Electron-hole liquid in ZnSe single crystals

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The recombination radiation and light amplification spectra are investigated in ZnSe cubic single crystals under high-power photoexcitation. It is shown on the basis of the experimental data on spontaneous luminescence and amplification of light, as well as of theoretical calculations of the emission spectra and of the gain, that electron-hole droplets (EHD) are produced in ZnSe at $T = 4.2$ K. The factors that lead to distortion of the EHD parameters (the equilibrium concentration n_0 of the electrons and holes in the droplet and its binding energy) are identified. The correspondingly corrected parameters are $n_0 = 10^{18}$ cm^{-3} and $\varphi = 4 \pm 1$ meV.

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§1. INTRODUCTION

It has been established by now that an electron-hole liquid (EHL) can be produced in a number of semiconductors.[1,2] Following the work done on Ge and Si, extensive research has been started lately into compounds in which polariton effects play an important role. EHL have thus been observed in the indirect-gap semiconductors GaP[3] and AgBr,[4] and recently this phase of electron-hole system was noted in the direct-gap compounds CdS[5], ZnO,[6] ZnSe,[7] and ZnTe.[8] Considerable progress towards the understanding the carrier condensation into EHL in polar semiconductors was attained as a result of the theoretical work initiated by Keldysh and Silin[9] and continued by Beni and Rice.[10]

The principal method of experimentally investigating the liquid phase of the carriers as one of the nonequilibrium states of a semiconductor is analysis of the radiation from crystals, i.e., an investigation of the luminescence spectra, as well as study of the spectra of light amplification. For EHL to be produced, sufficiently large concentrations of nonequilibrium carriers (NEC) are needed, so that in direct-gap semiconductors, in view of the short lifetimes of the NEC and of the excitons, large pumping by an electron beam or by optical methods (laser excitation) is needed.

Luminescence in the region of the intrinsic-absorption edge at high excitation levels in II–VI compounds was the subject of many studies (e.g., Refs. 11 and 12), in which, however, the laws governing the luminescence are differently interpreted. Thus, the observed new bands in the edge emission spectrum are interpreted by mechanisms that describe different processes in the gas of the free excitons of high density (these are elastic and inelastic exciton-exciton and exciton-electron interactions) in an electron-hole plasma (EHP).

All the foregoing phenomena are quite new and have not been extensively studied. Many unsolved problems seem to be common to a large number of crystals. In particular, there has been very little research into the thermodynamics of an electron-hole system, especially in direct-gap semiconductors.

We have investigated the edge luminescence and the optical-gain spectra of cubic ZnSe single crystals under conditions of strong excitation and low temperatures. The distinguishing features of the luminescence and light amplification in single-crystal ZnSe are explained within the framework of the model of electron-hole droplets (EHD). In §3 are described the experimental results on recombination radiation and light amplification. The principal parameters of the liquid phase are established in §4 on the basis of the obtained experimental data and of the theoretical luminescence and amplification spectra in EHL.

§2. EXPERIMENTAL PROCEDURE

We chose for the investigation of the luminescence the purest ZnSe single crystals grown from the gas phase and from the melt. The crystal quality was determined from the intensity of the emission of the exciton impurity complexes at low temperatures. The purest ZnSe samples were taken to be those in which the luminescence intensity of the exciton impurity complexes was minimal. Luminescence was observed from freshly cleaved surfaces of single crystals immersed in liquid helium.

The excitation source was the third harmonic of an AYG:Nd^{3+} laser ($h\nu = 3.51$ eV) operating intermittently ($f_{\text{rep}} = 12.5$ Hz, $\tau_p = 10$ nsec). The maximum excitation density in the plane of the sample reached 10^{24} cm^{-2} sec^{-1}. The luminescence signal was analyzed with

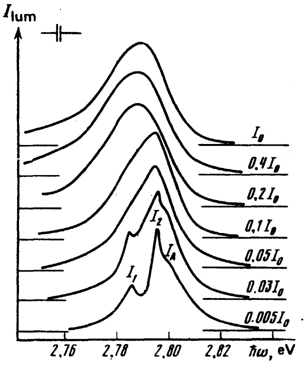

FIG. 1. Spontaneous luminescence spectra of ZnSe single crystals vs the excitation level.

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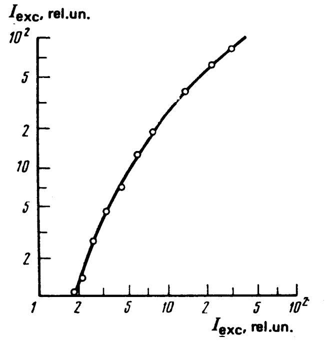

FIG. 2. Luminescence intensity vs excitation level (LIC) for ZnSe single crystals in the region $E_C = 2.786$ eV at 4.2 K.

a grating monochromator with linear dispersion 6 Å/mm. The spectrum registration was photoelectric, and synchronous detection was used.

To obtain the gain spectra, we compared the spectra of the spontaneous (I_{sp}) and amplified (I_{amp}) luminescence of a sample excited with a narrow strip of light. The strip width was ~0.05 mm, and the length was varied up to $l = 1$ mm, the excitation field along the strip remaining uniform. The dimensions of the excited region were monitored with a measuring microscope. The spontaneous luminescence, which was not subject to amplification or to reabsorption, since a thin surface layer was excited, was studied in a direction perpendicular to the plane of the sample [direction of I_{sp} in the inset of Fig. 3 (see below)]. We investigated the luminescence from the end face of the single crystal. This luminescence was amplified and passed through the entire length of the excited region. It is known[13] that the intensity of the spontaneous and amplified luminescence are connected by the relation

$$\frac{I_{amp}(\omega)}{I_{sp}(\omega)} = \frac{\exp[g'(\omega)l]-1}{g'(\omega)l}, \qquad (1)$$

where g' and l are respectively the resultant gain and the length of the excited region. Formula (1) was used to calculate the spectra of the optical gain.

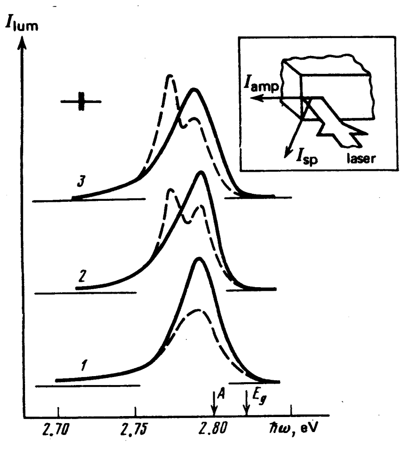

FIG. 3. Spectra of spontaneous (I_{sp}, solid line) and amplified (I_{amp}, dashed) luminescence at various excitation levels: 1—10^{23}, 2—$3\cdot10^{23}$, 3—$6\cdot10^{23}$ cm^{-2} sec^{-1}. The arrows A and E_g denote respectively the energy positions of the free exciton and of the width of the forbidden band in ZnSe at 4.2 K. The inset shows the experimental geometry.

§3. EXPERIMENTAL SPECTRA OF THE LUMINESCENCE AND OF THE LIGHT GAIN

Figure 1 shows the spectra of the spontaneous luminescence of single-crystal ZnSe as functions of the excitation level. At low excitation levels (~10^{22} cm^{-2} sec^{-1}) there are separated in the spectrum several weak lines with maxima $I_A \approx 2.80$, $I_2 = 2.795$, $I_1 = 2.786$ eV, due to luminescence of the free and bound excitons.[14] With increasing pump, the structure of the spectrum becomes smoothed out and only one wide band with a maximum at $E_c = 2.786$ eV. It is remarkable that further increase of the excitation level leads only to an increase of the radiation intensity, and the energy position of the maximum and the half-width of the new band remain constant. The half-width of the band, its energy position, the lux-intensity characteristics (LIC) do not make it possible to identify this band with the radiation produced by inelastic exciton-exciton or exciton-electron (hole) interaction, nor with the mechanism of a homogeneous electron-hole plasma. The foregoing properties are possessed by EHD radiation. In fact, when the EHD is formed, the concentration established in the droplet corresponds to the minimum average energy per electron-hole pair. With increasing excitation, the total concentration of the NEC is increased, as well as the volume occupied by the drops, up to a complete filling of the EHL space, but the concentration that determines the half-width and the energy position of the emission band remains the same in the droplets.

That EHD droplets are produced is attested also by the LIC shown in Fig. 1. At a low excitation level (< 10^{22} cm^{-2} sec^{-1}) the exponent of the LIC is close to 3, and with increasing pump it decreases. At maximum excitation, the LIC is close to linear. It was found in Ref. 15 that in the case of EHD the exponent of the LIC should range from 3 (corresponding to the start of the droplet formation) to 1 when the bulk of the excited electrons and holes recombine in the liquid phase.

The liquid phase of the NEC should have an appreciable gain (negative absorption), so that investigations of the spectral distribution of the gain constitute one of the methods of proving the existence of droplets. We have measured the spectra of the gain in ZnSe crystals as functions of the excitation level, using the procedure described in §2. Typical luminescence spectra obtained in geometries of spontaneous and amplified luminescence are shown in Fig. 3. These luminescence spectra were used to calculate by formula (1) the spectral behavior of the gain (Fig. 4). At low excitation level there is no gain (Fig. 4, curve 1). Starting with a certain excitation density, gain appears in the spectral region 2.76–2.78 eV and increases in absolute value with increasing pump. The energy position and the width of the gain spectrum remain practically constant (Fig. 4, curves 2 and 3). This might seem to correspond to the EHD emission mechanism, and these spectra are customarily used to determine the droplet parameters. An analysis of the results has shown, however, that the picture is

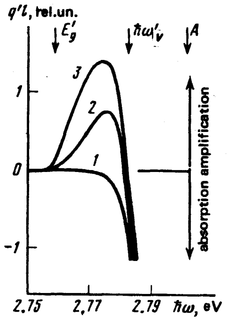

FIG. 4. Gain spectra vs. the excitation densities corresponding to the curves 1, 2, and 3 on Fig. 3. The arrows E_g', $\hbar\omega_v$, and A mark respectively the energy positions of the width of the renormalized forbidden band, of the violet edge of the gain spectrum, and of the free exciton.

more complicated. We shall return later to the calculation of the EHD parameters in ZnSe single crystals on the basis of a comparison of the spontaneous luminescence and gain spectra.

§4. EHD PARAMETERS

The main EHD parameters are the binding energy φ, i.e., the distance from the energy ground state of the electron-hole pair to the lower ($n=1$) exciton term, and the equilibrium carrier density n_0 in the droplet, corresponding to the minimum of $\langle E\rangle$. The simplest way of experimentally determining φ and n_0 is from the spectra of the optical gain. The liquid state of the NEC is a degenerate EHP, which should have considerable amplification properties on account of the inverted population in the spectral region $E_g' \leqslant \hbar\omega \leqslant E_g' + E_F^e + E_F^h$ (the inequality holds exactly at any temperature), where E_e^F and E_F^h are the Fermi energies of the electrons and holes, respectively. In the general case, for a degenerate EHD, the "red" boundary of the optical gain spectrum is determined by the renormalized gap width E_g', and the "violet" edge is given by

$$\hbar\omega_v=\mu=\frac{d}{dN}[N\langle E\rangle]=\langle E\rangle+n\frac{\partial}{\partial n}\langle E\rangle,$$

where $\mu = E_g' + E_F^e + E_F^h$ is the chemical potential of the system, and N is the total number of electrons and holes (n is their density). In the case of droplets, the second term in the right-hand side of (2) is zero.

Thus, by measuring the width of the gain spectrum we can determine the sum $E_F^e + E_F^h$ of the Fermi quasilevels, and by the same token the density of the pairs in the drop. On the other hand, the distance from the violet edge of the gain spectrum to the exciton ground state is equal to the droplet binding energy φ, since it is defined as the distance between the EHD ground energy state $\langle E\rangle$ and the free-exciton absorption. The parameters obtained in this manner for the EHD in ZnSe turned out to be $\varphi' = 16$ meV and $n_0' = 10^{17}$ cm^{-3}. This differs appreciably from the theoretical calculations of Beni and Rice,[16] who obtained $\varphi = 5$ meV and $n_0 = 3\times10^{18}$ cm^{-3}. It must be indicated that similar discrepancies between theory and experiment were observed also for some other direct-gap semiconductors.[17,18]

It seems to us that the explanation for this fact can be found in the peculiarity of light propagation in the case when EHD are produced. The excited region of the crystal is strongly inhomogeneous because of the subdivision of the NEC system into EHD (liquid phase) and the space between the droplets (which is in fact a low-density gas of free excitons). The recombination radiation that flows into the EHD should pass through the space between the droplets, which "cuts off" the short-wave of the spectrum on account of the Urbach intrinsic-absorption edge. This reabsorption affects mainly the radiation registered from the end face of the crystal. Distortions of this type should occur also in the case when the gain is measured by other known methods, for example by the Shaklee technique.[19]

We shall attempt to calculate theoretically the gain spectrum with account taken of the Urbach absorption edge $\alpha(\omega)$. Assume that the EHD occupies the fraction l_1/l of the radiating length l, and the space between the droplets occupies the fraction l_2/l. The measured gain $g'(\omega)$ is then

$$g'(\omega)=[g(\omega)l_1-\alpha(\omega)l_2]/l, \tag{3}$$

where $g(\omega)$ is the theoretical gain calculated, with allowance for the quasimomentum selection rule, from the formula[20]

$$g(\omega)\sim(\hbar\omega-E_g)^{1/2}\left[\left\{\exp\left[\frac{(\hbar\omega-E_g)m_h^*-E_F^e}{kT}\right]+1\right\}^{-1}+\left\{\exp\left[\frac{(\hbar\omega-E_g)m_e^*-E_F^h}{kT}\right]+1\right\}^{-1}-1\right], \tag{4}$$

where

$$m_h^*=m_h/(m_e+m_h),\qquad m_e^*=m_e/(m_e+m_h).$$

The gain $\alpha(\omega)$ for ZnSe single crystals near the intrinsic absorption edge was taken from Ref. 21. The ratio of the lengths l_1 and l_2 was chosen by comparing the theory with experiment.

The calculation results and the experimental gain spectrum are shown in Fig. 5. Curve 1 is the gain spectrum $g(\omega)$ without allowance for reabsorption [Eq. (4)]. Taking reabsorption into account, we obtain from (3) and (4) the plot for $g'(\omega)$ (curve 2). The points are the experimental data. We see that the agreement between the theoretical (with allowance for reabsorption) and experimental spectra is quite good.

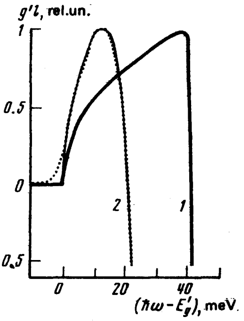

FIG. 5. Theoretical spectra of the EHD gain without (curve 1) and with allowance (curve 2) for reabsorption. The points mark the experimental gain spectrum.

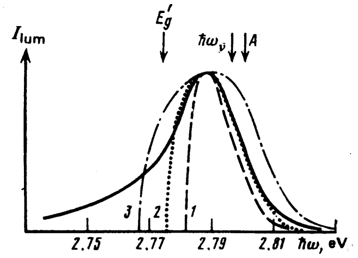

FIG. 6. Experimental (solid line) and theoretical (points, dashed, and dash-dot lines) EHD emission spectra. Curves 1, 2, and 3 were calculated for $T=40$ K and for NEC densities 5×10^{17}, 10^{18}, and 2×10^{18} cm^{-3}, respectively. The arrows E_g' and A are the same as in Fig. 4, while $\hbar\omega_v$ denotes the violet edge of the EHD spontaneous luminescence spectrum.

The gain spectra can thus not be used directly to determine the EHD parameters in direct-gap semiconductors. If a correction for reabsorption is introduced to reconcile the $g(\omega)$ spectrum, large errors appear in the short-wave part of the spectrum $g(\omega)$. In this respect the EHD spontaneous luminescence spectra contain more reliable information. In an investigation of the radiation from the surface of the sample (the I_{sp} direction on the inset of Fig. 3), the luminescence spectrum remains practically undistorted, and the depth of excitation is small, so that it becomes possible to compare the experimental data with the theoretical spectrum of the spontaneous luminescence of the EHD. The form of the luminescence spectrum for direct interband vertical transitions is described as follows[20]:

$$I(\hbar\omega)\sim(\hbar\omega-E_g)^{1/2}\left\{1+\exp\left[\left(-E_F{}^e+m_h{}^*(\hbar\omega-E_g)\right)\frac{1}{kT}\right]\right\}^{-1}$$
$$\times\left\{1+\exp\left[\left(-E_F{}^h+m_e{}^*(\hbar\omega-E_g)\right)\frac{1}{kT}\right]\right\}^{-1}. \qquad (5)$$

The calculation results are shown in Fig. 6. We see that agreement between the theoretical and experimental spectra is obtained only in the central part of the spectra. The difference between the long-wave wings of the spectra may be due to the part played in the radiation by the optical and acoustic phonons, which are not taken into account in the model. The short-wave part of the spectrum is stretched out because of the many-particle effects in the high-density NEC plasma.[22] It is possible, however, to estimate the principal parameters of the EHD, neglecting the already mentioned discrepancies between the theoretical and experimental spectra. The half-width of the spontaneous-spectrum band determines the carrier density in the droplet, and the distance between the violet boundary of the spectrum and the exciton ground state yields the EHD binding energy. The best agreement between the theoretical calculations with experiment was obtained for the density $n_0=10^{18}$ cm^{-3}, in which case the binding energy turned out to be $\omega=4\pm1$ meV. These values are quite close to the theoretical ones.[16]

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