PHYSICAL REVIEW B VOLUME 36, NUMBER 2 15 JULY 1987-I

Photoluminescence due to exciton-exciton scattering in GaSe under picosecond laser excitations

X. Z. Lu, R. Rao, B. Willman, S. Lee, A. G. Doukas, and R. R. Alfano
The Institute for Ultrafast Spectroscopy and Lasers, Department of Physics and Electrical Engineering,
The City College of New York, New York, New York 10031
(Received 28 October 1986)

Picosecond-laser-excited photoluminescence spectra in GaSe at room temperature have been measured and analyzed. Both spontaneous and stimulated emissions were attributed to the exciton-exciton scattering process in GaSe through a careful band-shape analysis. The exciton-photon coupling coefficient $\pi\alpha/\epsilon=3.3\times10^{-3}$ was obtained from the spontaneous emission spectra fit. The stimulated emission is well explained by the optical gain mechanism arising from the reverse absorption process of the exciton-exciton scattering.

I. INTRODUCTION

Over the years many experiments on the luminescence spectra of the gallium selenide (GaSe) semiconductor using different excitation techniques and configurations at various temperatures and excitation intensities have been performed.[1–13] Various mechanisms have been suggested to explain the observed luminescence spectra in GaSe. The origin of the spontaneous and stimulated emissions in GaSe at high excitation levels still remains controversial. At room temperature and high excitation intensities ($\sim10^8$ W/cm^2) the emission spectra from GaSe consist of two bands: a broad spontaneous band peaked at ~628 nm and a narrow stimulated one at ~646 nm. Most of the preceding publications attributed them to two different mechanisms without considering the correlation between those two bands. In fact, the feature that a sharp stimulated emission line appears at the low-energy side of a broad spontaneous band exists in many semiconductors and can be explained by a general theory based on different emission mechanisms. In this paper, we will show through a band-shape analysis that the spontaneous and stimulated emission bands in GaSe originate from the same mechanism—the exciton-exciton scattering process.

In Sec. II, we report on our experimental apparatus and techniques. The observation of the photoluminescence spectra at room temperature is discussed in Sec. III. Different theoretical models are presented in Sec. IV. Numerical calculations based on these theories are presented and compared to our experimental spectra in Sec. V. Discussion of the results are given in Sec. VI.

II. EXPERIMENTAL METHOD

The experimental setup used a mode-locked Nd:YAG (YAG denotes yttrium aluminum garnet) laser system Quantel YG401C including an oscillator, an acoustic-optic modulator, a pulse selector, a two-pass amplifier, and a second-harmonic generator. The excitation beam of 27 psec at 532 nm was focused on the sample surface to a spot of ~0.35 mm in diameter. The excitation beam was *s* polarized and nearly perpendicularly incident on the sample surface.

GaSe is a III-VI semiconductor which crystallizes in a layer structure. Three different periodic stacking sequences of the layers have so far been observed and described in the literature as β-, γ-, and ϵ-GaSe.[14] The corresponding periods embrace two, three, and two layers, respectively. The ϵ-GaSe which has D_{3h} symmetry[15] was used in the present work. The top valence band has a Γ_4^- symmetry and the lowest conduction band has a symmetry of Γ_3^+ at the center of the first Brillouin zone. The sample used was an ϵ-type GaSe thin-layer single crystal with the *c* axis perpendicular to the surface of the layer. The photoluminescence from the sample was collected by a lens of 15 cm focal length at an angle of 40° into a $\frac{1}{4}$-m Jarrell-Ash spectrometer. The signal was measured by a silicon-intensified-target detector coupled to an optical-multichannel analyzer (OMA-III), and stored in a PDP 11/23 + minicomputer. Corning 3-67 filters were placed in front of the spectrometer to eliminate the elastically scattered light from the sample. All photoluminescence spectra were recorded at room temperature by single shots of the laser. The resolution of the detection system was about 2 nm.

III. RESULTS

The photoluminescence spectra from GaSe at room temperature under the picosecond-pulse-laser excitation corresponding to the three excitation energies 0.5 μJ (weak), 2.0 μJ (medium), and 4.0 μJ (strong) per pulse are shown in Figs. 1(a), 1(b), and 1(c), respectively. The excitation intensities are 0.16×10^8, 0.64×10^8, and 1.3×10^8 W/cm^2, respectively. At low excitation intensities ($<0.5\times10^8$ W/cm^2) only one broad band peaked at ~628 nm (which agrees with Ref. 11) was observed. This band, as shown in Fig. 1(a), is attributed to the spontaneous emission in GaSe. Its intensity was found to be proportional to the excitation intensity. At medium intensity [see Fig. 1(b)], in addition to the spontaneous emission band at ~628 nm, there appears a sharp stimulated emis-

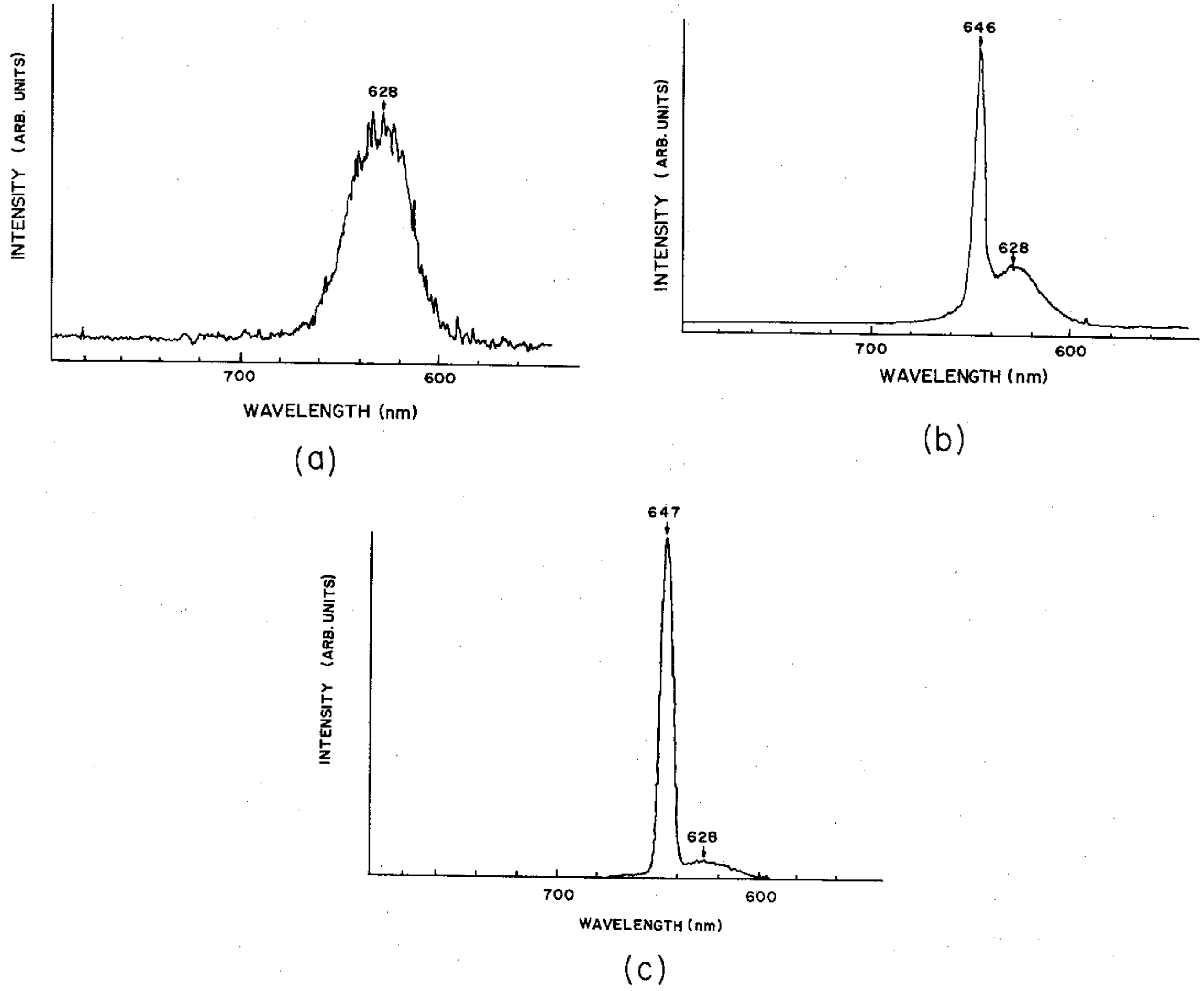

FIG. 1. Photoluminescence spectra excited by a picosecond 532-nm beam at three different excitation intensities: (a) $I = 0.16\times10^8$ W/cm^2, (b) $I = 0.64\times10^8$ W/cm^2, (c) $I = 1.3\times10^8$ W/cm^2.

sion line at 646 nm whose intensity increases superlinearly with the excitation intensity. At strong excitation intensity the stimulated emission peaked at ~647 nm dominates the entire emission spectra, as shown in Fig. 1(c). No impurity emission lines from our GaSe samples were observed because of the relatively high temperature (~300 K) in the experiment.

IV. THEORY

In highly excited semiconductors, exciton-exciton scattering and electron-hole plasma effects play significant roles in the luminescence spectra near the band edge of the material. Both mechanisms have been reported in various semiconducting compounds and also have been suggested to be important in the optical amplification and the laser action.

The electron-hole plasma (EHP) emission originates from recombination of electron-hole pairs. The spontaneous emission spectrum at high temperature with the k-selection rule is given by[16]

$$I_{\rm sp}(E) \propto (E-\tilde{E}_g)^{1/2} \exp\left[-\frac{E-\tilde{E}_g}{k_B T_e}\right], \tag{1}$$

where $\tilde{E}_g = E_p - \frac{1}{2}k_B T_e$, T_e is the electronic temperature, $\tilde{E}_g$ is the reduced band-gap energy, and E_p is the peak energy of the emission band.

The optical amplification gain spectrum is given by[17]

$$g(E) \propto I_{\rm sp}(E)\left[1-\exp\left[\frac{E-\Delta F}{k_B T_e}\right]\right], \tag{2}$$

where

$$\Delta F = F_e - F_h$$

is the energy difference between the quasi Fermi levels of the electron and the hole. As shown in Fig. 1 of Ref. 17, the peak of gain occurs on the low-energy side of the peak of $I_{\rm sp}(E)$ due to the excitation-induced reverse optical-absorption process of the stimulated emission.

The stimulated emission spectrum for unsaturated gain is given by[1]

$$I_{\rm st}(E)=I_0\exp(gL)\ , \tag{3}$$

where L is the length of the excitation region.

The emission due to exciton-exciton scattering can be expressed symbolically as $(E_K^{1s},E_{K'}^{1s})\rightarrow(h\nu,e\text{-}h)$. The spontaneous emission spectrum due to this process is given by[18]

$$I_{\rm sp}(E)\propto\frac{E\rho(E)}{(E-E_x)^2+(\pi\alpha/\epsilon)E_x^2}\,\frac{1}{k_BT_x}\int_0^\infty d\xi\int_0^\infty dt\frac{\sqrt{\xi}}{(1+\xi/E_b)^4}\exp\left[-t-\frac{1}{4t}\left[\frac{E_x-E_b-E-\xi}{k_BT_x}\right]^2\right]\ , \tag{4}$$

where $\rho(E)dE$ is the number of photon modes in the crystal between energies E and $E+dE$, where $\rho(E)\propto E^2$, E_x is the energy of the $1s$ exciton at $\mathbf{K}=0$, E_b is the binding energy of excitons, $E_x=E_g-E_b$, T_x is the exciton temperature, α and ϵ are the polarizability of excitons and dielectric constant of the material, respectively. Note that nonradiative exciton-exciton interaction, which is expected to be proportional to the exciton temperature T_x, should decrease the exciton lifetime and broaden the emission lines. This effect is implicitly reflected by the factor $(1/k_BT_x)$ outside the integral in Eq. (4).

The spectral gain due to exciton-exciton scattering process is given by[19]

$$g(E)\propto I_{\rm sp}(E)\left[1-\eta\exp\left[\frac{E-(E_x-E_b)}{k_BT_x}\right]\right]\ , \tag{5}$$

where

$$\eta=\frac{n_en_h}{n_x^2}\left[\frac{m_x^2}{m_em_h}\right]^{3/2}. \tag{6}$$

and $n_e,m_e;n_h,m_h$; and n_x,m_x are densities and effective masses of electron, hole, and exciton, respectively. Note that η increases with increasing temperature, excitation intensity, or length. A similar red shift of the optical gain peak relative to the spontaneous emission peak can be seen from Fig. 1 of Ref. 19. The stimulated emission spectrum in this model is also given by Eq. (3).

V. NUMERICAL CALCULATION AND FITTING DATA

The calculated spontaneous emission spectra at different electronic temperatures using the EHP model [Eq. (1)] are shown in Fig. 2 in which $E_p=1.973$ eV. The solid dots represent the experimental data of Fig. 1(b). The calculated high-energy tail fits the data well if we choose $T_e=400$ K. However, the sharp drop at the low-energy side of the theoretical curve cannot fit the experimental data at all.

The spontaneous emission spectra predicted by the exciton-exciton scattering model [Eq. (4)] are shown in Fig. 3(a) for different excitonic temperatures, and Fig. 3(b) for different exciton-photon coupling coefficient $\pi\alpha/\epsilon$. It is clear that the high-energy tail of the spectra is sensitive to the excitonic temperature T_x and the low-energy tail is sensitive to the choice of $\pi\alpha/\epsilon$. The best-fit result occurs at exciton temperature $T_x=500$ K and $\pi\alpha/\epsilon=3.3\times10^{-3}$, as shown in Fig. 3(b). Typical values of the exciton-photon coupling coefficient $\pi\alpha/\epsilon$ in semiconductors range from 10^{-4} to 10^{-3}, e.g., for the A exciton in CdS, the oscillator strength $4\pi\alpha=0.0142$ and the background dielectric constant $\epsilon=9.38$ were derived from resonant Brillouin scattering,[20] yielding $\pi\alpha/\epsilon=3.8\times10^{-4}$. The exciton-exciton scattering model gives a much better fit than the EHP model. Therefore, we believe that exciton-exciton scattering is the dominant mechanism responsible for the spontaneous emissions in GaSe at room temperature and high excitation levels ($\sim10^8$ W/cm^2).

The optical gain spectra calculated from the exciton-exciton scattering model [Eq. (5)] for $E_x=2.0$ eV, $E_b=0.020$ eV, and $T_x=500$ K are shown in Fig. 4(a) for different η, where $I_{\rm sp}(E)$ was taken from the experimental data of Fig. 1(b). We see that the gain curve is very close to the spontaneous emission spectrum when η is small. As η is increased, the gain peak shifts towards the low-energy side and the peak amplitude decreases. (The gain in the high-energy region of the spectrum becomes negative and is not shown in the figure.) This is because the optical absorption due to the reverse process, i.e., the creation of two $1s$ excitons with the annihilation of a pho-

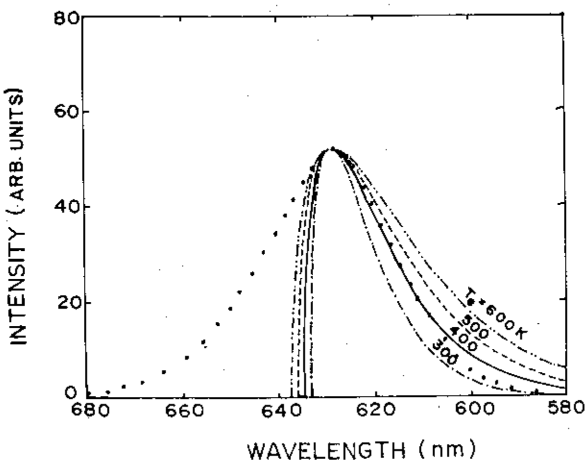

FIG. 2. Calculated spontaneous emission spectra from the EHP model [Eq. (1)] with $E_p=1.973$ eV and different electronic temperature T_e. The solid circles represent the experimental data of Fig. 1(b).

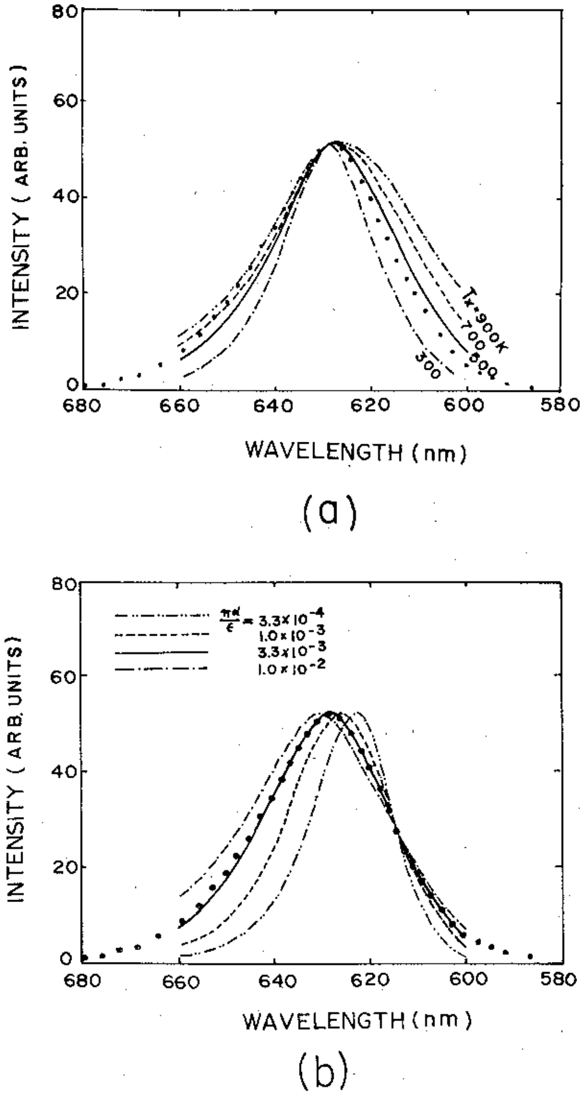

FIG. 3. Calculated spontaneous emission spectra from the exciton-exciton scattering model [Eq. (4)] with $E_x=2.0$ eV, $E_b=0.020$ eV, and (a) $\pi\alpha/\epsilon=2.5\times10^{-3}$ and different excitonic temperature T_x. (b) $T_x=500$ K and different exciton-photon coupling coefficient $\pi\alpha/\epsilon$. The solid circles represent the experimental data of Fig. 1(b). The best fit occurs at $E_x=2.0$ eV, $E_b=0.020$ eV, $T_x=500$ K, and $\pi\alpha/\epsilon=3.3\times10^{-3}$.

ton and a free electron-hole pair, becomes significant when the free-carrier density is increased. Since the reverse absorption band is located at higher energies than the emission band, a relative increase of magnitude of the reverse absorption reduces the gain in the high-energy part of the spectrum and accordingly leads to the red shift of the optical gain band.

The gain peak position relative to the spontaneous emission peak position at $T_x=500$ K, $E_x=2.0$ eV, and $E_b=0.020$ eV is plotted versus η in Fig. 4(b). If we assume the gain peak position is the same as the peak position of the stimulated emission [18 nm beyond the spontaneous one, as shown in Fig. 1(b)], we obtain $\eta=2.0$ in our experiment.

The calculated gain spectra for $\eta=2.0$ at different temperatures are shown in Fig. 4(c). The peak position shifts gradually towards low energies with the temperature rise and the peak amplitude decreases at the same time.

The stimulated emission profile (solid line) calculated from Eqs. (3) and (5) using the exciton-exciton scattering model is shown in Fig. 5. In our calculation, the maximum value of the optical gain in GaSe was normalized to 1000 cm^{-1}, which is a reasonable value derived from the literature.[9] The excitation length is estimated as $L=0.2$ mm. For comparison, we also show the observed stimulated emission spectrum (solid circles) of Fig. 1(b), as well as the calculated and observed spontaneous emission profiles in the same figure. These are good fits.

VI. DISCUSSION

The energy-conservation equation for exciton-exciton scattering emission process is given by

$$\left[E_x+\frac{\hbar^2K^2}{2m_x}\right]+\left[E_x+\frac{\hbar^2K'^2}{2m_x}\right]=h\nu+\left[E_x+E_b+\frac{\hbar^2k_e^2}{2m_e}\right]+\frac{\hbar^2k_h^2}{2m_h} .$$

If we neglect the contribution to the emitted photon from the changes in kinetic energy of the system,

$$h\nu\approx E_x-E_b=E_g-2E_b . \qquad (7)$$

Therefore, the peak position of the spontaneous emission should locate at $E_p=E_g-2E_b$, since E_g is a function of the lattice temperature which can be assumed to be reasonably the same as the ambient temperature due to the relatively slow response of the lattice to the picosecond excitation pulses. Thus $E_g=E_g(T=300\text{ K})=2.020$ eV and from Eq. (7) $E_p=h\nu=1.980$ eV ($\lambda_p\approx626$ nm). Experimentally, we obtained $\lambda_p=628$ nm which agrees with this estimate within our experimental precision. Notice that the exciton temperature T_x obtained from our experiment is considerably higher than room temperature due to fast transfer of energy from the optical pulse to the exciton system. Also, the threshold intensity of the stimulated emission in GaSe obtained in our experiment ($\sim10^8$ W/cm^2) is about 2 orders of magnitude higher than that given in Ref. 8 because the excitation length in our experiment (~0.2 mm) is much smaller.

According to Schluter,[21] GaSe is an indirect semiconductor with the top of its valence band located at the center Γ of the Brillouin zone, having the Γ_4^- symmetry, and the bottom of the conduction band situated at the M point (M_3^+ symmetry). Moreover, a relative minimum of the conduction band (Γ_3^+) at the Γ point happens to be a few tens of meV above the minimum of the M point.[21] The direct free exciton associated with the minimum Γ_3^+, with a binding energy of $E_b=20$ meV, becomes a resonant state with the continuum free-electron states of the indirect conduction-band minimum. Therefore, electrons in the indirect conduction band will jump into the direct free exciton levels at high-temperature and high-excitation conditions,[22] which increases the (direct) free exciton den-

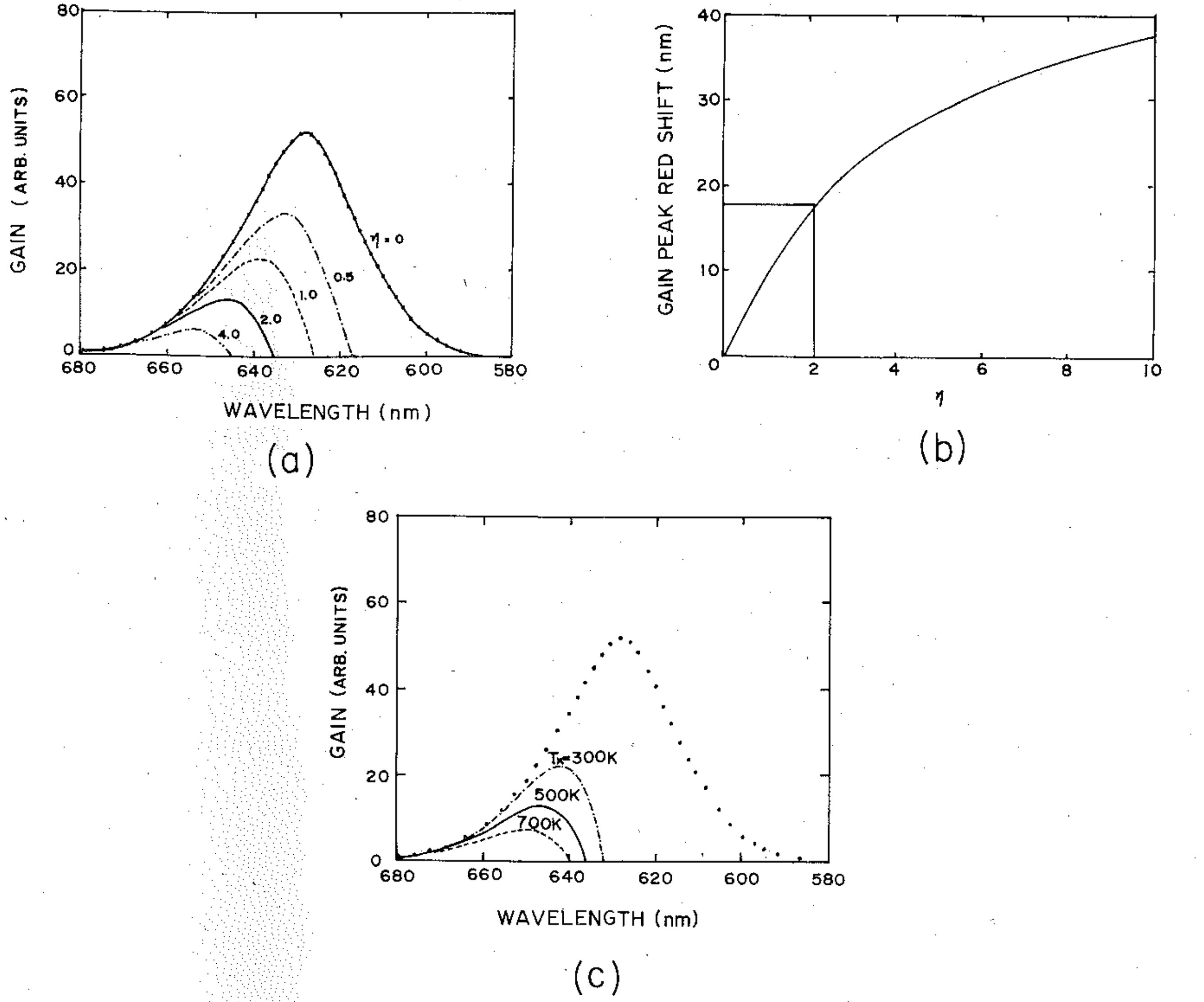

FIG. 4. (a) Calculated optical gain spectra due to exciton-exciton scattering in GaSe for $E_x = 2.0$ eV, $E_b = 0.020$ eV, $T_x = 500$ K, and different η. (b) Calculated optical gain peak red shift relative to the spontaneous emission peak vs η. (c) Calculated optical gain spectra in GaSe due to exciton-exciton scattering for $E_x = 2.0$ eV, $E_b = 0.020$ eV, $\eta = 2.0$, and different excitonic temperatures.

sity and favors the exciton-exciton scattering process.

At extremely high excitation intensities the excitons would dissociate into electrons and holes due to the screening of the Coulomb interactions in excitons by electrons and holes, and frequent collisions between excitons. They form EHP in most direct-gap semiconductors. Frova *et al.* (1977) found that exciton absorption bands in GaSe at $T = 4.2$ K disappeared in the limit of extremely high optical intensities due to formation of EHP. The critical density for the Mott transition from exciton to EHP in GaSe (Ref. 23) is $\sim 10^{18}$ cm^{-3} (corresponding to an average separation of ~ 100 Å). In our case, about 3% of the incident photons at 532 nm would be absorbed due to scattering;[24] for pulse energy 2 μJ, the number of photon delivered by each excitation pulse is

$$N_{\mathrm{ph}} \approx 1.5 \times 10^{11} .$$

These photons are distributed in a disk area of 0.35-mm diameter and 5-μm thickness. If we assume 100% quantum efficiency for exciton production, the exciton density in GaSe right after excitation of the laser pulse will be

$$n_x \approx 3 \times 10^{17} \text{ cm}^{-3} .$$

The exciton density attainable in our experiment is believed to be smaller than this estimate due to low quantum efficiency, and various exciton decay channels, etc. The actual exciton density in our experiment was much lower than the Mott transition threshold. Therefore, the exciton-exciton scattering (instead of the EHP) model is

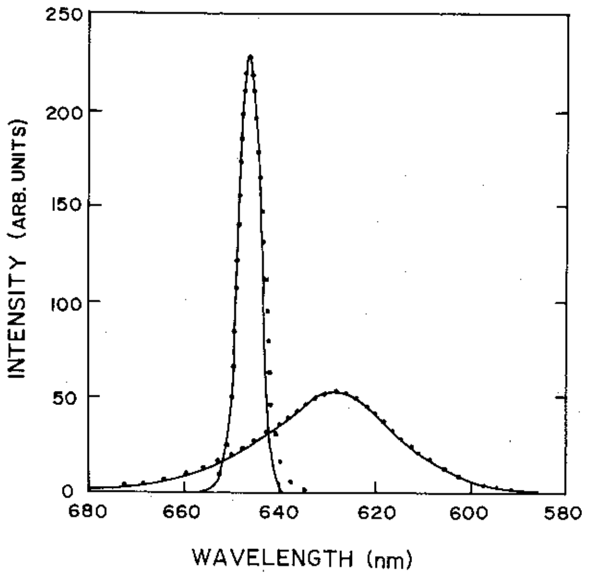

FIG. 5. Calculated stimulated emission profile (solid line) due to exciton-exciton scattering in GaSe for $E_x=2.0$ eV, $E_b=0.020$ eV, $T_x=500$ K, and $\eta=2.0$. The solid circles represent the experimental data points of Fig. 1(b).

the dominant mechanism in our photoluminescence experiment. The excellent fit of spectral shapes also supports the existence of excitons.

There is much evidence for the existence of exciton phenomena in GaSe at room temperature. Besson *et al.*[25] observed a very distinct $n=1$ direct exciton absorption peak in GaSe at room temperature and showed that it shifted towards red and weakened as pressure was increased. Capozzi[22] also observed the direct exciton luminescence in GaSe at room temperature in the backscattering geometry along the c axis. On the other hand, Voitchovsky and Mercier[14] found that emission lines due to impurity levels and $n \geqq 2$ exciton states disappeared at room temperature. Therefore, we believe scattering of the ground state excitons is the main mechanism responsible for the observed photoluminescence spectra even at room temperature in our experiment.

In conclusion, the exciton-exciton scattering process is the most probable mechanism responsible for both the spontaneous and the stimulated emissions in GaSe at room temperature and high excitation intensity. The high-energy and low-energy tails of the spontaneous spectra are sensitive to the exciton temperature and the exciton-photon coupling coefficient, respectively. A value of $\pi\alpha/\epsilon=3.3\times10^{-3}$ was measured. The amplitude and red shift of the stimulated emission with respect to the spontaneous emission are determined by the ratio η and the exciton temperature.

ACKNOWLEDGMENT

This work is supported by the Office of Naval Research.

---

[1] R. E. Nahory, K. L. Shaklee, R. F. Leheny, and J. C. Dewinter, Solid State Commun. **9**, 1107 (1971).
[2] T. Ugumori, K. Masuda, and S. Namba, Phys. Lett. **38A**, 117 (1972).
[3] R. C. C. Leite, E. A. Meneses, N. Jannuzzi, and J. G. P. Ramos, Solid State Commun. **11**, 1741 (1972).
[4] T. Ugumori, K. Masuda, and S. Namba, Solid State Commun. **12**, 389 (1973).
[5] J. P. Voitchovsky and A. Mercier, Phys. Status Solidi A **18**, 545 (1973).
[6] A. Mercier and J. P. Voitchovsky, Phys. Rev. B **11**, 2234 (1975).
[7] I. M. Catalano, A. Cingolani, M. Ferrara, and A. Minafra, Phys. Status Solidi B **68**, 341 (1975).
[8] I. M. Catalano, A. Cingolani, M. Ferrara, M. Lugara, and A. Minafra, Solid State Commun. **19**, 1115 (1976).
[9] Tadaki Ugumori, Kohzoh Masuda, and Susumu Namba, J. Phys. Soc. Jpn. **41**, 1991 (1976).
[10] T. Ugumori, K. Masuda, and S. Namba, Nuovo Cimento **38B**, 596 (1977).
[11] R. Baltramiejunas, V. Narkevicius, E. Skaistys, J. Vaitkus, and J. Viscakas, Nuovo Cimento **38B**, 603 (1977).
[12] A. Cingolani, M. Ferrara, and M. Lugara, Opt. Commun. **32**, 109 (1980).
[13] S. S. Yao and R. R. Alfano, Phys. Rev. B **27**, 2439 (1983).
[14] J. P. Voitchovsky and A. Mercier, Nuovo Cimento **22B**, 273 (1974).
[15] J. C. Irwin, R. M. Hoff, B. P. Clayman, and R. A. Bromley, Solid State Commun. **13**, 1531 (1963).
[16] Yuzo Yoshikuni, Hiroshi Saito, and Shigeo Shionoya, Solid State Commun. **32**, 665 (1979).
[17] Gordon Lasher and Frank Stern, Phys. Rev. **133**, A553 (1964).
[18] Tetsuo Moriya and Takashi Kushida, J. Phys. Soc. Jpn. **40**, 1668 (1976).
[19] Tetsuo Moriya and Takashi Kushida, J. Phys. Soc. Jpn. **40**, 1676 (1976).
[20] J. Wicksted, M. Matsushita, H. Z. Cummins, T. Shigenari, and X. Z. Lu, Phys. Rev. B **29**, 3350 (1984).
[21] M. Schluter, Nuovo Cimento **13B**, 313 (1973).
[22] V. Capozzi, Phys. Rev. B **23**, 836 (1981).
[23] Tadaki Ugumori, in *Semiconductors Probed by Ultrafast Laser Spectroscopy*, edited by R. R. Alfano (Academic, New York, 1984), Vol. 1, p. 109.
[24] S. S. Yao, J. Buchert, and R. R. Alfano, Phys. Rev. B **25**, 6534 (1982).
[25] J. M. Besson and K. P. Jain, Phys. Rev. Lett. **32**, 936 (1974).