High-temperature electron-hole liquid in layered InSe, GaSe and GaS crystals

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We have investigated the radiative recombination spectra of layered semiconductors belonging to the A^3B^6 group (InSe, GaSe, GaS) in the temperature range 4.2 K to 150 K, for optical excitation densities up to 3 MW/cm^2. We show that for high excitation densities an emission line appears in the luminescence spectra of these crystals whose origin is radiative recombination of electron-hole pairs in an electron-hole liquid (EHL) which forms at the *M*-point of the hexagonal Brillouin zone. Based on the results of our experiments and calculations of the ground state energies, we show that EHLs in InSe, GaSe and GaS are characterized by high critical temperatures and large values of their equilibrium densities: 40 K, 90 K, 130 K, and 6×10^{18} cm^{-3}, 1.7×10^{19} cm^{-3} and 2.3×10^{20} cm^{-3}, respectively.

1. INTRODUCTION

At high optical excitation densities, collective interactions transform the exciton gas in semiconductors into a new phase—the electron-hole liquid (EHL).[1] The critical temperature T_K below which the EHL can exist is different for different crystals: for Ge, $T_c \approx 8$ K, for Si, $T_c \approx 28$ K, for GaP, $T_c \approx 40$ K, etc. It is possible to create a high-temperature electron-hole liquid in a semiconductor with large exciton binding energy, along with strong anisotropy in its electronic spectrum and a large number of equivalent valleys. The first criterion can be realized in crystals possessing large electron and hole masses and small dielectric permittivities, the second in strongly anisotropic (two-dimensional) crystals.[2]

From this standpoint, the layered crystals InSe, GaSe and GaS are promising objects of study, since out of the various semiconductors with strongly anisotropic crystal structures our information on the energy spectra of these three is (at this time) the most complete. In addition, the technology now available can be considered satisfactory for obtaining perfect bulk single crystals of these materials which are natural for optical studies.[3]

Investigations of radiative recombination in GaSe,[4,5] InSe[6] and GaS[7,8] at low optical excitation densities have made it possible to ascertain the nature of the radiation lines in the photoluminescence spectra of these semiconductors. A number of experiments have shown that as the optical excitation density increases, the luminescence spectra of layered semiconductors in the A^3B^6 group undergoes a transformation; however, the mechanism which causes this transformation has not been unequivocably identified. The new lines which appear in the radiation spectra of gallium and indium selenide are considered by some authors[9–12] to be associated with exciton-exciton scattering processes, while other authors[9,13–15] connect them with the formation of an electron-hole plasma. According to Refs. 16 and 17, the radiative spectrum of gallium sulfide is reconfigured as the optical excitation density increases due to the appearance of an EHL; however, with regard to the conditions under which such a phase can form, e.g., its critical temperature, these two papers differ significantly in their predictions.

In light of this last statement, we decided that it would be interesting to carry out the complex photoluminescence studies of crystals of InSe, GaSe and GaS needed to establish to what extent the process of formation of the EHL in these crystals determines the observed reconstruction which their radiation spectrum undergoes as the level of optical pumping increases. In the second section of the paper, we study the conditions under which an EHL can form in each of these crystals, based on the available data on their band structures, values of effective masses and dielectric permittivities; in the third section, we present the experimental results, and finally in the fourth section we will try to draw some conclusions about the nature of EHLs in InSe, GaSe and GaS, estimate their parameters, and elucidate the role played by radiation originating from the decay of the EHL in the formation of the emission spectrum of each crystal.

2. ESTIMATES OF EHL GROUND STATE ENERGIES IN THE GaSe FAMILY OF SEMICONDUCTORS

Increasing the optical power incident on a sample increases the concentration of nonequilibrium carriers in the sample; at a certain threshold concentration, a new state of the system of electron-hole pairs becomes energetically allowed in the crystal. The total energy E_T of the *e-h* pairs is determined by the kinetic energy of the electrons and holes, along with their exchange and correlation energies. For the case of simple band structures the kinetic energy of electrons and holes can be calculated in standard fashion

$$E_{kin} = 0.3(3\pi^2 n\hbar^3)^{2/3}(1/m_e^* \nu_e^{2/3} + 1/m_h^*);$$

here, $m^* = (m_\perp^2 m_\parallel)^{1/3}$ is the density-of-states effective mass, and $m_{\perp,\parallel}$ are the carrier effective masses transverse to and along the crystal axis; ν is the number of equivalent valleys. To calculate the sum of the exchange and correlation energies, a simple universal expression was assumed in Ref. 18:

$$E_{corr} + E_{exch} = (-4.8316 - 5.0879 r_s)R/(0.0152 + 3.0426 r_s + r_s^2);$$

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here, R is the Rydberg constant of the exciton: $R = -\mu e^4/2\hbar^2\varepsilon_0^2$; ε_0 is the static dielectric permittivity; μ is the reduced mass of the exciton; $r_s = (3/4\pi n)^{1/3} a_{ex}^{-1}$ is a dimensionless parameter which characterizes the e-h pair density. The total energy of the e-h pairs equals $E_T E_{kin} E_{corr} E_{exch}$. Thus, when we know these parameters we can estimate the ground-state energy E_G of the e-h system as the minimum value of the function E_T at the corresponding equilibrium density n_0. By comparing the value of the quantity E_G with the binding energy of an exciton E_{ex} measured from the bottom of the conduction band, we can determine whether or not an EHL can exist in the crystal (the work function $\varphi = E_G - E_{ex}$ must not be negative). These parameters E_G and n_0 also determine the energy position of the EHL radiation line in the spectrum; its critical temperature is determined by the condition $E_G \sim 10\, kT_c$.[1,19]

Based on the available information about the band structure and parameters of InSe, GaSe and GaS, let us try to estimate EHL parameters for these crystals. According to the data in Ref. 20, the absorption edge in all these crystals originates from optical transitions between nondegenerate states, which are on the whole not strongly anisotropic.

In gallium selenide[21] and indium selenide,[22] the direct optical transitions take place at the center of the hexagonal Brillouin zone (the Γ point, specifically, $\Gamma_{4^-} \to \Gamma_{3^+}$), while indirect transitions take place between the top of the valence band and the bottom of the conduction band at the point M ($\Gamma_{4^-} \to M_{3^+}$). The widths E_g^Γ and E_g^M, which correspond to the direct and indirect gaps in these crystals, differ by a quantity ~ 10 meV. In gallium sulfide the absorption edge is due to indirect transitions ($\Gamma_{4^-} \to M_{3^+}$); the conduction band minimum, which is located at the M point, is ~ 500 meV lower in energy than the bottom of the conduction band at the center of the Brillouin zone.[8] Using the data assembled in the table, we can estimate E_G and n_0 for each of the crystals. At this time, the most reliable and complete information available is for gallium selenide. The values $m_{\perp,\parallel}^{e,h}$ at the Γ point were determined in Ref. 23 from experiments in crossed electric and magnetic fields; the value of the electron mass at the edge of the Brillouin zone was calculated using data from kinetics experiments.[24] For InSe, whose band structure, along with the value of the band dispersion, differs little from GaSe, the electron masses at the Γ point were determined from cyclotron resonance[25]; however, there was no experimental data on the values of $m_{\perp,\parallel}^h$ at the Γ point or the values of the electron masses at the Brillouin zone edge. In order to estimate the EHL parameters for InSe, we were obliged to use the hole masses for GaSe,[26] and to select the values of the electron masses at the zone edge based on the assumption that the ratio of the effective masses of electrons at the center to their masses at the edge of the Brillouin zone is identical for these two crystals. The magnitudes of the effective carrier masses in gallium sulfide were investigated in Ref. 27, and were estimated in Refs. 28 and 29 based on the results of Hall-effect and thermo-EMF measurements. The values of the dielectric permittivity are reliably known for all the crystals.

To calculate the Rydberg constant for excitons in the anisotropic case, the expression $R = \mu e^4/2\hbar^2\varepsilon_0^2$ is usually used, where the reduced mass of the exciton μ is chosen to be the value obtained from an "averaged" value of the effective carrier masses [the optical effective mass: $\mu = m_{oe} m_{oh}/(m_{oe} + m_{oh})$, where $m_{oe,h}^{-1} = 1/3(2/m_\perp^{e,h} + 1/m_\parallel^{e,h})$. The optical effective masses were calculated for GaSe and InSe, while in the case of gallium sulfide the mass $m_{e,h}^*$ given in Table I was used for $m_{oe,h}$. The value ε_0 is taken to equal $\varepsilon_0 = (\varepsilon_\parallel \varepsilon_\perp)^{1/2}$. The calculated values of the Rydberg constant for all these crystals are found to be in good agreement with available experimental data on the binding energies of their excitons.

These estimates of the EHL parameters indicate that the formation of an EHL from the direct edge in the crystals GaSe and InSe is energetically unfavorable; at the same time, formation of an EHL in the system of indirect excitons is possible for all three crystals. They also show that EHLs in layered group-A^3B^6 crystals must be characterized by rather large values of binding energy, and consequently by high critical temperatures as well as rather large equilibrium densities.

To conclude this section, we should point out that we consider all the values of EHL parameters presented in the table to be estimates, due to the limited accuracy in the determination of all the effective masses, especially for indium selenide and gallium sulfide; in addition, we have nowhere taken into account the interaction of particles with different wave vectors (i.e., at different band minima).

3. EXPERIMENTAL RESULTS

We investigated crystals of InSe, GaSe and GaS grown by the Bridgman method. The single crystals of InSe and GaSe consisted primarily of the ε-polytype (D_{3h}^1) with a certain admixture of γ-polytype (C_{3v}^5); the crystals of GaS were the β-modification (D_{6h}^4). We used both CW and pulsed excitation sources to excite the photoluminescence.

TABLE I.

Crystals	ε_0	Direct Transitions $\Gamma_{4^-} \to \Gamma_{3^+}$							Indirect Transitions $\Gamma_{4^-} \to M_{3^+}$						
						Exp.	Calculated						Calculated		
		$m_\perp^e$ (m_0)	$m_\parallel^e$ (m_0)	$m_\perp^h$ (m_0)	$m_\parallel^h$ (m_0)	E_{ex}^Γ (meV)	E_{ex}^Γ (meV)	E_G^Γ (meV)	$m_\perp^e$ (m_0)	$m_\parallel^e$ (m_0)	ν_e	E_{ex}^M (meV)	E_G^M (meV)	n_0 (cm^{-3})	T_c K
GaSe	8.8[27]	0.18	0.16	0.61	0.55	20	23	21	0.5	1.6	3	54	64	$1.7\cdot10^{19}$	76
InSe	9.6[30]	0.132	0.081	$m_h^*=0.5m_0$		14	13.2	12,5	$m_e^*=0.46m_0$		3	35	39	$6\cdot10^{18}$	46
GaS	10.6[31]	—	—	$m_h^*=2.3m_0$		—	—	—	$m_e^*=1.3m_0$		3	100	117	$2.3\cdot10^{20}$	140

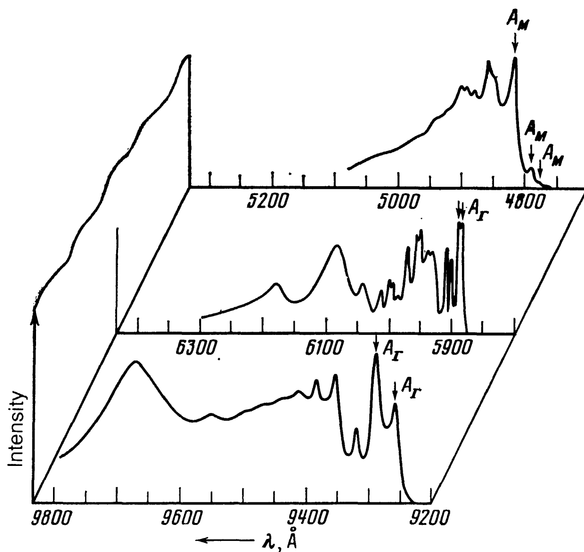

FIG. 1. PL spectra of InSe, GaSe and GaS (from bottom to top) for steady-state excitation. The excitation density was 5×10^{-2} W/cm^2, $T = 5$ K. A_Γ and A_M are lines caused by the decay of free excitons formed as the Γ and M points of the Brillouin zone.

The steady-state luminescence spectra were studied while the samples were excited by an LPM-11 laser ($h\nu_{ex} = 2.807$ eV). By focusing down the laser beam, we achieved an excitation density of ~ 5 W/cm^2. In the pulsed-measurement experiments we used an LGI-21 nitrogen laser ($h\nu_{ex} = 3.667$ eV) with a pulse length of ~ 10 nsec, a repetition rate of 30 Hz and a power of ~ 1.6 kW, along with an AL-202 nitrogen laser with analogous characteristic times but with a power per pulse of ~ 100 kW (in this case, by focusing down the laser beam we achieved densities of ~ 5 MW/cm^2). We weakened the excitation level by using neutral filters. The photoluminescence (PL) spectra were recorded for steady-state excitation by synchronous detection, while for pulsed excitation we used a stroboscopic system for photoelectric recording with a time resolution of ± 2 ns, and a DFS-12 spectrometer with 5 Å/mm dispersion. The samples were placed directly in the liquid helium; to measure the temperature-dependent behavior of individual lines of the PL spectrum, they were immersed in its vapor. The thermostat system allowed us to record the spectra in the temperature range 4.2 K to 300 K to an accuracy of ± 0.5 K. In order to conduct experiments in which the recombination radiation spectra from GaSe, InSe and GaS was spatially resolved, we used a system of lenses and crossed optical slits; this system allowed us to study the luminescence from various regions of the crystal with a resolution of $\sim 100\,\mu$m. All measurements were carried out on bulk samples ($10\times10\times2$ mm).

In Fig. 1 we show the emission spectra of InSe, GaSe and GaS crystals recorded under steady-state excitation at densities smaller than 10^{17} photons/cm$^2\cdot$sec (0.05 W/cm^2). For low optical excitation densities the recombination radiation spectra of these crystals are characterized by emission lines caused by radiative decay of free excitons (A) and exciton-impurity complexes.

When an excitation density of $\sim 10^{19}$ photons/cm$^2\cdot$sec (5 W/cm^2 in the steady-state excitation regime) is reached at temperatures $T < 40$ K, the PL spectra of indium selenide undergoes a significant modification: in the long-wavelength region of the spectrum a new broad line appears with $h\nu_{max} = 1.32$ eV. For steady-state exitation, reconstruction of the PL spectra of GaSe and GaS was not observed. In Fig. 2 we show the results of pulsed excitation studies of the PL spectra of these crystals; as the level of excitation increases, the radiative recombination line for free excitons (A_Γ) in GaSe (Fig. 2) is broadened, and on its long-wavelength side a new broad line (P) appears. For excitation densities in excess of 0.2 MW/cm^2, a new emission line is recorded in the PL spectrum of GaSe, with $h\nu_{max} = 2.073$ eV (the K-line). As the excitation density increases, the exciton-emission line (A_Γ) in InSe (Fig. 2) is broadened and its splitting disappears; for excitation densities $\gtrsim 6$ kW/cm^2, a broad line (the P-line) appears in its place. For excitation levels larger than 10 kW/cm^2, a new line appears in the emission spectrum of InSe with $h\nu_{max} = 1.32$ eV (the K-line). A similar reconstruction of the radiative-recombination spectrum is observed in gallium sulfide as the optical excitation density is increased: in the long-wavelength region of the PL spectrum a broad emission line appears—the K-line ($h\nu_{max} = 2.5$ eV), see Fig. 2. The appearance of K-lines for all the above crystals occurs with threshold behavior in the excitation density, and is accompanied by intensity saturation of the radiation line for free excitons.

The intensity of the K-line and its half-width have a characteristic temperature dependence in all the crystals. For convenience in comparison (Fig. 3) the spectra are normalized relative to the maximum of the K-line. The short-wavelength structure of the spectra and the K-line exhibit markedly different temperature dependences. For increas-

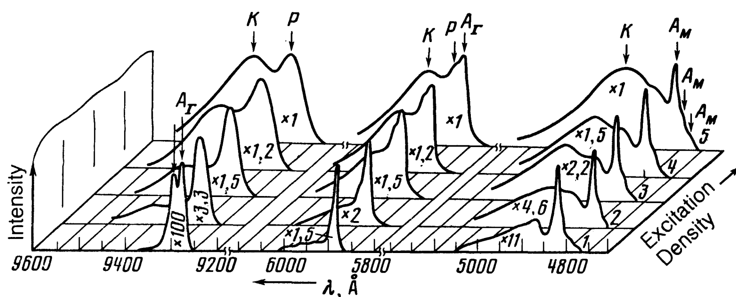

FIG. 2. PL spectra of InSe, GaSe and GaS (from left to right) for pulsed excitation. Density of excitation: in InSe, 1—$1.4\times10^{-4}I_0$, 2—$3.3\times10^{-3}I_0$, 3—$1.4\times10^{-2}I_0$, 4—$3.3\times10^{-2}I_0$, 5—$6.6\times10^{-2}I_0$; in GaSe, 1—$6\times10^{-3}I_0$, 2—$10^{-1}I_0$, 3—$5\times10^{-1}I_0$, 4—$7.5\times10^{-1}I_0$, 5—I_0; in GaS, 1—$10^{-2}I_0$, 2—$10^{-1}I_0$, 3—$2.5\times10^{-1}I_0$, 4—$4\times10^{-1}I_0$, 5—I_0 ($I_0 = 3$ MW/cm^2, $T = 5$ K).

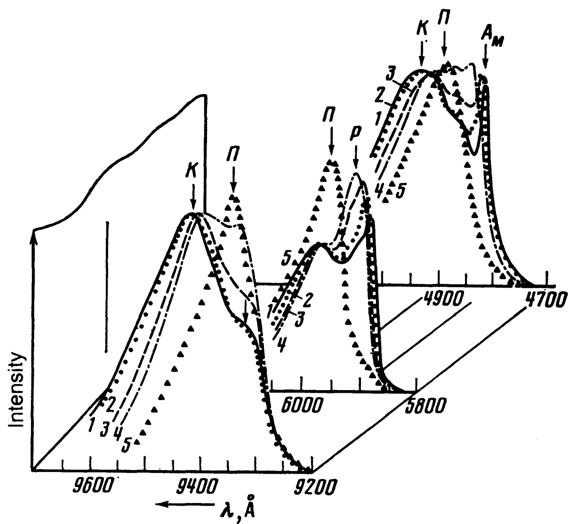

FIG. 3. Temperature dependence of the PL spectra of InSe, GaSe and GaS (proceeding inward) for pulsed excitation densities of $10^{-1}I_0$ for InSe and I_0 for GaSe, GaS ($I_0 = 3$ MW/cm²). The temperatures for curves 1–5 equalled 5, 10, 20, 30 and 45, respectively for InSe; 5, 45, 65, 75 and 100 K for GaSe; 5, 45, 65, 100 and 140 K for GaS. The spectra whose maxima are labeled П were recorded at those temperatures at which the K-lines disappears. The intensities of the K-lines are not normalized.

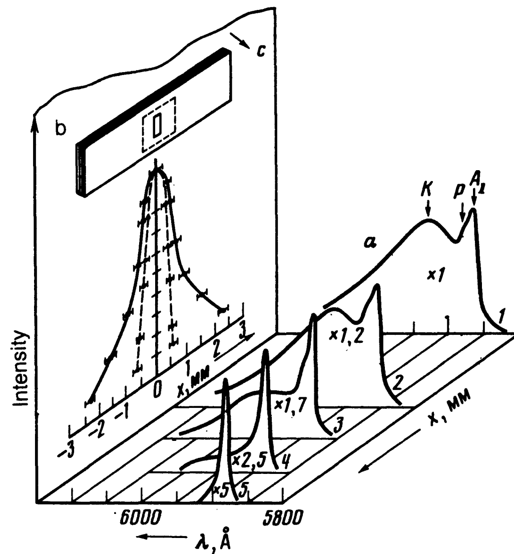

FIG. 4. PL spectra of GaSe recorded by the method of spatial resolution. The pulsed excitation density equalled 3 MW/cm², $T = 5$ K. (a)—PL spectra of GaSe recorded from different portions of the crystal surface, x is the distance from the center of the excitation region: 1—$x = 0$, 2—0.3, 3—0.5, 4—0.6, 5—1.6 mm. (b)—dependence of the K-line intensity (the dashed curve) and the A_Γ line (continuous curve) on the magnitude of the displacement x. On top: experimental geometry; the dashed lines show the excitation region (1.2×1.2 mm²), the continuous lines the region imaged by the spectrometer gap (0.1×0.8 mm²).

ing temperatures, the short-wavelength structure begins to dominate in the spectra, while undergoing a marked shift to lower energy, while at the same time, as the temperature increases a noticeable shift to the short-wavelength region is observed in the long-wavelength edge of the K-line, and also a certain shift in the maximum of the K-line toward the high-energy side, as the violet edge of the K-line is washed out (see Fig. 3).

In studying the PL of strongly excited crystals, one finds that important information is carried by the spatially-resolved luminescence spectrum. In Fig. 4 we show the radiative-recombination spectra for gallium selenide, recorded directly from the region of maximum excitation ($x = 0$) and from various portions of the unilluminated surface of the sample. Analogous spectra were also recorded for crystals of InSe and GaS. As is clear from Fig. 4, the K-line emission is localized to the region of excitation while the short-wavelength emission is recorded from the entire surface of the sample.

Additional information about distinctive features of the radiative recombination processes in crystals is provided by time-resolved spectra of PL generated by pulsed excitation. The PL spectra of indium selenide recorded after various time lapses τ_l relative to the beginning of the laser pulse are shown in Fig. 5. It is clear that for $\tau_l < 4$ ns the emission spectra are characterized by the presence of the short-wavelength A_Γ and P emission lines, and by the M emission line. For $\tau_l \geqslant 4$ ns, the K-line appears in the PL spectrum. The maximum intensity of the K-line corresponds to a time lapse $\tau_l \sim 10$ ns; for $\tau_l > 10$ ns the K-line begins to dominate the PL spectrum. At the end of the laser pulse some broadening of the K-line is observed. This broadening occurs out to $\tau_l \sim 40$ ns, after which the line shape is practically unchanged. An increase in the width of the K-line after the end of the laser pulse is also observed in the PL spectrum of gallium selenide. We did not observe any significant change in the emission spectra of GaS as the time lag was varied.

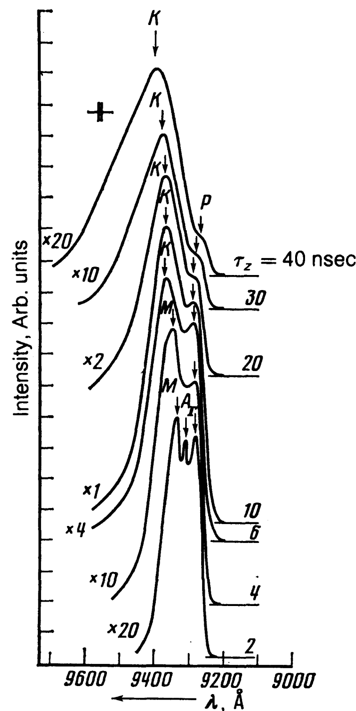

FIG. 5. Time evolution of the PL spectra of indium selenide. The pulsed excitation intensity equalled 0.2 MW/cm², $T = 5$ K.

4. DISCUSSION OF RESULTS

At sufficiently low optical excitation densities, the spectra of InSe, GaSe and GaS are characterized by sharp emission lines caused by radiative decay of direct and indirect excitons (Fig. 1). The nature of each of the radiation lines shown in Fig. 1 was discussed in detail in Refs. 8, 21, 22, 32 and 33. The PL spectra presented in the previous section were recorded on the same samples at high excitation densities (Fig. 2). The transformation of the PL spectra as the level of excitation is increased is a consequence of the reconstruction of the crystal energy spectrum which occurs in the presence of a high density of nonequilibrium charge carriers. The experimental data indicate that a characteristic feature of the emission spectra is the formation of a new line whose behavior with temperature and excitation density is generally the same for all the crystals. Distinctive features of the behavior of a K-line in the emission spectra are: a threshold excitation density for its appearance; its disappearance at $T_c \approx 40$ K (InSe), 90 K (GaSe) and 130 K (GaS); a decrease in its half-width due to a violet shift in its long-wavelength edge; a noticeable shift in its maximum toward the short-wavelength region as the temperature increases. All these things suggest to us that the K-line is a result of radiative recombination of e-h pairs in an EHL. Narrowing of the radiation line in the EHL and the shift of the line maximum to the short-wavelength region as the temperature rises can be explained by the thermal expansion of the EHL droplet, which leads to a decrease in the e-h pair density; this in turn causes a decrease in the value of the electron and hole chemical potentials measured from the bottoms of their respective bands, and lowers the energy per e-h pair in the EHL.[1]

The proximity in energy of the short-wavelength edge of the K-line to the radiation line for direct free excitons (the A_Γ line) in GaSe and InSe, and the values of the binding energies of direct excitons in these crystals (see Table I) in conjunction with the rather high temperature at which the K-line disappears from the spectrum, make interpretation of the nature of this line difficult in the context of a model which assumes that the EHL forms at the direct edge. Let us assume that the K-line in the emission spectra of GaSe and InSe is a result of recombination of e-h pairs in an EHL formed in the system of indirect excitons. This assumption is supported by the similarity between the radiative recombination spectra of the typically indirect semiconductor gallium sulfide and the spectra of gallium and indium selenide (at high excitation densities).

The results of those experiments which employ the method of spatial resolution (Fig. 4) to study the photoluminescence also become intelligible within the context of the EHL model. The presence of exciton luminescence originating from parts of the crystal far from the excitation region can be explained as a consequence of multiple reabsorption and re-emission of photons, which leads to radiation from excitons located at distances greater than the diffusion length of excitons in these crystals.

Let us now investigate the changes in the luminescence spectra of crystals of InSe and GaSe as a function of the time lapse relative to the beginning of the laser pulse. As an example we consider the experimental data for InSe. For a time lapse $\tau_l < 4$ ns, there is present in the PL spectrum a radiative recombination line associated with direct-gap excitons, an emission line associated with exciton-impurity complexes (the M-line) and the P-line. For $\tau_l \gtrsim 4$ ns, an emission line appears in the system which is due to the EHL. The width of the EHL radiation line remains practically unchanged up to the instant when the laser pulse ends; after it ends, the line width increases. This line broadening continues for a time $\tau_l \sim 40$ ns, after which the width of the EHL radiation line does not change. The main features of this time evolution of the K-line can be explained in the following way: an excitation light quantum has an energy $h\nu_{ex} = 3.667$ eV; since the width of the forbidden gap in InSe $E_g^\Gamma = 1.352$ eV (at $T = 4.2$ K), nonequilibrium ("hot") electrons and holes are formed, which after thermalization with the participation of optical phonons can acquire a temperature different from the temperature of the phonon subsystem as a result of interparticle interactions. Under these conditions, the EHL also has a relatively high temperature, which determines the density of e-h pairs in the EHL. At the end of the laser pulse, the temperature of the electron system drops due to interaction of the particles with acoustic phonons, and the temperature falls also, which in turn leads to an increase in the EHL density due to thermal compression.[1] The relatively short radiation time of the EHL (~ 40 ns) recorded in experiments using time resolution in InSe, GaSe and GaS is apparently due to the important role played by nonradiative recombination processes.

We can try to estimate the density of e-h pairs in the EHL by fitting the theoretically calculated radiative line shape to the experimental lines. The radiative line shape of an EHL which forms at the indirect edge is described for the case of an allowed transition by the expression[34]

$$I_{e\text{-}h}^{M}(h\nu) \sim \int_0^{h\nu-\Delta} \varepsilon^{1/2}(h\nu-\Delta-\varepsilon)^{1/2} F(\varepsilon)\, d\varepsilon,$$

and for the case of a forbidden transition by the expression

$$I_{e\text{-}h}^{M}(h\nu) \sim (h\nu-\Delta) \int_0^{h\nu-\Delta} \varepsilon^{1/2}(h\nu-\Delta-\varepsilon)^{1/2} F(\varepsilon)\, d\varepsilon,$$

where

$$F(\varepsilon) = \left[1+\exp\frac{\varepsilon-E_{F^e}}{kT}\right]^{-1}\left[1+\exp\frac{h\nu-\Delta-\varepsilon-E_{F^h}}{kT}\right]^{-1},$$

Δ is the renormalized width of the forbidden gap, and E_{F^e}, E_{F^h} are the quasi-Fermi levels of electrons and holes respectively at a given temperature T:

$$E_F(T) \simeq E_F^0[1-(\pi^2/12)(kT/E_F^0)^2].$$

Here $E_F^0 = (\hbar^2/2m^*_{e,h})(3\pi^2 n/\nu_{e,h})^{2/3}$ is the Fermi energy for electrons and holes. Fitting the theoretical radiation line shape of the EHL to the experimental line shape for the luminescence spectra of GaSe and GaS is made difficult by the poor resolution of the short-wavelength edge of the K-line. For indium selenide, this procedure allows us to estimate the density of e-h pairs in the liquid (Fig. 6a): $n \approx 9 \times 10^{18}$ cm^{-3} (forbidden transition).

Let us discuss the nature of the P-line recorded in the PL spectra of InSe and GaSe at high optical excitation densities. The proximity in energy of the P-line to the exciton radiation line (A_Γ) which is formed at the $K=0$ point in the Brillouin zone, and also the presence of the P-line at temperatures above 100 K, eliminates the possibility that the P-line is a result of radiative decay of e-h pairs in an EHL which forms at the direct edge. The appearance of the P-line at high optical excitation densities, the dependence of its line width on the level of excitation, and the significant line broadening as the temperature rises—all these facts lead us to postulate that the P-line in the PL spectrum of indium and gallium selenide appears as a result of the formation of an electron-hole plasma (EHP) at the $K=0$ point of the hexagonal Brillouin zone. To estimate the density of the EHP in an InSe crystal, we tried to fit the theoretical radiative line shape to the experimental one. We used the results of experiments with the same samples of InSe, in which the P-line dominated the PL spectra. The radiative line shape of an EHP formed at the direct-gap edge can be described by the formula

$$I_{e\text{-}h}^{\Gamma}(h\nu)\sim E^{1/2}\left\{1+\exp\left[\frac{1}{kT}\left(E\frac{m_h^*}{m_e^*+m_h^*}-E_F^e\right)\right]\right\}^{-1}\times\left\{1+\exp\left[\frac{1}{kT}\left(E\frac{m_e^*}{m_e^*+m_h^*}-E_F^h\right)\right]\right\}^{-1},$$

where E is the energy measured from the red edge of the radiation line. The values of the band structure parameters of InSe were chosen in accordance with the table. The calculated and experimental curves were superimposed so as to make their maxima coincide. The best coincidence was for an e-h pair density in the EHP of $n\approx1.1\times10^{17}$ cm^{-3} and a temperature of $T=15$ K (Fig. 6b).

Consequently, due to special features of the band structure of InSe and GaSe, it is possible to have an EHL in these crystals at the M-point of the Brillouin zone and an EHP at the Γ-point at the same time. For temperatures above T_c, two Mott transitions (metal-insulator transitions) can occur in these systems, one for the direct and one for the indirect exciton systems. In view of the fact that excitons formed at the direct and indirect edges have different radii, the Mott transitions in these systems will occur consecutively, first in the direct exciton system and then in the indirect system. The lowest order we can suppose that the interaction of excitons and e-h pairs with different wave vectors (i.e., direct- and indirect-gap) can be neglected, since the difference in momentum corresponds to an inverse lattice vector, while the effective masses of electrons at the Γ and M points of the hexagonal Brillouin zone are noticeably different. However, this question calls for a more careful investigation.

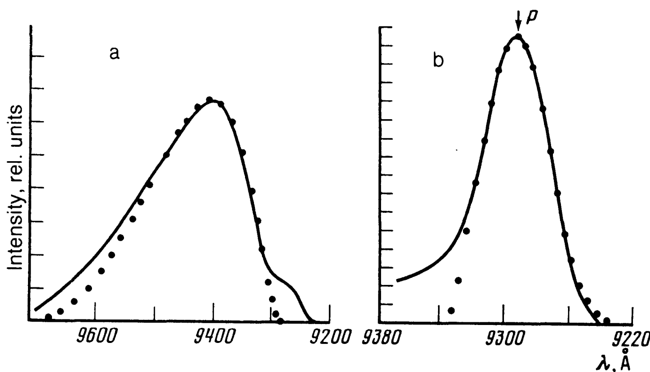

FIG. 6. A comparison of experimental (continuous curve) and theoretical calculations (points) for the EHD radiation line shape (a) and the EHP emission line (b) in InSe. The fitting parameters for case a are $n=9\times10^{18}$ cm^{-3}, $T=5$ K; in case b, $n=1.1\times10^{17}$ cm^{-3}, $T=15$ K (continuous curve).

Thus, in crystals of InSe, GaSe and GaS a high-density electron-hole liquid can form out of the system of photoexcited carriers at high optical excitation densities. In our view, what is interesting about the formation of EHLs in these crystals is the high critical temperature below which the new phase can exist in GaSe and GaS, and also the unusual situation in which the EHL which forms in the system of indirect excitons coexists in the excited region of the crystal with an EHP formed at the direct absorption edge. The collective processes described above may play an important role in the phenomena of optical bistability observed in GaSe.[35]

In conclusion we note that in our experiments excitation of the crystal occurred close to its surface region: the absorption coefficients are $\alpha_{abs}\sim6\times10^5$ (InSe), $\sim10^5$ (GaSe) and $\sim3\times10^4$ cm^{-1} (GaS) for the crystals in question at $h\nu_{ex}=3.667$ eV. The presence in such layers of an EHL and EHP, both of which are characterized by high density, is possible because of the unusual surface properties of layered crystals: surfaces of layered InSe and GaSe are characterized by small recombination velocities and small layer depths (less than 10 Å) of adsorbed atoms.[36]

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