# Study of electron–hole drops in ZnTe single crystals

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The luminescence spectra of ZnTe single crystals under strong optical excitation ($T = 4.2$ K) were investigated. It was observed that the luminescence spectrum consists of one emission line whose half-width and maximum depend little on the intensity of excitation. The results are explained on the basis of the model of emission of electron–hole drops (EHD). The binding energy of the drop ($\zeta_0 = 2$–$3$ meV) and the average carrier density in the drop ($n_0 = 2.5\times10^{17}$ cm$^{-3}$) are estimated by comparing the experimental data with the theoretical calculation of the emission line shape.

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Condensation of excitons into electron–hole drops (EHD) in direct-band II–VI semiconducting compounds differs from the drop formation in the indirect-band semiconductors Ge and Si, which have been sufficiently well investigated in this respect.[1] It follows from the theoretical estimates that the conditions for the appearance of EHD in typical direct-band II–VI semiconductors are less favorable than for Ge and Si. First, the carrier lifetime in the bands for the direct-band semiconductors are smaller by several orders of magnitude than for the indirect-band semiconductors, and this introduces its own peculiarities in the condensation process. Second, the presence of strong anisotropy and degeneracy of the bands in Ge and Si contributes to a lowering of the ground state energy of the EHD, thus greatly stabilizing the drop with respect to the gas of the free excitons.[3] However, in polar II–VI semiconductors the lowering of the ground state energy of the EHD is due to the strong interaction between the carriers and optical phonons. This question was considered theoretically for some semiconducting compounds in Refs. 3–5. It should be noted that the available experimental data [6–11] are far from sufficient to explain many singularities of the condensation of excitons into EHD in direct-band semiconductors.

The present paper deals, for the first time ever, with the question of drop formation in ZnTe single crystals. Luminescence of ZnTe at large excitation levels has been the subject of several studies, in which the singularities in the emission spectra were discussed on the basis of the exciton–exciton or exciton–electron interaction models, [12–14] or the model of Bose–Einstein condensation of polaritons of the upper branch.[15]

The luminescence of ZnTe single crystals was excited by the third harmonic of the emission of an AYG:Nd$^{3+}$ laser ($E = 3.56$ eV, $\tau = 10$ nsec, $f_{rep} = 12$ Hz). The luminescence measurements were made on freshly cleaved surfaces of crystals immersed in liquid helium ($T = 4.2$ K). The spectra were registered by a photoelectric method using synchronous detection; the linear dispersion of the spectral instrument was 6 Å/mm.

  

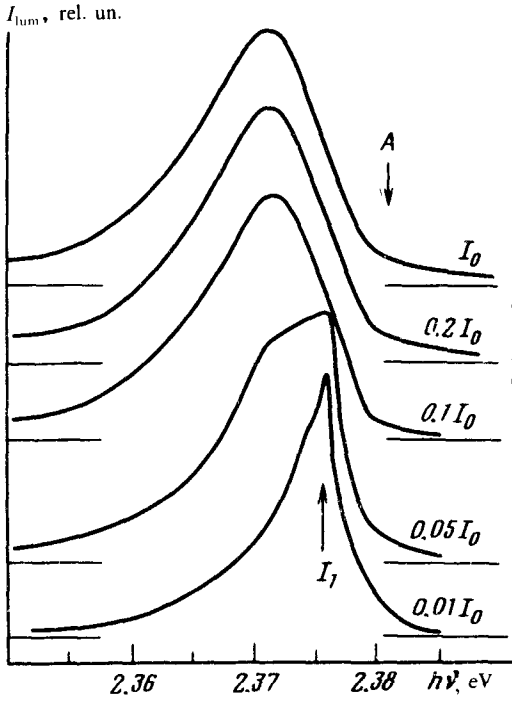


FIG. 1. Luminescence spectra of ZnTe single crystals as functions of the excitation level at $T = 4.2$ K and $I_0 = 3$ MW/cm$^2$. The arrows $A$ and $I_1$ denote the energy positions of the free exciton and of the exciton localized on the neutral zinc vacancy, respectively.

Figure 1 shows the luminescence spectra of ZnTe at various excitation intensities. At low excitation levels the spectrum has only one emission line with a maximum $E_1 = 2.2376$ eV. This line, according to Refs. 16 and 17, is due to emission of an exciton localized on a neutral vacancy of the zinc. In contrast to other studies, we did not observe more exciton-impurity complex lines, and this fact is one of the attributes of the quality of the investigated crystals. With increasing excitation level, a new line is formed on the long-wave wing of the spectrum, and further increase of the excitation makes this line more pronounced, with a maximum near $E_c = 2.371$–$2.372$ eV. The maximum of the new emission line does not shift, and the half-width ($\Delta \approx 12$ meV) increases only insignificantly (approximately 1–2 meV) when the excitation density is increased by one order of magnitude. The lux-intensity characteristic is initially linear with subsequent tendency for the exponent to decrease at extreme excitation intensities.

It seems to us that this behavior of the observed luminescence line can be explained by means of the model of emission of a strongly degenerate electron–hole plasma that has condensed into EHD. Calculation of the average energy per electron–hole pair shows that the minimum of this energy is close to the energy of the ground state of the exciton (Fig. 2). However, as indicated, allowance for the interaction of the electrons and holes with the *LO* phonons leads to a lowering of the minimum of the average energy, and by the same token to stabilization of the EHD. The carrier density in the drop corresponds to the energy minimum, and therefore this density can be used in the calculation of the shape of the EHD emission line. Estimates in accordance with

Ref. 2 show that the minimum of the average energy per $e$-$h$ pair is reached at a concentration $n_{\min} = 2.7\times10^{17}$ cm$^{-3}$. Knowing the concentration corresponding to the energy minimum, we calculate the emission line shape for several concentrations close to $n_{\min}$. For direct allowed interband transitions, in the case of a quasiequilibrium distribution of the electrons and holes in the bands, the emission line shape is described in the following manner:

$$I(h\nu)\sim\sqrt{h\nu-E_g}\left\{1+\exp\left[\left(-F_e+\frac{m_h}{m_e+m_h}(h\nu-E_g)\right)\frac{1}{kT}\right]\right\}^{-1}$$

$$\times\left\{1+\exp\left[\left(-F_h+\frac{m_e}{m_e+m_h}(h\nu-E_g)\right)\frac{1}{kT}\right]\right\}^{-1},$$

where $F_e$ and $F_h$ are the Fermi quasilevels. The "red" boundary of the spectrum is determined by the condition $h\nu_r = h\nu_v - (F_e + F_h)$. The "violet" boundary $h\nu_v$, in the case of drops, corresponds to a minimum of the $e$-$h$ pair energy, and can be used to determine the EHD binding energy. Fig. 2 shows the theoretically calculated emission-

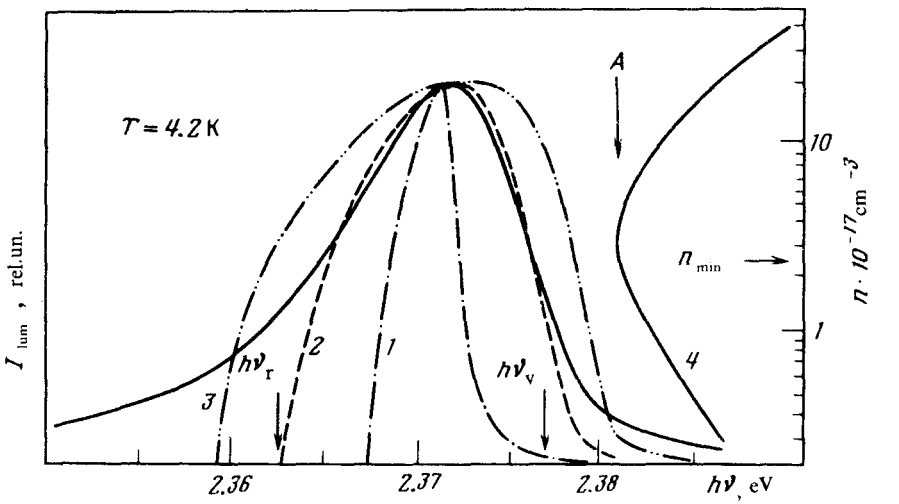


FIG. 2. Experimental (solid line) and theoretical (curves 1–3) EHD emission spectra. Curves 1, 2, and 3 correspond to concentrations $n = 10^{17}$, $2.5\times10^{17}$, and $4\times10^{17}$ cm$^{-3}$, respectively. Curve 4 is a plot of the ground state of the degenerate plasma against the carrier density (right-hand scale).

line shapes of a degenerate electron–hole plasma for three carrier densities close to $n_{\min}$. The same figure shows the experimental results. It is seen that the best agreement with theory takes place at $n_0 = 2.5\times10^{17}$ cm$^{-3}$. Attention is called to the strongly stretched long-wave edge of the radiation, which can be due either to interaction with phonons or to multiparticle interaction in the quasiparticle system.[5,18,19] The short-

edge of the emission line can be due either to deviation of the carrier distribution in the bands from quasiequilibrium, or to a continuous "background" caused by radiation in band–band transitions.[20]

Comparing the "violet" boundary with the exciton term in the state $n = 1$, we determine the binding energy in the EHD. As follows from Fig. 2, the EHD binding energy is approximately equal to $\zeta_0 = 2$–$3$ meV. It should be pointed out that it is very close to the theoretically calculated[4] energy of the ground state of the EHD in the close semiconducting compound cadmium telluride.


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