

EFFECTS OF EXCITATION-INDUCED OPTICAL ABSORPTION
IN HIGHLY EXCITED SEMICONDUCTORS

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ABSTRACT

The red shift of stimulated emission bands of various semiconductors with increasing pumping intensity or length of the excited region of the crystal is explained by the wavelength-dependent gain saturation due to relative increase in optical absorption. Several effects of excitation-induced negative gain are also discussed.

Stimulated emissions in undoped semiconductors have been studied by a number of investigators under intense optical or electron-beam excitations. It has often been observed that the stimulated emission band appearing on the lower energy side of the band edge shows a marked red shift with the increase of the excitation intensity or the length of the excited region of the crystal.¹⁾ Although this phenomenon appears to be very common to wide-gap semiconductors, there exists no general theory of this red shift.

In the present paper, we show that this shift is explained well by the change of the gain spectrum caused by the relative increase in the optical absorption, especially that due to the reverse process of the stimulated emission which produces the gain. Several recent experiments on highly excited semiconductors are also interpreted in terms of excitation-induced optical absorption.

It is well known in the field of laser physics that the optical gain generally decreases when the input light level is increased. This

gain saturation can be explained by the reduction of the population difference between the initial and the final states of the laser transition in the presence of intense resonant optical field. Since the optical gain is determined by the difference between the stimulated emission rate and the absorption rate, the population decrease in the initial state and the increase in the final state lead to the gain reduction, enhancing the relative contribution of the absorption process. In the case that the laser transition is related to some continuous energy band, as in semiconductors and organic dyes, this type of population change also causes variation of the gain spectrum, because the stimulated emission and reverse absorption spectra do not agree with each other in this case. Then, the spectrum of the emitted light changes with the intensity of the resonant radiation in the material. We attribute the red shift of the stimulated emission bands in various semiconductors mentioned above mainly to this effect. Some contribution may come from the population change due to other origin, which also gives a similar effect.

Figure 1 shows the emission spectra of a highly excited GaAs. The stimulated emission band denoted as [P] emerges from the low energy side of the P band and shifts towards lower energies with the excitation intensity. Then, another mechanism, which we ascribe to the luminescence from metallic electron-hole liquid state,²⁾ becomes dominant and its stimulated emission band appears on the low-energy side. The [P] band approaches asymptotically to an energy around 8 meV below the exciton energy $E_0^{1s} = (E_g - E_x^b)$ until it disappears. We attribute the spontaneous P emission band to a radiative exciton-exciton collision process and the [P] band to its stimulated process.^{3,4)} The spontaneous emission and optical gain spectra due to this process were calculated using a simplified interaction potential between the two excitons.⁴⁾ The results agreed well with the experimentally obtained spontaneous emission and small-signal gain spectra. These two spectra were almost

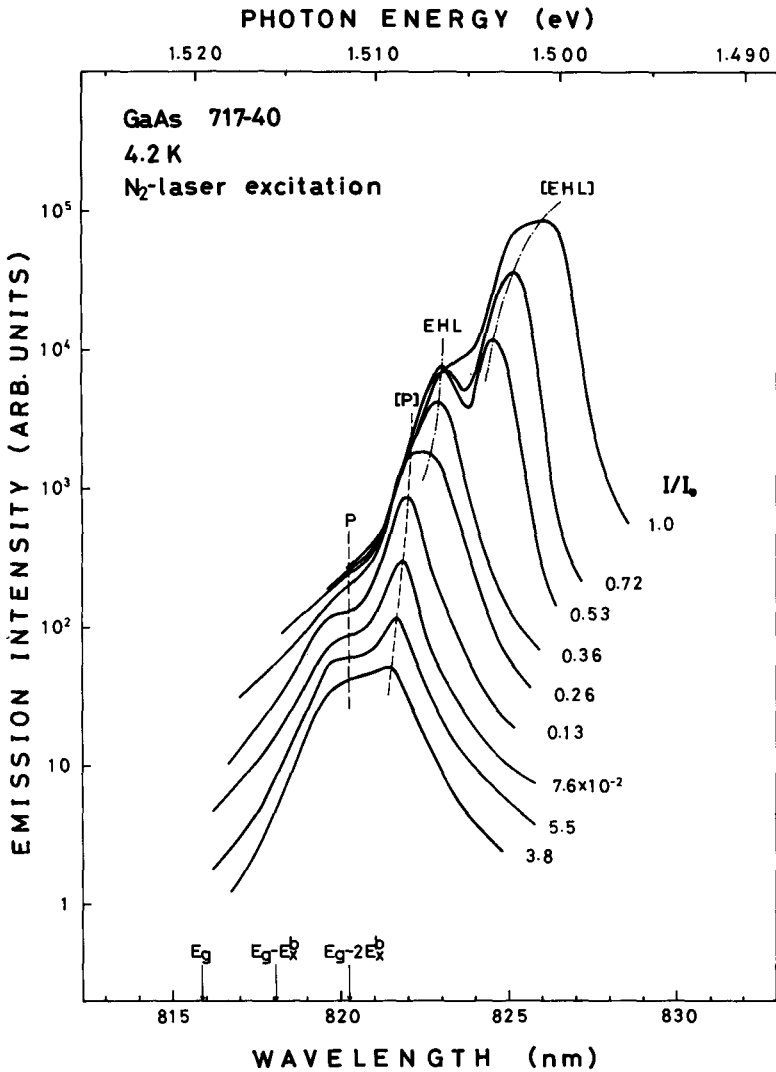


Fig.1. Emission spectra of nitrogen-laser-pumped GaAs observed in the direction parallel to the excited surface of the crystal. The excitation intensity is indicated by the ratio of the used intensity I to the maximum intensity $I_0 \approx 5\text{MW}/\text{cm}^2$. The band gap and exciton binding energies are denoted as E_g and E_x^b , respectively, and the stimulated emission bands are shown by [].

identical with each other.

Figure 2 shows the spectra calculated for the most important collision process of two ls excitons in which one exciton recombines to

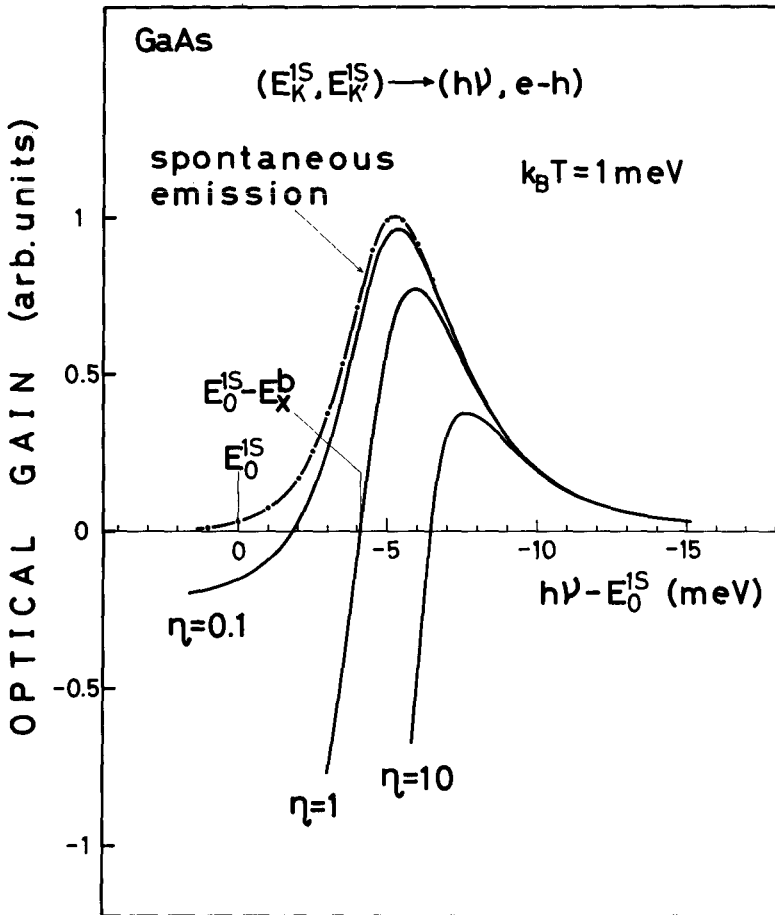


Fig.2. Calculated spontaneous emission (dashed curve) and optical gain spectra (solid curves) of GaAs due to radiative two $1s$ -exciton collision process. The parameter η is equal to $(N_e N_h / N_{1s}^2) \times (M^2 / m_e m_h)^{3/2}$, where N_{1s} , N_e and N_h are the densities and M , m_e and m_h are the masses of the $1s$ exciton, electron and hole, respectively. The energy of the $1s$ exciton with the momentum $\hbar K$ is denoted as E_K^{1s} .

emit a photon with energy $h\nu$, while the other dissociates into a free electron-hole pair.⁴⁾ Similarly evaluated absorption spectra due to the reverse process of the stimulated emission, *i.e.*, the optical absorption to create two $1s$ excitons with the annihilation of a free electron-hole pair, are plotted in Fig.3. The theoretical gain curve for $\eta = 0$ is identical with the spontaneous emission spectrum, which

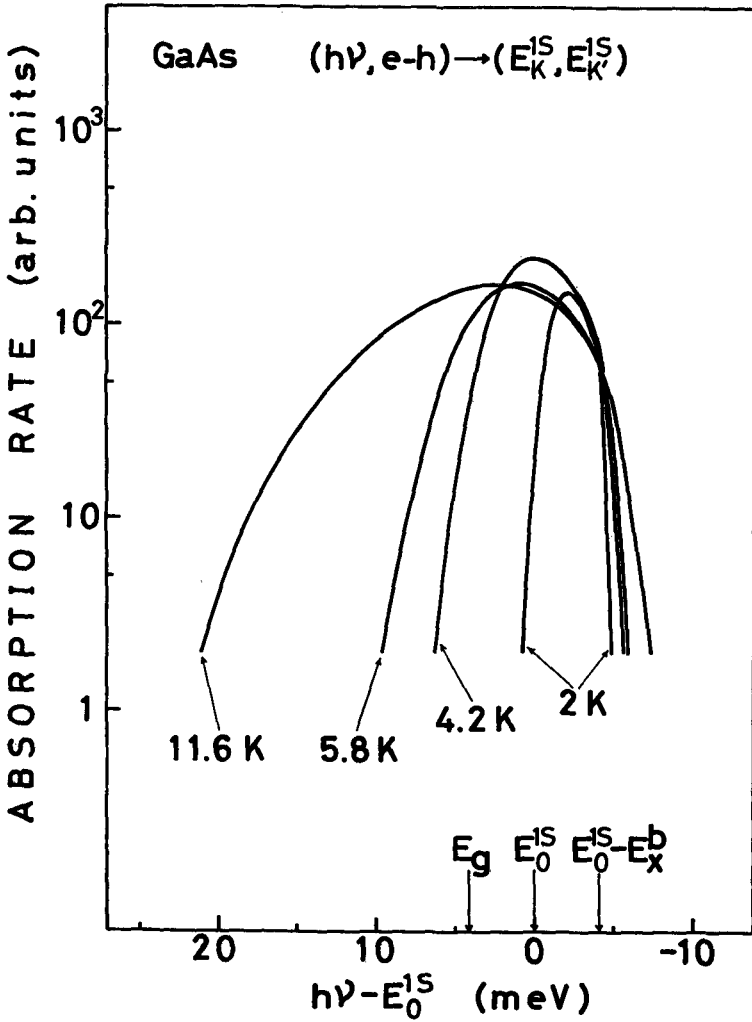


Fig.3. Optical absorption spectra of GaAs calculated for the process to create two 1s excitons with the annihilation of a free electron-hole pair.

agrees with the result on the small-signal gain spectrum in GaAs. As η is increased, the gain band is reduced and shifts towards lower energies. This is because the reverse absorption becomes significant with increasing η . As shown in Fig.3, this absorption band is located on the higher energy side of the emission band, so that the relative increase of the reverse absorption reduces the gain in the high-energy part of the spectrum and accordingly leads to the red shift of the gain

band.

In highly excited GaAs, the spontaneously emitted radiation is amplified in the crystal. When the power of this resonant radiation becomes intense enough, an increase of the population ratio of free carriers to excitons occurs corresponding to the gain saturation for the large signal. Then, the gain spectrum changes, the gain becoming very small or even negative at the high-energy part, while the change being relatively small at the low-energy part. Thus the resonant radiation spectrum and accordingly the emitted output spectrum shift towards lower energies. Since η is dependent on the resonant radiation power inside the crystal, the magnitude of the red shift depends on the excitation intensity, the length of the excited region of the crystal, and so on. It may be reasonable to consider that the free carrier densities N_e and N_h become close to the exciton density N_{1s} at the high intensity limit of the resonant radiation. In the case of GaAs, this corresponds to η of ~ 10 . Since the peak of the calculated gain curve for this value of η is shifted by ~ 8 meV from the exciton energy, the observed red shift of the [P] band is explained very well by the above theory.

Benoit à la Guillaume *et al.*⁵⁾ observed a red shift of the gain peak as a function of excitation time in an electron-beam pumped CdS crystal. They ascribed this gain mechanism to the exciton-electron collision process and explained the time variation by the rise of the electron and exciton temperatures T_e and T_{ex} . The ratio of the reverse absorption rate to the stimulated emission rate due to this process increases very rapidly when T_e is increased or when N_{1s} is decreased. Since the location of the reverse absorption band is higher in energy than that of the emission band, the relative increase in the reverse absorption shifts the gain band to the red as in the case of two-exciton collision process. From the energy position of the small-signal gain peak and the spectral shape of the spontaneous emission band locating

around the energy region of our interest, it seems to be more plausible to attribute the above gain mechanism to the exciton-exciton collision process. In this case also, we can explain the observed red shift by the relative increase of the excitation-induced optical absorption rates with time. The optical absorption due to the reverse processes of the radiative exciton-electron and exciton-exciton collisions will be enhanced by the rise of T_e and also by the increases of the free carrier density and the resonant radiation intensity (filling-up of trapping levels with time probably increases the lifetimes of the free carriers and excitons and also reduces the impurity-induced absorption below the band gap).

For the luminescence process of an excitonic molecule to leave a single exciton, similar red shift has been observed by several investigators.⁶⁻⁸⁾ In CuCl, for example, the M_L line increases in intensity much rapidly compared with that of the M_T line and shows an apparent red shift with the increase of the excitation intensity.⁷⁾ This result can be understood well again by considering the effect of the reverse absorption on the gain as follows. When the resonant radiation power is increased, the gain for the M_T line is saturated immediately because of the relatively long lifetime of the single transverse exciton. Gain saturation for the M_L line to leave the single longitudinal exciton with short lifetime becomes significant at higher radiation powers, and is stronger at the high-energy part than at the low-energy part for the same reason as mentioned above.

In Fig.2, the optical gain is negative in the high-energy part of the spectrum unless $\eta = 0$. This is because the stimulated emission is overcome by the reverse absorption in this spectral region. This negative gain explains the pumping-induced optical absorption below the band gap in highly excited CdS.^{9,10)} In GaSe, an intense stimulated emission band due to the exciton-exciton collision process was found to appear at 77 K under pulsed dye-laser excitation at 595 nm (~ 14 meV

below the exciton energy) where the absorption coefficient in unexcited crystals is small.¹¹⁾ This result is explained by our model as follows. The pumping light is first absorbed weakly to create free carriers, which then induce new absorption as discussed above. From the very high gain reported in the literature,¹⁾ excitation-induced optical absorption around 595 nm is estimated to become fairly large. Thus, the efficient pumping below the exciton energy is understood well by our theory.

Hildebrand and Göbel¹²⁾ measured the excitation spectrum for the stimulated emission band due to the exciton-exciton collision process in GaAs, *i.e.*, the [P] band of Fig.1, at 2 K. The spectrum measured at the excitation density of $\sim 10^5$ W/cm² was found to be located between the energies E_0^{1s} and $(E_0^{1s} - E_x^b)$. Compared with the theoretical absorption spectrum of Fig.3, we find that this result can be explained by the pumping-induced negative gain exactly in the same way as in the case of GaSe mentioned above. Recently it has been found that the excitation spectrum for the excitonic molecule luminescence in CdS has a broad structure-less band peaking around the exciton energy.¹³⁾ We attribute this band again to the above-discussed excitation-induced optical absorption such as due to the reverse processes of the radiative exciton-exciton and exciton-electron collisions.

In conclusion, it has been shown that the excitation-induced optical absorption as well as the stimulated emission plays an important role in the optical spectra of highly excited semiconductors. Since the energy position of the stimulated emission band often depends on the pumping power, the length of the excited region and so on, the measurement of the unsaturated gain spectrum, especially under the condition of negligible absorption, is important for the identification of the dominant gain mechanism.¹⁴⁾

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