High-temperature electron-hole liquid in layered gallium sulfide

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At a temperature $T = 5$ K and at excitation power densities $\gtrsim 0.2$ MW/cm^2, the luminescence spectrum of GaS contains an emission line which is due to radiative recombination of *e-h* pairs into an electron-hole liquid. The critical temperature of the liquid in GaS is estimated to be $T_c \sim 130$ K, the equilibrium density $n_0 \sim 2.3 \times 10^{20}$ cm^{-3}, and the binding energy of the liquid $E_l \sim 117$ meV.

At high optical excitation densities in germanium, silicon, and certain other semiconductors, a collective interaction of excitons gives rise to a new phase: an electron-hole liquid.[1] The critical temperature for the existence of an electron-hole liquid is usually low: $T_c \sim 21$ K in Si, ~ 8 K in Ge, ~ 5 K in GaAs, and ~ 50 K in CdS. The formation of a high-temperature electron-hole liquid is most likely in semiconductors with a large exciton binding energy, a large number of equivalent valleys, and a strongly anisotropic electron spectrum. Such a situation can be arranged in highly anisotropic (two-dimensional) crystals and also in crystals exhibiting large electron masses $m_e^{\perp,\|}$ and large hole masses $m_h^{i,\|}$, along with low dielectric constants ϵ_0.

In this sense, layered crystals are promising systems for the formation of a high-temperature electron-hole liquid. Among layered group III–VI semiconductors (InSe, GaSe, GaS), gallium sulfide occupies a special position in that it is obviously an indirect-gap semiconductor. In InSe and GaSe, the widths of the direct and indirect gaps are approximately the same (differing by something on the order of 10 meV), so that it becomes necessary to analyze the specific conditions for the formation of the electron-hole liquid. The maximum of the valence band in GaS lies at the Γ point in the hexagonal Brillouin zone; the absolute minimum of the conduction band is at the M point, 500 meV below the minimum of the conduction band at the Γ point.[2] Differential-absorption and photoluminescence spectra were analyzed in Refs. 2 and 3, and direct evidence was found for the existence of indirect excitons in GaS. The position of the exciton band was also found: $E_{\text{exc}} = 2594 \pm 2$ meV.

In the present experiments we studied GaS single crystals grown by the Bridgman method. The crystals are studied in the vapor of liquid helium. The luminescence of GaS is excited by a nitrogen laser (3371 Å) with a power of 100 kW, a pulse length ~ 10 ns, and a repetition frequency of 30 Hz. The spectra are recorded by means of a stroboscopic photoelectric detection system and a DFS-12 spectrometer with a dispersion of 5 Å/mm. Figure 1 shows the photoluminescence spectra of gallium sulfide recorded at various optical excitation densities. With increasing excitation density, a broad new band appears in the long-wave part of the photoluminescence spectrum (the K line, with $h\nu_{\max} = 2.495$ eV). The shape of the K line and the position of the

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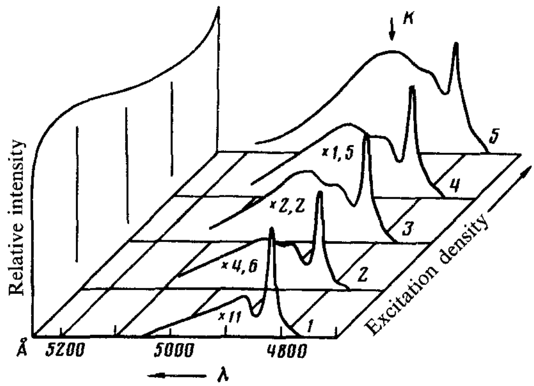

FIG. 1. Luminescence spectra of gallium sulfide at various excitation levels: 1—0.04I_0; 2—0.07I_0; 3—0.25I_0; 4—0.5I_0; 5—I_0. $I_0 \sim 3$ MW/cm^2.

maximum are independent of the excitation level. At the time at which this line appears, the intensity of the free-exciton emission line reaches saturation. The intensity of the K line and its width exhibit the typical behavior as a function of the temperature (Fig. 2). With increasing temperature, there is a significant shift of the long-wave boundary of the K line in the short-wave direction. The short-wave lines in the GaS luminescence spectrum undergo a significant long-wave shift with increasing temperature, while the energy position of the maximum of the K line shifts up the energy scale. The K line disappears when the temperature is raised above a threshold $T_c \sim 130$ K. At higher temperatures, there is a single broad emission band (the Π line) in the photoluminescence spectrum; its maximum shifts with the temperature in accordance with the change in the width of the band gap.

The behavior of the emission spectrum of gallium sulfide—the formation of the K line after a threshold excitation density is reached, the disappearance of this line at $T_c \sim 130$ K, the narrowing of the line with increasing temperature, as a result of a violent shift of its long-wave edge, and the shift of the maximum of the K line in the short-wave direction with increasing temperature—is consistent with the conclusion that the long-wave line in the GaS emission spectrum is caused by the radiative recom-

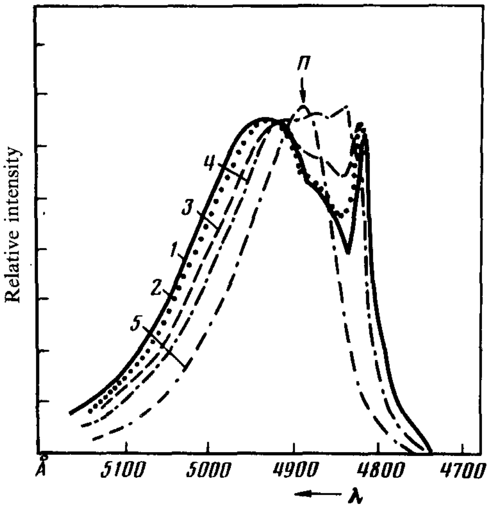

FIG. 2. Temperature dependence of the luminescence spectrum of gallium sulfide. $I_0 \sim 3$ mW/cm^2. 1—$T = 5$ K; 2—$T = 50$ K; 3—$T = 70$ K; 4—$T = 100$ K; 5—$T = 140$ K.

bination of *e-h* pairs into an electron-hole liquid, formed in a system of indirect excitons.

Taking into account the multivalley nature of GaS ($\nu_e = 3$), we can estimate the binding energy of the electron-hole liquid, calculating the total energy of the *e-h* pairs[4]:

$$E_t^{e\text{-}h} = 0.3(3\pi^2 n\hbar^3)^{2/3}\left(\frac{1}{m_e^*\nu^{2/3}} + \frac{1}{m_h^*}\right) - \frac{4.8316 + 5.0879 r_s}{0.0152 + 3.0426 r_s + r_s^2}R,$$

where $m_{e,h}^*$ are the effective masses of the state densities for electrons and holes, respectively, R is the Rydberg constant for the exciton,

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3}\frac{\mu e^2}{\epsilon_0\hbar^2}$$

is a dimensionless parameter, and μ is the reduced mass of the exciton. For numerical estimates we use the following parameters of the band structure of gallium arsenide: $m_e^* = 1{,}3m_0$ (Ref. 5), $m_h^* = 2{,}3m_0$ (Refs. 6 and 7), and $\epsilon_0 = 10.6$ (Ref. 8). The binding energy of the electron-hole liquid is assumed to be the minimum of the function $E_t^{e\text{-}h}(n)$. The results of our calculations show that the equilibrium density of *e-h* pairs in the electron-hole liquid is $n_0 \sim 2.3 \times 10^{20}$ cm^{-3}, and the binding energy is $E_l \sim 117$ meV. These values of E_l and n_0 must be regarded as estimates because of the imprecise determination of the effective masses. There are some pieces of evidence which make these values of E_l and n_0 look reasonable: An estimate of the binding energy of indirect excitons in GaS on the basis of the values of m_e^*, m_h^*, and ϵ_0 given above yields a value close to that found experimentally (Ref. 9, for example). The value found here for E_l is consistent with the experimental value of the critical temperature: $10kT_c \sim E_l$ (Ref. 10).

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