that the pressure leads to an increase of the minimal distance between the lower levels of Pr^{3+} in the directions of <100>. This decreases the contribution of the mechanism of transverse relaxation and increases the contribution of the slow-relaxation mechanism. The result is the minimum of ΔH in the direction <100>, which is characteristic of the slow-relaxation mechanism.

A more exact answer to the question of the nature of relaxation in YIG with Pr^{3+} ions can apparently be made by measurement of the angular and temperature dependences of ΔH at different pressures.

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OBSERVATION OF RADIATIVE RECOMBINATION ON THE SURFACE OF A SEMICONDUCTOR (GaAs)

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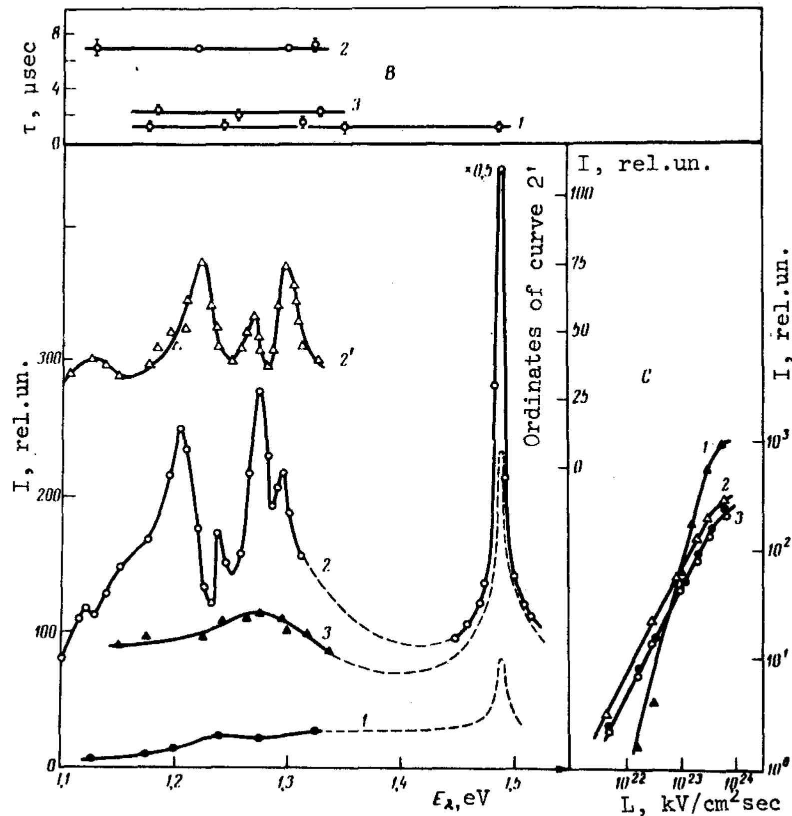
1. The influence of the surface of a semiconductor on the luminescence was established in a number of investigations, and in all the studied cases the surface served as a quenching factor caused by the intense nonradiative channel of surface recombination (see, e.g., [1 - 3]). So far no one has succeeded in observing the radiation produced by luminescence from surface centers. Yet experiments in this direction are of fundamental importance for several reasons. In view of the lowering of the crystal symmetry, the eased conditions for "cooling" of the free carriers on the surface [4, 5], etc., the question is raised whether radiative processes can exist at all on the surface of the semiconductor. For exciton radiation, this reduces to the question whether surface excitons can exist in principle. We are thus dealing with fundamental properties of the surface of semiconducting crystals.

On the other hand, the creation of a surface on which radiative processes predominate is important for the establishment of the nature of local centers, for the investigation of surface-phonon spectra, and also for laser physics.

2. Experiments aimed at observing surface radiation were performed on a high-emissivity material (GaAs) using a pulsed ($t_p \approx 3 \times 10^{-8}$ sec) ruby laser exciting a narrow (~1 μ) surface region. The maximum laser intensity (L) was 10^{24} kV/cm²sec. In addition to a sharp increase in the investigated signal, the use of the laser techniques is important when it comes to reducing the relative influence of nonradiative channels (particularly, because of the shift of the Fermi quasilevels towards the edges of the forbidden band and the ensuing inclusion of shallow centers [6]). As is well known, shallow centers are more capable of resonant energy exchange with release of phonons than are the deep and as a rule nonradiative centers. For the same reason, the surface mainly employed was the one obtained by cleavage along the (110) direction at low temperature in a neutral medium (liquid hydrogen). In this case a sufficiently large number ($\sim 10^{14}$ cm^{-2}) of shallow centers is produced on the surface [7]; on the other hand, the production of deep centers connected with structure or chemical-structure complexes is made difficult.

We investigated single-crystal samples of GaAs of two types: (I) n-type with $n_0 = 3 \times 10^{15}$ cm^{-3} and $\mu_n \approx 1.3 \times 10^3$ cm²/V-sec and (II) semiinsulating



Spectra (A), long-wave-section relaxation times (B), and lux plots (C) of GaAs radiation at 20°K. (1 - 3 pertain to samples of batch I; 2' pertains to samples of batch II); A, B: 1 - mechanically polished surface, 2, 2' - surface purified by cleavage along (110), 3 - surface after cleavage and exposure to air at 300°K for 24 hr. C: 1 - for peak with E_1 = 1.49 eV; 2 - for peak with E_3 = 1.275 eV, 3 - for peaks with E_2 = 1.3 eV (●) and E_4 = 1.2 eV (o).

with $\rho \simeq 2 \times 10^{8}$ ohm-cm. In addition to the cleaved surface, we investigated also real surface states produced by chemical etching (HNO_3:HF:H_2O = 3:1:2) and mechanical polishing. The laser photoluminescence spectra were measured from the unilluminated side of the sample with the aid of an IKS-12 monochromator and an FEU-62 photomultiplier. In the investigation of the impurity region of the laser photoluminescence we used an additional GaAs filter. In addition to the laser photoluminescence amplitude (I), we determined also the radiation kinetics I(t) (see [6]).

3. The figure shows the spectra, the times of long-duration relaxation, and the lux plots of the radiation of GaAs at 20°K. It is seen from the figure that in samples with "real" surfaces one observes only one band ($E_1 \simeq 1.49$ eV) for which $I \sim L^2$ and which is thus determined by the edge volume radiation. In the relaxation of the radiation, two sections are observed: a slower one with τ_1 on the order of microseconds, and a faster one (practically duplicating the laser pulse wave form) with $\tau_2 \lesssim 3 \times 10^{8}$ sec. A noticeable influence of the state of the surface on τ_1 was established. For example, τ_1 was increased by etching from 0.7 μsec (for a mechanically polished surface) to more than double the value.

After the cleavage, the amplitude of the edge radiation increased noticeably, and new peaks appeared in the long-wave region. The most pronounced were the peaks $E_2 \simeq 1.3$ eV, $E_3 \simeq 1.27$ eV, $E_4 \simeq 1.2$ eV, and $E_5 \simeq 1.13$ eV. The form of the IR spectrum was independent (in the investigated interval $L \geq 10^{22}$ kV/cm^{2}sec) of the intensity of the exciting light L. This corresponds to the following observed fact: the intensity of the observed peaks depends linearly on L up to the maximum laser excitations. The appearance of peaks for the samples I was accompanied also by a strong increase in the relaxation time (τ_1 increased by $\sim$5 - 10 times, τ_2 by $\gtrsim$30 - 50 times). For samples II, the cleavage led to the appearance of analogous peaks. However, the kinetics of the relaxation of the laser photoluminescence ($\tau_1 \simeq 0.7$ μsec, $\tau_2 \leq t_4$) remained unchanged.

Exposure of the samples at T = 300°K to an atmosphere of hydrogen gas had little effect on the positions and the shapes of the peaks. At the same time, exposure of the samples at the same T for a day in air led to the vanishing of the peaks E_2, E_4, and E_5 and to a decrease in the amplitude of the peak E_3.

4. Let us discuss the results briefly. The smallness of the quantum yield ($\eta << 1\%$), the weak dependence of the laser photoluminescence relaxation times on E_λ, and their increase after the cleavage (samples I) indicate that recombination exerts a decisive influence on the kinetics of the nonradiative surface channel. At the same time, for samples II the influence of the volume nonradiative channel predominates in the kinetics.

The positions of the bands E_5, E_2, E_3, and E_4 on the energy scale, and the linear character of the dependence of I on L at given E_λ, all offer unambiguous evidence of their "impurity" nature. On the other hand, the dependence of the given peaks on the state of the surface (their occurrence after the cleavage, their conservation after exposure at 300°K to an atmosphere of gaseous H_2, the vanishing of the peaks after contact with the chemically-active gas medium O_2 or $H_2O + O_2$ and after etching of a layer $\sim$150 Å), and the independence of their position of the doping of the volume, all indicate unambiguously that the observed peaks have a surface nature.

We have thus observed, for the first time, the phenomenon of radiation via surface centers in semiconducting crystals. The energy positions of these centers ("shallow" centers) agree qualitatively with the theoretical ones calculated for an atomically pure (110) surface of GaAs [8]. A detailed investigation of the characteristics of the radiation bands (their shapes, polarization, etc.) will make it possible to establish the feasures of the surface luminescence as compared with volume luminescence.

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GaSe, A NEW EFFECTIVE MATERIAL FOR NONLINEAR OPTICS

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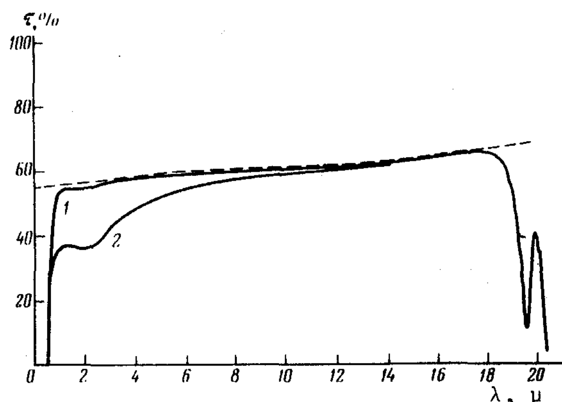
We have investigated the nonlinear optical properties of the semiconducting crystal GaSe, which belongs to the point group $\bar{6}$m2. We used p-type single crystals with carrier density 10^{15} cm^{-3} and mobility 25 cm^2/V-sec, grown by the Bridgman-Stockbarger method. The growth technique makes it possible to obtain single crystals up to 30 mm in diameter and more than 100 mm in length.

The GaSe crystal is transparent in the wavelength range from 0.65 to 18 μ (Fig. 1) and is of good optical quality. The absorption coefficient in the transparency region does not exceed 1 cm^{-1}.

We measured the ordinary refractive index and the birefringence index in the wavelength range from 0.63 to 10.6 μ. The dispersion of the refractive index in the transparency region is described with sufficient accuracy by the formulas

$$n_o^2 = A/\lambda^4 + B/\lambda^2 + C + D\lambda^2 + E\lambda^4,$$
$$n_e^2 = K + L/(\lambda^2 + M) + H\lambda^2, \quad (1)$$

where A = -0.05466, B = 0.48605, C = 7.8902, D = -0.000824, E = -0.00000273, K = 6.0476, L = 0.3423, M = -0.16491, H = -0.001042, and λ is measured in microns.



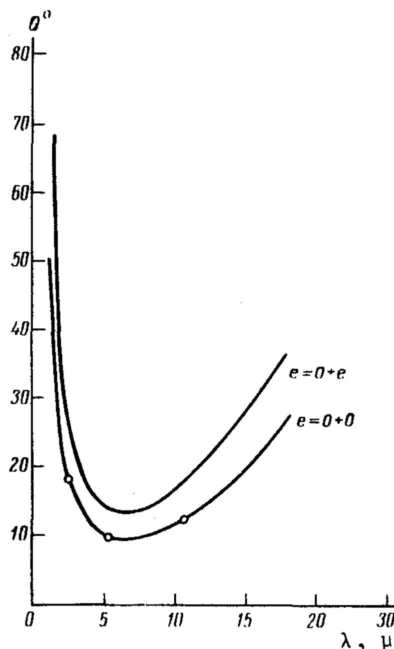


Fig. 1. Transmission spectrum of GaSe crystal: dashed curves - reflection loss, continuous curves - transmission spectrum: 1 - sample thickness 1.5 mm, 2 - 6.0 mm.

Fig. 2. Dependence of the phase synchronism angle for the second harmonic on the pump wavelength.