Study of electron-hole drops and of plasma in mixed $CdS_{1-x}Se_x$ crystals

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(Submitted 3 July 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 4, 230–235 (20 August 1978)

We have observed, for the first time ever, glow of highly excited mixed $CdS_{1-x}Se_x$ crystals. Depending on the crystal composition, this glow is attributed to recombination radiation of electron-hole drops or plasma. The concentration limits of the produced drops are established for a number of these crystals.

PACS numbers: 71.35. + z, 71.45. – d, 78.55.Hx

The question of the possible condensation of excitons into metallic electron-hole drops (EHD) in direct-band semiconductors, particularly in CdS and CdSe, is being extensively discussed in the literature of late. Theoretically, such a possibility was predicted by Keldysh and Silin,[1] who have shown that in polar crystals at high concentrations of electron-hole pairs the average energy per pair of particles, when account is taken of the interaction with the LO phonons, turns out to be lower than the exciton level and consequently the formation of the liquid phase becomes energywise favored. Direct calculations of the energy of the condensation with allowance for this circumstance, subsequently performed in Ref. 2, predict respective values 13 and 0 meV for CdS and CdSe crystals.

The question of the nature of the glow at high excitation levels was investigated experimentally by many workers. The first drop-based interpretation of recombination radiation in the CdS crystal was advanced in Ref. 3. The authors ascribed to the drop radiation the so-called *P*-band which was earlier interpreted as the result of the Auger process in exciton-exciton collisions.[4] This point of view was subsequently confirmed in studies[5,6] of the oscillations of the intensity in a magnetic field and of the optical orientation of the carriers. An opinion was advanced,[7,8] on the basis of a study of the spectral dependence of the amplification coefficient at high excitation levels, that the electron-hole liquid (EHL) drops are indeed produced in the CdS crystal, as well as in CdSe.

It was shown, however, in our earlier papers[9,10] that in the CdSe crystal there is no condensation into drops, and at high excitation levels, owing to the screening of the Coulomb interaction, a degenerate noncondensed electron-hole plasma (EHP) is produced. In a recent paper,[11] devoted to an investigation of the CdS and CdSe crystals, the opinion is advanced that the EHP is produced in both cases at high excitation intensities, and doubts are expressed there concerning the interpretation of Ref. 3. Thus, there is no meeting of minds in the hitherto published papers concerning the nature of the glow produced at high excitation levels in CdS and CdSe crystals.

In this connection, we have carried out a comprehensive investigation of the features of recombination radiation of the crystals CdS, CdSe and of the mixed crystals

$CdS_{1-x}Se_x$, for the purpose of studying the collective effects at high concentrations of the excitons and revealing the character of variation of these effects in a smooth transition from CdS via $CdS_{1-x}Se_x$ to CdSe. It is shown that in the pure CdSe crystal and in the mixed $CdS_{1-x}Se_x$ crystals, when x changes from 0.6 to unity, glow properties are observed that can be attributed to formation of an uncondensed EHP. At the same time in CdS and in mixed crystals with $x<0.6$, the glow at low temperatures can be ascribed to an EHL condensed into drops.

Experiment. We used bulk two-photon excitation of the crystals by a ruby laser (CdS) and a neodymium laser ($CdS_{1-x}Se_x$ and CdSe), both Q-switched and lasing at a lower-order transverse mode. The power of the focus beam incident on the crystals reached 170 and 100 MW/cm² for the neodymium and ruby lasers, respectively. We investigated plane-parallel single crystals grown from the melt, with an optical axis parallel to the surface, with different percentage compositions. In the investigation of the mixed crystals we chose the highest grade samples, with homogeneous composition, whose reflection spectra revealed exciton bands. At 4.2 K, the crystals were

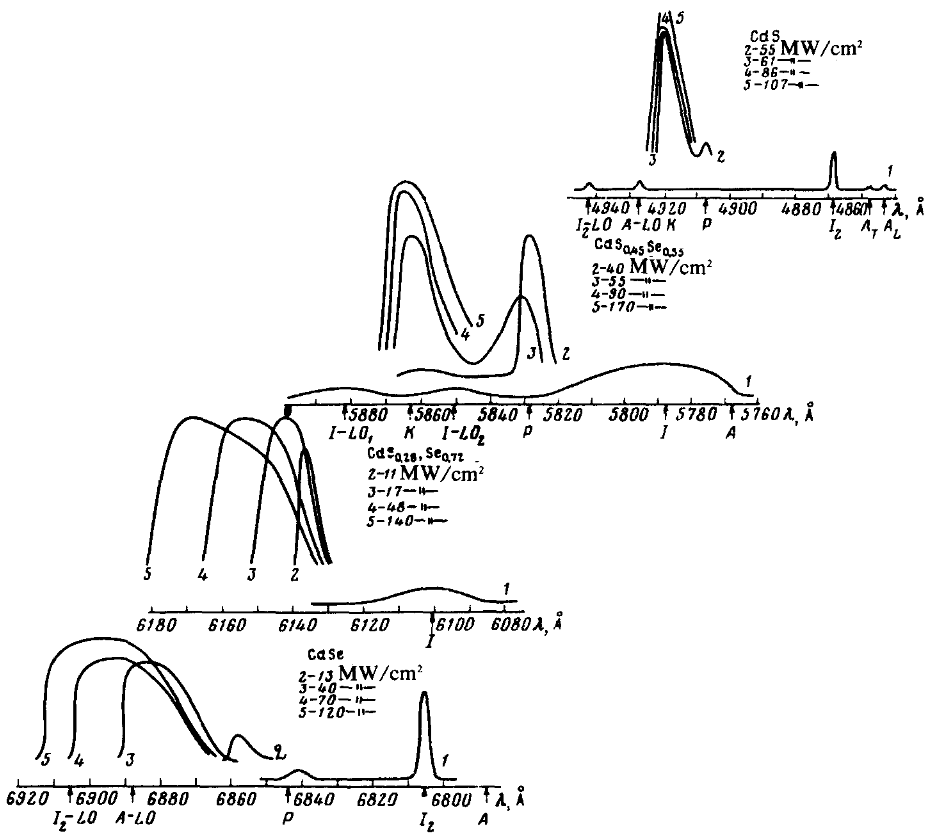

FIG. 1. Recombination-radiation spectra of $CdS_{1-x}Se_x$ crystals excited by a mercury lamp (curve 1) and by a laser (curves 2–5). The arrows on the abscissa axis indicate the positions of the A exciton measured from the reflection spectra; I—bound-exciton lines.

immersed in liquid helium, and at higher temperatures they were placed in the helium vapor. The registration was with a spectrograph having a dispersion 4 Å/mm by a photographic method. The crystal radiation was strongly polarized in a direction perpendicular to the C axis.

Figure 1 shows the results obtained with four samples of different composition at 4.2 K. Curves 1 in each case represent the spontaneous luminescence spectrum excited by a mercury lamp. Curves 2–5 were obtained by excitation with a laser beam of different intensity, as marked on Fig. 1. In all the considered cases, laser excitation produced a glow starting with a certain threshold pump power (curve 2). The glow had a characteristic mode structure (smoothed out on Fig. 1), attesting to the stimulated character of the process.

It is seen from the curves that the spectral behavior of the emission of the CdSe crystals and of the mixed crystals with $x > 0.6$ differ in principle from the behavior of the CdS crystals and the mixed crystals with $x < 0.6$. In the former case, at each pump level, only one emission band is observed and this band broadens with increasing intensity of excitation and shifts towards the red side (mainly on account of the shift of the sharp "red boundary"). With respect to its spectral position, the glow does not coincide with any of the excitonic recombination channels, and with respect to the aggregate of properties analyzed in detail in Refs. 9 and 10, it can be ascribed to radiation of a degnerate EHP. In the second case, at a slight excess of the pump power over threshold, two generation channels coexist simultaneously. One of the bands coincides with the predicted spectral position of the P band, while the other falls in a region where there are no exciton glow mechanisms, i.e., in a "pure" spectral interval (K band). When the pump power is increased, the P band attenuates and vanishes completely, and this is accompanied by a considerable enhancement of the K band. The spectral position of the K band does not depend on the intensity, and its red boundary coincides with the red boundary calculated in[3] for the EHL glow, i.e., it corresponds to the measured width of the band gap of the CdS crystal at an electron-hole pair concentration $n_0 \approx 2 \times 10^{18}$ cm^{-3}. The K band has a characteristic shape with an abrupt red edge, whereas the P band has a stretched-out red edge. The entire aggregate of the presented data makes it possible to interpret the behavior of the CdS crystal and of the mixed crystals with $x < 0.6$ from the point of view of production in them of EHD and of their simulated emission. The P-band glow observed simultaneously with the K band at near-threshold pumps attests to the coexistence of a drop (electron-hole) and gas (exciton) phases. A confirmation of such an interpretation follows also from an analysis of the temperature dependence of the glow, shown in Fig. 2 for CdS and CdSe. In CdSe crystal, with increasing temperature, the EHP band becomes narrower and "presses" towards the red boundary, whose position in each case is determined by the pump level. This behavior was attributed in Ref. 10 to the lifting of the EHP degeneracy at high temperatures. In the CdS crystal, when the temperature is raised all the way to ~ 60 K, the K emission band shifts in the red direction parallel to the shift of the A exciton, and beyond it much more rapidly. Up to ~ 60 K, a certain narrowing of the band is observed with increasing temperature, after which the band broadens considerably. These data attest to a change in the glow mechanism near 60 K, due apparently to a transition through the critical temperature T_{cr} for the EHD in CdS. In Ref. 8, T_{cr} is estimated approximately at 55 K, which is very close to the value obtained by us. Above T_{cr}, the principal recombination mechanism is apparently the radiation due to exciton-exciton collisions,[12] since curve 2 of

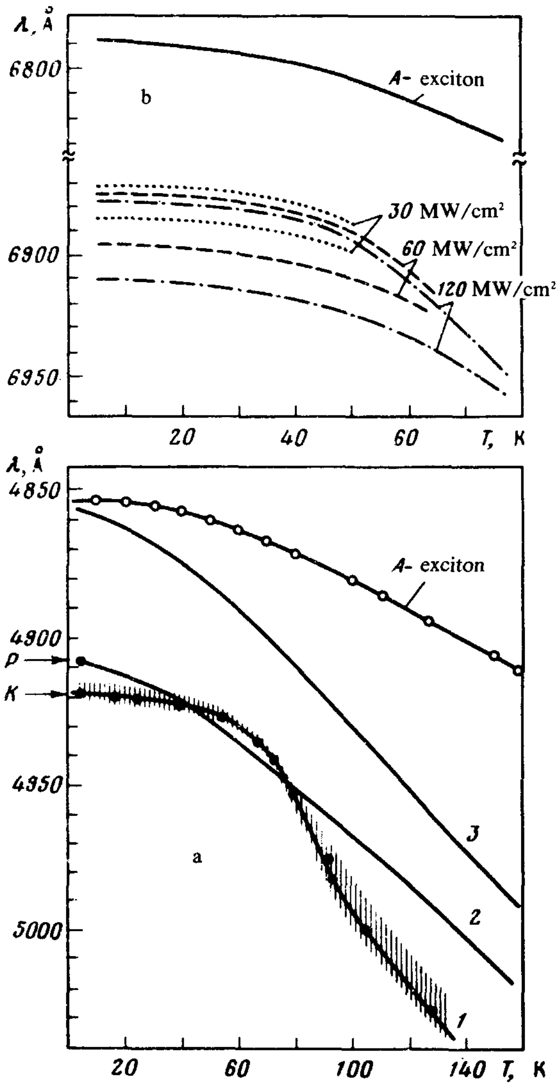

FIG. 2. Temperature dependence of the recombination-radiation bands in the crystals: a—CdS, 1—the shaded part corresponds to the width of the K band leveled at the 0.1 level of the maximum intensity, 2—calculated position of the P line,[12] 3—calculated position of the line corresponding to the exciton-electron interaction. b—CdSe, the positions of the red and violet recombination boundaries of the ion glow are shown for different excitation powers. The band limits are given at the 0.1 level of the maximum intensity.

Fig. 2 is closer to the experimental values than curve 3, which corresponds to exciton-electron interactions.

Thus, investigations of the system of mixed crystals $CdS_{1-x}Se_x$ have confirmed the theoretically predicted[2] conclusion that drops can exist in CdS but cannot be produced in CdSe. The concentration limits of drop production in the series of these crystals have also been established.

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