Radiation of electron-hole plasma in the CdSe crystal

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(Submitted January 19, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **23**, No. 5, 253–256 (5 March 1976)

The appearance of new radiation was registered following two-photon excitation of CdSe crystals, and is attributed, in accordance with its properties, to recombination radiation of an electron-hole plasma.

PACS numbers: 72.30.+q, 71.80.+j, 78.60.Dg

The numerous reported investigations of the luminescence spectra of strongly excited A_2B_6 crystals, especially CdS and CdSe, have so far not provided an unambiguous picture of the effect of exciton interaction in these crystals. On the one hand, a number of workers have observed new lines ascribed to excitonic molecules, to inelastic scattering of excitons and biexcitons, to exciton-electron interaction, and Bose-Einstein condensation of biexcitons and excitons (see the review[1] and[2–4]). Furthermore, there are indications[5] that in the CdS crystal the excitons are conserved up to concentrations 10^{18}—10^{19} cm^{-3}. On the other hand, on the basis of the luminescence spectrum of a one-photon-excited CdS crystal, it is concluded in[6] that the excitons decay and an electron-hole ($e-h$) plasma is produced even at excitation concentrations 10^{17} cm^{-3}. We have affected for the first time two-photon volume excitation of a CdSe crystal and demonstrated the formation of $e-h$ plasma at concentrations 10^{16}—10^{18} cm^{-3}.

Experiment. We used two-photon excitation of crystals with a Q-switched neodymium laser generating a single transverse mode. The focused beam power incident on the crystal ranged from 10^7 to 10^8 W/cm^2. The crystals were immersed in liquid helium. We studied single-crystal samples (grown from the melt) 1.5—2 mm thick, with optical axes parallel to the surface. The radiation was registered by a photographic method with a spectrograph having a dispersion 4 Å/mm. The excitation was with partially-polarized light, $\mathbf{E} \perp \mathbf{C}$; the crystal radiation was polarized, $\mathbf{E} \perp \mathbf{C}$.

Figure 1 shows the results. The lower curve (1) is the luminescence spectrum of the CdSe crystal when excited with a mercury lamp. The arrow denotes the A-exciton position, obtained from the reflection spectrum. In the case of laser excitation, the crystal emission has a threshold, and cannot be registered in practice until the excitation power reaches 13 MW/cm^2. At $J_{exc} = 13$ MW/cm^2, a relatively narrow band appears (curve 2), broadens with increasing pump power, and shifts towards longer wavelengths. The produced radiation does not agree in its spectral position with any of the known excitonic and impurity recombination channels, neither with the exciton A, nor with its replica on the longitudinal optical phonon (A—AO), nor with the bound exciton J_2 and its phonon replica (J_2—LO), nor with the exciton Auger recombination (the so-called P line), nor with a possible radiation of a biexciton and its Auger recombination

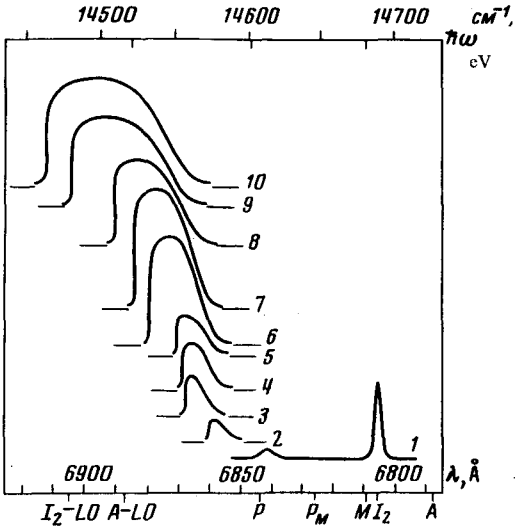

FIG. Luminescence spectra of CdSd crystal excited by a mercury lamp (curve 1) and by a neodymium laser (excitation powers, in MW/cm^2, respectively: 2—13, 3—13.5, 4—14.5, 5—15, 6—23, 7—15, 8—40, 9—70, 10—120). $T = 4.2$ °K.

(the lines M and P_M, respectively). The known published positions of all these lines are marked on Fig. 1. The bands have a peculiar shape, namely, they have abrupt red edges and diffuse violet edges. This shape, insofar as we know, was not obtained in earlier experiments, where a more or less stretched out long-wave "tail" was observed.

Discussion of results. According to rough estimates, the lower limit of the exciton concentration corresponded to $N_{\min} = 2 \times 10^{16}$ cm^{-3}, and the upper limit to $N_{\max} = 1.4 \times 10^{18}$ cm^{-3} (it was assumed that the exciton lifetime is 0.5 nsec and the coefficient of the two-photon absorption is 0.1 cm/MW[7]). At these exciton concentrations, in the CdSe crystal, the effects of interaction between them should become very strong. In fact, the "limiting" exciton concentration, corresponding to the case of their "dense" packing, is estimated from the relation $N_{\text{lim}} \cdot (4/3)\pi a_{\text{exc}}^3 = 1$ and is equal to 2.4×10^{17} cm^{-3}. If we introduce, as is customary, the dimensionless parameter $r_s = r/a_{\text{exc}}$, where r is the distance between excitons, then N_{lim} corresponds to $r_s = 2$. Under these conditions the interaction should lead to a breaking of the bond between the individual electron and hole and to formation of $e-h$ plasma.[8] It is predicted theoretically (see e.g., the reviews[9,10]) that owing to the exchange and correlation interaction of the electrons and holes the width of the forbidden band decreases with increasing carrier density N, and this should lead to a shift of the red boundary of the recombination radiation to the long-wave side. Simultaneously with the increase of N, the occupation of the bands by the carriers increases, and consequently, the recombination radiation band should experience a broadening (equal roughly to the sum of the chemical potentials of the electrons and holes ($\mu_e + \mu_h$). Calculations show also that at $T = 0$ the average energy per pair of particles should have a minimum as a function of the concentration. Therefore, at high concentrations a liquid phase (drops) or a noncondensing $e-h$ plasma can be produced in principle. A distinguishing spectral attribute of such formations should be independence of the spectral position of the recombination radiation line of the excitation intensity in the case of a drop, and

the presence of such a dependence in the case of a plasma. It is seen from the experimental results that the spectral position of the new emission depends strongly on the pump power, and consequently favors the formation of the $e-h$ plasma.

We have carried out a rough calculation of the shift of the red boundary of the spectrum and its broadening as a function of the number N of the $e-h$ pairs, starting with the assumption that a plasma is produced. If we compare the experimentally obtained red boundary of the spectrum at the minimal excitation level with the calculated boundary, then it corresponds to a concentration $N_{min} = 0.2\times10^{18}$ cm^{-3}. The maximum concentration is estimated at $N_{max} = 0.5\times10^{18}$ cm^{-3}. In order of magnitude, these values agree with the estimates given above. An additional confirmation of the conclusion that we are dealing with a system in which the excitons have disintegrated and an $e-h$ plasma was produced is the vanishing, observed in[3], of the exciton bands in the absorption and reflection spectra at $N = 10^{17}-10^{18}$ cm^{-3}.

As to the widths of the recombination-radiation bands, they turn out to be smaller than $\mu_e+\mu_h$ at all concentrations. The reason for the narrowing is probably that at a crystal thickness 1.5—2 mm an essential role is played by the amplification processes, and the contour of the recombination and radiation curve is determined also by the spectral distribution of the gain. The previously emphasized peculiarity of the form of the recombination-radiation bands, namely, the abrupt red edge and the diffuse violet edge, also agrees with the contour calculated under the assumption of an $e-h$ plasma.[6] This form was experimentally registered here for the first time.

We assume therefore, that the volume-excited new radiation in the CdSe crystal is due to recombination of the produced electron-hole plasma.

[1]R. Levy and J. B. Grun, Phys. Status Solidi [a] **22**, 11 (1974).
[2]H. Kuroda, S. Shionoya, H. Saito, and E. Hanamura, Solid State Commun. **12**, 533 (1973).
[3]I. Kh. Akopyan and B. S. Razbirin, Fiz. Tverd. Tela **16**, 189 (1974) [Sov. Phys. Solid State **16**, 113 (1974)]; I. Kh. Akopyan, E. F. Gross, and B. S. Razbirin, Pis'ma Zh. Eksp. Teor. Fiz. **12**, 366 (1970) [JETP Lett. **12**, 251 (1970)].
[4]J. Vaitkus, R. Baltramiejunas, and V. Niunka, J. Phys. Chem. Solids **35**, 159 (1974).
[5]J. F. Figueira and H. Mahr, Phys. Rev. **B7**, 4520 (1973).
[6]V. G. Lysenko, V. I. Revenko, T. G. Tratas, and V. B. Timofeev, Zh. Eksp. Teor. Fiz. **68**, 335 (1975) [Sov. Phys.-JETP **41**, 163 (1975)].
[7]F. Bruckner, B. S. Dneprovskiĭ, and V. U. Khattatov, Kvantovaya Elektron. **1**, 1360 (1974) [Sov. J. Quantum Electron. **4**, 749 (1974)].
[8]L. V. Keldysh, in: Eksitony v poluprovodnikakh (Excitons in Semiconductors), Nauka, p. 5.
[9]Ya. Pokrovkiĭ, Phys. Status Solidi [a] **11**, 385 (1972).
[10]P. Vashishta, P. Bhattacharyya, and K. S. Singwi, Nuovo Cimento **23**, B172 (1974).