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Electron-hole drops in ZnSe single crystals

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Edge luminescence is investigated in strongly excited ZnSe single crystals. It is established that at $T = 4.2$ K the luminescence is due to recombination radiation of electron-hole drops (EHD). Comparison of the theoretical calculations with the experimental data yielded the carrier density in the drop, $n_0 = 10^{18}$ cm^{-3}, and the EHD binding energy, 4–7 meV.

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Formation of electron-hole drops (EHD) in Ge and Si single crystals has been reliably established by numerous experiments.[1] It was shown[2,3] that in semiconductors with curved bands the drop formation is aided by the band structure. Preliminary calculations for direct-band crystals have shown that the drop energy is less than the energy of the ground state of the exciton, i.e., the drop is not stable. In[4–6], however, it was shown theoretically that drops can be produced in polar semiconductors, and the interaction of the electron-hole system with the optical phonons stabilizes the liquid phase versus the exciton gas. The most reliable EHD experiments were performed on CdS single crystals.[7–10] In addition, radiation of EHD was observed in GaAs,[11,12] CdSe,[9] ZnO.[13] The question of drop formation in direct-band crystals can nevertheless not be regarded as completely answered, so that additional investigations of EHD in direct-band semiconductors are needed.

We have investigated the edge luminescence of ZnSe single crystals under strong excitation and have found that the results can be explained by starting with the EHD model. It should be pointed out that edge luminescence of ZnSe was investigated in[14,15], but the singularities of the luminescence spectra were explained by using models of inelastic exciton-exciton and exciton-electron interaction.

The luminescence of ZnSe single crystals was excited by the third harmonic of an AYG:Nd^{3+} laser. The investigated single crystals were grown from the melt. The maximum excitation density when the beam was focused on the sample surface was $I_0 = 3$ MW/cm^2. The measurements were made on freshly cleaved single crystals which were immersed in liquid helium. The photoluminescence was registered with a grating monochromator having a linear dispersion 6 Å/mm. The spectra were recorded by photoelectric means with the use of synchronous detection.

The ZnSe photoluminescence spectra at various excitation levels are shown in Fig. 1. In the case of weak excitation the edge radiation consists of narrow lines with maxima $I_1 = 2.796$; $I_2 = 2.790$ and $I_3 = 2.781$ eV, due to luminescence of exciton-impurity complexes.[16] With increasing excitation level, the structure of the spectrum becomes smoothed out and only one broad band appears in the spectrum, with a maximum at $E_k = 2.785$ eV. The position of the maximum and the shape of this emission

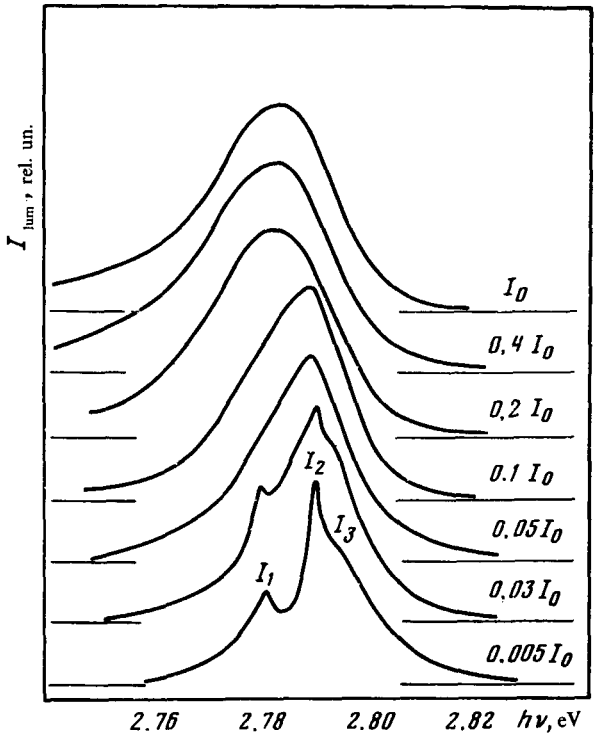

FIG. 1. Luminescence spectra of ZnSe single crystals.

line vary little with the sample excitation level. The maximum of the band is located 15 meV away from the ground state of the exciton. The exponent of the lux-intensity characteristic is close to unity, and at extremely high excitation intensities it saturates. Neither the half-width of the new band nor the other characteristic attributes make it possible to identify it with radiation produced in inelastic exciton-exciton or exciton-electron interaction.

In all probability the observed radiation is due to emission of a strongly degenerate electron-hole plasma that has condensed into EHD. Let us calculate the average energy per electron-hole pair as a function of the density of the pairs and let us determine the concentration corresponding to the minimum of the average energy. At $T=0$ in the ϵ_0 approximation,[2] the average energy per e-h pair in the electron-hole liquid is equal to:

$$< E(n) > \equiv < E(r_s) > = \frac{2.21}{r_s^2} - \frac{1.832}{r_s} + E_{\text{corr}}(r_s), \tag{1}$$

where $r_s=(1/a_0)(3/4\pi n)^{1/3}$; a_0 is the Bohr radius of the exciton, equal to 33 Å for ZnSe. The correlation energy $E_{\text{corr}}(r_s)$ was calculated on the basis of the results of[3]. Calculation with (1) shows that the energy minimum is equal to $\langle E(n)\rangle_{\min}=-0.94E_{ex}$, i.e., it is somewhat higher than the energy of the exciton ground state (Fig. 2). However,

allowance for the interaction of the electrons and the holes with the *LO* phonons lowers the minimum of the energy per pair of particles[4,5] so that the latter can condense into EHD. The carrier density corresponding to the minimum *e-h* pair energy is $n_0 = 10^{18}$ cm^{-3}. In the case of condensation this concentration should be equal to the concentration in the drop. Knowing the concentration of the energy minimum, we calculate the shape of the emission line and determine, by comparison with experiment, the "violet" end point of the spectrum, and by the same token the EHD binding energy.[1)] For direct allowed interband transitions, in the case of a quasi-equilibrium distribution of the electrons and holes in the bands, the emission line shape is described by the relation:

$$I(h\nu) = \left\{1 + \exp\left[\left(F_e + \frac{m_h}{m_e + m_h}(h\nu - E_g)\right)\frac{1}{k_B T}\right]\right\}^{-1} \left\{1 + \exp\left[\left(E_h + \frac{m_e}{m_e + m_h}(h\nu - E_g)\right)\frac{1}{k_B T}\right]\right\}^{-1}, \tag{2}$$

where F_e and F_h are the Fermi quasilevel for the electrons and holes. The "red" end point of the spectrum for direct transition is determined by the band filling

$$h\nu_{\text{red}} = h\nu_v - (F_e + F_h). \tag{3}$$

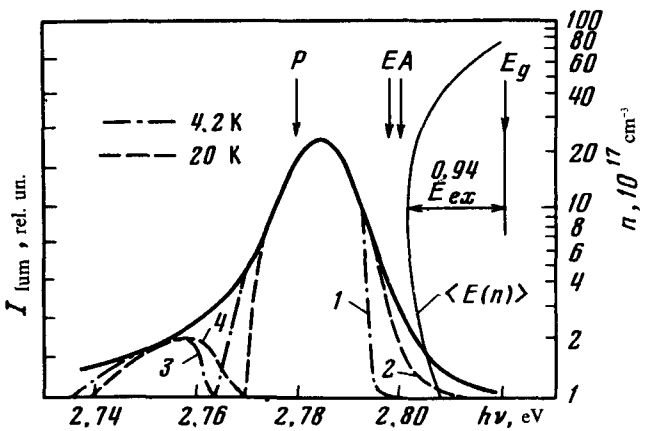

FIG. 2. Spectral distribution of EHD emission at maximum excitations (solid line), as well as line shape calculated from formula (2) (curves 1 and 2) and formula (4) (curves 3 and 4). The points show the dependence of the average energy $\langle E(n)\rangle$ per *e-h* pair on the concentration. The arrows *A*, *E*, and *P* mark the positions of the emission maxima of the free exciton and of the lines of the exciton-electron and exciton-exciton interactions, respectively.

The solid line in Fig. 2 corresponds to the experimental spectrum, while lines 1 and 2 correspond to the theoretical curves calculated at $n_0=10^{18}$ cm^{-3} for $T=4.2$ and 20 K, respectively. It follows from the comparison that the theory agrees satisfactorily with the experiment only in the central part of the spectrum. The theory and experiment do not agree in the short-wave regions of the spectrum, a fact noted also in other papers.[17] The long-wave radiation produced beyond the abrupt "red" end point of the theoretical spectrum may be due to multiparticle interactions of the carriers in the EHD, as well as to interactions with the phonons. We have attempted to estimate the contribution of the radiative transitions with participation of *LO* phonons to the long-wave wing of the emission spectrum, using the formula (we assume for simplicity that the matrix element of the transition is constant):

$$I(h\nu)=\int_0^{h\nu'}\sqrt{\epsilon}\sqrt{h\nu'-\epsilon}\left\{1+\exp\left[(\epsilon-F_e)\frac{1}{k_BT}\right]\right\}^{-1}\times\left\{1+\exp\left[(h\nu'-\epsilon-F_h)\frac{1}{k_BT}\right]\right\}^{-1}d\epsilon, \tag{4}$$

where $h\nu'=h\nu+E_{\text{phon}}-E_g$; $h\nu$ is the energy of the emitted photon. Curves 3 and 4 of Fig. 2 correspond to calculation in accord with (4) for $T=4.2$ and 20 K, respectively. We see that the interaction with the phonon leads to contraction of the "red" end point, although other mechanisms cannot be excluded.

The short-wave radiation undergoes reabsorption compared with the long wave radiation, and therefore this edge of the spectrum is distorted. It must be indicated that the "violet" edge is sensitive to the temperature of the radiating system of the nonequilibrium carriers. Since the electron temperature can differ from that of the lattice in the case of strong excitations,[17,18] it plays the role of one more parameter when it comes to comparing the theory with experiment. It is seen that for $T=20$ K the agreement between theory and experiment is better for the short-wave edge than at 4.2 K.

Thus, by comparing the experiment with theoretical calculations we can determine the EHD binding energy. Assuming that the binding energy is defined as the distance between the minimum of the energy per *e-h* pair and the energy of the exciton ground state, we obtain a value 4–7 meV. It should be noted that the EHD binding energy is determined more accurately from the enhancement spectra,[7,9] but in our case, because of the smallness of the coefficient, we were unable to measure the enhancement spectrum with sufficient accuracy.

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[1)]In the case of drops, the minimum of the *e-h* pair energy coincides with the "violet" end point of the EHD emission spectrum.[1]

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