Optical spectroscopy of extrinsic recombinations in gallium selenide

Vito Capozzi
Dipartimento di Fisica, Università di Bari, via Amendola 173, I-70126 Bari, Italy

Maurizio Montagna
Dipartimento di Fisica, Università di Trento, I-38050 Trento, Italy
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Luminescence at energy lower than the absorption edge has been investigated in crystals of GaSe, containing different degrees of lattice disorder, as a function of temperature, of photoexcitation intensity, and of excitation energy. At low excitation intensity, the extrinsic luminescence is composed of broad overlapping bands that present a blue shift when the temperature increases. Their shape and intensity is strongly dependent on the laser excitation frequency and on the degree of lattice disorder. The results are discussed in terms of a model involving the recombination of shallow donors and free electrons with deep acceptors. These two recombination mechanisms and those involving free and bound excitons are found to be competitive. Their relative importance is strongly dependent on the concentration of structural defects, on the temperature, on the excitation intensity, and on the excitation frequency.

I. INTRODUCTION

The photoluminescence (PL) spectrum of the layered semiconductor GaSe is quite complex at low temperature: it contains either intrinsic sharp lines due to the excitonic recombinations[1-4] or extrinsic bands at lower energy connected to lattice defects or impurities.[5] The PL spectrum is very rich in lines, because of the particular GaSe band structure near the optical-absorption edge: the conduction band has an indirect minimum at point M of the Brillouin zone (BZ), which is only 25 meV lower than the direct minimum.[6,7] These two minima can both be populated by the photoexcited carriers, and then radiative recombinations from states associated with direct and indirect gaps simultaneously occur.[2-4,8] The shape of the PL spectra is therefore very sensitive to temperature (T),[9,10] excitation intensity (J),[1,11] and excitation energy.[12,13]

The excitonic luminescence of GaSe from 580 to about 620 nm has been extensively studied by several groups.[1,3,4,14] Apart from some details, concerning the energies of the indirect excitonic recombinations, the different authors agree with the interpretation of these intrinsic lines as due to free, as well as bound, direct and indirect excitonic emissions.[3,4,8,14]

Comparatively, very poor information is available about the emission bands related to the defect levels localized in the forbidden energy gap at energy lower than 2 eV.[5]

In this work we present the PL results for three kinds of GaSe samples grown by the Bridgman method and containing different degrees of structural disorder. The luminescence properties strongly depend on the structural disorder of the lattice layers formed either during growth or when cleaving the slices. We investigated the broad PL bands between 600 and 900 nm which generally dominate the emission spectra of GaSe below 100 K at very low excitation intensities. The shape and intensity of these bands are very sensitive to the structural quality of the samples.

The extrinsic emissions are attributed to two competitive recombination processes: (i) donor-acceptor–pair recombinations, which are the most important mechanism at very low J, and (ii) free-electron–acceptor transitions–a dominant process at higher optical intensity, at which the excitonic luminescence is still weak. Donor and acceptor states are produced by intrinsic structural defects.

II. EXPERIMENTAL PROCEDURE

The GaSe crystals were grown from the melt by using the Bridgman-Stockbarger method.[15] X-ray analysis and excitonic transmission spectra have shown that the investigated samples have the hexagonal ϵ structure and contain stacking faults.[16] The ingots were cleaved in slices about 0.1 mm thick along the layer planes. The fresh, cleaved surfaces appeared as smooth as a mirror, although they contained a few fine cracks, probably produced during the cleavage.

The samples were put in a continuous-flow liquid-He cryostat whose temperature could be varied from 2 to 300 K. They were illuminated (in a direction forming a $\pi/4$ angle with respect to the c axis) using the 514.5-nm line of a cw Ar-ion laser, whose light beam was focused on a spot of about 100 μm diameter. The emission light was collected at $\pi/2$ from the front surface of the crystal. For the energy-selective luminescence spectra and for the luminescence-excitation measurements, a dye laser (Rhodamine-6G, pumped by the Ar-ion laser) with a linewidth of about 1 cm^{-1} was used as a variable monochromatic light source. Two crossed polarizing filters

were placed before and after the sample in order to strongly reduce the intensity of the background luminescence of the dye laser scattered by the sample.

The luminescence was analyzed by a double-grating spectrometer (linear dispersion of 2.5 Å/mm) with a very weak stray light, such that we could measure the PL-response at frequencies very close (a few cm^{-1}) to the exciting-laser line. The signal, detected by a cooled RCA C31034 photomultiplier, was recorded using photon-counting techniques. The laser intensity absorbed by the samples was varied by means of a set of calibrated neutral-density filters.

III. EXPERIMENTAL RESULTS

A. General properties of the PL spectra and sample quality

Figure 1 shows the PL spectra measured at $T=80$ K and at $J=6$ W cm^{-2} of three GaSe samples chosen on the basis of the different relative intensities of the emission features.

The spectra of Fig. 1 can be divided into two parts: the high-energy PL contribution, above 1.98 eV, formed by the lines DFE, DBE, IFE, and IBE (intrinsic lines), and the low-energy part below 1.98 eV, characterized by broad emission bands (extrinsic luminescence). (See caption for all definitions.)

The origin of the intrinsic lines is due to various excitonic recombination processes.

(a) The line DFE at 2.098 eV is the well-known zero-phonon emission of the $n=1$ direct free exciton in the triplet state.[1]

(b) The line DBE at 2.078 eV is due to the recombination of direct excitons bound to neutral-acceptor centers.[4]

(c) The emission IFE at 2.035 eV is attributed to the one-LO-phonon replica of the indirect free-excitonic recombination associated with the indirect conduction band at the M point of the BZ.[3,4,8]

(d) The structure IBE at 2.002 eV is assigned to the radiative recombination of indirect excitons bound to deep neutral-acceptor centers.[4]

Further properties of these four lines as a function of J, T, and excitation energy are discussed in detail in Ref. 4.

In Fig. 1(a) the line DFE [full width at half maximum (FWHM) of 10 meV] is the most intense emission with respect to either the other intrinsic lines or to the very broad and weak extrinsic luminescence band at lower energy. This kind of PL spectrum is typical of the "high-quality" samples (type A) with a low density of defects and cleaved without strains (no cracks appeared on the cleaved surfaces).

In Fig. 1(b) the line DFE is broader and is still the main emission, but the intensities of the excitonic recombinations DBE, IFE, and IBE are increased with respect to those of Fig. 1(a). The small peak at 2.113 eV on the high-energy tail of DFE is due to the recombination of direct excitons from the $n=2$ level. The extrinsic luminescence is now more intense than that in Fig. 1(a), and consists of a broad band (FWHM of ≈ 0.19 eV) centered at 1.62 eV. This spectrum is typical of the crystals of "intermediate quality" (type-B samples) showing a few cracks on the surface that are usually produced during the cleavage.

In Fig. 1(c) the direct excitonic recombinations DFE and DBE are practically absent, while the indirect excitonic lines IFE and IBE are the main features. Moreover, the extrinsic luminescence is, in this case, more intense with respect to the intrinsic lines and shows a broad band (FWHM of ≈ 0.26 eV) centered at 1.71 eV. Spectrum (c) of Fig. 1 belongs to the "poor-quality" samples

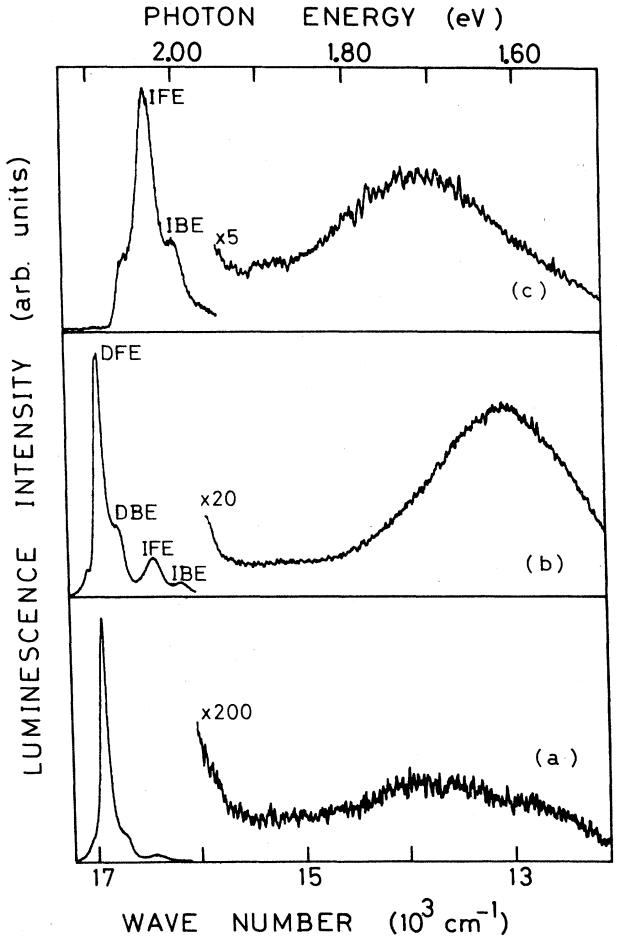

FIG. 1. Luminescence spectra of three Bridgman-grown ϵ-GaSe samples measured by pumping into the conduction band with the 514.5-nm laser line at $T=80$ K and with an excitation intensity of 6 W cm^{-2}. Spectrum (a) is relative to type-A samples containing a low density of lattice defects and are cleaved without strains. Spectrum (c) is observed in type-C samples, which contain many fine cracks on the cleaved surfaces and a higher degree of lattice disorder. Spectrum (b) is observed in type-B, which are of intermediate quality. DFE denotes direct free exciton, DBE direct bound exciton, IFE indirect free exciton, and IBE indirect bound exciton. For each spectrum the intensity scale of the part at energies lower than 1.98 eV is relative to that of the high-energy side. The relative sensitivity factors for the PL intensity are indicated. The spectral resolution is of 10 cm^{-1}.

containing a high density of defects and a lot of cracks on the cleaved surfaces (type-*C* samples).

The shape and relative intensity of the PL spectra of GaSe are sample dependent, as shown in Fig. 1, and they also change with the illuminated spot on the same sample, especially as far as the type-*C* samples are concerned. Moreover, the shape and intensity of the extrinsic luminescence change as a function of T and J; for the intrinsic lines such dependences have been reported in Ref. 4 and we do not discuss them in this work anymore. However, it is worth noting, in Fig. 1, the relative intensity of the lines DFE and IFE: there is an enhancement of the indirect excitonic recombinations with increasing structural disorder of the samples [see Figs. 1(a) and 1(c)]. This could be due to the growth of nonradiative transitions, which seem to affect the direct excitonic recombinations more than the indirect ones. In particular, in Fig. 1(c) we observe a structure at about 2.061 eV on the high-energy tail of the IFE, which can be attributed to zero-phonon lines (ZPL's) of the indirect excitons having a Rydberg of about 30 meV.[4,17] This would locate the bottom of the indirect conduction band (ICB) at about 2.09 eV for $T=80$ K, as reported in Ref. 7. The appearance of the ZPL is due to the relaxation of the selection rule of the wave vector for indirect transitions from the M to Γ points of the BZ. Since this effect increases with the density of the lattice defects and impurities of the samples, the ZPL is resolved only in the type-*C* sample. Zero-phonon (ZP) transitions of the indirect excitons in GaSe have also been observed in absorption measurements.[17,18]

At low temperature the majority of the Bridgman-grown crystals give PL spectra of the type depicted in Fig. 1(b). Type-*A* samples constitute $\approx 10\%$ of the samples characterized by luminescence techniques. Hence, in the following the results we discuss only type-*B* samples.

B. Excitation-intensity dependence of the PL spectra

Shown in Fig. 2 is the evolution of the PL spectra, at $T=80$ K, of a type-*B* sample, for different values of J. By decreasing the excitation intensity, we observe that the extrinsic luminescence becomes more and more important with respect to the excitonic lines. Moreover, the shape of the extrinsic bands changes by lowering J and becomes more structured. In particular, we see in Fig. 2 that at excitation intensities lower than 10^{-2} W cm^{-2} it is possible to resolve two extrinsic bands $B1$ and $B2$ centered at 1.88 and 1.62 eV, respectively. For values of J lower than 10^{-3} W cm^{-2}, the excitonic lines have nearly disappeared. It should be remarked that by decreasing J, for the type-*A* samples as well the extrinsic luminescence becomes dominant, and at the lowest intensities we could measure the extrinsic bands are more structured and narrower than those of Fig. 2(d).

Figure 3 shows the dependences of the luminescence intensities of the line DFE, those of the extrinsic bands $B1$ and $B2$, and that of the integrated total luminescence (TL) as a function of J from 10^{-3} to 10 W cm^{-2} for a type-*B* sample, at $T=80$ K.

We mention that the points in this figure have been obtained by focusing the laser beam on the samples in two different ways. The solid symbols show the luminescence intensities obtained by focusing the excitation light on a small spot (diameter ≈ 100 mμ), so as to obtain high values of J, which are, however, limited by the damaging of the sample for heating. By decreasing J, the PL signal is more and more difficult to measure. So, it was necessary to defocus the laser beam in order to illuminate a larger area of the sample surface to get a higher emission intensity. The open symbols of Fig. 3 were obtained in this last case. The solid lines of the double-logarithmic plot of Fig. 3 are the fits with a power law $L \sim J^s$. The behavior of the DFE intensity is superlinear $s=1.4\pm0.1$) over the entire range of J investigated. Similar results were obtained for the other excitonic recombinations DBE, IFE, and IBE.[14]

On the other hand, the band $B2$ shows a linear dependence with J ($s=1.0\pm0.1$) in a wide range of J up to

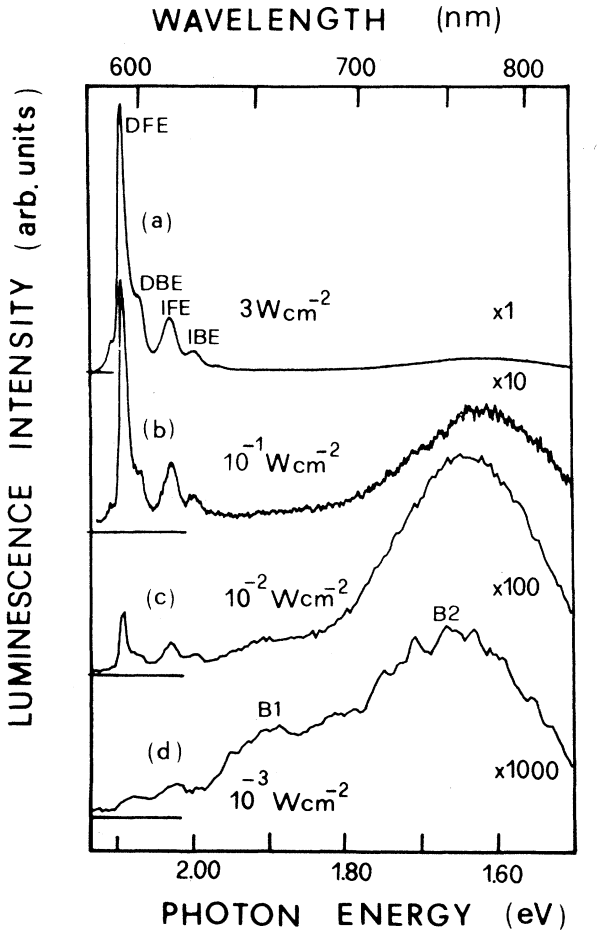

FIG. 2. Luminescence spectra of a Bridgman-grown ϵ-GaSe sample (type *B*) measured by excitation into the conduction band with the 514.5-nm laser line at $T=80$ K and for different excitation intensities. $B1$ and $B2$ are two extrinsic emission bands. The other labels have the same meaning as in Fig. 1. The amplification factor is indicated for each spectrum on the right side. The spectral resolution is of 10 cm^{-1}.

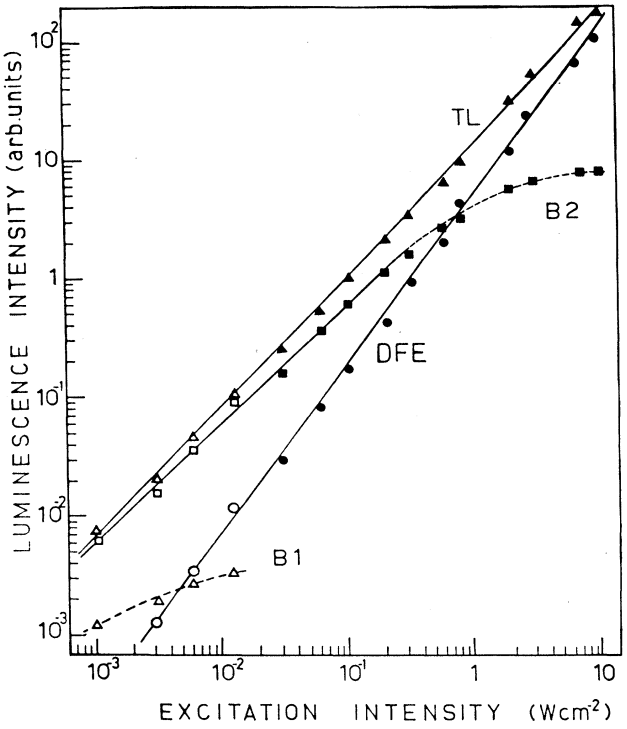

FIG. 3. Logarithmic plots of the integrated intensity of the direct-free-excitonic line (DFE), of the total luminescence (TL) of the spectra, and of the two extrinsic emission bands $B1$ and $B2$ shown in Fig. 2, vs the excitation intensity (J) at $T=80$ K. The solid and open symbols were obtained from illuminated spots on the sample of about 0.1 and 1 mm, respectively. The solid lines are the least-squares fits of the experimental intensities (L) to the power law $L \approx J^s$. The exponent s is equal to 1.4±0.1 for the DFE line, to 1.0±0.1 for the $B2$ band, and to 1.2±0.1 for the TL plot.

about 0.3 W cm^{-2}, followed by a saturation trend (dashed line).

As for the band $B1$, we observe that the saturation regime for this recombination process already occurs in the range of J from 10^{-3} to 10^{-2} W cm^{-2}. Moreover, the total luminescence intensity of the emission spectrum in the visible range shows a superlinear dependence as a function of J (plot TL), where $s=1.2\pm0.1$ over four decades. This behavior indicates that the quantum yield of the excitonic luminescence increases with J and it shows the importance of the nonradiative transitions.

C. Temperature dependence of the PL spectra

A few PL spectra measured as a function of T with the 575-nm laser line at $J=4$ W cm^{-2} are reported in Fig. 4 for a type-B sample. At liquid-He temperature [spectrum (a)], the intrinsic luminescence is very structured and there are three different contributions of the excitonic recombinations: the first group of lines, at energy higher than 2.096 eV, are attributed to free or weakly localized direct excitons;[8,10,19] the second group (the features BE) from about 2.058 to 2.096 eV are due to the recombinations of direct bound excitons;[8,10,20] the third group—between 1.922 and 2.058 eV—are assigned to the recombination of free and bound indirect excitons and their phonon replicas.[4,8,14] By increasing T, the first group of lines (which at T larger than 40 K merges into the emission DFE) becomes more and more intense with respect to the other radiative recombinations. In contrast, the intensity of the BE lines decreases rapidly versus T, and they disappear one by one starting from those at higher energy. This behavior is characteristic of the bound-exciton recombinations, which, in this case, are due to excitons bound to ionized donors.[14] For T larger than 40 K these lines disappear completely. Above 50 K the emission DBE appears and the intrinsic part of the PL spec-

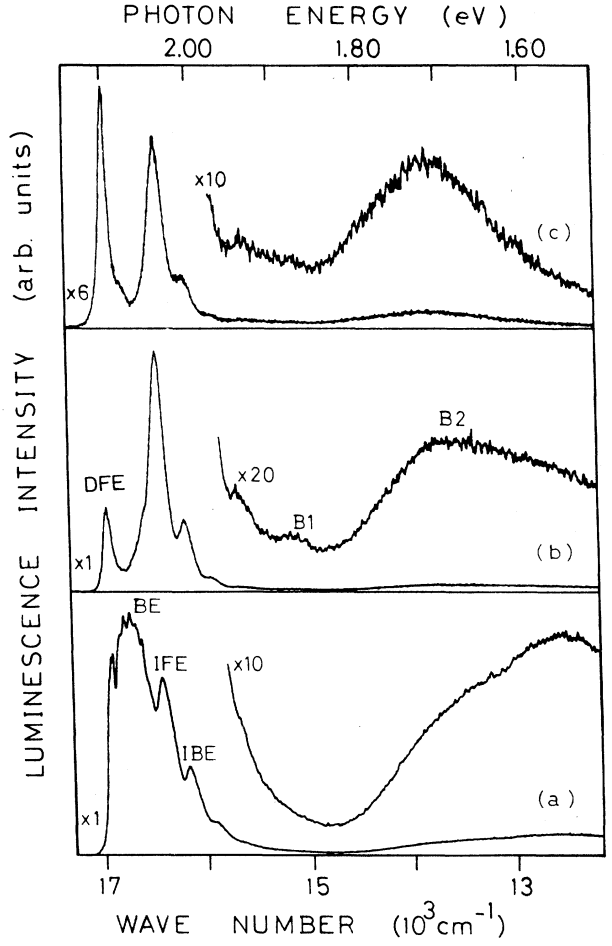

FIG. 4. Luminescence spectra of a Bridgman-grown ϵ-GaSe sample (type B) measured at different temperatures: (a) 4 K, (b) 43 K, and (c) 65 K. The spectra were obtained by excitation into the bottom of the direct conduction band at 575 nm and at an excitation intensity of 4 W cm^{-2}. The PL-intensity scale of spectrum (c) has been expanded by a factor of 6 with respect to spectra (a) and (b): the luminescence is quenched by the increasing temperature. The low-energy part of each spectrum is also shown in an expanded scale of the intensity (by the indicated factors), in order to better show the shape of the extrinsic luminescence $B1$ and $B2$. The spectral resolution is 10 cm^{-1}.

trum is formed by the four excitonic lines discussed above [Fig. 4(c)]. As for the indirect excitonic recombinations IFE and IBE, their intensity first increases up to about 40 K and then decreases with respect to the luminescence of direct excitons. Further details and properties of these three groups of lines as a function of T are discussed in Ref. 10.

For each temperature investigated, the extrinsic emission is more intense and broader in the samples containing a large density of structural defects or impurities (crystals of type C) with respect to the samples of good quality (type A). Moreover, the intensity of the extrinsic luminescence decreases rapidly with respect to that of the excitonic emissions as a function of T, in all three types of samples. In particular, for T larger than 180 K the whole extrinsic luminescence completely disappears and the luminescence spectra nearly coincide with the line DFE with a small contribution of the IFE emission. When T increases, we observe a blue shift and a narrowing of the band emission $B2$. The maximum of this band shifts from 1.55 to 1.70 eV for T rising from 4 to 65 K. The FWHM, which is about 0.21 eV at $T=65$ K [Fig. 4(c)], becomes much larger in spectrum 4(a), where the low-energy side of the extrinsic band could not be measured, because the quantum efficiency of the photomultiplier falls rapidly for wavelengths longer than 850 nm.

We have found that the total luminescence intensity of the spectra decreases about 10^3 times from 2 to 300 K. This result clearly indicates a temperature decrease of the quantum yield of the radiative processes. We think that the damping of the total luminescence efficiency versus T is likely due to the temperature increase of the nonradiative recombinations (which are in competition with the radiative transitions).

D. Excitation spectra

To better understand the nature of the extrinsic luminescence of GaSe and from which states it is excited, we measured the PL excitation spectra (PLES) of the emission $B2$ by detecting the signal of the maximum of this band. In Fig. 5(a) we show an example of PLES of the band $B2$—for a type-B sample—recorded at 1.62 eV and $T=80$ K. We also measured the PLES at different energies along the high- and low-energy tails of the band $B2$ and we found that they have shapes very similar to that of spectrum (a) of Fig. 5.

For comparison, we also show the PLES of the line DBE at 2.078 eV [Fig. 5(b)]. This spectrum looks like the excitonic absorption spectrum of GaSe at 80 K (Ref. 13) and its shape is very similar to that of the PLES of the line DFE, which presents line-narrowing effects, as discussed in Ref. 12. Its main structure at 2.098 eV corresponds to the excitation of the ground state of direct free excitons. Further, Fig. 5(b) shows that the recombination process of the direct bound excitons which originate the line DBE is efficient when exciting into the direct conduction band (DCB).

On the other hand, spectrum (a) of Fig. 5 presents a broad feature in the region between the edges of the two conduction-band minima and a deep minimum centered at the spectral position of the DFE line. In particular, the PLES of band $B2$ has a long tail at an energy lower than the DFE.

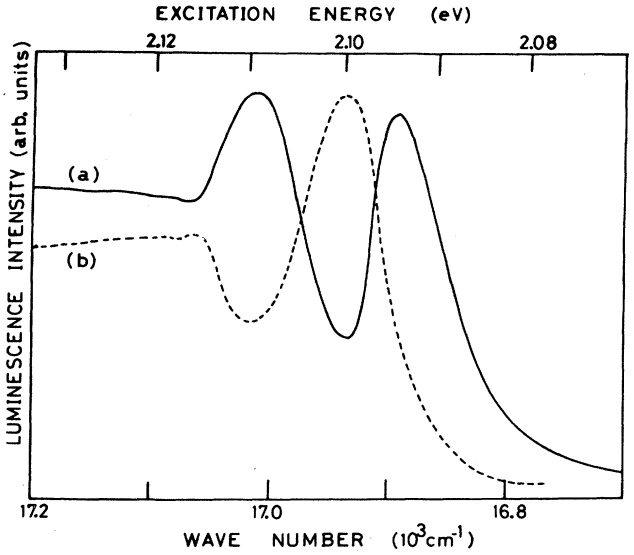

FIG. 5. Luminescence-excitation spectra at $T=80$ K of a Bridgman-grown ϵ-GaSe sample (type B) measured by scanning a dye laser ($J=10$ W cm^{-2}) and detecting the emission light of (a) the maximum of the extrinsic band $B2$ at 1.62 eV, and (b) the direct-excitonic line DBE at 2.078 eV, shown in Fig. 2.

The different shapes of these two PLES indicates the existence of competition between the mechanisms of the recombination processes from which the emission band $B2$ originates and the mechanism responsible for the formation and recombination of the direct excitons. Moreover, we remark that both spectra of Fig. 5 are flat and quite intense when exciting into the conduction band. In fact, the shape of the PL spectra does not change at all if we pump at higher and higher energies, starting from the bottom of the direct conduction band. However, in Fig. 5 we see that the fluorescence of band $B2$ is very intense when we excite electrons in the valley of the ICB whose bottom is about 6 meV lower than the $n=1$ level of the direct excitons.[7]

The PL-excitation spectra of band $B1$ centered at about 1.88 eV (Fig. 2) were not easy to measure accurately, because this structure appears resolved, from the generally more intense band $B2$, only at the lowest values of J, as shown in Fig. 2. However, qualitative information concerning the PLES of band $B1$ can be obtained by the PL spectra from measurement with selective excitation at different energies on the tail of the absorption edge.

E. Energy-selective PL spectra

In Fig. 6 we show PL spectra of a type-B sample obtained at 80 K by excitation at three different laser frequencies on the low-energy tail of the indirect-absorption edge. In this figure we observe an enhancement of the extrinsic luminescence with respect to the excitonic lines, when the excitation energy decreases.

With respect to spectrum (a) of Fig. 2—obtained by excitation into the conduction band—we see that in this case the extrinsic luminescence is much stronger. More-

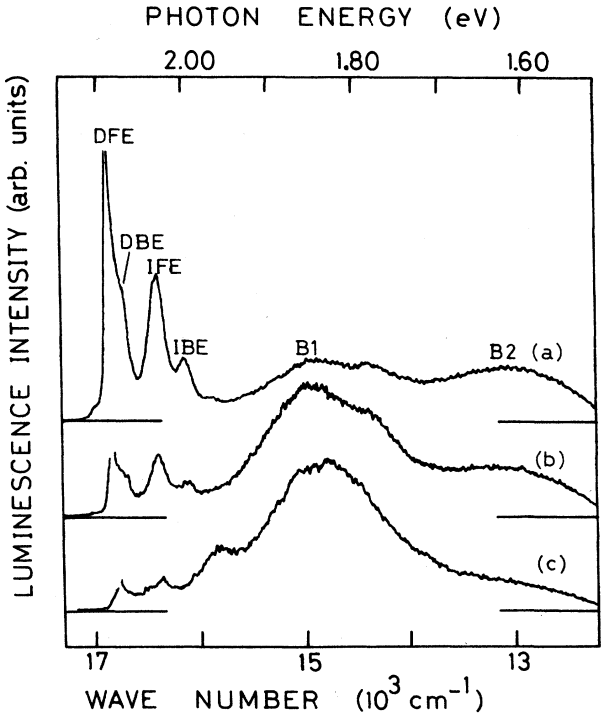

FIG. 6. Energy-selective luminescence spectra at $T=80$ K of an ϵ-GaSe sample (type B) obtained with excitation at different laser frequences on the low-energy tail of the excitonic absorption band: (a) 2.091 eV, (b) 2.087 eV, and (c) 2.083 eV. The structures at energies higher than 1.98 eV are due to various excitonic recombinations, whereas the bands at lower energy are extrinsic emission bands below the absorption edge. For the meaning of the labels, also see the captions of Figs. 1 and 2. The excitation intensity and the spectral resolution were 5 cm^{-1} and 5 W cm^{-2}, respectively. During the scan across the excitation energy, the fluorescence and diffused light of the laser line were stopped. This gives the missing portion of the spectrum on the peak of the line DBE.

over, the extrinsic luminescence is more structured and the main bands $B1$ and $B2$ are more resolved than in Fig. 2. We observe that the intensity of band $B2$ decreases when the laser energy is lowered along the indirect-absorption tail, in agreement with the PLES results of Fig. 5(a).

In contrast, the intensity of band $B1$ increases more and more, and $B1$ becomes the dominant emission band when we excite at energies lower than the indirect minimum of the conduction band. Further, Fig. 6 shows that this band is structured and at least two main features are observed.

Thus, the extrinsic luminescence of GaSe consists of different bands which are enhanced or quenched depending on the exciting energy.

IV. MODEL FOR EXTRINSIC LUMINESCENCE

A. Summary of the experimental results

A model for the extrinsic luminescence in GaSe should reproduce the above experimental results, which are now summarized.

(a) At low temperature ($T<200$ K) the PL spectra consist of the excitonic emission lines (intrinsic luminescence) and the extrinsic luminescence at lower energy, composed by broad overlapping bands. The relative intensity among the direct and indirect excitonic lines and also between the intrinsic and extrinsic emissions depends strongly on the quality of the crystals. Namely, the intensity of the extrinsic luminescence increases with the defect density and lattice disorder of the samples.

(b) The extrinsic luminescence can be separated into two bands, $B1$ and $B2$, because of their different behavior. These bands dominate the PL spectra at very low J. At 80 K the intensity of $B2$ varies linearly with J up to ~ 0.5 W cm^{-2} and then it begins to saturate, whereas the intensity of $B1$ already saturates at $J\sim 10^{-3}$ W cm^{-2}. On the contrary, the intensity of the intrinsic lines depends superlinearly on J and they appear only when $B1$ begins to saturate. The superlinear behavior of the total integrated luminescence intensity indicates the importance of nonradiative recombinations.

(c) At 4 K the direct free combinations can be observed only in high-quality samples and, in general, the intrinsic luminescence is dominated by the recombination of the direct bound excitons. By increasing T, the BE lines progressively decrease and disappear at about 40 K. For $T>\sim 40$ K the direct free-exciton emission becomes more and more important and persists up to room temperature.

(d) By increasing T, the intensity of the extrinsic luminescence decreases with respect to that of the excitonic lines and also in absolute value. The spectral position of band $B2$ shifts towards higher energy and the band narrows, when T increases.

(e) The PL-excitation spectra of the excitonic lines are different from those of the extrinsic bands, evidence of competition between the two kinds of recombination processes.

(f) The energy-selective PL spectra show an enhancement of band $B1$ and a quenching of $B2$ when exciting on the low-energy tail of the absorption edge, at energies lower than the ICB minimum.

B. Donor-acceptor–pair recombinations

Extrinsic bands involving localized states in the energy gap can originate from the following recombination processes:

$$D^0+A^0\rightarrow D^+ + A^- + \text{photon}\ , \tag{1a}$$

$$D^0+h\rightarrow D^+ + \text{photon}\ , \tag{1b}$$

$$e+A^0\rightarrow A^- + \text{photon}\ , \tag{1c}$$

where D^0, A^0 and D^+, A^- are the neutral and ionized donor and acceptor centers respectively; e and h stand for electron and hole.

The energy of the photon emitted in one of the processes (1) will depend on different parameters: for example, in a donor-acceptor–pair (DAP) recombination the total energy released will be[21]

$$\delta E = E_g - (E_A + E_D) + E_{AD} \ , \tag{2}$$

where E_g is the energy gap, E_A and E_D are the acceptor and donor ionization energies, respectively, and E_{AD} accounts for the DAP interaction. If the donors and acceptors are considered point-charge defects, the last term of the (2) assumes the simple expression[21]

$$E_{AD} = q^2/\epsilon_0 r \ , \tag{3}$$

where q is the electronic charge, ϵ_0 is the static dielectric constant, and r is the donor-acceptor–pair distance.

If r is comparable with the lattice constant, expression (2) yields a line spectrum which is characteristic of transitions between closely spaced donor and acceptor pairs, as observed, e.g., in GaP.[22] When the DAP separation is large with respect to the lattice constant, the term $e^2/\epsilon_0 r$ tends to zero and the DAP lines merge into an unresolved emission.

Since in GaSe the defects are related to the stacking faults which involve extended regions, E_A, E_D, and E_{AD} are not discrete values and no sharp lines are expected in the optical spectra.

In addition, homogeneous broadening of the emission can be present. In fact, for zero-phonon transitions all the δE energy is emitted in a photon, but, in general, phonons can assist the electronic transition. Strong electron-phonon interaction is usually observed for deep donor and acceptor centers which produce important lattice distortion.

C. Donor and acceptor levels in GaSe

The crystals of GaSe (not intentionally doped) grown by the Bridgman method are highly compensated and contain in the energy-gap donor and acceptor levels whose energies do not depend on the chemical nature of the impurities; their densities increase with the structural disorder of the samples.[15] In the following we will be mainly concerned with type-B samples, because the largest part of the Bridgman-grown crystals show PL spectra similar to those of Fig. 2.

Our samples present an electrical p-type conductivity with $N_A - N_D \sim 10^{15}$ cm^{-3} and $N_A + N_D \sim 10^{17}$ cm^{-3}, where N_A and N_D are the concentrations of acceptors and donors, respectively.[15]

Shallow donor levels ($D1$) about 6 meV below the ICB (i.e., $\sim$12 meV from the direct excitonic ground state) have been found in the optical spectra of p-type samples of GaSe.[7,11,23]

Three main groups of acceptor levels have been observed by electrical-transport measurements, in Bridgman samples grown in different laboratories. Manfredotti *et al.*[24] observed acceptor states diffused in energy and lying between 0.18 and 0.21 eV above the valence band (VB), with a density of about 10^{16} cm^{-3}. Their samples are very similar to ours. In fact, they are p type with a total acceptor density of $\sim 10^{17}$ cm^{-3} and are highly compensated with $N_A - N_D \sim 10^{16}$ cm^{-3}. Further, as also found in our samples,[15] most of the acceptor states ($\sim 10^{17}$ cm^{-3}) are located on a shallow level ($A0$) 30 meV above the VB. These trapping levels, detected by means of different electrical transport techniques, are generally attributed to intrinsic defects generated by structural disorder, mainly stacking faults. The acceptor level ($A1$) at 0.20 eV with a density of $\sim 10^{16}$ cm^{-3} was shown to be characteristic of relatively pure crystals of Bridgman p-type GaSe.[25] The formation of direct bound excitons, giving rise to the DBE line, was attributed to the presence of the $A1$ acceptor centers.[4]

In our crystals deeper acceptor levels ($A2$) 0.44 eV above the VB and with a density of $\sim 10^{13}$ cm^{-3} have been detected by means of the space-charge-limited-currents technique.[26] The same level has also been detected in other p-type GaSe samples, with the same concentration and diffused 0.42 and 0.46 eV.[27] These deep $A2$ levels should be the neutral-acceptor centers which bind the indirect excitons via the formation of indirect-bound-exciton states, whose recombinations give the line IBE.[4] These acceptor centers were classified as "giant traps" because of their very large capture cross sections ($\sim 10^{12}$ cm^2).[27] They are not associated with point defects, but to somewhat extended regions of defects, as dislocations or stacking faults.

For the above structure of extrinsic centers it results that, at very low temperature and in the absence of optical excitation, the Fermi level is localized on the acceptor level $A1$ at 0.2 eV. All the donor states are ionized and so are almost all the acceptor centers, except for $N_{A^0} = N_A - N_D \sim 10^{15}$ cm^{-3} acceptors, which are neutral. They are the deepest, namely all the 10^{13}-cm^{-3} acceptors $A2$ and 10^{15} cm^{-3} of the $A1$ ones.

D. Discussion

As discussed in Sec. III, the extrinsic luminescence can be divided into two bands, $B1$ and $B2$, because of their different experimental behavior.

The $B1$ band is very efficiently excited by pumping below the absorption edge (Fig. 6) in correspondence to the $D1$ donor energies, and it presents a saturation trend at very low J (Fig. 3). This behavior clearly indicates that donor states are involved in the recombination processes. The strong dependence of the PL spectra on the excitation frequency at 80 K is quite surprising [compare, e.g., Figs. 2(c) and 6(b)]. The absence of thermal equilibrium among different electronic states involving donor levels is evident here. Similar effects were found in regard to the direct- and indirect-free- and bound-excitonic states and were attributed to the complicated structure of the conduction band, with two nearly resonant minima, and to the presence of nonradiative recombinations.[10] The latter dominate the kinetics of recombination even at low temperature in a wide range of excitation intensities, as it results from the superlinear behavior of the intensity of the total integrated luminescence (TL plot of Fig. 3). The energy position of band $B1$ centered at 1.88 eV (FWHM of $\sim$0.15 eV) is in agreement with DAP transitions of electrons from the neutral shallow-donor levels $D1$, lying about 2.08 eV above the VB for $T = 80$ K,[7] to deep neutral-acceptor states $A1$ centered at $E_{A1} \sim 0.20$ eV above the VB. It should be noted that about 99% of the neutral acceptors are in the $A1$ level at low temperature

and low excitation intensity. The shape of $B1$, which shows broad structures (see Fig. 6), should resemble the energy distribution of neutral acceptors. However, a distribution of donor-acceptor interaction energies, as well as a homogeneous broadening due to a phonon-assisted transition, could affect the actual line shape.

The $B1$ band is less efficiently excited by pumping in the conduction band. It, however, dominates the luminescence spectrum for very low J, but tends to saturate already at 10^{-3} W/cm^2. Band $B2$ becomes the dominant one at higher J. This suggests that band $B2$ is due to a different and competitive recombination mechanism.

In fact, $B2$ is very efficiently excited in the indirect edge, with a deep minimum in the excitation spectrum at the DFE energy [Fig. 5(a)]. Moreover, band $B2$ does not appear after resonant excitation in the donor levels, as is clear from the excitation spectrum of Fig. 5 and the selective PL spectra of Fig. 6. These results, together with the saturation behavior of $B1$, indicate that emission $B2$ corresponds to a recombination process which is competing with those giving rise to the excitons and $B1$ emissions. Via excitation in the conduction band, band $B2$ saturates at much higher J than that at which $B1$ does, when the excitonic luminescence becomes the dominant one. This suggests that $B2$ originates from electron states higher in energy than the $D1$ levels. Therefore, we propose that $B2$ is due to the recombination of free electrons with neutral acceptors, i.e., process (1c). In this way, the observed behavior of the intensities as a function of J is also well reproduced (see Fig. 3). In fact, when the donor states are no longer available for free electrons, the latter can recombine either with neutral acceptors or with free holes. The probability of recombination of free electrons with neutral acceptors is expected to be proportional to the product of the relative densities, and then to J if the density of neutral acceptors can be considered constant, as is the case at low J: $P_{e-A^0} \sim n A^0 \sim J$.

On the other hand, the probability of exciton recombination $P \sim np$ is expected to be proportional to J^2 at low values of J. A saturation of electron-acceptor recombination will occur at higher J when the exciton luminescence is dominant.

As discussed before, at low J and low T, the acceptor centers which are neutral are the deepest ones: the 10^{13} cm^{-3} of $A2$ levels at 0.44 eV and the deepest 10^{15} cm^{-3} lying above the Fermi level localized on the A 1 levels at about 0.2 eV. The zero-phonon energy for electron recombination with the $A1$ neutral acceptors is expected at 1.89 eV, being the bottom of the ICB at about 2.09 eV for $T=80$ K.[17] The $B2$ band appears at lower energies and extends over a wide spectral range starting from about 1.8 eV (see Figs. 2 and 4). It is possible that the $A2$ levels, due to their high cross section, in site of their low density, have an important role. Their zero-phonon transitions are expected to be centered at 1.65 eV corresponding to the maximum of $B2$ (Fig. 2). However, transitions of $A1$ acceptors strongly coupled to phonons could also account for the observed shape of the $B2$ band. The role of $A1$ acceptors seems to be supported by the temperature behavior of the shape of $B2$, which shows a blue shift and a narrowing effect (Fig. 4). At very low temperature there is a sharp separation across the Fermi level between neutral and ionized acceptors. By increasing T, the Fermi level (in p-type samples and at low J) moves towards higher energies and the separation between A^0 and A^- becomes less sharp. In this way neutral-acceptor states at lower energies become available for electron capture. This effect can account for the blue shift of the luminescence as well as for the narrowing: if at low temperature only the diffused high-energy tail of the Al acceptor was available, by increasing the temperature the distribution of A^0 progressively resembles that of $A1$, giving rise to progressive blue shift and sharpening of the luminescence.

V. CONCLUSIONS

The present results give some further information on the complex kinetics of the e-h recombination in GaSe. According to the model of Ref. 1, the photoexcited electron-hole pairs can recombine through two competing channels: the first concerns the formation and recombination of free and bound excitons, and the second refers to the electrons which thermalize at the bottom of the indirect conduction band. Thermalization can take the electrons to occupy the donor states, from which they can relax, radiatively or nonradiatively, onto the acceptor levels. A high density of structural defects favor nonradiative and extrinsic radiative recombination, giving rise to low quantum yield and to strong luminescence bands in the forbidden gap, respectively. Low temperature and low excitation intensities favor extrinsic recombinations with respect to the excitonic ones. As the direct-exciton ground state is only a few meV higher than the bottom of the indirect minimum, the electrons thermalized in the indirect minimum can also contribute to the population of the direct-exciton states, besides to that of the indirect ones and to the donor states. This process is favored by high temperatures and excitation intensities and by low concentrations of structural defects. Under these conditions, the excitonic lines dominate the luminescence spectrum of GaSe and the extrinsic luminescence saturates. Saturation of the band $B1$, attributed to donor-acceptor–pair recombination, occurs at very low excitation intensities. On the other hand, the intensity of band $B2$ tends to saturate at quite higher excitation intensity, when the excitonic luminescence dominates the fluorescence. We propose that the $B2$ band originates from the recombination of free electrons, mainly at the indirect minimum, with neutral-acceptor levels. This mechanism of recombination should be the dominant one at an excitation intensity which is sufficiently high in order to saturate the donor levels, but sufficiently low to have a low concentration of holes and therefore a small probability of forming excitons.

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