Electron-hole liquid in CdSe crystals

V. S. Dneprovskiĭ, V. I. Klimov, and E. D. Martynenko
M. V. Lomonosov Moscow State University

(Submitted 26 January 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **33**, No. 6, 324–328 (20 March 1981)

The spectra of the spontaneous exciton luminescence of CdSe (8 K) single crystals, which were scanned in time with a resolution of 2×10^{-11} sec, are examined. The samples were excited by high-power ultrashort light pulses. The results of the spectrochronographic measurements are explained by the formation of an electron-hole liquid in a straight-band semiconductor.

PACS numbers: 71.25.Tn, 71.35. + z

Studies of the high-density excitons in non-straight-band semiconductors such as germanium and silicon have shown that at temperatures below some critical value and at a sufficiently high exciton concentration the latter condense into drops of the electron-hole liquid (EHL).[1] The question of the existence of the EHL in *straight-band* semiconductors has not been answered until now. In spite of the large amount of experimental data (see the review article[2] and the citations therein), it is not definitively clear whether the excitons condense into EHL drops with some equilibrium particle concentration in such semiconductors as CdS and CdSe, or only the formation of a nonequilibrium electron-hole plasma (EHP) is possible with a concentration that depends on the excitation intensity.

We examine in this paper the spontaneous exciton-luminescence spectra of highly excited CdSe crystals, which were scanned in time with a time resolution of 2×10^{-11} sec. The experimental results can be explained by the formation of an EHL in the semiconductor.

Lamellar CdSe single crystals with a thickness of 1–2 μm were investigated. The samples were excited by a train of 15–20 ultrashort pulses (USP) of light ($\lambda_S = 530$ nm) with a duration of 5×10^{-12} sec for an invidual pulse in the first half of the train. The pump radiation, which was polarized perpendicularly to the optical axis of the crystals, was directed at a 45° angle to the $(1\bar{2}10)$ plane. The diameter of the excitation region was chosen to be no larger than 50 μm in order to exclude amplification processes.

Figure 1 shows the luminescence spectra of a CdSe (8K) crystal at different pumping intensities (S). At high excitation levels ($S > 0.5$ MW/cm^2) three lines—P, L, and Q—were observed in the spectrum. The P line ($\lambda = 684.7$ nm at $S\sim0.6$ MW/cm^2; $\lambda = 685.3$ nm at $S\sim1$ MW/cm^2) was dominant in the $S < 1.5$-MW/cm^2 region; the L line was dominant in the interval from 3.5 to 9 MW/cm^2, and its position and width ($\lambda = 688$ nm and $\Delta\lambda = 6$ nm) were almost independent of the pump power; the Q line, which appeared on the long-wave wing of the L line at $S\sim9$ MW/cm^2, broadened considerably and shifted toward longer wavlengths with increasing excitation level.

The luminescence spectra at $T = 77$ K in the $S > 0.5$-MW/cm^2 region consisted of

 0021-3640/81/06308-05$00.60

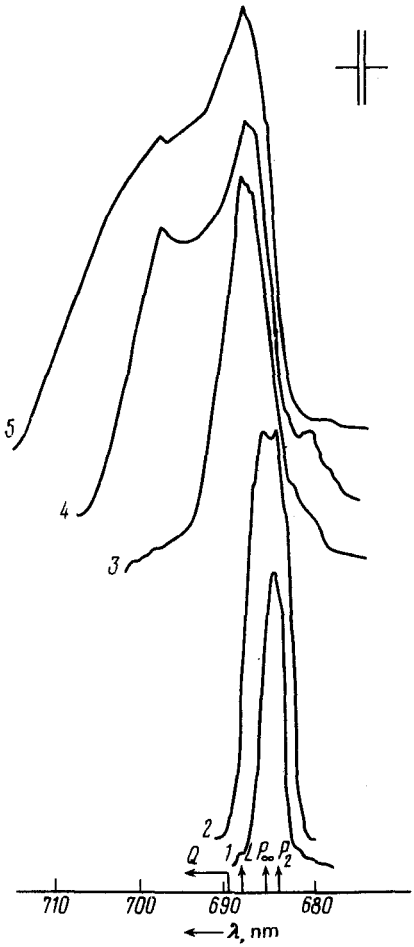

FIG. 1. Luminescence spectra of CdSe (8K) for excitation by a train of ultrashort pulses: 1) $S = 0.006S_0$, 2) $S = 0.02S_0$, 3) $S = 0.07S_0$, 4) $S = 0.5S_0$, 5) $S = S_0$; $S_0 = 100$ MW/cm^2.

two lines—P and Q. The P line was dominant at $S < 2$ MW/cm^2, while the Q line was dominant at $S > 5$ MW/cm^2.

The special, high-transmission spectrograph, which we have used earlier[3] in conjunction with an FER-2 high-speed photoelectronic recorder (time resolution 20 psec and spectral resolution 1.5 nm), was used to investigate the time-scanned luminescence spectra of the CdSe crystals (8K). At $S \sim 20$ MW/cm^2 the L line (Fig. 2), whose width and position were almost unchanged with time ($\lambda \sim 688$ nm and $\Delta\lambda \sim 6$ nm), was dominant in the spectra after excitation. Within 40–60 psec the emission maximum was abruptly shifted toward shorter wavelengths to $\lambda \sim 685$ nm. The luminescence line subsequently shifted smoothly to $\lambda \sim 682$ nm. The delay times (Δt) of the luminescence-intensity maximum and the characteristic times (τ) for the luminescence intensity decay by a factor of e were measured for different portions of the spectrum (Fig. 3). The delay of the L line did not exceed 20–30 psec (the time resolution of the method) and the P line appeared with a delay of 70–80 psec. The value of τ was 60 psec for the L line and ~ 20 psec for the P line.

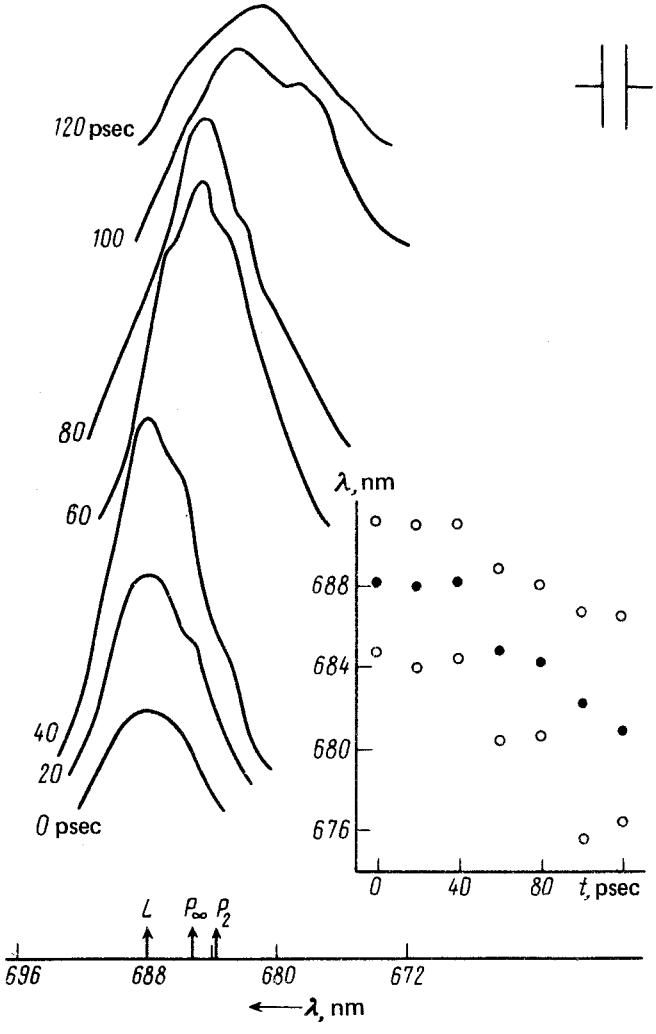

Fig. 2. Time-scanned luminescence spectra of CdSe (8 K and $S = 20$ MW/cm^2) for excitation by a single ultrashort pulse and graphs of the time variation of the position of the maximum of the luminescence line (•) and of its fronts (○) (the position of the fronts was determined from the 0.5 level of the intensity maximum).

The properties of the P line (position and movement of the maximum with a change in the pumping intensity) can be explained by the inelastic exciton-exciton scattering process.[4] The L line appeared at high pump powers at an exciton density of $\sim 10^{17}$ cm^{-3}. Its spectral properties—the variability of the position and width with a change in pump power as well as the variability of the line parameters in the time-scanned luminescence spectra—can be explained by the formation of EHL drops in the semiconductor. The existence of the EHL can also be used to explain the absence of the L line in the time-scanned spectra[3] at $T = 77$ K (a temperature above the critical value[2]).

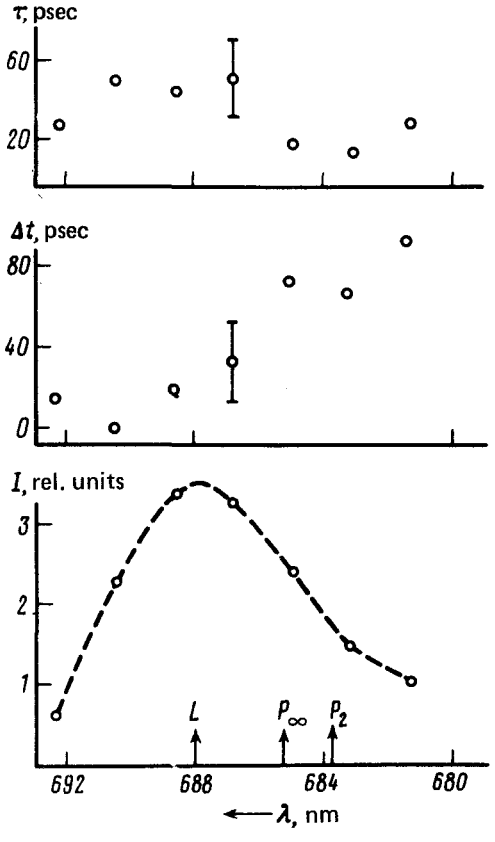

FIG. 3. Integrated luminescence spectrum of CdSe (8K) for excitation by a single ultrashort pulse and graphs of the dependence of τ and Δt on the luminescence wavelength.

Thus, only a high-density exciton gas apparently exists up to values of $S \sim 1.5$ MW/cm^2 in the excited volume, in which radiative recombination occurs primarily because of inelastic exciton-exciton collisions (the P line). At $S > 1.5$ MW/cm^2 (Fig. 1) the exciton density apparently reaches the critical value, at which EHL drops are formed (the L line). As the excitation level increases the volume of the liquid phase increases at some equilibrium concentration of particles (the shape and position of the emission line are unchanged). When the entire excited volume is filled with the EHL, a further increase in the pump power leads to an increase in the particle concentration—the system behaves like an EHP, the corresponding emission line (Q) is broadened, and it is shifted toward longer wavelengths. The results of the time studies can apparently be explained in the following manner. The electron-hole pairs produced by the excitation pulse in a time not exceeding 20–30 psec are condensed into drops. The number of particles in a drop decreases primarily because of the action of two processes: radiative recombination of the electron-hole pairs inside the drop and particle evaporation from its surface.[1] The first process leads to an exponential decrease of the number of particles in a drop and dominates in the initial stage of its breakup when the drop volume is quite large; the second process plays the principal role when the drop volume is small. Thus, the first 40–60 psec after the drop formation correspond to their exponential breakup with a characteristic time of 60 psec, which is then replaced by rapid evapora-

tion (the transition from the L to the P line in the time-scanned spectra). The subsequent shift of the luminescence line toward shorter wavelengths is apparently attributable to the increased probability of exciton scattering into states with low quantum numbers as their concentration decreases (the transition from the P_∞ line to P_2).

We estimated the concentration of electron-hole pairs and the EHL binding energy from the width of the L line and from the position of its short-wave fall-off (Fig. 1): 9×10^{17} cm^{-3} and 9 meV, respectively.

In conclusion, the authors wish to thank L. V. Keldysh for a discussion of the work, and G. O. Müller and O. N. Talenskiĭ for providing the CdSe samples.

1. T. Rice, J. Hensel, T. Phillips, and G. Thomas, Electron-Hole Liquid in Semiconductors (Russ. Transl., Mir, Moscow, 1980).
2. G. O. Müller and R. Zimmerman, Proc. 14th Int. Conf. Phys. Semicond., Edinburgh, 1978, p. 165.
3. V. S. Dneprovskiĭ, V. I. Klimov, and E. D. Martynenko, Dokl. Akad. Nauk SSSR 253, 1109 (1980) [Sov. Phys. Dokl. 25, 629 (1980)].
4. H. Liebing, P. Mengel, and W. Ruppel, Status Solidi B 72, 431 (1975).

Translated by Eugene R. Heath
Edited by S. J. Amoretty