Effect of picosecond-laser-driven shock waves on spontaneous and stimulated emissions in GaSe

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

Shock waves in GaSe semiconductors were produced by high-power picosecond laser pulses. Spontaneous and stimulated emissions in GaSe were used to probe the effect of shock waves. Under the laser-driven shock loading, a 24-nm spectral red-shift of the spontaneous-emission peak position, which corresponds to 14-kbar shock pressure, was detected. Significant line broadening of the spontaneous emission is attributed to the shock-wave-induced collision mechanism. The observed larger red-shift of 36 nm and the intensity decrease of the stimulated-emission peak were explained by the shock-wave-induced band-gap shrinkage through the gain-reduction mechanism based on the exciton-exciton scattering process in GaSe.

I. INTRODUCTION

Over the past 40 years, shock-wave research has been an active area because of its technological importance.[1] The generation of high pressure by shock waves differs in essence from generation by conventional methods in that it relies on the inertial response of matter to rapid acceleration rather than on static constraints applied by a fixed apparatus. The application of mode-locked picosecond laser pulses for the generation of ultrahigh pressure and short-duration shock waves[2-6] has brought about the possibility of studying the properties of condensed matter under extreme high pressure and temperatures.[7] The fast energy transfer from macroscopic mechanical disturbance to microscopic electronic and vibrational states in condensed media are key processes responsible for chemical and physical changes.

Recently, we have reported[7,8] picosecond-laser-excited spontaneous photoluminescence studies of GaSe layered semiconductors subject to high-power picosecond-laser-induced shock pressures. It is well known that the energy band structure of semiconductors changes under pressure. For GaSe, the energy band gap shrinks under pressure, causing the shift of both the absorption and luminescence spectra to the red. The spectral shift of the spontaneous-emission band gives a measure of the shock pressure generated by the pump beam. Furthermore, by delaying the probe beam with respect to the pump beam, we were able to map out the entire shock profile.

In this paper, we will extend our previous work and investigate spontaneous- and stimulated-emission spectra from GaSe under different probe intensities with and without the application of the laser-driven shock pressure. At low probe intensity, in addition to a spectral red shift, we have observed, for the first time, a broadening in spontaneous-emission line due to shock-wave-induced exciton collisions. At higher intensities, the effects of shock waves on the stimulated emission in GaSe have also been investigated. Previously, we have correlated and modeled

both spontaneous and stimulated emission in GaSe to the same origin: exciton-exciton scattering process. The purpose of the present paper is to reveal the shock effect on both spontaneous and stimulated emission and explain them using this model.

II. EXPERIMENTAL ARRANGEMENT AND TECHNIQUE

A schematic diagram of the experimental setup is shown in Fig. 1. A pump-and-probe technique was used to observe the shock effect on the photoluminescence emission in GaSe. A Quantel Nd:YAG laser (YAG denotes yttrium aluminum garnet) of 30 psec pulse width and 35 mJ pulse energy at 1.064 μm was utilized as the pump beam to generate shock waves in the aluminum foil. An R-70 filter was inserted in the pump beam to eliminate the fluorescence emission from the flashlamps in the YAG laser system. The shock wave was launched into the GaSe sample located behind the aluminum foil. Part of the infrared pulse was frequency doubled by passing it through a potassium dihydrogen phosphate (KDP) crystal to produce 27-psec laser pulses at 532 nm. This pulse was used as a probe beam. It was delayed through a white cell approximately by 39 nsec relative to the arrival of the pump beam at the aluminum foil. This was necessary to observe the maximum effect of shock pressure. The pulse selection of the YAG laser system was monitored by a fast photodiode coupled to a Tektronix 7104 oscilloscope.

The thickness of the GaSe sample was about 50 μm with the c axis of the crystal parallel to the thickness of the sample. The aluminum foil had a thickness of 20 μm. The sample and the aluminum foil were loaded between two $\frac{1}{4}$-in.-thick Pyrex plates and clamped tightly. Mineral oil was added to the interface of the sample and aluminum foil to ensure efficient mechanical coupling. The pump beam was focused by a 15-cm-focal-length lens to a 450-μm-diam. spot on the aluminum foil which ensured planarity of the shock wave and a peak power densi-
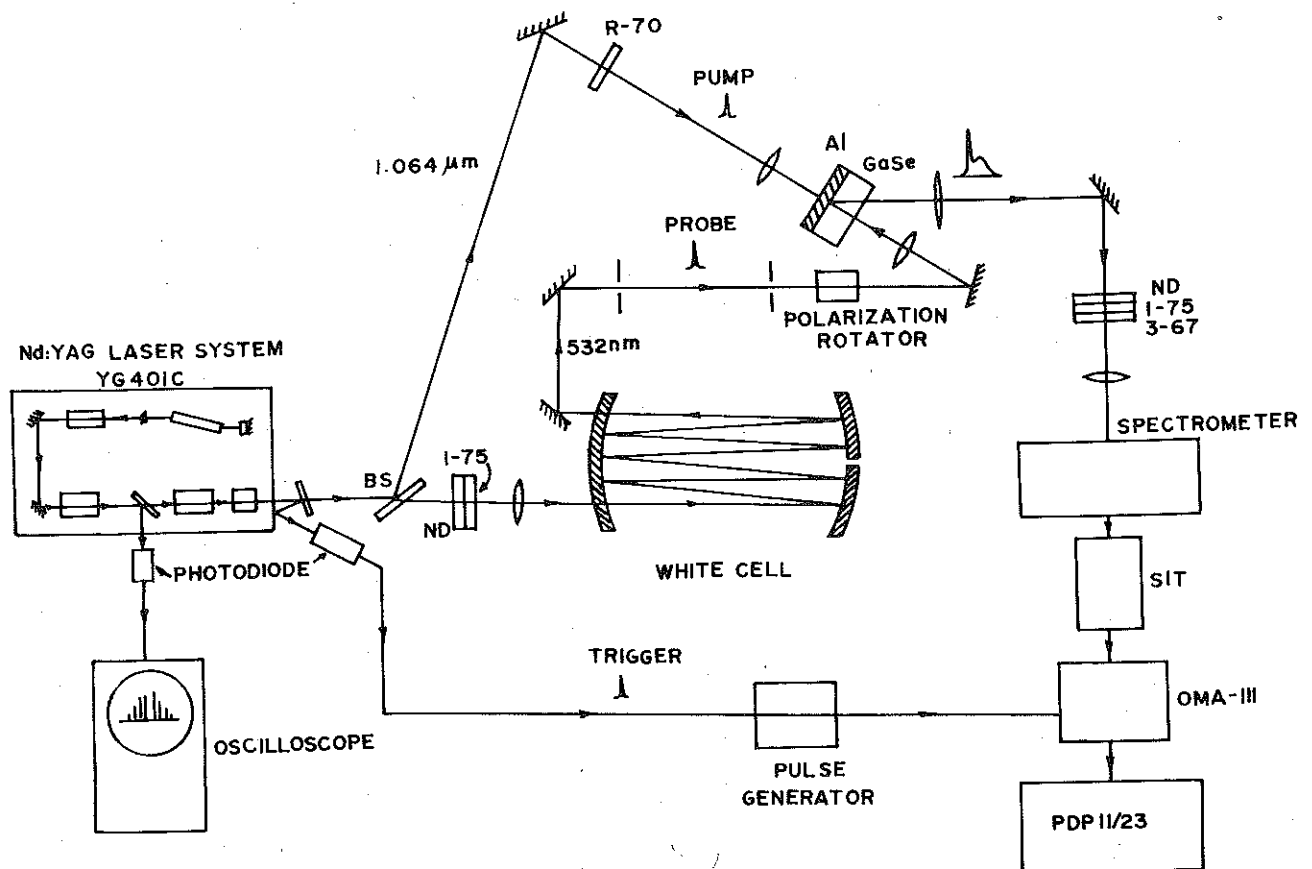
LU, RAO, WILLMAN, LEE, DOUKAS, AND ALFANO

FIG. 1. Schematic diagram of the experimental setup.

ty of $\sim 7 \times 10^{11}$ W/cm^2. The probe pulse was focused to a 350-μm-diam. spot by a 15-cm-focal-length lens on the sample. The thickness of the probed region was approximately equal to the penetration depth of the 532-nm laser beam in GaSe which is ~ 5 μm. Proper care was taken in aligning the two beams. Since the pump beam damaged the aluminum foil, a different spot on the aluminum foil was employed each time that a shock was generated.

The emitted light was collected by a lens of 15 cm focal length and focused onto a $\frac{1}{4}$-m Jarrell-Ash spectrometer. Corning 3-67 filters were placed in front of the spectrometer to eliminate the elastically scattered light from the sample. The signal was detected by a silicon-intensified target coupled to an optical multichannel analyzer OMA III (Princeton Applied Research), and stored in a PDP11/23 PLUS host computer. The trigger pulse obtained from the laser firing was used to synchronize OMA scans. The resolution of the detect system was about 2 nm. All spectra were recorded at room temperature by single shots of the laser.

III. RESULTS AND DISCUSSION

A. Shocked spontaneous emission

The effect of shock waves were found to be most salient for the delay time between the pump and probe beam $\tau \sim 39$ nsec. When τ increased from 39 nsec to above 100 nsec, the shock effects gradually weakened and disappeared. At $\tau \leq 30$ nsec, no shock effect was observed.

This feature agreed with our previous results (see Fig. 3 of Ref. 7). The typical spectra showing the shock effects on both spontaneous and stimulated emissions in GaSe are displayed in Figs. 2, 3, and 4 for $\tau = 39$ nsec and probe intensities 0.17×10^8, 0.68×10^8, and 1.3×10^8 W/cm^2, respectively. Under the shock loading, the spontaneous-emission peak was red-shifted by 28 nm (Fig. 2) and 24 nm (Fig. 3).

The energy band gap in GaSe shrinks with increasing pressure or temperature:[7,9]

$$E_g(T,P) = 2.020 \text{ eV} - (0.47 \text{ meV K}^{-1})(T - 300 \text{ K})$$
$$- (6.2 \text{ meV kbar}^{-1})P , \qquad (1)$$

where $T = 300$ K is the lattice temperature which does not change much during the shock loading.[7] The peak energy of the spontaneous emission due to the exciton-exciton scattering process is

$$E_p = E_g - 2E_b . \qquad (2)$$

Taking the partial derivative with respect to the pressure, one obtains

$$\frac{\partial E_p}{\partial P} = \frac{\partial E_g}{\partial P} - 2\frac{\partial E_b}{\partial P} .$$

The reported value for the change of the exciton binding energy with uniaxial static pressure is[9]

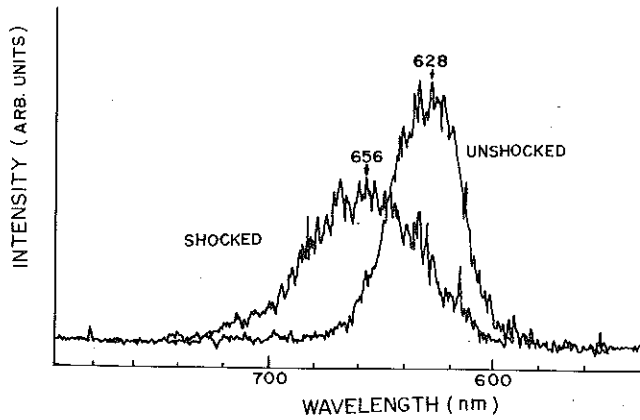$$\frac{\partial E_b}{\partial P} = -0.6 \text{ meV kbar}^{-1} ,$$

FIG. 2. Unshocked (right) and shocked (left) spontaneous-emission spectra at low probe intensity $(0.17 \times 10^8$ W/cm^2).

FIG. 4. Unshocked (right) and shocked (left) stimulated-emission spectra at high probe intensity $(1.3 \times 10^8$ W/cm^2).

therefore

$$\frac{\partial E_p}{\partial P} = -5.0 \text{ meV kbar}^{-1} \ . \tag{3}$$

The experimentally observed reds-shift of 71 meV (Fig. 3) gives the value of laser-induced shock pressure in GaSe to be in the range of 14 kbar. This shock-pressure magnitude has been confirmed by our recent transducer measurements.[3]

Significant line broadening in the spontaneous-emission spectra under the shock loading was clearly and repeatedly observed. This is shown in Figs. 2 and 3. The following four features are apparent for spontaneous-emission profiles.

(1) The magnitude of broadening ranges from 20 to 30 nm. In Fig. 2 the full width at half maximum (FWHM) is 39 nm for the unshocked spectrum and 67 nm for the shocked spectrum. In Fig. 3 the FWHM of the spontaneous curves is 36 nm for the unshocked and 62 nm for the shocked case.

(2) This broadening occurred at different delay times. It is found that the amount of broadening is proportional to the red-shift of the spontaneous-emission peak position.
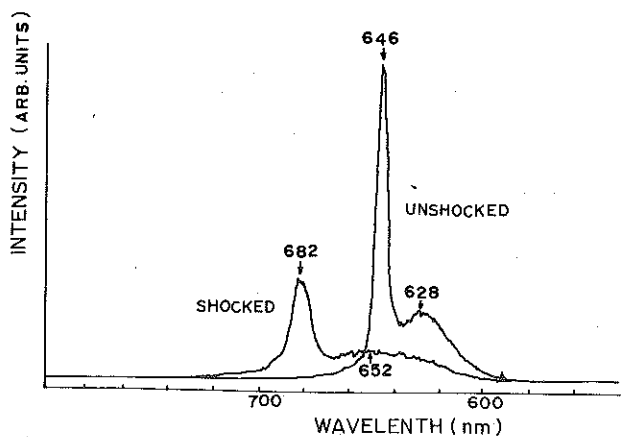

FIG. 3. Unshocked (right) and shocked (left) stimulated-emission spectra at medium probe intensity $(0.68 \times 10^8$ W/cm^2).
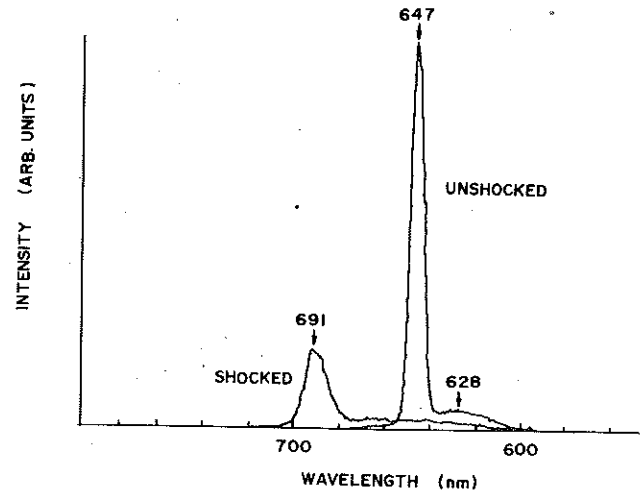
(3) The peak amplitude decreases under shock loading such that the integrated spontaneous-emission intensity (area) approximately remains same for both shocked and unshocked spectra.

(4) The broadened spontaneous spectrum has a Lorentzian profile.

The observed line broadening of the spontaneous-emission profile is attributed to the shock-wave-induced collision process in condensed matter. The emitting excitons in the shocked region all suffer from additional collisions with the entire array with a directional particle velocity u_p. The collision frequency for each exciton is

$$f_c = a^2 u_p N_{\text{mol}} \ , \tag{4}$$

where a is the Bohr radius of the exciton in GaSe which is[10] ~ 32 Å, N_{mol} is the molecular density in GaSe which is $\sim 2 \times 10^{22}$ cm^{-3}. The particle velocity at 14 kbar is about 2×10^4 cm sec^{-1}. Therefore, the collision broadening $\Delta \nu = 2 f_c / \pi \sim 2.5 \times 10^{13}$ Hz or $\Delta \lambda \sim 33$ nm which agrees well with the observed value.

Since the collision frequency is proportional to u_p which is related to the shock pressure P by the jump condition[1] $P - P_0 = \rho_0 U_s u_p$, where U_s is the shock velocity, and ρ_0 and P_0 are density and pressure in the unshocked region, the shock-wave-induced collision broadening is expected to be proportional to the red-shift of the spontaneous-emission peak. The collision broadening is homogeneous and has a Lorentzian line shape.[11] This is also confirmed by our experiment. From the fact that the shocked spontaneous emission has the same integrated intensity as the unshocked one we deduce that the elastic collision (phase-perturbing collision) plays a main role in our line-broadening mechanism because inelastic collision (quenching collision) will decrease the number of emitting excitons and reduce the integrated intensity significantly.

Note that the usual pressure broadening which is crucial for gaseous systems essentially comes from an increase in particle density and a decrease in mean free path due to high pressure. This cannot be significant in condensed matter because of its extremely small compressibil-

ity (typically $\rho/\rho_0 \sim 1.2$ at $P = 200$ kbar). Our shock-wave-induced exciton collision broadening is a new mechanism which is directly related to the unique nature of the shock waves and exciton in condensed matter.

B. Shocked stimulated emission

Typical experimental stimulated spectra, both unshocked and shocked, are displayed in Fig. 3. There are three salient features evident from the shocked spectra.

(1) The stimulated peak is red-shifted due to the shock pressure by 36 nm (in Fig. 3) which is greater than the spontaneous shift of 24 nm (in Fig. 3, under the same shock loading condition).

(2) The spectrum is considerably broadened.

(3) There is an intensity decrease of the stimulated emission under laser-driven shock pressure.

According to the exciton-exciton scattering model for the photoluminescence emission in GaSe, the relation between the optical gain and the spontaneous-emission spectrum is given by[12]

$$g(E) \propto I_{sp}(E)\left[1 - \eta \exp\left[\frac{E - (E_g - 2E_b)}{k_B T_x}\right]\right], \quad (5)$$

where

$$\eta = \left[\frac{n_e n_h}{n_x^2}\right]\left[\frac{m_x^2}{m_e m_h}\right]^{3/2}. \quad (6)$$

The stimulated-emission profile for unsaturated gain is given by[13]

$$I_{st}(E) = I_0 \exp(gL). \quad (7)$$

The broadening of the stimulated-emission spectrum is a direct consequence of the broadening of the spontaneous-emission spectrum I_{sp}, as seen from Eq. (5). Since the ratio η depends on temperature, excitation intensity, and excitation length, we can approximately use the same value of 2.0 for η, as derived from our preceding paper. However, since the shock pressure shrinks the energy band gap, η increases to an effective value of

$$\eta' = \eta \exp\left[\frac{-\Delta E_g + 2\Delta E_b}{k_B T_x}\right],$$

with

$$\Delta E_g = -6.2\,\frac{\text{meV}}{\text{kbar}} \times 14\,\text{kbar},$$

$$\Delta E_b = -0.6\,\frac{\text{meV}}{\text{kbar}} \times 14\,\text{kbar},$$

$$T_x = 500\,\text{K},$$

therefore

$$\eta' = 10.$$

The increased effective value of η causes both the larger red-shift of the stimulated-emission peak relative to the spontaneous peak and the intensity decrease of the stimulated emission under the shock loading condition. As η increases from 2 to 10, the gain peak value calculated from Eq. (5) will decrease from 12.5 to 1.8 (arbitrary units). The peak intensity ratio of the shocked and unshocked stimulated emission will be $I'/I = \exp[(g'-g)L]$ $\sim \exp[-0.86gL]$. Using[10] $g \sim 1000\,\text{cm}^{-1}$ and $L \sim 10\,\mu\text{m}$, we obtain $I'/I \sim 0.4$. This estimate agrees with the observed quenching factor quite well. Physically, the shrunken band gap due to the applied shock-pressure results in lowering the quasi-Fermi level of electrons and generating more free electron and hole pairs which in turn produces additional stimulated absorption causing quenching of the stimulated emission.

In conclusion, picosecond-lase-driven shock waves appear to be a very powerful technique to study properties of condensed matter under extremely high pressure. The observed red-shift of the spontaneous-emission peak under shock loading gives an estimate of 14 kbar for the laser-driven shock pressure in our experiment. The significant line broadening of the spontaneous emission is attributed to the shock-wave-induced exciton collision mechanism. The larger red-shift and intensity decrease of the stimulated-emission peak under the same shock loading condition were explained by the shock-wave-induced band-gap shrinkage through the gain-reduction mechanism based on the exciton-exciton scattering process in GaSe.

[1]G. E. Duvall and G. R. Fowles, in *High Pressure Physics and Chemistry*, edited by R. S. Bradley (Academic, London and New York, 1963), Vol. 2, p. 209.

[2]P. S. Peercy, E. D. Jones, J. C. Bushnell, and G. W. Gobeli, Appl. Phys. Lett. **16**, 120 (1970).

[3]K. P. Leung, S. S. Yao, and R. R. Alfano, in *Shock Waves in Condensed Matter, 1983*, edited by J. R. Asay, R. A. Graham, and G. K. Straub (Elsevier, Amsterdam, 1984), p. 343.

[4]P. E. Schoen and A. J. Campillo, Appl. Phys. Lett. **45**, 1049 (1984).

[5]B. L. Justus, A. L. Huston, and A. J. Campillo, Appl. Phys. Lett. **47**, 1159 (1985).

[6]A. L. Huston, B. L. Justus, and A. J. Campillo, Chem. Phys. Lett. **122**, 617 (1985).

[7]K. P. Leung, S. S. Yao, A. G. Doukas, and R. R. Alfano, Phys. Rev. B **31**, 942 (1985).

[8]R. Rao, X. Z. Lu, A. G. Doukas, S. Lee, B. Willman, P. Harris, and R. R. Alfano, Proceedings of the International Conference on Lasers, 1985 (unpublished), pp 171—177.

[9]V. V. Panfilov, S. I. Subbotin, L. F. Vereshchagin, I. I. Ivanov,

and R. T. Molchanova, Phys. Status Solidi B **72**, 823 (1975).

[10]T. Ugumori, K. Masuda, and S. Namba, J. Phys. Soc. Jpn. **41**, 1991 (1976).

[11]W. Demtroder, *Laser Spectroscopy* (Springer-Verlag, Berlin, 1982), pp. 90—100.

[12]T. Moriya and T. Kushida, J. Phys. Soc. Jpn. **40**, 1676 (1976).

[13]R. E. Nohory, K. L. Shaklee, R. F. Leheny and J. C. Dewinter, Solid State Commun. **9**, 1107 (1971).