 semiconductors are traditional luminescent materials with a wide forbidden band. The widths of the forbidden band of solid solutions correspond to the full spectrum of visible light and partially to the ultraviolet spectrum. This fundamentally allows their use as the basis of semiconductor sources and receivers of visible and ultraviolet light [1, 2]. In this connection, the problem of developing theoretical methods for studying the energy distribution of localised photoelectrons and photoholes in non-porous materials in order to calculate photoconductivity and photoluminescence spectra is currently urgent.

2. Methods.

In the proposed model a quantitative theory of low-temperature photoluminescence caused by radiative recombination of localised excitons in semiconductor solid solutions (and possibly in amorphous semiconductors) is constructed. In constructing the theory, the tunnel energy relaxation of excitons on localised states in the model of a deeply localised hole is taken into account and the exciton photoluminescence spectrum is calculated.

Solid solutions represent a special class of disordered solids in which the crystalline long-range order in the arrangement of the nodes of the spatial lattice is preserved, and the disorder is due to the random arrangement of substituent atoms at the nodes of at least one of the sublattices. As in the case of amorphous or glassy compounds, the presence of disorder in a semiconductor solid solution leads to the appearance of localised states for electrons and holes in the forbidden band. These states are intrinsic, they arise due to the fluctuation deviation of the solid solution composition in this region of space from the average. In this work [6], in the analysis of photoluminescence spectra of $CdS_{1-X}Se_X$ solid solutions, a model of exciton localisation is proposed, according to which an exciton is a hole strongly localised on composition fluctuations and bound an electron by its Coulomb field. The inequality $\alpha \ll \alpha_B$ where α is the radius of localisation of the hole, serves as a criterion for the applicability of this model. It has been confirmed in experiments on selective resonant excitation of localised exciton states and in the study of their hidden anisotropy in $CdS_{1-X}Se_X$ and also used for the analysis of experimental data [6]. In the present work, the theory of tunnel energy relaxation of excitons on localised states in the model of a deeply localised hole is constructed and the exciton photoluminescence spectrum is calculated; the dependence of the position of the maximum of the luminescence band and its half-width on the choice of the exciton lifetime is theoretically investigated.

A computer model of low-temperature energy relaxation of excitons to localised states (in the forbidden band) for the case of a strongly localised hole, when the hole, moving from one localisation centre to another, "pulls" the electron associated with it is build. In the considered model, the excitation energy of a localised exciton is determined by the following expression

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

where E_0 is the width of the forbidden band (mobility gap), ε is the binding energy of the hole at the localisation centre, counted from the hole mobility boundary, $\varepsilon_B = e^2/(2æ\alpha_B)$ is the Bohr binding energy of the electron on the hole, æ is the static dielectric permittivity. Since at $\alpha \ll \alpha_B$ the dependence of ε_B (and α_B) on ε can be neglected, the photoluminescence spectrum I(hw) is determined by the energy function of the hole distribution p(ε) and has the following form:

$$I(hw) = p(E_0 - hw - \varepsilon_B) \qquad (2)$$

The distribution p(ε) is formed by the competition of two processes, namely the radiative recombination of the exciton, characterised by the lifetime τ_0, and the tunnelling relaxation of the hole along the tail of the density of states. The tunnelling jump time $t_d(r)$ depends exponentially on the distance r between the localisation centres

$$t_d(r) = w_0^{-1}\exp(2r/\alpha) \qquad (3)$$

where the value of α is close to the hole localisation radius taking into account the inequality $\alpha \ll \alpha_B$, and for w_0 we take into account $w_0 \sim 10^{13}c^{-1}$.

At low temperature, it is sufficient to consider only the hole transitions ε =>> ε' to deeper states (ε' > ε). The values τ_0, w_0 and α are considered as parameters of the theory and their possible dependence on ε is neglected. Regarding the energy density of localised hole states g(ε), it is assumed that it decreases sufficiently rapidly to the depth of the forbidden bond, i.e. with increasing ε. In specific calculations and evaluations, we will approximate g(ε) by the exponent

$$g(\varepsilon) = g_0\exp(-\varepsilon / \varepsilon_0) \qquad (4)$$

thus introducing two more parameters g_0 and ε_0 into the theory. To find the distribution function p(ε), we use the model developed in [3] to describe interpair recombination in amorphous semiconductors, modifying this theory with respect to localised excitons.

Similar problems have been solved in a number of papers and the closest to the model under consideration is [5], but it considers only the kinetics of photoluminescence at small times and takes into account only the first jump in the energy relaxation process, whereas the proposed model studies the energy distribution of localised excitons under steady-state illumination conditions.

Turning to a more rigorous theory, we note that the state of a localised exciton is characterised by the hole binding energy ε and the distance r to the nearest unfilled state with a higher binding energy ε'> ε. The population degree f of the state (ε, r) satisfies the kinetics equation

$$\frac{f(\varepsilon,r)}{\tau(r)} = \Gamma(\varepsilon)[1 - f(\varepsilon,r)] \qquad (5)$$

or

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

Here the lifetime τ(r) is defined from the expression

$$\tau(r) = \frac{\tau_0\tau_d(r)}{\tau_0 + \tau_d(r)} \qquad (6)$$

and the function Γ(ε) is represented as

$$\Gamma(\varepsilon) = \frac{G(\varepsilon)}{g(\varepsilon) - p(\varepsilon)} \qquad (7)$$

where G(ε)dε is the rate of arrival to states (ε, ε+dε) from delocalised states or from states with lower binding energy. The energy distribution function of holes, which determines the shape and position of the photoluminescence maximum, is related to f(ε,r) by the integral relation

$$p(\varepsilon) = g(\varepsilon)\int_0^\infty f(\varepsilon,r)4\pi r^2\rho(\varepsilon)e^{-V(r)\rho(\varepsilon)}dr \qquad (8)$$

where $V(r) = 4\pi r^2/3$ a $\rho(\varepsilon)$ is defined as follows

$$\rho(\varepsilon) = \int_\varepsilon^\infty [g(\varepsilon') - p(\varepsilon')]d\varepsilon' \qquad (9)$$

The probabilities $\omega_{пр}(\varepsilon)$ and $\omega_{рек}(\varepsilon)$ that the exciton in the state ε, will respectively make a tunnelling jump or recombine radiatively are determined. The fulfilment of the condition

$$\omega_{пр}(\varepsilon) + \omega_{рек}(\varepsilon) = 1 \qquad (10)$$

can be used to determine the accuracy of numerical calculations. From expressions (5) and (7) we have

$$\omega_{пр}(\varepsilon) = \int_0^\infty \frac{f(\varepsilon,r)}{\tau_d(r)G(\varepsilon)} g(\varepsilon)4\pi r^2\rho(\varepsilon)e^{-V(r)\rho(\varepsilon)}dr \qquad (11)$$

The energy generation rate G(ε), the distribution function p(ε) and the probability $\omega_{пр}(\varepsilon)$ are related by an additional integral relation

$$G(\varepsilon) = [g(\varepsilon) - p(\varepsilon)]\frac{I}{\rho(0)}e^{\int_0^\varepsilon d\varepsilon' \omega_{пр}(\varepsilon')\frac{g(\varepsilon') - p(\varepsilon')}{\rho(\varepsilon')}} \qquad (12)$$

Equations (5) to (9) form a closed system of integral equations, which were solved numerically by iteration for certain values of parameters τ_0, w_0, α, g_0, ε_0 and variable I.

3. Results and Discussions

The shape of the long-wavelength wing of exciton absorption of the studied samples is exponential, the value of ε_0 was determined from the transmission spectrum and this value was used in the calculation as a parameter characterising the decay of the density of localised exciton states [4]. Photoluminescence in A_2B_6 structures, in the considered model, is determined by recombination of excitons localised on fluctuations of composition, which is accounted for by the exciton lifetime τ_0. Fig. 1 shows the values of the function p(ε), which determines the luminescence spectrum of one of the $CdS_{1-X}Se_X$ solid solution compositions, for the values of the parameter $\tau_0 := 0.1\cdot10^{-8}$s, $0.3\cdot10^{-8}$s, $0.6\cdot10^{-8}$s, curves 1, 2, and 3, respectively. The parameters $w_0=10^{13}s^{-1}$, α=7Å, $g_0=41{,}82\cdot10^{21}sm^{-3}эВ^{-1}$, $\varepsilon_0= 0.0055$eV and variable $I=10^{23}sm^{-3}s^{-1}$ were used in the numerical calculations [4]. The perpendicular arrows in Fig. 1 denote the position of the maximum $4\cdot\varepsilon_0$, $4{,}4\cdot\varepsilon_0$ и $4{,}55\cdot\varepsilon_0$ of the p(ε) function defining the luminescence spectrum of the $CdS_{1-X}Se_X$ solid solution calculated for the exciton lifetime values $\tau_0 := 0.1\cdot10^{-8}$s, $0.3\cdot10^{-8}$s и $0.6\cdot10^{-8}$s, curves 1, 2 and 3, respectively.

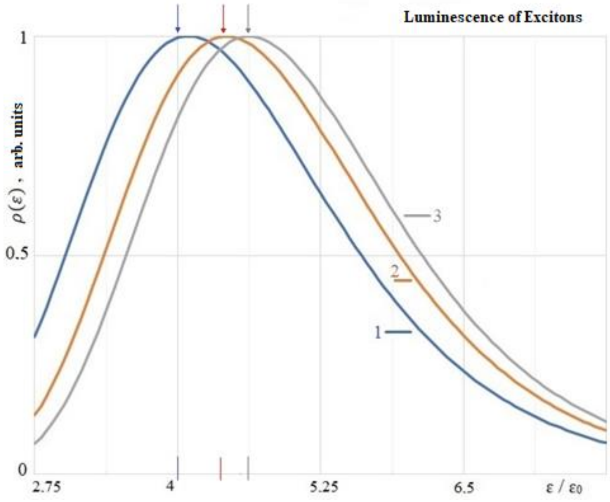

Fig. 1. Values of the function p(ε), which determines the luminescence spectrum of the $CdS_{1-X}Se_X$ solid solution composition, for the values of the parameter $\tau_0 := 0.1\cdot10^{-8}$s, $0.3\cdot10^{-8}$s, $0.6\cdot10^{-8}$s, curves 1, 2, and 3, respectively.

The constructed theoretical model naturally explains the behaviour of the luminescence spectrum with increasing exciton lifetime τ_0 (Fig. 1), the increase of which leads to a linear increase in the total concentration of excitons, the energy dependence of which is defined by the function p(ε). As was expect at longer lifetime of excitons τ_0 they have time to relax by tunnelling jumps to deeper energy states and the maximum of the distribution is shifted towards larger ε. In Fig. 1, the position of the maximum of curve 2 (vertical arrows) is shifted relative to curve 1 by the value of $0.4\cdot\varepsilon_0$ and the position of the maximum of curve 3 relative to curve 2 is shifted by the value of $0.15\cdot\varepsilon_0$. The accuracy of numerical calculations in the constructed model can be estimated using the equality

$$\int_0^\infty [1-\omega_{пр}(\varepsilon)]\cdot G(\varepsilon)d\varepsilon = I \qquad (13)$$

where G(ε) is the rate of exciton generation into states with binding energy ε, determined from expression (12). The excitation intensity of exciton states I for all cases of numerical calculation was equal to $I=10^{23}sm^{-3}s^{-1}$.

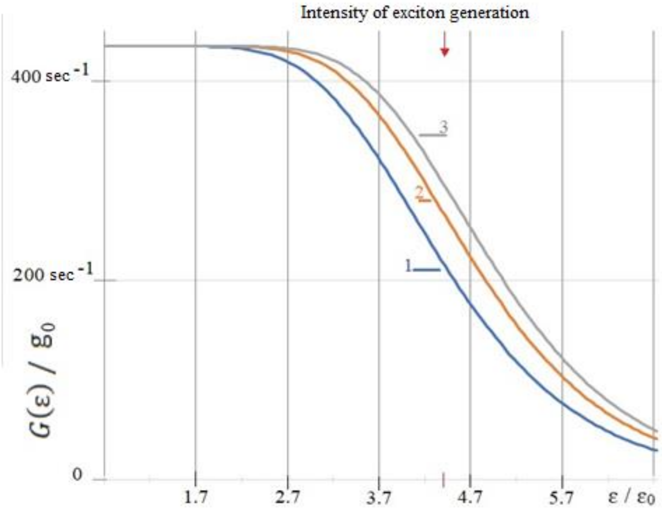

Fig. 2. Exciton generation rate G(ε) into states with binding energy ε calculated for different exciton lifetimes $\tau_0 := 0.1\cdot10^{-8}$s, $0.3\cdot10^{-8}$s and $0.6\cdot10^{-8}$s, curves 1, 2, and 3, respectively.

Fig. 2 shows the energy density of the generation rate G(ε) calculated for different exciton lifetimes $\tau_0 := 0.1\cdot10^{-8}$s, $0.3\cdot10^{-8}$s and $0.6\cdot10^{-8}$s, curves 1, 2, and 3, respectively. The perpendicular arrow marks the position of the $4.4\cdot\varepsilon_0$ maximum of the p(ε) function, which defines the luminescence spectrum of the $CdS_{1-X}Se_X$ solid solution, for the parameter value $\tau_0 := 0.3\cdot10^{-8}$s, curve 2, respectively in Fig. 1. Fig. 2 shows the coincidence of the initial exciton generation values near the mobility edge, which is a consequence of the equality of the parameter $I=10^{23}sm^{-3}s^{-1}$ to the photoexcitation intensity. The splitting of G(ε) functions is observed at $\varepsilon \sim \varepsilon \sim \varepsilon_{max}$, where ε_{max} is the position of the maximum of the exciton photoluminescence spectrum, in Fig. 2 ε_{max} is indicated by a vertical arrow, excitons through tunnel jumps go to deeper energy states and the values of G(ε) function corresponding to the maximum of the distribution function p(ε) increase and are shifted towards larger ε. The influence of the nature of the dependence of the density of states g(ε) on the photoluminescence band shape is illustrated in Fig. 3.

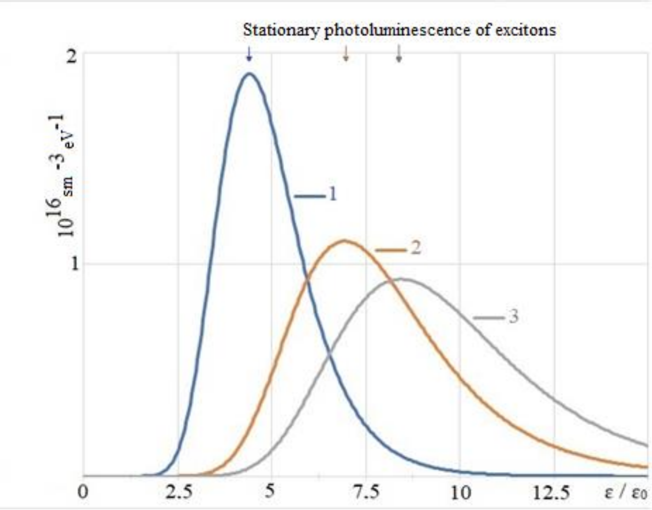

Fig. 3. Values of the function p(ε) determining the luminescence spectrum of the $CdS_{1-X}Se_X$ solid solution for values of the parameter λ := 0.0, 0.025 and 0.05, curves 1, 2 and 3, respectively.

The three-parameter function presented below was used as g(ε) in the calculation of the curves

$$g(\varepsilon) = g_0 \exp\left[-\left(\frac{\varepsilon_0}{\varepsilon} + \sqrt{\frac{\varepsilon_1}{\varepsilon}}\right)^{-1}\right] \qquad (14)$$

where $\varepsilon_1 = \lambda \cdot \varepsilon_0$, λ is a dimensionless quantity and determines the magnitude and shape of the density of exciton states [4,7]. The energy dependence of the density of states p(ε) calculated by formula (14) for three different values of $\lambda = \varepsilon_1/\varepsilon_0$ is shown in Fig.-3. It can be seen that with increasing λ the maximum of exciton distribution shifts towards larger values of ε (i.e., to the long-wave region of the spectrum), since the decline of the density of states into the depth of the forbidden bond becomes more gentle with increasing λ.

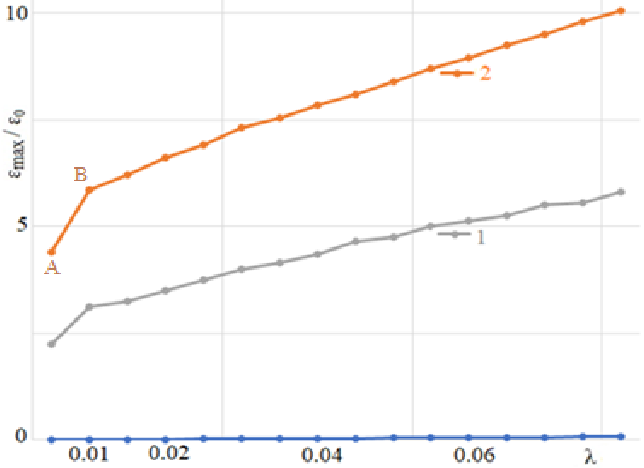

Fig. 4. Variation of half-width and position of maximum of the exciton luminescence spectrum for the values of the parameter λ := 0.0, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, 0.065, 0.07, 0.075 and 0.08, Fig. 1 and 2, respectively.

In this work, in contrast to the calculations in [7], the values of the function p(ε) only for recombining excitons at values of the parameter λ:= 0.0, 0.025 and 0.05, curves 1, 2, and 3, respectively, are calculated and shown in Fig. 3. The vertical arrows in Fig. 3 indicate the positions of the maxima of the p(ε) functions for curves 1, 2 and 3, respectively. The dependence of the maximum position and luminescence half-width on the value of the parameter λ, according to formula (14), were calculated in more detail and illustrated in Fig. 4. The figures in Fig. 4 characterise the change in the half-width and the shift in the position of the maximum of the exciton luminescence spectrum for values of the parameter λ := 0.0, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04, 0.045, 0.05, 0.055, 0.06, 0.065, 0.07, 0.075 and 0.08, fig.1 and 2, respectively. As can be seen from Fig. 4 (Fig. 1), the half-width of the exciton luminescence spectrum varies linearly reaching a value of the order of $6 \cdot \varepsilon_0$. The dependence of the maximum position shift in the exciton luminescence spectrum for the given values of the parameter λ at the above characteristic parameters of the $CdS_{1-X}Se_X$ solid solution is thus determined in Fig. 4 (Fig. 2). A noticeable change in the position of the maximum of the energy distribution function p(ε) is observed at the transition to the three-parameter function (14) at points A and B calculated for λ:=0.0 and λ:=0.01, where the shift of the maximum position at points A and B reaches the order of 1.45·ε_0. Further, as can be seen from Fig. 4 (Fig. 2), the dependence of the maximum position on λ of the functions p(ε) varies linearly reaching a value of the order of 10·ε_0.

4. Conclusions

Quantitative regularities of low-temperature luminescence spectra of $CdS_{1-X}Se_X$ solid solutions, where the main channel of recombination of non-equilibrium carriers is their capture to localised states caused by fluctuations of solid solution concentration, have been studied. In the constructed model, the function p(ε) defining the luminescence spectrum of the solid solution and the energy density of the generation rate G(ε) for different exciton lifetimes have been calculated. For a more detailed comparison of theoretical calculations with experimental data [4,7], the three-parameter function (14) with the characteristic parameter λ was used for the function g(ε), the value of which noticeably affects the change in the half-width and position of the exciton luminescence spectrum maximum, which is confirmed by the results of numerical calculations.

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