# Direct and indirect electron-hole plasmas in gallium selenide

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A detailed study of the electron-hole plasma in the indirect semiconductor GaSe is presented. The simultaneous presence of direct and indirect *e-h* plasmas in highly excited GaSe is expected as a consequence of the almost degenerate direct and indirect gaps. Simultaneous plasmas have been clearly observed in spontaneous emission measurements. Only the amplification channel associated with the indirect *e-h* plasma is observed in the stimulated emission and optical gain spectra at low temperature. Both *e-h* plasmas give rise to light amplification above 70 K with different optical gain coefficients. The mechanisms involved in the competition between the two amplification channels and their dependences on sample temperature and pumping intensity are discussed. An experimental determination of the photogenerated *e-h* pair densities, obtained by using a particular calibration technique of the experimental setup, allowed us to carry out the theoretical line-shape analysis of emission and gain bands, without uncertainties of the values of the physical parameters involved in the calculations.

## INTRODUCTION

The band structure of GaSe near the optical-absorption edge consists of an indirect minimum of the conduction band at the point $M$ ($M_3^+$ symmetry) of the Brillouin zone lower than the direct minimum ($\Gamma_3^+$) located at the $\Gamma$ point. The top of the valence band lies at the center of the Brillouin zone and has the symmetry $\Gamma_4^-$. The energy difference between the direct and the indirect gap is of only 25 meV.[1,2] This particular band structure has led some to believe that the electron-hole (*e-h*) plasma could be a three-component fluid containing direct ($\Gamma$) and indirect ($M$) electrons and ($\Gamma$) holes. This statement is supported by spontaneous luminescence measurements performed in strongly excited GaSe (up to 2.6 MW/cm$^2$) at 2 K.[3] The emission spectrum consists of two bands, localized at 592 and 602 nm, respectively, that are ascribed to the recombination of simultaneously occurring direct and indirect *e-h* plasmas. The reported Mott thresholds for the existence of direct and indirect *e-h* plasma are $n=4\times10^{16}$ and $n=2\times10^{17}$ cm$^{-3}$, respectively. Yao and Alfano,[4] who carried out photoluminescence spectroscopy measurements by means of a picosecond laser source (peak intensity up to 710 MW/cm$^2$) in a temperature range between 77 and 300 K, found two interesting features. The first is that the emission spectrum consists of two bands: a low-energy band (605 nm at 77 K), ascribed to a stimulated emission involving an indirect *e-h* plasma (IEHP) recombination, and a high-energy band (591.8 nm at 77 K), ascribed to the exciton-electron scattering emission process. The second feature Yao and Alfano found is that at 300 K, at a photogenerated electron density around $3\times10^{17}$ cm$^{-3}$, such an exciton-electron emission undergoes a continuous transition into a direct *e-h* plasma emission (DEHP). All these results seem to suggest that DEHP and IEHP can simultaneously occur in GaSe. Therefore one should expect that the *e-h* plasma in GaSe can supply two different optical amplification channels.

Stimulated emission and unsaturated optical gain experiments have shown that only one optical gain channel, localized in the IEHP energy region, operates in GaSe at the highest excitation intensities.[5–8] No experimental evidence of a direct plasma optical gain has been reported up to now. This feature seems to be in striking contrast to the above-mentioned interpretation of the spontaneous emission spectra.

The aim of this work is to achieve a better understanding of the radiative recombination processes and of the optical amplification mechanisms in highly excited GaSe. We have carried out spontaneous and stimulated emission and optical gain measurements in GaSe below and above the critical Mott density in a temperature range between 10 and 300 K.

## EXPERIMENTAL PROCEDURE

The GaSe single crystals were obtained from a melt by the Bridgman-Stockbarger technique or grown by the iodine transport method. The cleaved samples, whose quality was previously tested, varied in thickness between 2 mm and 10 $\mu$m. The samples were mounted on the cold finger of a temperature-controlled cryostat operating in the range 10–300 K by means of a closed-cycle He refrigerator. The excitation source was a flow-type $N_2$ pumped dye laser operating at two different wavelengths: at 575 nm, i.e., quasiresonant with the GaSe direct energy gap, by using Rhodamine 6G dye; and at 530 nm, i.e., the excitation wavelength of Refs. 3 and 4, by using the Coumarin 121 dye. The maximum focused peak power density was $I_0=6$ MW/cm$^2$ with pulse duration of 1 ns and a repetition rate of 10 pulse/s. A 45° geometry, with respect to the $c$ axis of the sample, was adopted for collecting the luminescence from the

 

cleaved face of the crystal. A 90° geometry was used in stimulated emission and optical gain measurements. The emission was analyzed by a 600-mm monochromator and the spectra were recorded by using a boxcar technique. An absolute measurement of the photogenerated *e-h* pair density, which is a fundamental quantity for evaluating the strength of the cooperative processes, has been obtained by calibrating the boxcar analyzer output with a reference monochromatic light signal from a Nd:YAG (YAG denotes yttrium aluminum garnet) second-harmonic pumped Quantel dye laser having a well-known intensity and a pulse duration comparable to the integration time response of the photomultiplier tube (PMT). Then the *e-h* pair density scale was normalized to the photoluminescence signal intensity corresponding to the arising of the EHP photoluminescence band, i.e., to the Mott critical density. This calibration technique allows us to evaluate the *e-h* pair density $n$ from the peak intensity of the experimental spectra. One can calculate the main $n$-dependent physical quantities (i.e., electron and hole Fermi energies, gap reduction, etc.) required to carry out theoretical fits of the experimental line shapes without free parameters, as described later.

The experimental method used to measure unsaturated optical gain was similar to that of Shaklee *et al.*[9] In order to avoid misfits in the gain spectrum measurements due to low gain processes or fast saturation effects, we adopted an optical arrangement which allowed us to measure gain coefficients from 10 to $10^4$ $cm^{-1}$ by controlling the sample excited length down to 1 $\mu$m.

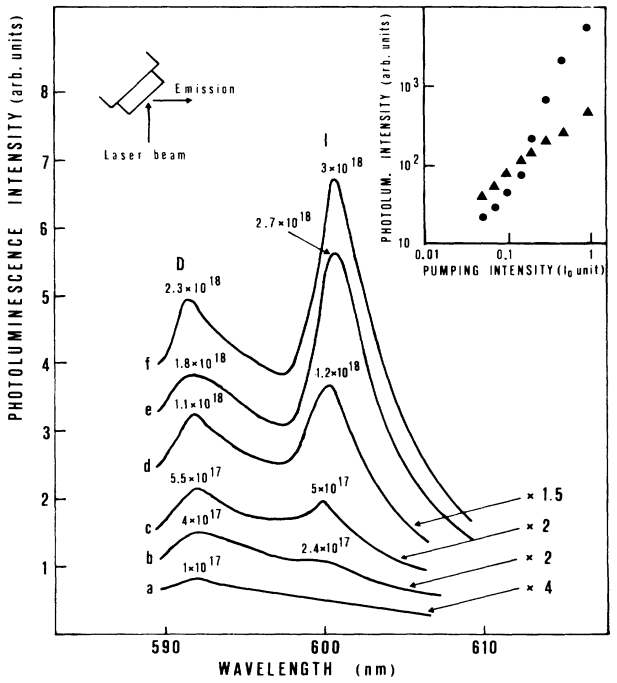


FIG. 1. Spontaneous emission spectra at 10 K and at different pump intensities of a 1-mm thick GaSe sample: curve *a*, $0.05I_0$; *b*, $0.2I_0$; *c*, $0.31I_0$; *d*, $0.5I_0$; *e*, $0.8I_0$; and *f*, $I_0$. The *e-h* pair densities corresponding to the peak intensities are reported on each spectrum. Inset: pumping intensity dependences of *D*-band (triangles) and of *I*-band (dots) amplitudes at 10 K for a thin (10 $\mu$m) GaSe sample.

## RESULTS

The spontaneous photoluminescence spectra of GaSe at 10 K, below the Mott threshold, only show the well-known emission bands due to excitonic radiative recombination processes, i.e., exciton-electron scattering (*A* band localized at 590.7 nm) and exciton-exciton collision (*B* band at 598.8 nm).[10,11] At high intensity these spectra change considerably. Figure 1 shows the typical evolution of 1-mm thick GaSe sample emission spectra, recorded in the 45° geometry at 10 K and for different pumping intensities (from $0.05I_0$ to $I_0$). The *e-h* pair densities reported on the curves of Fig. 1 have been measured by means of the experimental method described in the previous section. At the lowest value of excitation (curve *a*), one band, located at 592 nm (the *D* band), is observed. When the intensity is increased, a new spontaneous band appears (the *I* band) which lies at 599.5 nm and shows a linear dependence on the excitation up to $0.2I_0$. Both the spontaneous *D* and *I* bands appear over threshold pump levels corresponding to the calculated critical Mott densities at 10 K for the DEHP ($4\times10^{16}$ $cm^{-3}$) and IEHP ($2\times10^{17}$ $cm^{-3}$), respectively. With a further increase in the excitation intensity the *D* band displays a linear dependence while the *I* band becomes superlinear and its peak shifts up to 601 nm at maximum pump intensity. It is worth noting that in the thinnest sample (10 $\mu$m) even in the 45° geometry a stimulation effect of the *I* band, above $0.2I_0$, is always predominant and much more evident than in thick samples, showing a larger red shift (peak position up to 604.5 nm at $I_0$). The amplitude intensity dependences of both the *D* and *I* bands are shown in the inset of Fig. 1 for a 10-$\mu$m thick GaSe sample at 10 K. Practically, the GaSe photoluminescence spectrum at 10 K and above the Mott thresholds shows two different spontaneous broad emission bands (the *D* and *I* bands) and, above an *e-h* pair concentration of about $3\times10^{17}$ $cm^{-3}$, the *I* band clearly shows a stimulation on its low-energy side. On the other hand, the energy positions of the *D* band and of the excitonic lines (*A* and *B*) agree well with the results reported in Refs. 4 and 12, where a slow and continuous transition from the excitonic recombination processes to an *e-h* plasma has been observed in GaSe. In Fig. 2 we report the emission spectra at various temperatures, recorded under the same conditions as curves *b* and *e* of Fig. 1, i.e., at $0.2I_0$ (just above the indirect critical Mott density at 10 K) and at $0.8I_0$, respectively. In the low intensity spectrum *b* at 10 K the *D* band is predominant. If the temperature increases, the *I* band grows and reaches its maximum amplitude at $T=70$ K, then it decreases up to 120 K, where it disappears. The high intensity spectrum *e* is characterized by two main bands (*D* and *I*) localized at 10 K at 592 and 601 nm, respectively. The amplitude of the *D* band decreases with the temperature, while the amplitude of the *I* band

weakly increases up to about 70 K, then decreases. At 120 K both bands have the same amplitude. In the inset of Fig. 2, the temperature dependence of the peak energies of both the $D$ and $I$ bands at the maximum pump intensity are reported, together with those relative to the exciton-electron ($A$) and exciton-exciton ($B$) bands observed below the Mott threshold. It is worth noting that these different dependences allow us to exclude that the $D$ and $I$ bands could be of excitonic origin. On the contrary, their similar behavior suggests that the two bands $D$ and $I$ can be ascribed to a similar type of recombination process. The observed decrease of the $I$ band at relatively high temperature (120 K) can be ascribed to the thermal increase of the Mott threshold and to the experimental geometry unsuitable for the observation of amplified luminescence. These difficulties can be overcome by using a much more powerful laser source (as in Ref. 4). The alternative way we have chosen for studying the EHP stimulated emission was the 90° geometry in thin GaSe samples, which always show a stronger stimulated emission because of the lower diffusion of the photoinjected $e$-$h$ pairs, resulting in a higher EHP generation rate. In Fig. 3 several 90° geometry stimulated emission spectra of a thin GaSe sample (10 $\mu$m) obtained at different temperatures and at $0.5I_0$ pump intensity, are reported. The amplitude of the $I$ band increases up

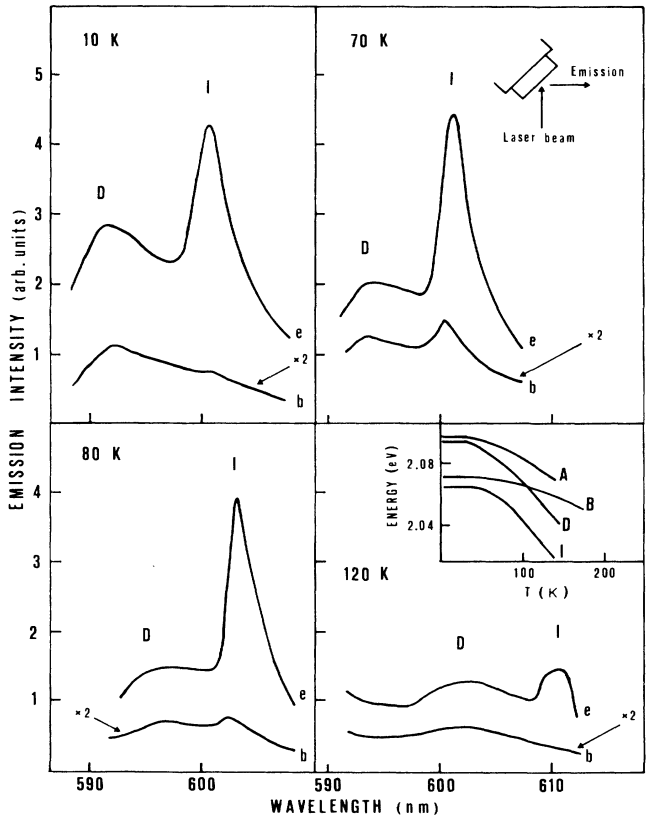


FIG. 2. Temperature evolution of curves $b$ ($0.2I_0$) and $e$ ($0.8I_0$) of Fig. 1, at 10, 70, 80, and 120 K, respectively. Inset: temperature dependences of the $D$ and $I$ bands of Fig. 2 and of the $A$ (exciton-electron) and $B$ (exciton-exciton) bands.

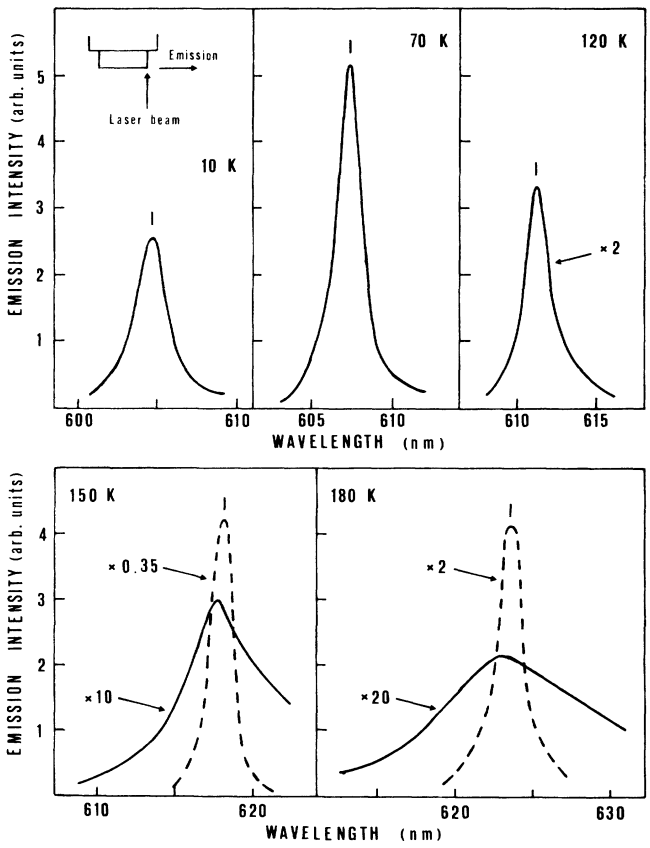


FIG. 3. Stimulated emission spectra of a thin (10 $\mu$m) GaSe sample at $0.5I_0$ (continuous curves) and at $I_0$ (dashed curves) pump intensities, recorded at different temperatures.

to 70 K, while it decreases and the band broadens toward the $D$-band energy region when the temperature is increased over 120 K. At the maximum dye laser intensity the $I$ line stimulated emission is present up to the highest temperatures, as shown by the dashed spectra in Fig. 3. Such a result is quite general, because it is independent of the pumping wavelength and of the growth technique, and is in complete agreement with Ref. 4. Finally, it is worth noting that the temperature dependence of the amplitude for the stimulated emission band in Fig. 3 is similar to that reported in Fig. 2 for the $I$ band.

Figure 4 shows unsaturated optical gain spectra of the same GaSe sample of Fig. 3 (10 $\mu$m) at three different temperatures; the spectra were obtained under resonant pumping (continuous curves) and at the maximum dye laser intensity. At 10 K the spectrum is characterized by only one band, centered at 604.5 nm, with a maximum value of the gain coefficient $g$ of the order of $10^3$ $cm^{-1}$, related to the stimulated emission of the $I$ band. Systematic measurements of the $g$ coefficient in the $D$-band energy range, carried out with narrow slits (10 $\mu$m) and at different pump levels in order to avoid saturation effects due to high gain processes ($g = 10^4 - 10^5$ $cm^{-1}$), allow us to exclude the possibility that the $D$ band could have optical gain at low temperature. By increasing the

temperature up to 70 K the optical gain of the $I$ band is enhanced ($g=1100$ cm$^{-1}$) and only over 80 K does a new gain band on the high-energy side of the $I$ line arise, which is related to the $D$ band and has a moderate gain (100 cm$^{-1}$). It is worth noting that such a new gain band is also evident in nonresonant pumping conditions (530 nm), when the $I$ band seems to gain less (see dashed curves in Fig. 4).

## DISCUSSION

The theoretical expression for the shape of luminescence arising from *e-h* plasma emission with the **k**-selection rule, i.e., typically for direct transitions, is given by[13]

$$I(h\nu)\propto(h\nu-E_g')^{1/2}f_e\left[\frac{m_h}{m_e+m_h}(h\nu-E_g')\right]\times f_h\left[\frac{m_e}{m_e+m_h}(h\nu-E_g')\right]. \quad (1)$$

When **k**-selection rules are not to be considered, i.e., for zero-phonon indirect transitions, we have[13]

$$I(h\nu)\propto\int_0^{h\nu-E_g'}(h\nu-E_g'-E)^{1/2}\sqrt{E}f_e(E)\times f_h(h\nu-E_g'-E)dE\ . \quad (2)$$

In Eqs. (1) and (2) $m_e$ and $m_h$ are the electron and hole effective masses respectively, $f_e$ and $f_h$ are the Fermi functions for electrons and holes, and $E_g'$ is the reduced energy gap. The use of Eqs. (1) and (2) needs the quantitative knowledge of the *e-h* pair density $n$ and of some $n$-dependent parameters like the electron and hole Fermi energies ($F_e$ and $F_h$, respectively) and the gap reduction $E_{xc}'$. In order to carry out, with no free parameters, the fit between our experimental line shapes and the above-reported theoretical models, we have used our experimental *e-h* pair density to calculate $F_e$, $F_h$, and $E_g'$ by means of the degenerate electron gas model.[14] In such a model $F_e$ and $F_h$ are evaluated by means of a temperature-dependent Fermi energy formula and the gap reduction is calculated by using an approximate equation for the exchange-correlation energy, based on a suitable plasmon pole model. Therefore the EHP chemical potential $\mu$ is calculated starting from the general relation $\mu=F_e+F_h+E_g'$.

Our fitting procedure shows that the $D$ band can only be fitted by Eq. (1) for **k**-conserving direct transitions as in Ref. 4, while the $I$ band is only fitted by Eq. (2) for zero-phonon indirect transitions. In Fig. 5 the fits for the spontaneous $D$ and $I$ broad bands of a typical photoluminescence spectrum of GaSe at 10 K are shown. The experimentally determined *e-h* pair densities are $n=8.5\times10^{17}$ and $5.5\times10^{17}$ cm$^{-3}$, which give gap reductions of 48 and 50 meV for the $D$ and $I$ bands, respectively. Since the $I$ band is fitted by only the **k**-nonconserving model, this one has been considered in fitting the gain spectrum of GaSe at 10 K, which is characterized by the $I$ band only at the maximum pump intensity. The results of this calculation are shown in Fig. 6. The observed agreement between theoretical and experimental curves has been obtained by using the values of physical parameters reported in the same figure and calculated with the degenerate electron gas model previously described.[14] The peak position and the crossover energy positions (i.e., the reduced gap and the chemical potential) strictly correspond to those deduced from the experimental gain spectra.

The results of these comparisons, together with the temperature dependences of the $I$ and $D$ bands (inset of Fig. 2), allow us to affirm that the spontaneous emission spectrum of GaSe, at low temperature and above the critical Mott density, is characterized by the simultaneous recombination of a direct *e-h* plasma and of an indirect *e-h* plasma, in agreement with the conclusion of Ref. 3. We ascribe this effect to the GaSe band structure and to the quasiresonant energies of the direct and in-

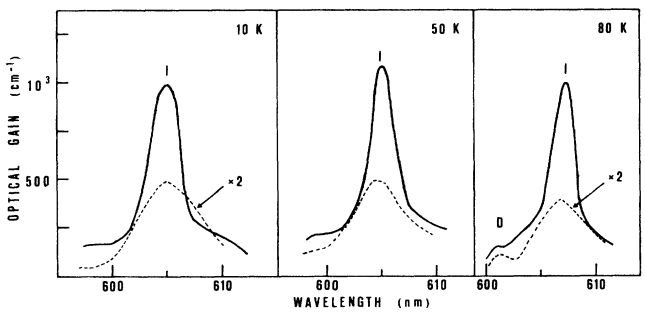


FIG. 4. Gain spectra of the thin GaSe sample (10 $\mu$m) at different temperatures recorded under 575-nm (solid lines) and 530-nm (dashed lines) optical pumping.

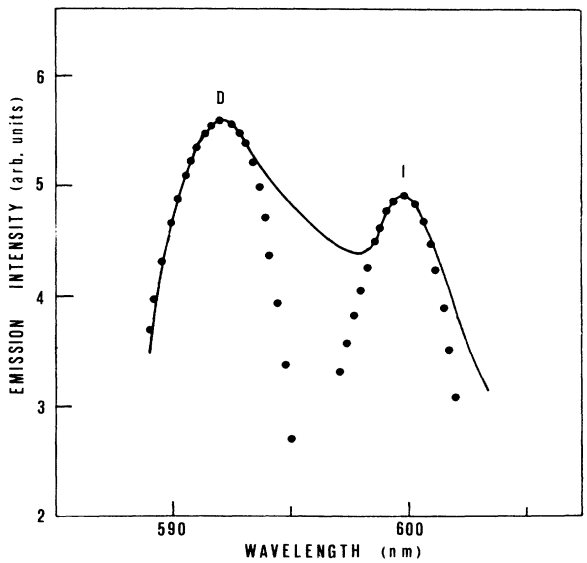


FIG. 5. Fit of the experimental spontaneous emission spectrum of GaSe at 10 K (solid line) with the theoretical models for the luminescence arising from EHP recombination (dots). The $D$ line has been fitted by using Eq. (1), while the $I$ line has been fitted by using Eq. (2).

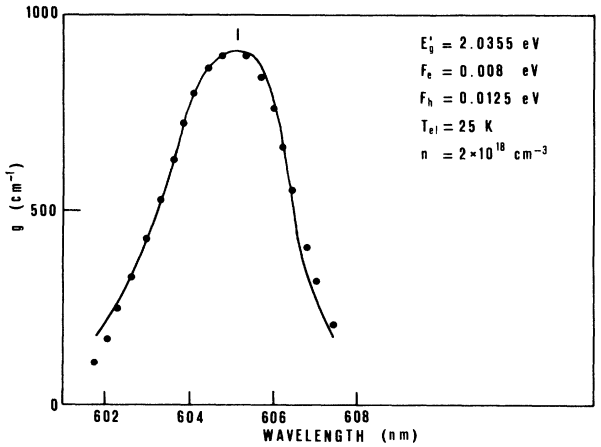


FIG. 6. Fit of the experimental gain spectrum of GaSe at 10 K (solid line) with Eq. (2) (dots).

direct gaps, which cause the simultaneous population of both the conduction minima under strong optical pumping. On the contrary, the optical gain and the stimulated emission spectra give evidence that, below 70 K, only the IEHP recombination shows optical amplification. Moreover, our gain measurements allow us to conclude that the absence of the predicted DEHP strong gain should not be connected to a gain saturation effect, as proposed in Ref. 3. In order to explain such a behavior we must invoke the competition of some loss mechanism with the optical amplification processes in the DEHP system. We tentatively attribute the absence of this DEHP optical amplification to the presence of the IEHP stimulation which is always predominant at low temperatures. In fact, the presence of the amplifying degenerate *e-h* system in the indirect gap, at an energy quasiresonant with the direct gap, strongly affects intrinsic self-absorption effects of the emitted DEHP photons. Such self-absorption effects consist of both free-electron intraband absorption at the *M* point and IEHP absorption and can be taken into account because of the zero-phonon nature of the IEHP transitions,[15] which increases the absorption probability. Since an underestimated value of the self-absorption coefficient for such a process is about $10^3$ cm$^{-1}$, no laser action is expected by DEHP in the presence of IEHP, as can be seen in Figs. 3 and 4, for temperatures below 70 K. On the other hand, at temperatures well above 70 K, a broadening of the *I* band in the *D*-band energy region is observed (Fig. 3) and the *D* band appears in the gain spectrum under both pumping conditions (Fig. 4). Such a feature can be ascribed to the statistical electron thermal pumping from the *M* indirect minimum to the near Γ direct one. This thermal pumping not only modifies the two plasma relative densities, but also reduces the general intrinsic self-absorption process of the DEHP photons, thus allowing the moderate *D*-band optical gain (about 100 cm$^{-1}$) detection. This interpretation agrees with the results reported in Ref. 4, where a DEHP is observed only at 300 K and under picosecond excitation, when no IEHP stimulated emission occurs.

As regards the IEHP emission process, we find a particular temperature dependence of both spontaneous and stimulated emission amplitudes. The results previously discussed show an enhancement of the IEHP emission for temperatures ranging between 10 and 70 K, and a decrease of the same process for further increasing temperatures. In order to explain such a feature, a further temperature-dependent band filling mechanism for the indirect gap can be considered, which, adding to the optical pumping itself, increases the IEHP density up to 70 K. This mechanism can be related to the presence of a dense band of localized donor and acceptor levels in the direct gap having a concentration of about $10^{17}$–$10^{18}$ cm$^{-3}$ and depending only on the structural defects rather than on the doping itself.[16] Such levels give origin to a large number of emission lines (named TR, i.e., trap recombination lines) characterizing the GaSe photoluminescence spectrum and extensively studied below the Mott threshold.[16–20] The salient feature of these lines is their thermal quenching above 50 K, due to the ionization of the impurity levels, which causes a strong increase of the direct free-exciton density, as shown by luminescence experiment.[19] Practically, the TR quenching results in an increase of the *e-h* pair density which, below the degeneration regime, gives origin to bound states (free exciton). On the contrary, above the Mott threshold the TR disappearance gives origin to unbound states causing a free–*e-h*-pair population increase. Since the electrons in the TR donor levels thermalize in the lowest conduction minimum, this process produces an enhancement of the IEHP density. This mechanism also explains the observed behavior of the optical Mott threshold for the IEHP in the range 10–70 K: the IEHP is well established at 70 K and not at 10 K, for pumping intensity just above the theoretical threshold (Fig. 2, curve *b*). For further temperature increases such a mechanism does not contribute more to the EHP population mechanism. On the contrary, the inverse thermal jump from *M* to Γ minimum predominates.

## CONCLUSIONS

Our experimental results show that the GaSe spontaneous emission in a wide temperature range is characterized by the simultaneous radiative recombination of a DEHP and an IEHP. Only the IEHP recombination channel shows optical gain below 70 K. Above this temperature the DEHP optical amplification appears with a moderate gain ($g = 100$ cm$^{-1}$).

By taking into account the particular GaSe band structure, the quasiresonant energy gaps, and the competition between losses and population mechanisms within the two optically amplifying *e-h* plasmas, a phenomenological model has been developed which explains the above-mentioned results. The data presented allow a better comprehension of the optical properties of both the direct and the indirect *e-h* plasmas in GaSe.

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