Shock-wave-induced collision broadening of the photoluminescence spectra in GaSe

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Significant spectral broadening of the photoluminescence in GaSe under the picosecond-laser-driven shock pressure has been observed for the first time. The broadening of the spontaneous emission was found to be proportional to the shock pressure and attributed to a shock-wave-induced exciton collision mechanism due to the directional motion of particles in the shocked region.

There are significant differences[1–4] between the observed physical and chemical properties of condensed matter which is shocked and hydrostatically compressed at the same pressure and temperature. Production of the picosecond-laser-driven shock waves offers a new powerful technique to study the properties of semiconductor circuits and devices at very high pressures with a table-top laser facility. Recently, we reported[5] on the spontaneous and stimulated emission from GaSe at different excitation intensities and attributed both the spontaneous and stimulated emission to the same origin—exciton-exciton scattering process. In this letter, photoluminescence spectral line broadening observed under picosecond-laser-driven shock loading in GaSe is reported for the first time which is attributed to enhanced excitonic collision processes associated with the shock wave.

A pump-and-probe technique was used to observe the shock effect on the photoluminescence emission in GaSe. The GaSe sample of 50 μm thickness with the c axis perpendicular to the layers was attached to an aluminum foil of thickness 20 μm. A Quantel Nd:YAG laser of 30 ps pulse width and 35 mJ pulse energy at 1.064 μm was focused to a 450-μm-diam spot on the Al foil surface to generate shock waves which propagated through the Al foil into the GaSe sample. A 532-nm probe beam of 27 ps pulse width was focused to a 350-μm-diam spot onto the GaSe surface. The photoluminescence from GaSe was dispersed by a 1/4-m spectrometer and detected by a silicon-intensified target coupled to an optical multichannel analyzer OMA III, and stored in a PDP11/23 + computer.

Typical spontaneous emission spectra from GaSe with and without shock loading are shown in Fig. 1. The salient features displayed in Fig. 1 are red shift of 28 nm and broadening of the shocked spectrum relative to the unshocked one.

The emission due to exciton-exciton scattering can be expressed as $(E_K^{1s}, E_{K'}^{1s}) \rightarrow (h\nu, e-h)$. The spontaneous emission spectrum due to the exciton-exciton scattering process is given by[6]

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

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 $K=0$, E_b is the binding energy of excitons, $E_x = E_g - E_b$, T_x is exciton temperature, α and ϵ are the polarizability of excitons and dielectric constant of the material, respectively. The peak energy is located at $E_p = E_g - 2E_b$. Figure 2 shows a comparison between the observed spontaneous emission spectrum (solid dots) and the calculated one (solid line) from Eq. (1) with $E_x = 2.0$ eV, $E_b = 0.020$ eV, $T_x = 500$ K, and the coupling coefficient $\pi\alpha/\epsilon = 3.3\times10^{-3}$.

It is a well known fact that the direct energy band gap of GaSe shrinks under pressure causing the red shift of the photoconductivity, absorption, and luminescence spectra.[7–9] With the reported static values of[10] $\partial E_g/\partial P = -6.2$ meV(kbar)$^{-1}$ and $\partial E_b/\partial P = -0.6$ meV(kbar)$^{-1}$ we obtain the (hydrostatic) pressure coefficient of the peak energy $\partial E_p/\partial P = -5.0$ meV(kbar)$^{-1}$. There is evidence[11] showing that the stress anisotropy of the shock compression could be neglected in many cases. The red shift of 28 nm (84 meV) displayed in Fig. 1 deduces a shock pressure of $\sim$17 kbar. To see if this approximation is reasonable, we also performed an independent measurement of the shock pressure in the same experimental setup by an x-cut quartz transducer technique.[12] The pressure of $\sim$15 kbar was obtained which confirmed our approximation.

Significant line broadening of the spontaneous emission spectra under the shock loading was clearly and repeatedly observed. The magnitude of broadening was about 24 nm for a shock pressure of 17 kbar, as displayed in Fig. 1. It was

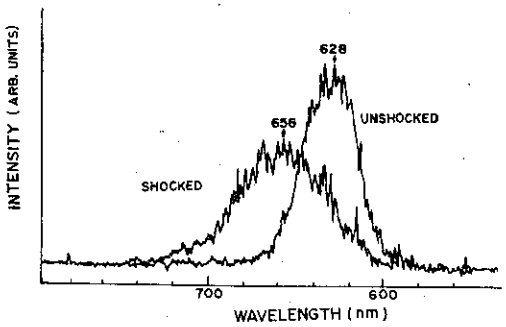

FIG. 1. Observed unshocked and shocked spontaneous emission spectra from GaSe at room temperature and excitation intensity 17 MW/cm^2.

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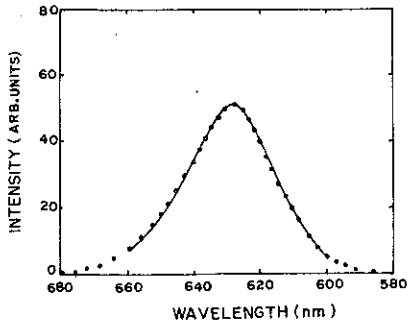

FIG. 2. Calculated spontaneous emission spectrum from the exciton-exciton scattering model of Eq. (1) with $E_x = 2.0$ eV, $E_b = 0.020$ eV, $\pi\alpha/\epsilon = 3.3\times10^{-3}$, and $T_x = 500$ K. The solid dots represent the experimental unshocked spontaneous spectrum.

found that the peak amplitude decreased under shock loading such that the integrated spontaneous emission intensity (area) approximately remains the same as that of the unshocked spectrum.

It was reported[13] that although the electronic (or excitonic) temperature in the probed region ($\sim$434 K) was considerably higher than the room temperature due to heating effect by the probe beam, no significant temperature rise due to the shock wave loading was detected. The Doppler linewidth at temperature T_x due to the thermal motion of the emitting excitons is given by[14]

$$\delta\lambda_D = \frac{2\lambda_p}{c}\left(\frac{2kT_x \ln 2}{M_x}\right)^{1/2}, \tag{2}$$

where λ_p is the peak wavelength of the emission and M_x is the exciton mass. If this mechanism was responsible for the observed line broadening (of a factor of 2, approximately), the temperature would increase by a factor of 4 due to the shock loading, i.e., the exitonic temperature would exceed 1700 K in the shocked region which is definitely unrealistic. Also, a Doppler broadened line should have a Gaussian profile[14] which disagrees with our observed Lorentzian line shape. Therefore, the possibility of temperature effect causing the linewidth increase due to the shock loading can be safely excluded.

The probed region in our experiment formed a disk of 350 μm in diameter and 5 μm in thickness (the penetration depth of the 532-nm probe beam in GaSe). Since the shock pressure is proportional to the pump beam fluence,[12] transverse inhomogeneity of the shock pressure over the disk area (350 μm in diameter) originated from the Gaussian profile of the pump beam (450 μm in diameter) intensity should be less than 20%. There was also a longitudinal inhomogeneity of the shock pressure in the direction of shock wave propagation due to pressure decay in space. In our picosecond laser-driven shock wave case, the shock decay time was measured[13] to be $\sim$70 ns, corresponding to a decay length of $\sim$140 μm. Thus, the longitudinal variation of pressure in the shocked region was less than 0.5 kbar. However, the observed line broadening corresponded to a pressure variation from zero to twice the mean value of the shock pressure as deduced from the observed red shift. Therefore, neither transverse nor longitudinal inhomogeneity of the shock pressure can explain the observed large line broadening.

The observed line broadening of the spontaneous emission is attributed to the shock-wave-induced exciton collisions. When a shock front propagated through the sample, all molecules behind it would gain a particle velocity u_p via the intermolecular bonding, but excitons would not, since there was no such tight bonding between excitons or between exciton and molecules. Therefore, 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 $f_c \approx a^2 u_p N_{\rm mol}$, where a is the Bohr radius of the exciton in GaSe which is[15] $\sim$32 Å, $N_{\rm mol}$ is the molecular density in GaSe which is $\sim 2\times10^{22}$ cm^{-3}. The particle velocity at 17 kbar is about 2×10^4 cm s^{-1}. Therefore, the collision broadening at 17 kbar is $\Delta\nu = 2f_c/\pi \sim 2.5\times10^{13}$ Hz or $\Delta\lambda \sim 33$ nm which agrees well with the observed value. It should be noted that collisional broadening is homogeneous and should have a Lorentzian line shape.[14] This is also clearly shown in Fig. 1. Since the collision frequency is proportional to u_p which is related to the shock pressure P by the jump condition[11]: $P - P_0 = \rho_0 U_s u_p$, where U_s is the shock velocity, ρ_0 and P_0 are density and pressure in unshocked region. The shock-wave-induced collision broadening is expected to be proportional to the shock pressure. This is confirmed by our experimental data as shown in Fig. 3. The observed line broadening from different pairs of unshocked-shocked data plotted against the applied shock pressure displays a linear dependence. A pressure coefficient of line broadening for the spontaneous emission of GaSe $\sim$1.3 nm/kbar is obtained.

The observation that the shocked spontaneous emission has the same integrated intensity as the unshocked one suggests that the elastic collision (phase-perturbing collision) plays a major 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 latter effect cannot be significant in condensed matter because of its extremely small

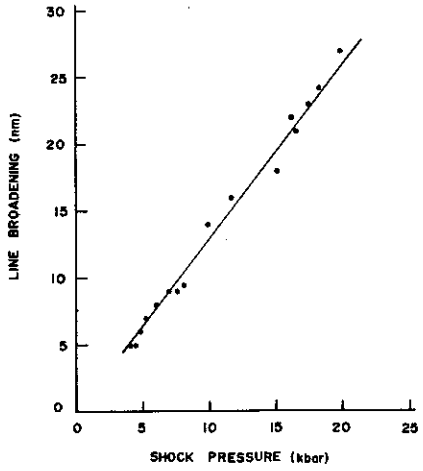

FIG. 3. Observed wavelength broadening of the spontaneous emission spectrum from GaSe vs shock pressure.

compressibility (typically $\rho/\rho_0 \sim 1.2$ at $P = 200$ kbar). The shocked-wave-induced exciton collision broadening is a new mechanism different from the usual pressure broadening and directly related to the unique nature of the shock waves and excitons in condensed matter.

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