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Fluctuation theory of donor-acceptor pair luminescence in compensated semiconductors

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We propose a self-consistent quantitative fluctuation theory of donor-acceptor pair luminescence in compensated semiconductors at constant excitation. The theory succeeds in explanation of main peculiarities of luminescence, including lineshape and position. It also allows to extract such an important material parameter as compensation with high dgreee of precision.

1 Introduction Although doped wide-band-gap semiconductors are rather intensively studied due to their importance in optoelectronic applications (see e.g. Ref. [1]), the understanding of the fundamental principles that govern the optical processes in such systems has been achieved only recently [2, 3]. It turned out that most of such materials are strongly compensated and their properties are extremely sensitive to the Coulomb fluctuating fields, which originate from the charged donors and acceptors. For instance, it was explicitly shown [2], [4], that the kinetics of donor-acceptor pair (DAP) photoluminescence (PL), in the presence of such fields, is described by a non-exponential function, which is even slower than the Kohlrausch stretched exponential function. Similarly, cw DAP PL of such materials is strongly affected by the same fields [3, 5–7]. Previously [3], we have analyzed the excitation intensity dependence of DAP PL for heavily-doped and compensated ZnSe:N using a simplified model, where we considered only the changes in the quasi-Fermi level of a minority dopant, while the quasi-Fermi level of the majority dopant was assumed to be constant. The experimentally observed strong shift of the PL to the blue under increasing excitation has been explained by the shift of the minority dopant (donor) quasi-Fermi level due to occupation of higher energy levels by the photoexcited electrons participating in the radiative recombination. At extremely low excitations almost all donors (as minority dopants) are empty and thus positively charged. In addition to these, the equivalent number of negatively charged as well as many neutral acceptors (as majority dopants) are present in the material. Therefore, in the presence of the potential fluctuations, the starting value of the quasi-Fermi level for donors is minus infinity whereas for acceptors it is a constant, which does not change much under low excitations. Such an approach adequately explained the experimentally observed excitation intensity dependent spectral shifts, but failed to explain the pronounced asymmetry of the PL.

In this work we present a complete quantitative theory of cw DAP PL in compensated semiconductors for the case of $T = 0$ K. In contrast to the simplified model [3], we now consider a random

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distribution of both donor and acceptor energy levels with the probability determined by the free energy of the Coulomb fluctuations frozen at the sample's growth temperature. Moreover, this approach is completely symmetrical with respect to the type of majority dopant; thus, if donors are majority dopants, the quasi-Fermi level starting value for acceptors tends to plus infinity, whereas for donors it is a finite quantity (see also below).

2 Theory As before [2–4] we begin with the expression for the energy $h\nu$ of the emitted photon of the DAP PL in the presence of the potential fluctuations

$$h\nu = E_{\mathrm{DA}} + \frac{e^2}{\varepsilon R} + U[\varphi]\,. \tag{1}$$

Here, the fluctuation term, $U[\varphi]$, has a collective nature and is determined by $\varphi(\boldsymbol{r}_{\mathrm{D}}) - \varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R})$, which is the difference between values of random potential at the sites of a given donor (with a coordinate $\boldsymbol{r}_{\mathrm{D}}$) and an acceptor, separated by the distance R; E_{DA} is the energy difference between the donor and acceptor levels in the absence of the Coulomb energy, $e^2/\varepsilon R$; e is the electron charge and ε is the static dielectric constant of the material. Further below, we shall use $E = h\nu - E_{\mathrm{DA}}$ as the emission energy, instead of $h\nu$.

Following, Ref. [3] we assume that under the steady-state excitation, in the presence of the potential fluctuations, the electrons occupy donor and acceptor levels below the corresponding quasi-Fermi levels, μ_{D} and μ_{A}, respectively. In this case the number of electrons on donors and acceptors will be determined by the step-functions $\Theta[\mu_{\mathrm{D}} - e\varphi(\boldsymbol{r}_{\mathrm{D}})]$ and $\Theta[\mu_{\mathrm{A}} - e\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R})]$, correspondingly, with μ_{D} and μ_{A} are to be self-consistently determined through the excitation intensity G ($\mathrm{s}^{-1}\,\mathrm{cm}^{-3}$). Therefore, the concentrations of neutral donors and acceptors averaged over the potential fluctuations (denoted by the angle brackets with the corresponding subscript) are defined as

$$N_{\mathrm{D}}^{(0)} = N_{\mathrm{D}}\langle\Theta[\mu_{\mathrm{D}} - e\varphi(\boldsymbol{r}_{\mathrm{D}})]\rangle_{\{\varphi\}}\,, \tag{2}$$

$$N_{\mathrm{A}}^{(0)} = N_{\mathrm{A}}\langle 1 - \Theta[\mu_{\mathrm{A}} - e\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R})]\rangle_{\{\varphi\}} = N_{\mathrm{A}}\langle\Theta[-\mu_{\mathrm{A}} + e\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R})]\rangle_{\{\varphi\}}\,, \tag{3}$$

where N_{D} and N_{A} are the total concentrations of donors and acceptors, respectively. Since the PL intensity depends on the concentration of neutral species, we present the DAP PL intensity $I_{\mathrm{E}}(G)$ per unit energy interval near E as:

$$I_{\mathrm{E}}(G) = 4\pi N_{\mathrm{A}} N_{\mathrm{D}} \int_0^\infty \mathrm{d}R\, R^2 W(R)\, P(R) \times \left\langle \delta\left\{ E - \frac{e^2}{\varepsilon R} + e[\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R}) - \varphi(\boldsymbol{r}_{\mathrm{D}})] \right\} \Theta[\mu_{\mathrm{D}} - e\varphi(\boldsymbol{r}_{\mathrm{D}})]\, \Theta[-\mu_{\mathrm{A}} + e\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R})] \right\rangle_{\{\varphi\}}. \tag{4}$$

Here $W(R) = W_{\max} \exp[-2R/R_{\mathrm{B}}]$ (where $W_{\max}$ is a pre-exponent and R_{B} is the Bohr radius of the shallowest impurity) is the probability of radiative transition of the electron from the donor to the acceptor [8] and the δ-function reflects the conservation of energy in the recombination process and $P(R)$ is a normalized probability distribution function for the inter-impurity separation. In the framework of the nearest-available-neighbor model (see, for example, [3, 9]) for compensated materials $P(R) \sim R^{-6}$. Since, the resulting expression for $I_{\mathrm{E}}(G)$ contains the exponential function $W(R)$ in the integrand, the power dependence of $P(R)$ does not play a mjor role, and one can put $P(R) = 1$ for simplicity. Furthermore, assuming 100% quantum efficiency, the integrated intensity of DAP PL coincides with G:

$$G = \int_{-\infty}^{\infty} I_{\mathrm{E}}(G)\,\mathrm{d}E = 4\pi N_{\mathrm{A}} N_{\mathrm{D}} \int_0^\infty \mathrm{d}R\, R^2 W(R)\, \langle\Theta[\mu_{\mathrm{D}} - e\varphi(\boldsymbol{r}_{\mathrm{D}})]\, \Theta[e\varphi(\boldsymbol{r}_{\mathrm{D}} + \boldsymbol{R}) - \mu_{\mathrm{A}}]\rangle_{\{\varphi\}}. \tag{5}$$

This equation determines $\mu_{\rm D}$, $\mu_{\rm A}$ as functions of G, when complemented by the charge neutrality condition:

$$N_{\rm D} - N_{\rm D}^{(0)} = N_{\rm A} - N_{\rm A}^{(0)} \,, \tag{6}$$

The averaging procedure defined as [10]

$$\langle (\ldots) \rangle_{\{\varphi\}} = \frac{\int (\ldots)\, \mathcal{D}\varphi \, \exp\left(-F\{\varphi\}/T_g\right)}{\int \mathcal{D}\varphi \, \exp\left(-F\{\varphi\}/T_g\right)}, \tag{7}$$

where we assume that the fuctuations are frozen at the temperature T_g. The free energy of Coulomb fluctuations

$$F\{\varphi\} = \frac{\varepsilon}{8\pi} \sum_{\boldsymbol{k}} k^2 (1 + R_s^2 k^2) \, (u_{\boldsymbol{k}}^2 + v_{\boldsymbol{k}}^2) \tag{8}$$

is expressed through the Fourier-components $u_{\boldsymbol{k}} = {\rm Re}\,(\varphi_{\boldsymbol{k}}\, {\rm e}^{i\boldsymbol{kr}}), v_{\boldsymbol{k}} = {\rm Im}\,(\varphi_{\boldsymbol{k}}\, {\rm e}^{i\boldsymbol{kr}})$ of the fluctuating potential $\varphi(\boldsymbol{r}) = \dfrac{1}{\sqrt{V}} \sum\limits_{\boldsymbol{k}} \varphi_{\boldsymbol{k}}\, {\rm e}^{i\boldsymbol{kr}}$ (V is the volume of the system). In principle, one should bear in mind that the screening radius R_s:

$$R_s^2 = \frac{\varepsilon T_g}{8\pi (N_{\rm A} - N_{\rm A}^{(0)})\, e^2} \tag{9}$$

depends on G, since $N_{\rm A}^{(0)}$ is excitation intensity dependent. However, such a dependence is rather weak, and if we assume acceptors as the minor dopant (see below) then at low G we expect $N_{\rm A}^{(0)} \ll N_{\rm A}$ and we will assume $R_s^2 = \varepsilon T_g/(8\pi N_{\rm A} e^2)$.

Equation (6) after averaging in Eqs. (2, 3) using Eqs. (7, 8) reduces to

$$N_{\rm A}\left[1 - {\rm erf}\left(-\sqrt{\frac{\varepsilon R_s}{2e^2 T_g}}\,\mu_{\rm A}\right)\right] = N_{\rm D}\left[1 - {\rm erf}\left(-\sqrt{\frac{\varepsilon R_s}{2e^2 T_g}}\,\mu_{\rm D}\right)\right], \tag{10}$$

where ${\rm erf}\,(x)$ is the error function. Now, using in Eq. (4) the Fourier representations $\delta(x) = \dfrac{1}{2\pi} \int\limits_{-\infty}^{\infty} {\rm d}A \, \exp\,(iAx)$, $\Theta(x) = \dfrac{1}{2\pi i} \int\limits_{-\infty}^{\infty} \dfrac{{\rm d}A}{A - i\delta} \, \exp\,(iAx)$, where $\delta \to +0$ we can calculate the Gaussian integrals over $u_{\boldsymbol{k}}$ and $v_{\boldsymbol{k}}$ using approach developed in Ref. [10]. The resulting integrals are calculated with the help of the formula ${\rm e}^{-\alpha^2 A^2} = \pi^{-1/2} \int\limits_{-\infty}^{\infty} {\rm d}y \, {\rm e}^{-y^2 - 2\alpha A y i}$ and then we obtain

$$I_{\rm E}(G) = 4\pi N_{\rm A} N_{\rm D} \int\limits_0^{\infty} {\rm d}R \, R^2 W(R) \frac{1}{2\pi} \sqrt{\frac{\varepsilon R}{e^2 T_g [R/R_s - 1 + \exp(-R/R_s)]}}$$

$$\times \, \exp\left\{ - \frac{\varepsilon R [E - e^2/(\varepsilon R)]^2}{4e^2 T_g [R/R_s - 1 + \exp(-R/R_s)]} \right\} \int\limits_{-\infty}^{\infty} {\rm d}y \, {\rm e}^{-y^2} \Theta(y - y_{\rm D}) \, \Theta(y_{\rm A} - y) \,. \tag{11}$$

Here

$$y_{\rm D} = \left[-\mu_{\rm D} + \frac{1}{2}\left(E - \frac{e^2}{\varepsilon R}\right)\right] \sqrt{\frac{\varepsilon R}{e^2 T_g [R/R_s - 1 + \exp(-R/R_s)]}} \,, \tag{12}$$

$$y_{\rm A} = \left[-\mu_{\rm A} - \frac{1}{2}\left(E - \frac{e^2}{\varepsilon R}\right)\right] \sqrt{\frac{\varepsilon R}{e^2 T_g [R/R_s - 1 + \exp(-R/R_s)]}} \,. \tag{13}$$

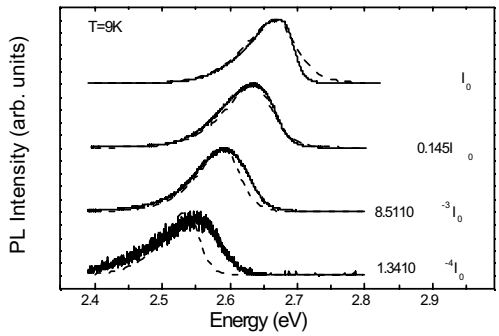

Fig. 1 Comparison of the calculated PL lineshapes for various excitation intensities (dashed lines) and the low temperature experimental data for compensated ZnSe:Cl, N (solid lines).

From the condition $y_D \le y_A$ we obtain the appropriate regions of R-integration as $E - \dfrac{e^2}{\varepsilon R} \le \mu_D - \mu_A$. At last, introducing the dimensionless quantities:

$$\widetilde{E} = \frac{\varepsilon R_s E}{e^2}, \qquad \xi = \frac{2R_s}{R_B}, \qquad \eta = \frac{e^2}{4T_g \varepsilon R_s}, \qquad \tilde{\mu}_{D,A} = \sqrt{\frac{\varepsilon R_s}{2e^2 T_g}}\,\mu_{D,A} \tag{14}$$

we arrive to the final expression

$$I_E(G) = \frac{\pi R_s^3 N_A N_D W_{max} \xi^3}{8\sqrt{\pi}} \sqrt{\frac{\varepsilon R_s}{e^2 T_g}} \int_0^\infty du\, \frac{u^{5/2}}{\sqrt{u - 1 + \exp(-u)}} \exp\left\{-\xi u - \frac{\eta(\tilde{E}u - 1)^2}{u[u - 1 + \exp(-u)]}\right\}$$
$$\times \left\{ \mathrm{erf}\left(\frac{\sqrt{2}\,u\tilde{\mu}_D - \sqrt{\eta}(\tilde{E}u - 1)}{\sqrt{u[u + 1 - \exp(-u)]}}\right) - \mathrm{erf}\left(\frac{\sqrt{2}\,u\tilde{\mu}_A + \sqrt{\eta}(\tilde{E}u - 1)}{\sqrt{u[u + 1 - \exp(-u)]}}\right)\right\} \Theta\left(\frac{1}{u} - \widetilde{E} + \frac{\widetilde{\mu}_D - \widetilde{\mu}_A}{\sqrt{2\eta}}\right). \tag{15}$$

Making analogous actions in Eq. (5) we get

$$G = 2\pi\, N_A N_D R_s^3 W_{max} \int_0^\infty du\, u^2 \exp(-\xi u) \int_{y_{min}}^\infty dy \exp(-y^2)$$
$$\times \left\{ \mathrm{erf}\left(\frac{\sqrt{2}\,u\tilde{\mu}_D + \sqrt{u - 1 + \exp(-u)}\; y}{\sqrt{u[u + 1 - \exp(-u)]}}\right) - \mathrm{erf}\left(\frac{\sqrt{2}\,u\tilde{\mu}_A - \sqrt{u - 1 + \exp(-u)}\; y}{\sqrt{u[u + 1 - \exp(-u)]}}\right)\right\}, \tag{16}$$

where $y_{min} = (\tilde{\mu}_A - \tilde{\mu}_D)\sqrt{u/[2(u - 1 + \exp(-u))]}$.

The Eqs. (15), (16) together with Eq. (10) are the central result of our theory for DAP PL of compensated semiconductors. It is useful to note that the theory possesses the natural property: its results remain invariant with respect to the change $N_D \rightleftharpoons N_A$, $\tilde{\mu}_D \rightleftharpoons -\tilde{\mu}_A$.

3 Comparison with experiment We used these formulas for quantitative description of our low-temperature experimental spectra of PL from ZnSe co-doped with N and Cl, where the donors are the majority dopant. In this situation, as we noted in the introduction, at comparatively low excitation intensities when the number of neutral acceptors is small the quasi-Fermi level for donors turns out practically constant whereas for acceptors it changes very noticeably with excitation. From Eqs. (10), (15), (16) one can see that the shape of the PL spectrum and its position in the energy scale at given excitation intensity are determined by the values: N_D/N_A, $\tilde{\mu}_D$, $\tilde{\mu}_A$, ξ, η, $e^2/(\varepsilon R_s)$, and E_{DA}. In Fig. 1 we show the normalized experimental data obtained for the sample with the nominal dopant concentrations $N_D = 6 \times 10^{17}$ cm^{-3} and $N_A = 3 \times 10^{17}$ cm^{-3} at different excitation intensities (1.34×10^{-4}, 8.51×10^{-3}, 1.45×10^{-1}, and 1 in arbitrary units for the data from the left to the right in Fig. 1)

together with the fitting according to our theory (the dashed curves, for which the ratios of the corresponding G values are the same as the experimental ratios). Numerically, we obtained the following: $N_D/N_A = 10$, $\tilde{\mu}_D = 0.906$, $\xi = 4$, $\eta = 0.1736$, $e^2/(\varepsilon R_s) = 0.0625$ eV, $E_{DA} = 2.785$ eV; in this case we obtained from Eq. (16) the next values for $\tilde{\mu}_A$: 3.41, 2.90, 2.50, and 2.22 in ascending order of the excitation intensity. As one can see from Fig. 1, the agreement between the theory and experiment is rather good, with the exception of the case of the lowest excitation intensity, where the experimental uncertainty is very large. The discrepancy with nominal concentrations of acceptors ($N_A = 3 \times 10^{17}$ cm^{-3}) in this sample could mean that uniform distribution of impurities corresponding to the nominal concentrations of dopants in the material does not occur.

Summarizing, we can conclude that the theory proposed in the present paper is capable to describe quantitatively main peculiarities of the DAP PL from compensated doped semiconductors. The theory admits further development, above all at the case of non-zero temperatures. Besides, it would be usefully to verify the non-uniform distribution of dopants in such materials.

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