

Characteristics of the temperature dependence of the radiative recombination intensity of $\text{GaS}_x\text{Se}_{1-x}$ crystals

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We studied the luminescence spectra of $\text{GaS}_x\text{Se}_{1-x}$ ($0 < x \leq 0.6$) for $T \geq 1.8$ K during Cu-vapor laser excitation ($\lambda_1 = 5105 \text{ \AA}$, $\lambda_2 = 5782 \text{ \AA}$). By varying the temperature from 4.2 to 1.8 K during excitation by the yellow laser line (λ_2), we found an increase in the quantum radiation output for $\text{GaS}_{0.1}\text{Se}_{0.9}$ by a factor of 1000. It is assumed that during such excitation at 1.8 K an exciton is formed at an ionized defect with a very weakly associated hole, which is opened to the system because of thermal dissociation at $T \geq 4.2$ K.

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Low-temperature luminescence in crystals has been studied in Refs. 1–3. The spectra of all the compounds were nearly identical and had similar properties. In this work we studied the emission of $\text{GaS}_x\text{Se}_{1-x}$ compounds with $0 < x < 0.6$ excited by a Cu-vapor pulsed laser. The excitation wavelengths were the green line $\lambda_1 = 5105 \text{ \AA}$ ($h\nu_1 = 2.428 \text{ eV}$) and the yellow line $\lambda_2 = 5782 \text{ \AA}$ ($h\nu_2 = 2.144 \text{ eV}$). The pulse duration was 10 nsec, the repetition frequency 4.5 kHz, and the pulse power without focusing 3 kW. The experimental arrangement has been described in detail in Ref. 4. The measurements were made at temperatures $T \geq 1.8$ K. It is known² that the width of the forbidden band in $\text{GaS}_x\text{Se}_{1-x}$ increases with increasing sulfur content. Therefore, the emission spectra for excitation by both the green and the yellow line may only be obtained for compounds with $x = 0.1, 0.3, \text{ and } 0.5$. Important properties were found in the behavior of the emission as a function of temperature for different excitation energies in the $\text{GaS}_{0.1}\text{Se}_{0.9}$ crystal.

According to Refs. 2 and 5, excitation with $h\nu_1 = 2.428 \text{ eV}$ is band-band for this crystal, while for $h\nu_2 = 2.144 \text{ eV}$ it has the nature of impurity excitation (the quantum energy is less than the width of the forbidden band). Regardless of the nature of excitation (λ_1 or λ_2), at 4.2 K the spectrum consisted of a number of narrow lines (Fig. 1) characterized by the total time of luminescence quenching $\tau \sim 100\text{--}300$ nsec. On further cooling to 1.8 K during band-band excitation, the luminescence intensity increased somewhat without a change in the luminescence quenching time. In the case of impurity excitation a temperature decrease from 4.2 to 1.8 K was accompanied by an increase in the luminescence intensity (the intensities of all the lines increased by approximately 10-fold!) and by a simultaneous sharp increase in the extinction time (100-fold!) Thus, the quantum yield of luminescence increased by almost three orders of magnitude. Moreover, lines neither appeared nor disappeared in the spectrum. Such

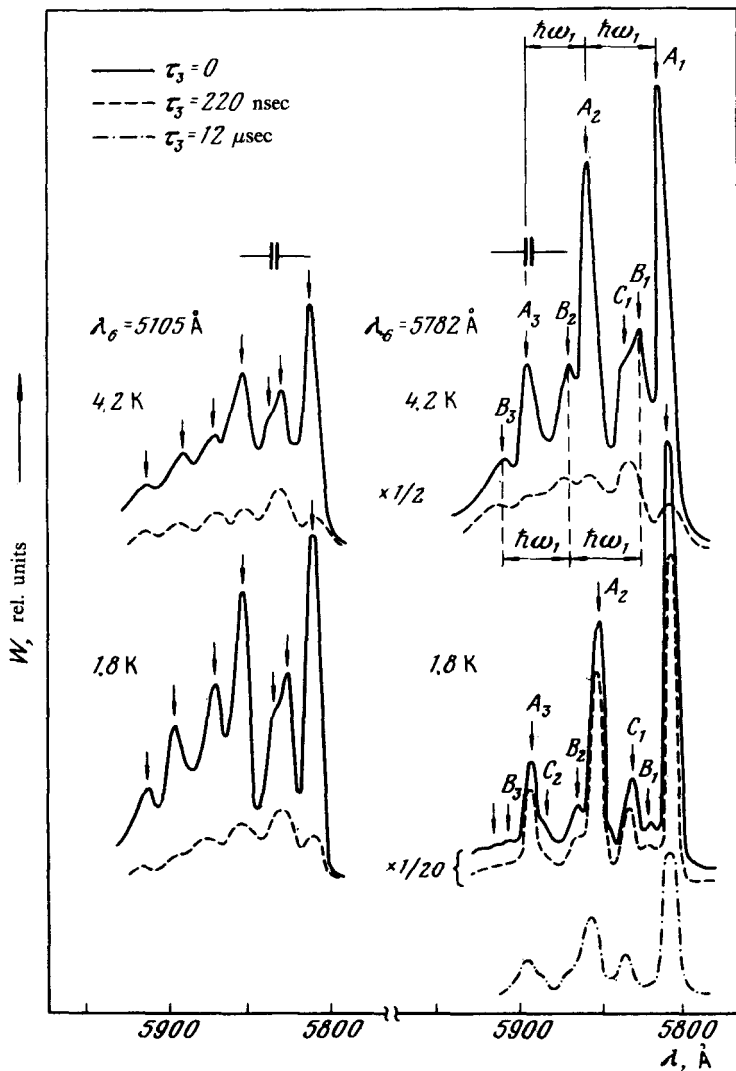


FIG. 1. Luminescence spectra of $\text{GaS}_{0.1}\text{Se}_{0.9}$ crystals with band-band excitation ($\lambda_1 = 5105 \text{ \AA}$) and impurity excitation ($\lambda_2 = 5782 \text{ \AA}$) at 4.2 and 1.8 K for various delays relative to the pump pulse.

an anomalously-large increase in the luminescence intensity for a temperature change of 2 K is unusual and calls for a special discussion.

Before considering the nature of the observed changes, we shall make several remarks concerning the luminescence spectrum of $\text{GaS}_{0.1}\text{Se}_{0.9}$. The emission lines (see Fig. 1) A_1 , A_2 , and A_3 as well as B_1 , B_2 , and B_3 differ by the same energy. It is natural to assume that A_2 (B_2) and A_3 (B_3) are the phonon echos of A_1 (B_1), characterized by the emission of one and two phonons, respectively. The phonon energy $\hbar\omega_1 \approx 15.5 \text{ MeV}$ is close to the phonon energies of 15 and 16 meV as the point M in the Brillouin zone⁽⁶⁾ in

ϵ -GaSe. We consider first the nature of the emission for $T > 4.2$ K. As long as the form of the spectra and the extinction times are independent of excitation (λ_1 and λ_2), we may assume the same mechanism for emission. It was shown in Ref. 2 that the emission spectra of $\text{GaS}_x\text{Se}_{1-x}$ compounds for $x > 0.1$ are due to indirect transitions. Thus, in Ref. 2 the radiative transition of the majority carrier (hole) to an impurity center, whose role is played by a donor associated with the indirect band, is assumed to be the mechanism for radiative recombination. In studies of $\text{GaS}_{0.1}\text{Se}_{0.9}$ crystals the behavior of the A lines for $T > 4.2$ K satisfies this mechanism completely. Actually, for an impurity mechanism for recombination the energy of the emitted photons satisfies the relation $h\nu = E_G - E_D - \sum \hbar\omega_i + E$, where E_G is the width of the forbidden band, E_D is the donor ionization energy, $\hbar\omega_i$ is the energy of the photons participating in the transition (for a non-photon transition $\hbar\omega_i = 0$), and E is the kinetic energy of the hole. In the experiment a shift of the A lines to shorter wave-lengths by 9 \AA was observed when the temperature was increased from 4.2 to 40 K. Since E_G is practically unchanged at these temperatures, the short-wavelength shift of 3.5 MeV (9 \AA) corresponds to the kinetic energy of the hole $E \sim kT \approx 3.5 \text{ meV}$ (at 40 K). A subsequent long-wavelength shift of the A lines with increasing temperature is explained by a decrease in E . The decay time for the A lines of 100–300 nsec is determined by the non-radiative capture of free holes. The B lines are probably constrained by another donor center.

In order to understand the sharp variation of the emission intensity in the 4.2–1.8 K temperature interval during excitation by the yellow line, we shall attempt to clarify the nature of the basic difference between the two excitation methods (λ_1 and λ_2). The green line energy $h\nu_1 > E_G^I$, the width of the forbidden band at the point I . In a crystal, these photons produce electron-hole pairs. The electrons are trapped by positively-ionized charged donor centers, and then recombine with free holes. In the case of impurity excitation ($h\nu_2 = 2.144 \text{ eV}$) an electron and a hole are produced directly near a charged donor center. Moreover, the electron is ejected to a bound state of the donor. In order to explain the growth of the emission intensity and an increase in the decay time, it is necessary to assume that the hole is also localized near the donor center, thereby decreasing the probability of its nonradiative recombination. In order for such a localization to occur, it is necessary that the hole have a finite affinity energy E_{af} for the neutral donor center.¹⁸⁾ In fact, since the effect disappears completely on increasing the temperature from 1.8 to 4.2 K, E_{af} must be quite small and on the order of kT at 4.2 K, i.e., 0.3–0.4 meV. Since the hole was localized near a neutral donor, the excitation which has been produced may therefore be called excitonic and be localized at the ionized donor. It is known,^{18,9)} that such excitations are stable only for certain mass ratios of the electron and the hole. There is apparently no reliable criterion for exciton stability at a charged center for an arbitrary dispersion law. In fact, the values of the effective masses in a given compound are not known, and it is therefore not possible to check the stability of such a compound by a theoretical calculation. However, all the data given above suggest that at $T = 1.8 \text{ K}$ excitation by the yellow line to the formation of an exciton in $\text{GaS}_{0.1}\text{Se}_{0.9}$ which is localized at a charged center.

In conclusion, the level of a stable exciton-impurity complex (EIC) should lie

below the level of a free exciton. According to our results, the position of one of the EICs in $\text{GaS}_{0.1}\text{Se}_{0.9}$ is determined at low temperatures ($T \leq 4.2 \text{ K}$) by the quantum energy $h\nu$ which corresponds to line A_1 . At the same time the energy of a free exciton (indirect) in this compound, determined in Ref. 5 by absorption data, is less (by about 10 MeV) than the energy of this EIC. We believe that the energy values of the indirect exciton band in $\text{GaS}_x\text{Se}_{1-x}$ which are given in Ref. 5 appear reduced at small values of x .

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¹J.P. Voitchovsky and A. Mercier, J. Phys. Chem. Sol. **36**, 1141 (1975).

²G.L. Belenkii, R. Rh. Nani, E. Yu. Salaev, and R.A. Suleimanov, Phys. Stat. Sol. (a) **31**, 707 (1975).

³N. Kuroda and Y. Nishina, Phys. Stat. Sol. (b) **72**, 81 (1975).

⁴V.E. Stopachinskii, Zh. Eksp. Teor. Fiz. **72**, 592 (1977) [Sov. Phys. JETP **45**, 310 (1977)].

⁵C. Depeursinge and Le Chi Thanh, Proc. 13th Intern. Conf. Phys. Semicond., Rome (1976).

⁶S. Jandle, J.L. Brebner, and P.M. Powell, Phys. Rev. **B13**, 686 (1976).

⁷J.P. Voitchovsky and A. Mercier, Nuovo Cim. **22B**, 273 (1974).

⁸E. Johnson, Optical Properties of Semiconductors, Mir, Moscow, 166 (1970).

⁹E.I. Rashba, Fiz. Tekh. Poluprovodn. **8**, No. 7 (1974) [Sov. Phys. Semicond. **8**, No. 7 (1975)].