Changes in the emission spectra of CdSe electron-hole plasma occurring as a result of rapid slowing down of the intraband relaxation

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A huge short-wave broadening of the luminescence spectrum of an electron-hole plasma (EHP) from 690 nm to the laser pump line (530 nm) as a result of excitation of CdSe (at 80 K) by strong ultra-short light pulses has been detected. A *B*-luminescence band, which is associated with the corresponding valence *B* subband, is clearly seen in the broadened spectrum. The broadening which was observed is attributable to the slowing down of the intraband energy relaxation of the EHP to a time comparable to the recombination time.

The polar scattering of *LO* phonons is the principal mechanism of the intraband energy relaxation of carriers in the direct-gap semiconductors such as CdS and CdSe. Since the time scales of this process are less than 0.1 ps, the time necessary for a complete energy relaxation should not exceed several picoseconds, even in the case of a strong interband excitation, where the excess carrier energy is close to 1 eV. As was noted in several places,[1–5] however, these times can be much larger. In the present letter, we will show that at high carrier concentrations the time of the intraband energy relaxation is comparable to the recombination time scale.

We studied lamellar CdSe crystals (at 80 K) of thickness 40–100 μm with interband excitation by ultrashort second-harmonic laser pulses from a neodymium laser (photon energy 2.339 eV) with a pulse length $\leqslant 10$ ps and energy $W = 5$–30 μJ (the corresponding concentrations of the excited carriers $n_e > 10^{18}$ cm^{-3}). In recording the emission spectra we projected an image of the crystal face, which scattered the enhanced luminescence light along with the image of the excited region, onto the spectrograph gap.

At $W = 13$ μJ (Fig. 1a) we observed a Q band (at 690 nm) of a spontaneous luminescence ($\lambda = 690$ nm) and an R band of a stimulated luminescence, whose position and shape are well described by the emission spectra of electron-hole plasma (EHP) (the temperature $T_e = 150$ K, $n_e = 1.2 \times 10^{18}$ cm^{-3}) which were calculated with allowance for the direct and indirect recombination of carriers (which is accompanied by the emission of an *LO* phonon).[5] Two amplification peaks are clearly seen in the stimulated luminescence: R_i (700 nm), which is linked with the indirect transitions and R_d (690 nm), which is linked with direct transitions [the spectral distance between them (25 ± 3 meV) is close to the energy of the *LO* phonon in CdSe, $\hbar\omega_{LO} = 26$ meV; Ref. 6]. An increase in the energy of ultrashort pump pulses to 30 μJ (Fig. 1b) produced radical changes in the luminescence spectrum in the form of the appearance of an emission "tail," which extends almost to the laser pump line, and a new luminescence *B* band (at 644.6 nm), which clearly is due to the recombination of

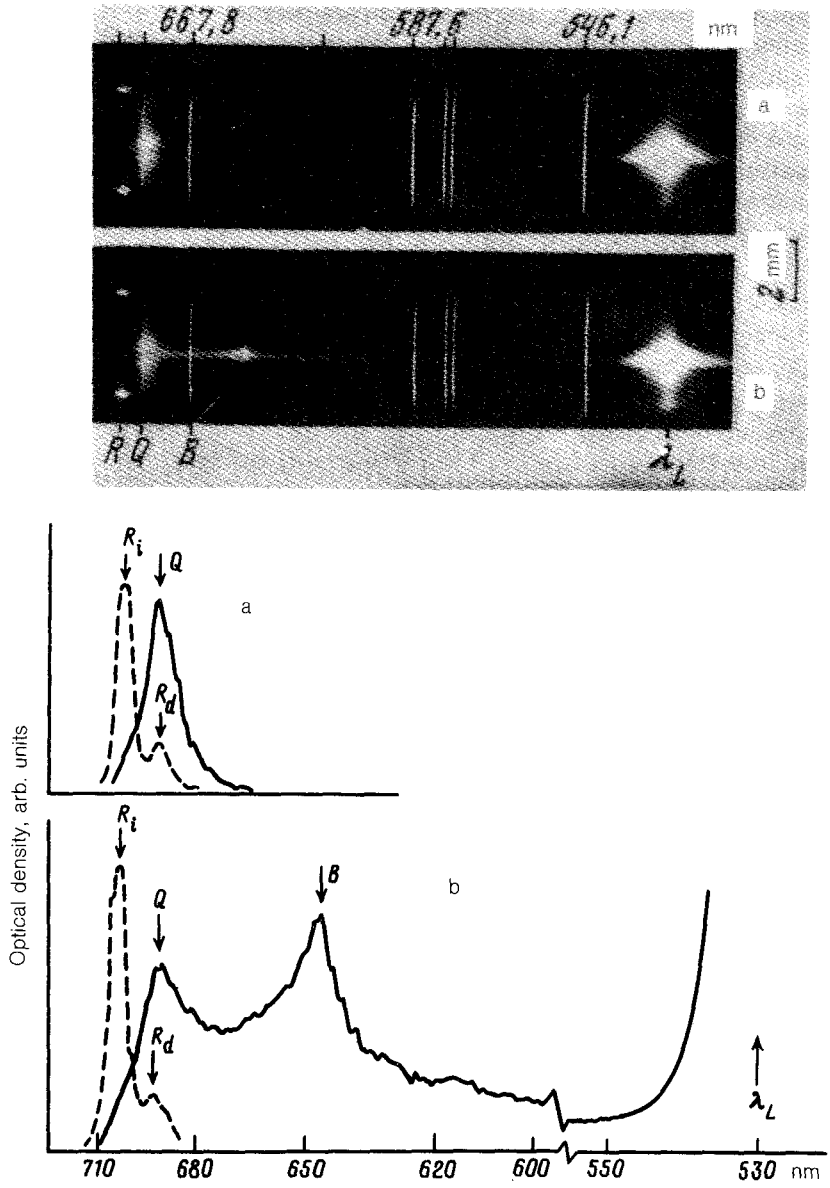

FIG. 1. Luminescence spectra of CdSe (at 80 K) and their densitometer traces at (a) $W = 13\ \mu$J and (b) 30 μJ (solid line—emission from the excitation region; dashed line—emission of an intensified luminescence scattered by a crystal).

holes from the B subband of the valence band, whose population is comparable to that of the A subband. This spectrum cannot be described by assuming the existence of an electron-hole plasma with a stabilized electron temperature. Clearly, this spectrum is due to the emission of a plasma, whose temperature during the recombination de-

creases from several thousand kelvin to several hundred kelvin (because the energy of the excitation quantum greatly exceeds the width of the band gap, the initial temperature of the electron-hole plasma is $T_e > 10^3$ K). The high temperature of the recombining electron-hole plasma accounts for the long short-wave emission tail and the effective filling of the valence B subband.

At $W = 13$ μJ (Fig. 1a) the photoexcited carriers thus lose virtually all of the excess energy over a time much shorter than the time scale of the plasma recombination [0.3–0.8 ns in CdSe (Ref. 5)] and the spectra records only the emission of rather cold EHP, whose temperature is about 150 K. At $W = 30$ μJ (Fig. 1b) the rate of the energy relaxation decreases to the extent that the emission is strongly affected by the superheated plasma at the initial stage of its cooling. The slowing-down effect is seen only near the maximum carrier concentration which manifests itself particularly clearly in the spatial distribution of the emission intensity: The B band and the short-wave luminescence tail are present in the emission from that part of the excitation region which has the largest carrier density (the central part).

The energy loss of the nondegenerate EHP, $W(\mathbf{q})$, as a result of the interaction with the LO phonon mode which corresponds to the wave vector $\mathbf{q}$, is given by

$$W(\vec{q}) = \hbar\omega_{LO} R(\vec{q}) \frac{\epsilon_\infty^2}{|\epsilon|^2} \left[N_{LO}(\vec{q}) + 1 - \exp\left(\frac{\hbar\omega_{LO}}{kT_e}\right) N_{LO}(\vec{q}) \right]. \quad (1)$$

where $N_{LO}(\mathbf{q})$ is the number of phonons in a state with the wave vector $\mathbf{q}$, ϵ is the longitudinal permitivity of the EHP ($|\epsilon|^2 = \epsilon_1^2 + \epsilon_2^2$; ϵ_1 and ϵ_2 are the real part and the imaginary part of ϵ, respectively), ϵ_∞ is the rf permittivity,

$$R(\vec{q}) = \frac{\Omega q^2}{2\hbar e^2} |V_{\vec{q}}|^2 \frac{\epsilon_2}{\epsilon_\infty^2} \exp\left(-\frac{\hbar\omega_{LO}}{kT_e}\right)$$

is the emission rate of LO phonons (ignoring the screening), V_q is the matrix element of the polar electron (hole)–phonon coupling[7], and Ω is the volume. The cooling of the EHP is accomplished primarily through phonons, whose wave vectors q_0^e and q_0^h correspond to the maximum emission rate of phonons by the electrons and holes, respectively. In a random-phase approximation we have $q_0^{e,h} = \omega_{LO}(m_{e,h}/3kT)^{1/2}$ (Ref. 8) (m_e and m_h are the effective masses of the carriers). The cooling of the EHP may slow down for two main reasons: 1) filling of the phonon modes with wave vectors close to $q_0^{e,h}$, which reduces the expression in the square brackets in Eq. (1), and 2) screening of the electron(hole)–phonon coupling, which increases $|\epsilon|$.

The filling of the phonon modes has a strong effect on the rate of the energy loss of the EHP when the temperature of phonons in the states with wave vectors q_0^e and q_0^h is close to the temperature of the EHP, T_e. The removal of energy from the EHP in this case occurs over a time τ_a characteristic of the decay of LO phonons to the acoustic phonons. In the case of CdSe with the lattice temperature 80 K, τ_a is approximately 4 ps (Ref. 9), while the relaxation time of the total excess energy of the electron-hole pair is close to 100 ps, consistent with the time scale for the recombination of the EHP. The critical concentrations $N_f^{e,h}$ for the filling can be found from the condition $R(q_0^{e,h})\tau_a = \exp(-\hbar\omega_{LO}/kT_e)$:

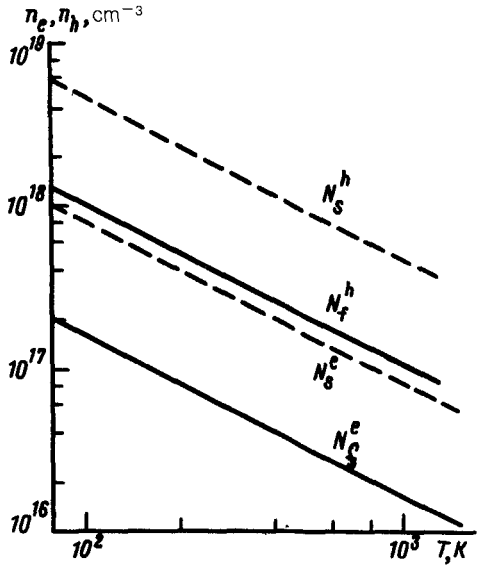

FIG. 2. Temperature dependence of the critical concentration for the filling of the phonon modes $N_f^{e,h}$ (solid line) and the screening of the electron(hole)–phonon coupling $N_s^{e,h}$ (dashed line); the indices e and h correspond to the electron–phonon coupling and hole–phonon coupling, respectively.

$$N_f^{e,h} = 0.055\hbar\omega_{LO}^2\epsilon_\infty^2 m_{e,h}/(\pi e^2\epsilon_p\tau_a kT_e), \tag{2}$$

where $\epsilon_p = \epsilon_0\epsilon_\infty/(\epsilon_\infty - \epsilon_0)$, and ϵ_0 is the static dielectric constant. Relation (2) shows that $N_f^{e,h} \propto m_{e,h}$; hence, $N_f^e < N_f^h$. An increase in the carrier concentration thus initially shuts off the electron channel of the energy relaxation and then the hole channel. The effective slowing-down of cooling of the EHP due to the filling of the phonon states occurs if $n_e > N_f^h$. This condition is satisfied for the concentrations obtained experimentally (at $T_e \geqslant 80$ K we have $N_f^h < 10^{18}$ cm^{-3}; Fig. 2). Note that an increase in the EHP temperature decreases the critical value of N_f^h. Consequently, the filling has a stronger effect in the initial stages of cooling of the EHP.

The square modulus of the dielectric constant near the resonance for $\epsilon_2(\omega = \omega_{LO}, q = q_0^{e,h})$ can be written in the form $|\epsilon|^2 = \epsilon_\infty^2(1 + \epsilon_2^2/\epsilon_\infty^2)$; here the critical values of the concentration $N_s^{e,h}$ for the screening are determined from the condition $\epsilon_2(\omega_{LO}, q_0^{e,h})/\epsilon_\infty = 1$. It follows from this condition that

$$N_s^{e,h} = 0.055\hbar\omega_{LO}^3\epsilon_\infty m_{e,h}/(e^2 kT_e). \tag{3}$$

For CdSe ($\epsilon_0 = 9.4$, $\epsilon_0 = 6.2$; Ref. 6) the ratio $N_s^{e,h}/N_f^{e,h} = 4.7$ (it does not depend on the temperature T_e or on the effective carrier mass). The screening comes into play, therefore, at higher carrier concentrations than those at which the filling occurs (Fig. 2). We note, however, that at concentrations $n_e > N_s^{e,h}$ the screening suppresses the phonon mode filling, since in this case we have $|\epsilon(\omega_{LO}, q_0^{e,h})|^2 \propto n_e^{-2}$ and $W(q_0^{e,h}) \propto 1/n_e$. The rate at which the phonon states are filled at high carrier concentration levels therefore decreases, rather than increases, with increasing n_e.

At carrier concentrations $n_e \geqslant 10^{18}$ cm^{-3}, which correspond to the excitation levels used by us, the phonon mode filling and the screening of electron–phonon coupling are highly efficient processes which clearly slow down appreciably the energy relaxation of the carriers and which lead to a considerable, experimentally observed, short-wave broadening of the EHP emission band.

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