Condensation of nonequilibrium electron-hole pairs near impurity centers in cadmium sulfide crystals

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(Submitted July 1, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 3, 157–160 (5 August 1976)

It is shown that at low temperatures the nonequlibrium electron-hole (e-h) pairs are bound with shallow neutral impurity centers to form multiparticle complexes that serve as nuclei for condensation into an electron-hole liquid.

PACS numbers: 71.80.+j, 78.60.Dg

The question of the origin of the so-called M bands in the emission spectra of straight-band semiconductors at low temperatures has remained unclear to this day. These bands lie near the exciton-impurity-complex (EIC) lines, as a rule on the low-energy side, and appear in the spectra at average e-h pair densities $\bar{n}_{e,h}$ on the order of the concentration n_d of the corresponding defects with which the EIC are connected. The appearance of the M bands in CdS and CdSe crystal is attributed in[1] to biexciton emission. In[2,3], however, serious arguments are advanced against the biexciton interpretation of the origin of M bands, and it is shown in particular that they are closely connected with the corresponding impurity centers in CdS crystals. We note that the mechanism proposed in[2]

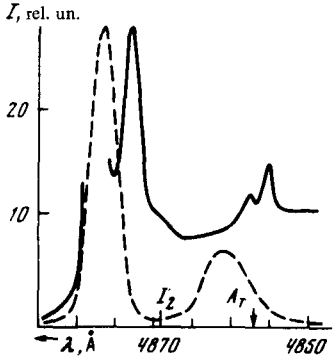

FIG. 1. Excitation spectra from the region of the maximum and on the long-wave edge of the M band at $T = 1.4$ °K and a pump $j \sim 3$ MW/cm^2. The solid and dashed curves correspond to the wavelengths 4876 and 4890 Å, respectively.

for the induced radiative decay of an EIC with emission of an acoustic phonon explains the nonlinear restructuring of the spectrum in the region of the $M(P_M)$ bands only at average e-h pair concentrations $n_{e,h} \lesssim n_d$ (see also[4]).

In this communication we attempt to show that the M band in the CdS spectra is the result of the binding of the nonequilibrium e-h pairs with a neutral donor center. The multiple EIC produced as a result of this binding is the nucleus of the condensation of the nonequilibrium carriers and excitons into an electron-hole liquid (EHL).[5]

We investigated the M-band photoexcitation spectra in high-purity CdS crystals in which the content of the donor impurities responsible for the EIC lines I_2 did not exceed 10^{15} cm^{-3}. The concentration of the acceptor impurities was several orders smaller, so that the spectra did not contain noticeable traces of the EIC I_1. The excitation spectra were recorded with a tunable dye laser. To decrease the induced radiative recombination at helium temperatures, the laser emission was focused on the crystal into a spot measuring 10×10 μ. This made it possible to excite average nonequilibrium e-h pair densities up to 10^{18} cm^{-3} by laser pumping.

Figure 1 shows the M-band excitation spectra measured for one of the investigated CdS samples at $T = 1.4$ °K. The experiment was performed in the following manner. Polarized light $\mathbf{E} \perp \mathbf{C}$ was applied to the crystal from a pulsed dye laser (lasing line half-width 1 Å, duration of single pulse 8 nsec, pulse repetition frequency 10^2 Hz). A double monochromator with resolution 0.2 Å registered continuously with the laser scan the luminescence signal at fixed frequencies within the M band. At large powers, two response spectra are observed in the excitation spectra, in the region of the exciton state $A_{n=1}$ and near the long-wave wing of the band I_2. The resonance near the EIC I_2 appears at pumps $j \gtrsim 10^5$ W/cm^2 and moves, as j increases up to 15 MW/cm^2, towards lower energies (about 2.5 meV) within the limits of the M-band width. The excitation spectra show that the M band can be excited not only via exciton generation but also directly by light of frequency close to the EIC I_2 line. This points to a connection between the M band and the impurity centers and excludes an interpretation of its origin within the framework of the biexciton concept.[1)]

Figure 2 illustrates the development of the emission spectrum in the region

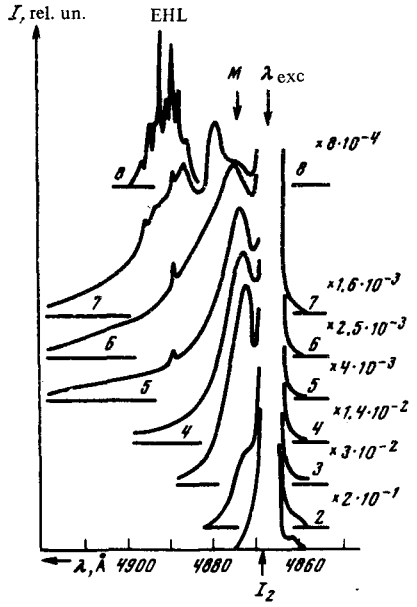

FIG. 2. Recombination spectra in the region of the M band following laser excitation (λ_{sec} = 4867 Å) and at T = 1.4 °K. Spectra 1—8 correspond to pumps 0.01, 0.02, 0.03, 0.3, 1, 3, 5, and 10 MW/cm^2 and to T = 1.4 °K.

of the M band when excited with laser light close in frequency to the EIC I_2 line. The M band is produced at an excitation power $j \gtrsim 10$ kW/cm^2. With increasing pump, in the interval 10^4—10^6 W/cm^2, and increase takes place in the band intensity and width, and its maximum shifts slightly towards longer wavelengths. At certain threshold pumps of the resonant excitation, $j \gtrsim 3$ MW/cm^2, the M band turns into an emission band corresponding to an electron-hole liquid with equilibrium e-h pair density $n_0 \sim 10^{18}$ cm^{-3} and binding energy $\phi \lesssim 12$ meV.[5] In Fig. 2, spectra 7 and 8 correspond to spontaneous and induced radiative recombination of the electron-hole liquid, respectively. Thus, in the same experiment we realized optical excitations of carriers in the immediate vicinities of the Fermi surfaces of the electron and hole bands in the electron-hole liquid.

The described experiments can be explained qualitatively by assuming that the weakly bound centers in CdS, particularly the neutral donors, serve as condensation centers for nonequilibrium carriers. Up to several dozen e-h pairs can be bound to each center to form multiparticle exciton-impurity complexes (poly-EIC) that are stable to decay into free excitons. At low exciton concentrations, the formation of poly-EIC is due to attraction to the impurity. With increasing number of localized excitons, the role of the impurity as a condensation center weakens (particularly because of screening effects). Nonetheless, the interparticle interaction leads to a lowering of the average energy per e-h pair and to further attraction between carriers. Starting with a certain number of pairs localized near the center, the role of the impurity becomes negligibly small and the average particle density near the center tends to a limiting value close to the equilibrium value of the density in the electron-hole liquid. As a result, the poly-EIC is transformed into a nucleus of the electron-hole liquid, corresponding to the CdS emission spectra to a restructuring of the M band into the emission band of the electron-hole liquid.

As a result of the interparticle interactions, the average energy per particle pair in the poly-EIC is different, but remains close enough to the EIC ground-state energy. The formation of such complexes can therefore result either from the binding of the free excitons with the center, and via laser emission of sufficient power, close in frequency to the EIC I_2 line. It is known that induced absorption accompanied by an increase of the number of pairs per unity in the poly-EIC, can be characterized by an exceedingly large oscillator strength.[7] If it is assumed that the emission probabilities of the poly-EIC and EIC are of the same order ($w_R \sim 10^9$ sec^{-1}), then at donor concentrations $n_d \sim 10^{15}$ cm^{-3} the effective excitation of the poly-EIC sets in at a resonant-excitation power $j > 10^4$ W/cm^2, which is in agreement with experiment. The M band appears at larger pumps as n_d increases.

If we compare the radiative time τ_M for the poly-EIC ($\tau_M < 2$ nsec in the M band) with the time τ_p of the radiative decay of e-h plasma of corresponding density, $n_{e,h} \sim 10^{16} - 10^{17}$ cm^{-3}, then we obtain for the amplification factor

$$\rho = \frac{\tau_p}{\tau_M} = \frac{|\Psi(0)|^2_{ex}}{n_{e,h}} \frac{1}{\pi a^3_{ex} n_{e,h}},$$

which determines the degree of electron-hole correlation, corresponding values $\rho = 30$ to 3. It follows therefore that the electron-hole correlations in poly-EIC are appreciable, and therefore the excitons in poly-EIC, in contrast to an electron-hole liquid, seem to retain their individuality, at least if the number of e-h pairs localized in the field of the center is not large. We note finally that in the case of an electron-hole liquid there would be no "gap" in the M-band excitation spectra.

The authors thank L. V. Keldysh, É. I. Rashba, and T. G. Tratas for exceedingly useful discussions.

[1)]The maximum in the excitation spectrum near EIC I_2 cannot be the result of resonant two-photon excitation of a biexciton, for in this case the biexciton emission line should be shifted by half the binding energy of the biexciton towards lower energies relative to the line of two-photon resonant absorption.[6] Under the conditions of our experiment the maxima of the photoexcitation and emission spectra of the M band practically coincide.

[1]S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Commun. **12**, 223, 227 (1973).
[2]A. F. Dite, V. I. Revenko, V. B. Timofeev, and P. D. Altukhov, Pis'ma Zh. Eksp. Teor. Fiz. **18**, 579 (1973) [JETP Lett. **18**, 341 (1973)].
[3]V. G. Lysenko and V. B. Timofeev, Fiz. Tverd. Tela **18**, 1030 (1976) [Sov. Phys. Solid State **18**, 588 (1976)].
[4]H. Liebing, P. Mengel, and W. Ruppel, Phys. Status Solidi [b] **72**, 431 (1975).
[5]V. G. Lysenko, V. I. Revenko, T. G. Tratas, and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 180 (1974) [JETP Lett. **20**, 77 (1974)]; Zh. Eksp. Teor. Fiz. **68**, 335 (1975) [Sov. Phys. JETP **41**, 163 (1976)].
[6]E. Hanamura, Solid State Commun. **12**, 951 (1973).
[7]A. A. Gagolin and E. I. Rashba, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 690 (1973) [JETP Lett. **17**, 478 (1973)].