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Luminescence of layered compounds excited by high-intensity two-photon pumping*

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High-intensity excitation luminescence measurements in three layered semiconductors (GaSe, GaS, and PbI_2) are reported. The excitation is achieved by two-photon pumping. Some new results are obtained: direct-gap emission in GaS and anti-Stokes "photon replica" in PbI_2. Spontaneous spectra of GaSe and PbI_2 show emission due to cooperative processes recombination, also giving stimulated emission. The optical gain of PbI_2 has been measured.

Usually, high-excitation properties of semiconductors are studied by one-photon pumping, and the nitrogen laser is the typical excitation source. The use of a highly absorbed radiation in the investigation of semiconductor properties, however, has the drawback that surface properties of the particular sample can influence the measurement. From this point of view, better results can be obtained exciting the sample by two-photon pumping; in fact, the nonlinear absorption coefficient of semiconductors for band-band direct transitions is of the order of 0.1 cm/MW and, consequently, an excitation power flux in the range 1 – 10 MW/cm^2 gives a unity-volume transition rate $W \simeq 10^{24}$–10^{25} cm^{-3} sec^{-1}.

In a previous work the present authors have measured the nonlinear absorption of GaSe, GaS, and PbI_2.[1] Also in these materials, the nonlinear absorption for direct band-band transitions is of the order of magnitude quoted above and, consequently, high excitation can be achieved by using high-power Q-switched lasers.

In the present work we report the results of an investigation of photoluminescence spectra of these materials excited by two-photon pumping. Some new effects, which have not previously been observed, appear: in GaS a spontaneous emission band associated to the direct energy gap, and in PbI_2 a novel nonlinear effect, which gives emission at energies higher than the fundamental gap, explainable by a "photon-replica" emission assisted by the photons of the exciting beam. In GaSe and PbI_2 stimulated emission associated to cooperative emission phenomena is observed.

EXPERIMENTAL

The measurements have been carried out by using a neodymium and a ruby Q-switched giant-pulse lasers; both lasers have 200-MW peak power and 20 nsec pulse duration. The ruby laser was used for excitation of GaS and PbI_2, the neodymium one for GaSe. The luminescence collected either perpendicularly or in the same direction of the exciting beam, was analyzed by a double-grating monochromator with a photomultiplier followed by a storage oscilloscope. Uniformity tests on the laser beam have been carried out as described in Ref. 1. Alternatively, the light emission was photographically recorded by a spectrograph.

The optical gain was measured by the same method which is utilized in one-photon experiments.[2] This method involves the measurement of the intensity of light, emitted by the sample perpendicularly to the exciting beam, as a function of the dimension L of the exciting rectangular spot along the direction of emission; the incident photon flux is kept constant. Since the important parameter in this kind of experiment is L, it is carefully controlled by an adjustable micrometric slit, and a high-quality imaging optics.

The equation connecting the luminescence intensity to L is

$$\mathfrak{L} = [\mathfrak{L}_0 / g(I_0)](e^{g(I_0)L} - 1), \tag{1}$$

where $\mathfrak{L}_0$ is the spontaneous emission and $g(I_0)$ is the optical gain in cm^{-1}. All measurements have been carried out at 80 °K using a vacuum liquid-nitrogen cryostat.

RESULTS AND DISCUSSION

Figure 1 shows the photoluminescence spectrum of GaS excited by two-photon pumping by the ruby laser. In the inset the dependence of integrated light intensity is plotted against exciting flux I_0. The slope 2 of the log-log plot confirms the two-photon optical-pumping mechanism for the two observed bands. Of these two bands, the first one (I band) at 2.56 eV has been previously observed by one-photon excitation and has been attributed to free-exciton recombination, associated with the indirect gap.[3] The other one (D band), which is at an energy close to that of the direct gap, has been normalized to account for the self-absorption of the sample by multiplying by the correction factor $\alpha d/(1 - e^{-\alpha d})$, where α is the one-photon absorption coefficient[4] and d is the thickness of the

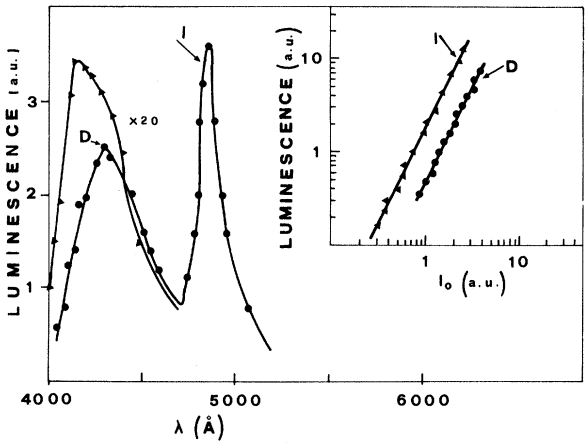

FIG. 1. Luminescence spectrum of GaS at 80 °K excited by ruby two-photon pumping. The band D after correction for self-absorption is showed by triangles (▲).

sample along the direction of light collection. After applying this correction, the peak is at about 20 meV below the direct energy gap. This is the first observation of direct emission in gallium sulphide. At this point it is not possible to be more conclusive about the origin of this emission; it could be associated, for example, with resonant states localized between the two gaps due to isoelectronic impurities as observed in some III-V compounds.[5]

Anyway, it is clear that the free carriers produced by the two-photon-excitation process thermalize either to the direct-band minimum or to the indirect one, and in both cases they undergo radiative recombination.

Figure 2 shows the emission spectrum at 80 °K of GaSe excited by the neodymium laser. Also in this case two bands are observed, but the situation is quite different.

The high-energy band (FE) at 5900 Å (2.1 eV) is due to free-exciton recombination.[6] The other, about 22 meV below the free exciton, shows a different evolution with incident intensity. In fact, in contrast to the case of GaS in which both bands have the same dependence on I_0, in GaSe the FE band is linear with I_0, whereas the L band is quadratic (see Fig. 3). Moreover, it is to be noted that the L band is more prominent than the FE one in the investigated intensity range.

The energy position of these bands and their evolution with pumping allow one to conclude that the L band is due to a cooperative excitonic process. In fact, when cooperative excitonic processes are involved, the emitted light intensity of the free exciton varies as $I_0^{1/2}$ (this is valid when cooperative recombination is dominant compared to single-exciton recombination[7]), owing

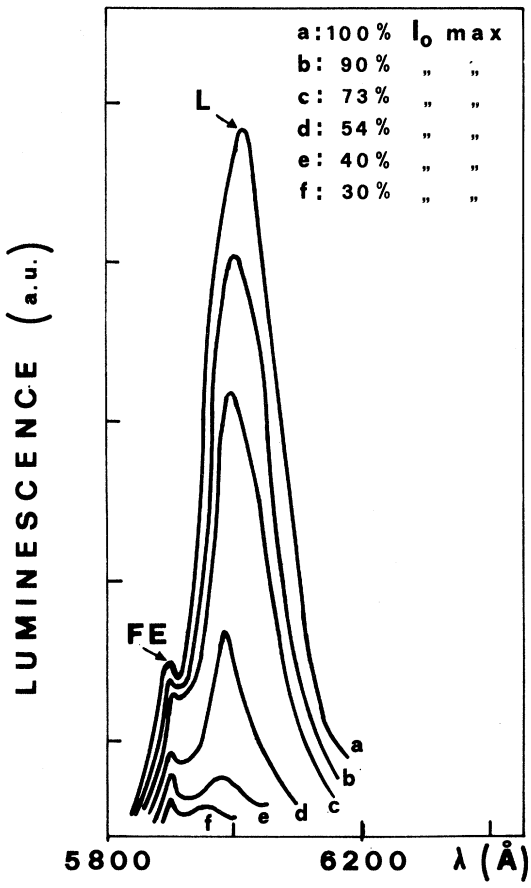

FIG. 2. Luminescence spectra of GaSe at various pumping intensities: $I_{0\,\max} = 10\ \mathrm{MW/cm^2}$.

to the depletion of free excitons through the collision channel in linear excitation experiments. The cooperative band is linear with I_0 in the same excitation range. When a quadratic excitation is used, as in two-photon experiments, the dependences becomes I_0 and I_0^2, respectively, in agreement with Fig. 3.

The band L has been widely studied by high-intensity one-photon excitation by various authors[8] and also by some of the present ones.[6,9] From the analysis of the optical-gain spectra we attribute the L band to an inelastic exciton-exciton collision.[9]

Also in the two-photon-excitation case, the L band shows stimulation effects when the emission light is collected perpendicularly to the direction of excitation; in this case the emitted intensity is first quadratic with I_0, as discussed above in connection with Fig. 3, therefore, the dependence becomes strongly superquadratic, breaking out in saturation effects. The threshold of the superquadratic branch is dependent on the quality of

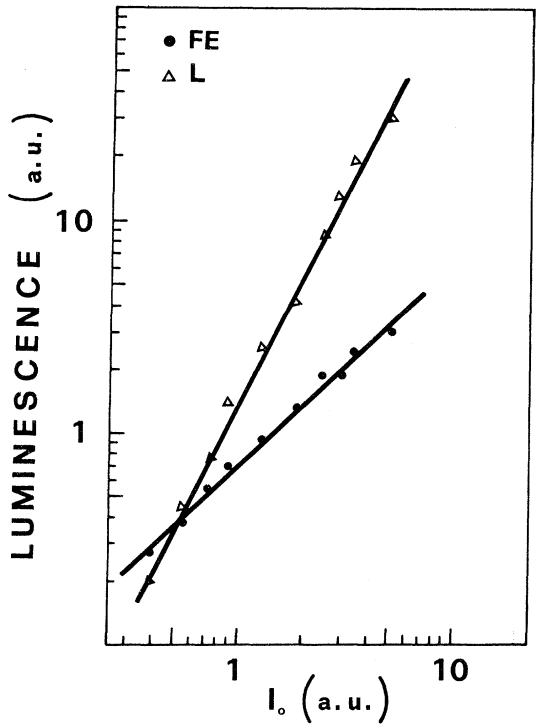

FIG. 3. Dependence of FE and L band of GaSe on incident power flux.

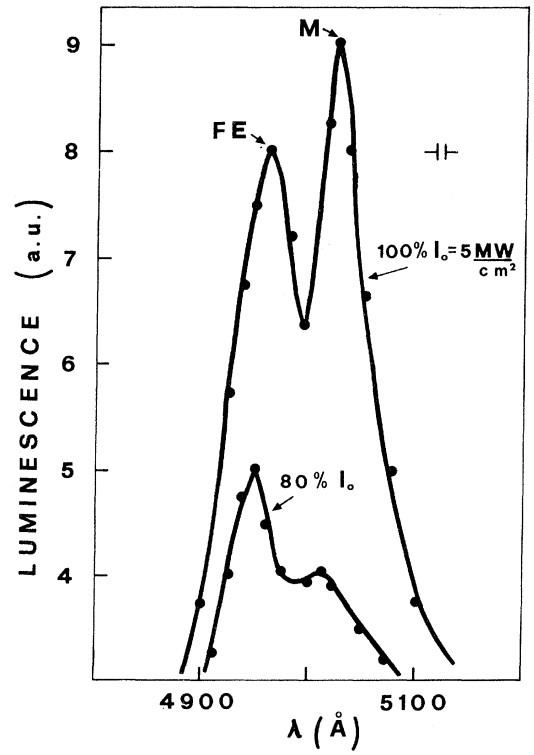

FIG. 4. PbI_2 luminescence spectra at two exciting intensities.

the samples, and is located around 6 MW/cm^2. This value is consistent with the exciton density required to have population inversion and then stimulated emission.[10]

Figure 4 shows the spectrum of PbI_2, ruby-laser excited, at two different excitation levels. Also in this case free-exciton luminescence is observed at 4980 Å (2.49 eV), together with a lower energy band (M) 25 meV below the free exciton.

In Figure 5 the dependences of the emission intensity of both bands is plotted against I_0. In contrast to the case of GaSe the exciton band grows quadratically, whereas the M band has a fourth-power dependence. In spite of this, for PbI_2 the band M can be again assigned to a cooperative phenomenon; in fact by comparing Figs. 2 and 4 is evident that, in the same excitation intensity range, the band L is prominent compared to the free-exciton one in GaSe, while in PbI_2 the band M is comparable to the free-exciton one only at the highest intensities.

This behavior explains the difference in the observed slopes. In fact, by the kinetic model of reference cited above,[7] it follows that when the free-exciton depletion by the cooperative recombination channel is not the dominant effect, i.e., when the excitonic density is not too high, the recombination kinetics is dominated by the free-exciton recombination, which is linearly dependent

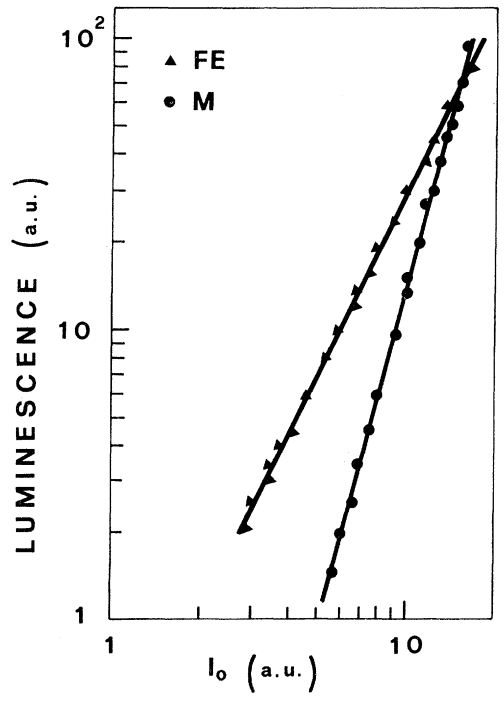

FIG. 5. Dependence of FE and M band of PbI_2 on incident flux power.

on the generation rate and then quadratic on I_0.

With regard to the nature of band M in PbI_2, it is difficult to discriminate among the various cooperative processes, since the value of the exciton binding energy E_b is very controversial.[11] Both an excitonic molecule and an exciton-exciton collision mechanism are consistent with the values of E_b, whereas the I_0 dependence and the energy position rule out such possibilities as phonon replicas and exciton-electron collision, respectively. Anyway, band M also presents stimulation effects as it is shown in Fig. 6, which is obtained in the same geometry used for GaSe. The stimulated emission peak is displaced by about 10 meV toward lower energies relative to the spontaneous band. This is also a commonly observed effect (it is present in GaSe[8] and other materials[12]) and it can be explained, if the exciton-exciton collision is the pertinent mechanism, by a stimulated absorption which gives a negative optical gain at the high-energy side of the emission band, shifting the peak to lower energies.

In Fig. 7 typical spectra of optical-gain measurements of band M are reported. In this figure the stimulated emission intensity is plotted against the length of the exciting spot and the impinging power density is constant ($I_0 = 8$ MW/cm^2). The dependence is exponential over nearly three decades. Fitting Eq. (1) to experimental points gives $g = 450$ cm^{-1}. Actually, the optical gain depends on I_0 and a square dependence is expected as shown in the inset of the figure.

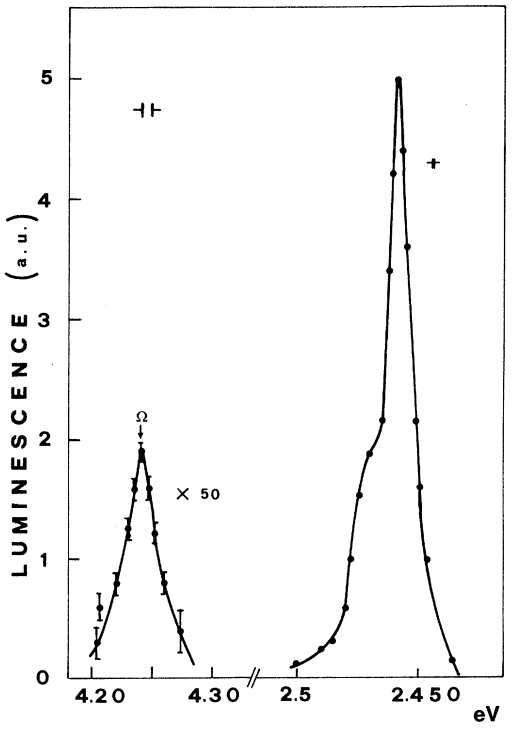

FIG. 6. Stimulated emission of PbI_2 associated to the band M. The "photon replica" Ω is also shown.

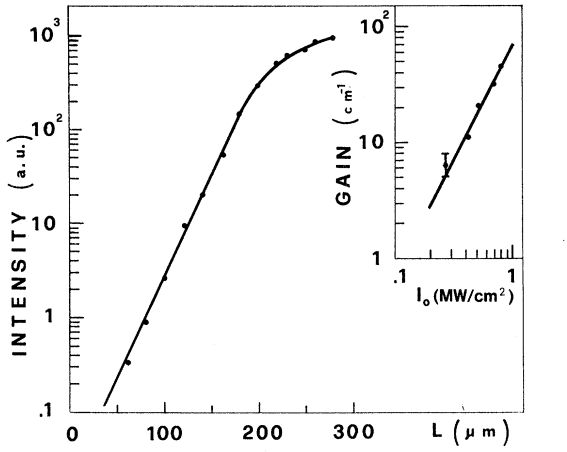

FIG. 7. Optical-gain measurements in PbI_2 (see text). The inset shows the dependence of gain on incident power flux.

Figure 6, for PbI_2, shows an emission band Ω at 2925 Å (4.24 eV), detected in the same geometry of band M. The band Ω is 10^4 times weaker than band M and is localized well above the energy gap of PbI_2. The energy displacement of the two bands is exactly 1.78 eV (i.e., the ruby-laser energy). We suggest that band Ω can be due to an anti-Stokes photon replica of band M. Such a nonlinear effect has been theoretically predicted and experimentally observed in InP.[13] Qualitatively, the mechanism responsible for Ω emission can be understood assuming that the relaxation time of "states" responsible for emission is much less than the laser-pulse duration, and that the emission process which originates the band M is "controlled" by the laser-beam electric field.

At present the weakness of the Ω band does not allow a more detailed experimental analysis of the effect, e.g., measurement of the emission time dependence and its evolution with exciting intensity. Anyway, the exciting intensity dependence, in a small range, is clearly superlinear, even if it is difficult to measure the exact slope.

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