Radiative recombination under conditions of screening of the Coulomb interaction in CdS crystals

V. G. Lysenko, V. I. Revenko, T. G. Tratas, and V. B. Timofeev

Institute of Solid State, USSR Academy of Sciences

(Submitted June 27, 1974)
ZhETF Pis. Red. **20**, 180–185 (August 5, 1974)

We investigate recombination radiation (RR) and the restructuring of the energy spectrum of CdS crystals in the case of high nonequilibrium densities of the electron-hole pairs. We show that at pair densities n_e, $n_h \geq 10^{18}$ cm^{-3} and at low temperatures ($T = 4.2$–100 °K) the RR spectrum corresponds to direct interband recombination of the electron-hole plasma.

In the limiting case of high nonequilibrium electron-hole (e-h) pair densities, when the interparticle distances r become comparable with the exciton Bohr radius r_B (i.e., $r_s \equiv r/r_B \sim 1$), the exciton concept becomes meaningless because of the screening of the Coulomb interaction, and the RR spectrum of the semiconductor should correspond to recombination of the electron hole plasma (EHP). Under these conditions the valence band and the conduction band become filled in accordance with the given e-h pair concentration and the temperature, and the energy spectrum itself becomes restructured as a result of exchange correlation interaction in the system of high-density electrons and holes.

We investigated the RR of high-purity CdS samples (donor and acceptor impurity concentration $\sim 10^{15}$ cm^{-3}) excited by a pulsed N_2 laser (power and single-pulse duration 2 kW and 10 nsec respectively, pulse repetition frequency 10^2 Hz). To decrease the contribution of the induced luminescence, the N_2-laser radiation was focused on the crystal into a spot measuring approximately 10 μ. The CdS spectrum was observed in a direction normal to the excited surface and was registered with a spectrometer of 0.2 Å resolution. A stroboscopic system for photoelectric registration has made it possible to perform time measurements with a resolution 2 nsec.

1. The principal changes occurring in the RR spectrum of CdS at $T = 4.2$ °K and when the pump power is increased from 10^5 W/cm^2 to 2×10^7 W/cm^2 are shown in Fig. 1a. The lower curve is the luminescence spectrum obtained after excitation with an ordinary mercury lamp. Figure 1 shows the exciton-impurity-complex (EIC) lines I_1 and I_2, the free exciton line A_T ($\lambda = 4853.4$ Å), and the position of the energy gap E_g. When the laser pump power is increased, a new band begins to grow on the long-wave side of the EIC line I_2 (or the M line).[1,2] When the number of e-h pairs averaged over the volume is increased, the width of this band increases, and its "red" boundary is appreciably shifted towards lower energies.

We shall show first that the position of this band on the energy scale, its width, and also the motion of the "violet" and "red" boundaries of its spectrum with increasing pair density correspond to the EHP recombination. To this end, using the method developed in[3,4], we calculate the average energy $\langle E(n)\rangle$ per e-h pair as a function of the pair density or of dimensionless parameter r_s. At $T = 0$ and at the CdS band parameters $m_e = 0.205$, $m_{h\parallel} = 0.7$, and $m_{h\perp} = 5.0$[5] we obtain for the average energy per pair the following expression (in meV):

$$\langle E(n)\rangle = \langle E_{kin}\rangle + \langle E_{exch}\rangle + \langle E_{corr}\rangle$$

$$= 61.4/r_s^2 - 52.9/r_s + \langle E_{corr}\rangle, \text{ meV} \qquad (1)$$

The values of $\langle E_{corr}\rangle$ for different r_s and n are listed in the table. The calculated position of the minimum of $\langle E(n)\rangle$ corresponds to $r_s \sim 2$ and $n \sim 2 \times 10^{18}$ cm^{-3}, and practically coincides with the nearest A_T exciton term.

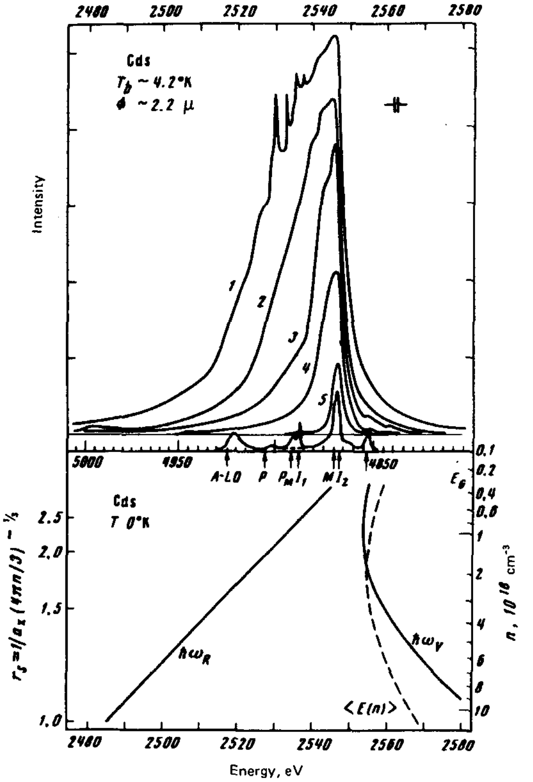

FIG. 1. a) Recombination radiation spectra (1—5) at respective excitation-power densities 16 mW/cm^2, 5 mW/cm^2, 1.4 kW/cm^2, 440 kW/cm^2, and 150 kW/cm^2. b) Dependences of the average energy $\langle E(n)\rangle$ per pair of particles, and of the "violet" and "red" boundaries $\hbar\omega_V$ and $\hbar\omega_R$ of the recombination spectrum, on the carrier density n in the plasma or on the dimensionless parameter r_s.

r_s	1	1.5	2.0	2.5
n, cm^{-3}	$1.13\cdot10^{19}$	$3.35\cdot10^{18}$	$1.41\cdot10^{18}$	$7.23\cdot10^{17}$
$<E_{corr}>$ meV	22.8	18.7	16.3	14.6

The obtained value of $\langle E(n)\rangle$ was then used to determine the "violet" and "red" boundaries of the recombination spectrum at different densities of the e-h plasma. At $T=0$, the "violet" boundary $\hbar\omega_V$ corresponds to recombination directly from the Fermi surfaces of the electron and hole bands, and is equal to the chemical potential W of a system of N electron-hole pairs:

$$\hbar\omega_V \equiv W = \frac{d}{dN}[N < E(n) >] = < E(n) + n\frac{\partial}{\partial n} <E(n)> . \qquad (2)$$

The "red" boundary of the RR spectrum, neglecting the dependence of the corrections to the kinetic energy on k, is shifted relative to $\hbar\omega_V$ towards lower energies, by an amount equal to the sum of the Fermi energies of the electrons and holes $\mu_e^0 + \mu_h^0$. The calculated dependences of $\hbar\omega_V$, $\hbar\omega_R$, and $\langle E(n)\rangle$ on the density n or the parameter r_s at $T=0$, shown in Fig. 1b, describe satisfactorily the position and the motion of the boundaries of the RR spectrum, as well as the width of the spectrum, as functions of the average number of the pairs in the plasma.

2. Figure 2 shows the form of the RR spectrum of an e-h plasma at different temperatures and at a practically constant pair density averaged over the volume (the pump was constant at $j\sim5\times10^6$ W/cm^3. We point out first that owing to thermodissociations there are no EIC in the spectra above 25 °K. With increasing temperature, the RR band of the e-h plasma broadens, mainly as a result of the smearing of the violet part of the spectrum. This smearing corresponds to temperature broadening of the electron and hole distribution functions. We have attempted to approximate the shape of the e-h plasma spontaneous-recombination spectrum by means of an expression that is valid for the model of noninteracting particles. Recognizing that the interband transitions have a directly allowed character, and assuming a quasiequilibrium distribution in the electron and hole bands, we obtain for the shape of the spontaneous spectrum

$$I_{sp}(\hbar\omega, \mu_e^T, T) \sim \sum_{\mathbf{k}_e = -\mathbf{k}_h = \mathbf{k}} f_e f_h \delta[\hbar\omega - \epsilon_e(\mathbf{k}) - \epsilon_h(-\mathbf{k})] . \qquad (3)$$

Here

$$f_{e,h} = \left[1 + \exp\frac{\epsilon_{e,h}(\mathbf{k}) - \mu_{e,h}^T}{k_0 T}\right]^{-1}$$

are the electron and hole distribution functions, μ_e^T and μ_h^T are the Fermi quasilevels, and $\hbar\omega$ is the energy reckoned from the "red" boundary of the spectrum. The dashed lines in Fig. 2 are the result of approximating the shape of the spectrum with allowance for reabsorption, and at the values of the parameters n and T indicated for each spectrum. The correction for reabsorption reduces to multiplication of (3) by the factor $\{1 - \exp[-\alpha(\hbar\omega)l]\}/\alpha(\hbar\omega)l$, where l is the carrier diffusion displacement length ($l\sim1.5\ \mu$), and $\alpha(\hbar\omega)$ is the absorption coefficient ($\alpha < 0$ in the case of amplification).

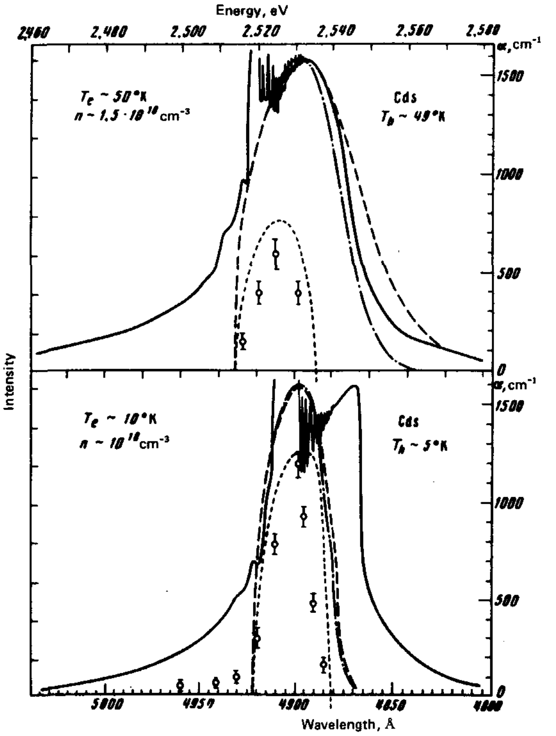

FIG. 2. Recombination radiation spectra (solid) and amplification spectra (circles) for EHP at $T=5$ and 49 °K. The dashed and dash-dot lines show the approximations of the spectrum shapes for the noninteracting-particle model without and with allowance for reabsorption, respectively.

Figure 2 shows, for 5 and 49 °K, the measured (circles) and calculated (points) distributions of the gain. The spectrum of the gain $\alpha(\hbar\omega)$ is connected with the shape of the spontaneous luminescence spectrum $I_{sp}(\hbar\omega)$ by the relation

$$\alpha(\hbar\omega) \sim I_{sp}(\hbar\omega)\left[\exp\frac{\hbar\omega - \mu_e^T - \mu_h^T}{k_0 T} - 1\right] . \qquad (4)$$

At helium temperatures, an e-h plasma of density $\sim10^{18}$ cm^{-3} is characterized by large gains or negative-absorption coefficients ($\alpha \gtrsim 10^3$ cm^{-3}). Therefore in the region of the maximum values of $\alpha(\hbar\omega)$ and when the condition $\alpha l \gtrsim 1$ is satisfied the RR experiences a strong amplification (lasing is observed if feedback is present in the system). As a result, intense narrow peaks with a faster-than-linear dependence on the power density and on the dimensions of the excitation region appear in the corresponding region of the spectrum (see Figs. 1 and 2). We emphasize that at helium temperatures the position of the maximum of the induced luminescence (of the maximum of the gain curve) of an e-h plasma with equilibrium density $\sim10^{18}$ cm^{-3} coincides exactly with the so-called P band, which was previously attributed to exciton-exciton collisions.[6,7]

We note in conclusion that at helium temperatures and at average e-h pair volume concentrations exceeding $\overline{n} > 10^{16}$ cm^{-3}, the EHP and electron-impurity complex bands in the spontaneous RR spectra of CdS (I_2 and M bands) are observed simultaneously. This means that regions that differ greatly in their e-h density are produced in the volume of the crystal. It is important that the position of the minimum of the average energy pair of particles $\langle E(n) \rangle$ estimated from the amplification spectra at helium temperatures and for pair density $\sim 10^{18}$ cm^{-3}, is localized approximately 10 meV below the exciton term A_T. It is therefore convenient for the nonequilibrium carriers to become condensed into plasma bunches having the equilibrium density value for the given T ($\sim 10^{18}$ cm^{-3}), and this may be one of the causes of the observed inhomogeneity in the carrier volume density.

A detailed discussion of the kinetics and of the spectral properties of EHP recombination radiation in CdS crystals will be published separately.

[1] S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Comm. **12**, 223 (1973).
[2] A. F. Dite, V. I. Revenko, V. B. Timofeev, and P. D. Altukhov, ZhETF Pis. Red. **18**, 579 (1973) [JETP Lett. **18**, 341 (1973)].
[3] W. F. Brinkman, T. M. Rice, P. W. Anderson, and S. T. Chui, Phys. Rev. Lett. **28**, 961 (1972); W. F. Brinkman and T. M. Rice, Phys. Rev. **7B**, 1508 (1973).
[4] M. Combescot and P. Nozieres, J. Phys. C5, 2369 (1972).
[5] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).
[6] C. Benoit a la Guillaume, J. M. Debever, and F. Salvan, Phys. Rev. **177**, 567 (1969).
[7] D. Magde and H. Mahr, Phys. Rev. Lett. 24, 890 (1970).