Mixing of hole bands in electron-hole plasma of CdS crystal

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The dependence of the degree of polarization of recombination radiation of electron-hole plasma in CdS samples on the optical-pump intensity is investigated. With increasing pumping, the intensity of the forbidden-polarization emission (**E** ∥ **c**) increases more rapidly than that of the allowed polarization (**E** ⊥ **c**). It is proposed to attribute this phenomenon to a mechanism that mixes the hole bands (A, B, C) via interparticle interaction in the dense plasma. The short-range electron-hole potential needed to obtain qualitative agreement with the experimental results is estimated.

1. INTRODUCTION

The valence band in uniaxial CdS crystals, which stems from the $3p$ shell of the sulfur atom, is split by the spin-orbit interaction and by the hexagonal crystal field into three bands, A, B, and C (Ref. 1). The selection rules allow dipole transitions from band A to the conduction band, of s type, only when the electric field **E** of the light wave is perpendicular to the optical axis c; transitions from bands B and C are allowed at any polarization of the light.[2] Although these rules are rigorously satisifed only for Bloch waves with zero momentum, the deviations from them due to the presence in the exciton wave function of Bloch waves with momenta from a small but finite vicinity of the Brillouin-zone center are very small. It is usually assumed that in all the weakly-coupled states near the edge of the absorption band the holes come from the hole band A.

Mutual screening of the excitons makes them unstable as their density increases. It is known by now that in substances in which the carrier lifetime is long enough, at high densities the exciton gas either becomes ionized to form an electron-hole plasma (EHP) (the Mott transition), or condenses at sufficiently low temperatures into drops of a dense electron-hole liquid (EHL) the Keldysh transition).

In the direct-band semiconductor CdS the exciton lifetime is of the order of 10^{-9} s. Numerous experimental studies of strongly pumped CdS (see, e.g., Refs. 3–5) indicate that this time is sufficient to thermalize the carriers, but too short to complete the process of separation into EHL drops and a tenuous exciton gas under conditions where this should be expected to occur in analogy with Ge (Ref. 6) and Si (Ref. 7) and according to theoretical calculations.[3,8] Practically almost all experimental results agree with the idea that the tendency of the EHP to produce drops leads to a substantially inhomogeneous continuous distribution of the particle density in space. Besides the regions with high density that corresponds to a minimum of the free energy per particle pair (droplike clusters), there exist regions with a more rarefield plasma. With increasing pump, the total volume of the clusters increases. Although the characteristics of this distribution have not yet been investigated, what matters to us here is only the undisputed fact that the average plasma density increases with increasing pump.

As the carrier density in the EHP increases, the interactions between particles assume a larger role and the index that numbers the hole bands can no longer be expected to be a conserved quantum number. With increasing admixture of band B or C in band A, the ratio of the EHP luminescence intensities changes with change of polarization. Starting from these premises, we investigate here the influence of optical pumping on the spontaneous-luminescence spectra of EHP in both polarizations.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The CdS samples, grown from the gas phase in the form of platelets 4–45 μm thick, with the c axis in the plane of the platelet, were placed in a helium thermostat with nondepolarizing windows at a temperature ≈4.5 K. Figure 1d shows

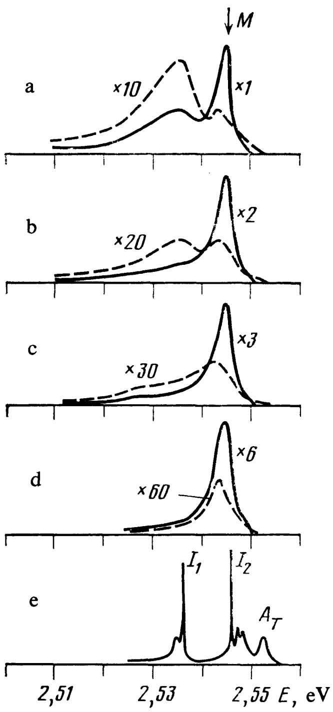

FIG. 1. Recombination-radiation spectra of CdS crystal in the polarizations **E**⊥**c** (solid curves) and **E**∥**c** (dashed curves) at various optical-pumping levels in MW/cm^2): a) 12, b) 5.5, c) 3, d) 1.4, e) excitation with mercury lamp. Crystal thickness $d = 4.5$ μm, temperature in thermostat 4.5 K, excitation-spot diameter ⩽10 μm.

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the luminescence spectrum of a crystal of thickness $d = 45$ μm with polarization $\mathbf{E} \perp \mathbf{c}$ at a low optical-pumping level, viz., excitation by the $\lambda = 365$ nm line of a mercury lamp. The lines of the free exciton (A_T) and of the excitons bound to a neutral donor (I_2) and to an acceptor (I_1) are marked. The density of minute impurities in this sample was $\sim 10^{15}$ cm^{-3}.

Strong optical excitation was produced with a pulsed nitrogen laser (pulse repetition frequency 500 Hz, pulse duration ≈ 10 ns). The radiation was focused on the crystal surface in the form of a spot with diameter $\leqslant 10\,\mu$m, thereby hindering the onset of stimulated emission in the EHP band.[3,5] The excited section of the surface was carefully chosen to minimize the possible depolarizing action of surface defects. The luminescence from the region on the opposite side of the crystal directly under the excitation spot was projected on the entrance slit of a DFS-24 monochromator. The emission spectra were recorded by a standard photoelectric system.

The spectra of the recombination radiation with allowed ($\mathbf{E} \perp \mathbf{c}$, solid lines) and forbidden $\mathbf{E} \parallel \mathbf{c}$, dashed lines) polarization at different pump levels 10^6–10^7 W/cm^2 and at a thermostat temperature $T = 4.5$ K are shown in Figs. 1a–1d. They show, besides the plasma radiation, also the so-called M band, whose origin is not yet completely clear.[9,10] Under the conditions of our experiments it is natural to relate the M band with the emission of I_2 complexes from regions where the EHP density is low, which are broadened and shifted towards the red part of the spectrum by interaction with the surrounding nonuniform plasma. It can be seen from Fig. 1 that the EHP radiation intensity increases with increasing pump, and that the forbidden-polarization intensity increases more rapdily than the allowed. This is illustrated by Fig. 2, which shows the ratio of the integral (in the 2.555–2.505 eV region) intensities $I_\parallel$ and $I_\perp$ of the forbidden- and allowed-intensity luminescence as a function of the optical-pump level H. The maximum degree of depolarization for this experiment reached $\approx 15\%$. We note that the intensity ratio at the maximum of the M band is practically independent of the pump and amounts to $\approx 4\%$, but does depend on the sample and on the choice of the location of the exciting spot on the crystal surface, ranging from 1 to 5% in different experiments. This background depolarization can be due not only to failure to satisfy the rigorous selection rules but also to surface defects. It is important to emphasize that the observed growth of $I_\parallel(H)/I_\perp(H)$ is not due to overheating of the system, for raising the thermostat temperature to 35 K (approximately the Fermi energy of the holes at a density $\sim 10^{18}$ cm^{-3}), at a constant pump level, altered noticeably the spectral distribution of the radiation (in particular, the M band almost vanished), but did not influence the polarization ratio within the limits of experimental error.

3. DISCUSSION

The observed growth of the ratio $I_\parallel(H)/I_\perp(H)$ can be naturally ascribed to the growth of the average EHP density. The denser the plasma the more frequent the collisions between its particles. The long-range part of the Coulomb potential is a smooth function of the coordinates and cannot lead to interband transitions. The hole mixing can cause only an interaction over distances on the order of size of the unit cell, where the potential depends strongly on the distance. For estimates it is convenient to separate this short-range part of the potential:

$$U = \Omega_0 U_0 \delta(\mathbf{r}), \qquad (1)$$

where Ω_0 is the unit-cell volume, and U_0 is the interaction between particles brought to within a distance $\sim \Omega_0^{2/3}$ between them. The process of EHP recombination without mixing is illustrated in Fig. 3a. The mixing of the hole bands can be illustratively represented as a virtual transition of an A-hole to band B via collision with another particle (an electron in Fig. 3b). The wave function of the hole from band A acquires as a result a wave-function admixture from band B, where other selection rules hold. The entire process of radiation having a forbidden polarization is shown in Fig. 3b. It is clear that since the collision is inevitable to amplitude of the "forbidden" transition will contain an extra power of the plasma density n. Since the relative velocities of the colliding particles are small, it is necessary to allow for their Coulomb interaction. This allowance reduces[11] to appearance, in all the matrix elements, of factors ψ_k for each entering or leaving pair of charged particles. For oppositely charged particles we have[12]

$$\psi_k^2 = (2\pi/ka)\,[1-\exp(-2\pi/ka)]^{-1}, \qquad (2)$$

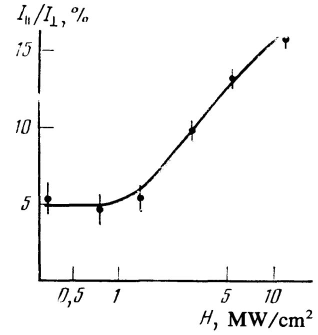

FIG. 2. Ratios $I_\parallel/I_\perp$ of integral emission intensities of Cd crystal in the polarizations E∥c and E⊥c vs optical pumping level H.

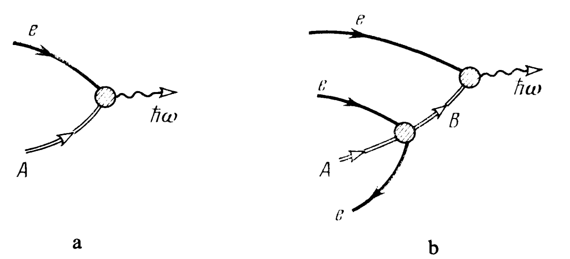

FIG. 3.

where a is the exciton Bohr radius and k is the electron momentum, since the velocity of the heavy hole can be neglected.[1] The factor (2) shows how the Coulomb attraction distorts the relative-motion plane wave in the "reaction region," where the mixing potential (1) acts. Since $ka < 1$, for electron-hole collisions the quantity ψ_k^2 increases the corresponding matrix elements by approximately an order of magnitude. The ratio of the transition probabilities is calculated in standard fashion and is equal to

$$\frac{I_{\parallel}}{I_{\perp}} = \left(\frac{p_B}{p_A} \frac{U_0 \Omega_0}{E_{AB}} \right)^2 \int \frac{d\mathbf{k}_1 d\mathbf{k}_2 d\mathbf{p}}{(2\pi)^9} \psi_{\mathbf{k}_1}^2 \psi_{\mathbf{k}_2}^2 \psi_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{p}}^2 n^e(\mathbf{k}_1) n^e(\mathbf{k}_2)$$
$$\times n^A(\mathbf{p}) [1 - n^e(\mathbf{k}_1+\mathbf{k}_2+\mathbf{p})] \left\{ \int \frac{d\mathbf{k}}{(2\pi)^3} \psi_{\mathbf{k}}^2 n^e(\mathbf{k}) n^A(\mathbf{k}) \right\}^{-1}, \tag{3}$$

where $E_{AB} = 0.016$ eV is the distance between bands A and B, $p_{A,B}$ are the matrix elements of the dipole transition from the valence bands to the conduction band, and $n(\mathbf{k})$ is the Fermi distribution function. For order-of-magnitude estimates we can put $p_A \sim p_B$, assume the temperature to be zero, and use in ψ_k^2 the Fermi momentum, after which we get

$$I_{\parallel}/I_{\perp} \sim (U_0 n \Omega_0 \psi_{k_F}^2 / E_{AB})^2. \tag{4}$$

In view of the foregoing estimate of ψ_k^2, it can be seen that a potential U_0 on the order of several electron volt, a density $n \approx 3 \cdot 10^{18}$ cm^{-3}, and $\Omega_0 \approx 10^{-22}$ cm^{-3} suffice to explain the observed phenomenon qualitatively. Detailed calculations of the spectrum shapes are difficult because there is no known exact experimental method of determining the density distribution in the EHP from the value of the pump. A fit, carried out in Ref. 3, of the experimental spectra for the allowed component to the simplest calculation of the line shape, without allowance for ψ_k^2 and for the red tails due to the quasiparticle finite lifetime, can claim only order-of-magnitude agreement.

4. CONCLUSION

The increase of the intensity ratio $I_{\parallel}/I_{\perp}$ with increasing optical pump can thus be related to interband hole mixing due to interparticle interaction in the plasma. We have considered electron-hole interaction, inasmuch as for an analogous interaction between holes the factor ψ_k^2 would lower, on account of the Coulomb interaction, the probability of finding two holes close to each other, and a much larger potential U_0 would be necessary to obtain agreement with the experimental results. The presence of the M band in the spectra made it impossible to separate the contribution of the plasma to the overall radiation length; it would be desirable to perform analogous experiments in purer samples with lower donor density.

It is known[3,4] that at low temperatures the electron-hole plasma of CdS absorbs radiation of frequency higher than $\omega_0 \approx 2.542$ eV and amplifies radiation with $\omega \lesssim \omega_0$. This makes it difficult for the M band radiation to undergo multiple reflections from the crystal faces. To demonstrate the multiple reflections play no significant role in plasma radiation, in some experiments the surface segment was excited by diffuse radiation— a "pit" was produced beforehand on the surface by high-power laser beam. An estimate shows that the radiation emerging through a perfect crystal boundary under the conditions of our experiments (the light recorded emerged at angles $\lesssim 0.1$ to the normal) is depolarized very little. The finite ratio $I_{\parallel}/I_{\perp}$ as the pump is decreased is caused therefore by the depolarizing action of the surface defects as well as by the change of the selection rules brought about by the change of the finite time of the light pulse, by the distribution of the carrier quasimomenta around the Brillouin-zone center, and others.

Band mixing should manifest itself also in a change of the dielectric constant ε_{ij} of a uniaxial crystal by a powerful optical pump.[13]

[1)] In the qualitative estimates we have neglected the effect of screening on the behavior of the wave function at the origin.

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