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Simultaneous direct and indirect recombinations in the electron-hole plasma of GaSe

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In honor of Emanuel Mooser's 60th birthday

Abstract. We measured the spontaneous recombination luminescence spectra of the electron-hole plasma in GaSe at liquid He temperature. In order to reduce the effects of inhomogeneous carrier density, we worked with pinholes and thin samples. Since direct and indirect conduction band minima are almost degenerate in GaSe, we assume that the plasma contains direct as well as indirect electron–hole pairs. We observe two lines which we assign to simultaneously occurring direct and indirect recombinations. Our novel model accounts well for spectral positions and line shapes of the experimentally observed emissions. Best fits of our spectra yield the densities of the different carrier species and their temperature.

Introduction

The optical spectra of strongly excited GaSe have been studied for a long time already (see e.g. [1, 2, 3, 4]). The difficulties in their interpretation, according to our opinion, is due to the particular band structure of GaSe, where the indirect minimum of the conduction band (at the M point of the Brillouin zone) is only 25 meV lower than the direct minimum (at Γ) [5, 6]. Therefore, we have to expect that optical excitation populates both direct and indirect band edges [7]. The optical spectra of weakly excited GaSe however are in most cases dominated by direct transitions. In addition, direct as well as indirect optical transitions are fully allowed only if the polarization of the light is parallel to the *c*-axis of the hexagonal crystal [8].

At lowest excitation intensities (of the order of 1 Wcm^{-2}), direct free exciton luminescence is easy to observe in good crystals [9]. For the luminescence from phonon assisted recombination of indirect excitons it is easier to work at liquid N_2 temperature than at liquid He temperature [10]. To our knowledge, zero-phonon transitions of the indirect free exciton have been observed in absorption measurements only [6]. At intermediate pump intensities (of the order of 10^4 Wcm^{-2}), the luminescence spectra show a low energy tail which has been interpreted in terms of exciton–exciton interactions [7]. Both, direct–direct and direct–indirect exciton–exciton recombination – processes which also can be stimulated optically –

have been invoked to explain the observed spectra. At pump intensities above about 10^5 Wcm^{-2}, the e-h (electron-hole) pair density is expected to be above the Mott value, the carriers form an e-h plasma.

Low temperature luminescence spectra of strongly excited GaSe feature the following properties (see Fig. 3 and [1] or [12]): The emission consists of mainly two lines; the line at lower energy can be found as much as three Rydbergs below the free exciton ground state [3]; and a pronounced low energy tail is present. Moreover, on this low energy line moderate optical gain has been observed [13]. In this report, we present carefully measured spontaneous luminescence spectra of GaSe at liquid He temperature and for carrier densities which are above the excitonic Mott density. The recent progress in the theory of e-h plasmas in semiconductors [14, 15] allows us to discuss these luminescence spectra quantitatively. According to our model, in GaSe this plasma is a three component fluid containing direct (Γ) electrons, indirect (M) electrons and holes (Γ); thus the two strong peaks which are observed in the luminescence spectra of highly excited GaSe are due to simultaneously occurring direct and indirect zero–phonon e-h recombinations. Since the two conduction band minima occur almost at the same energy in GaSe, the probability for these indirect transitions is relatively high permitting to observe moderate optical gain.

Experimental

The GaSe samples investigated were obtained by transport reaction or by the Bridgman method. The thickness of the crystal platelets varied between about 5 and 15 μm, which is comparable to the penetration depth of the exciting light. They were immersed in superfluid He and excited optically, either by the frequency doubled emission at 532 nm of an YAG:Nd (Y–Al-garnet doped with Nd) laser or by the light of a Rhodamine 6G laser. The excitation pulses had a duration of about 70 ns and a repetition rate of 75 Hz. The illuminated spot on the sample had a diameter of about 20 μm. The luminescence was collected from the front surface of the sample, in a direction which had an inclination of $\pi/4$ with respect to the c-axis. We placed a pinhole into the focal plane of the collecting lens, so that light coming from the excited volume only was detected. The luminescence was analyzed by a double spectrometer and detected by a photomultiplier tube, the spectra were recorded using boxcar techniques.

The intensity absorbed by the crystals varied between 0.2 and 3 MW cm^{-2}. Assuming an absorption coefficient of 10^3 cm^{-1}, a dielectric constant of 9.3 [16] and a lifetime of 0.1 ns [12, 17], we estimate total e-h pair densities ranging from 0.5 to $10 \cdot 10^{17}$ cm^{-3} at the surface of the sample. These densities are above the Mott value for direct e-h pairs which is about $4 \cdot 10^{16}$ cm^{-3} [18]. For indirect e-h pairs this value is about $2 \cdot 10^{17}$ cm^{-3}. The spectra, as shown in Fig. 3, are characterized by two main emissions, one at about 595 nm and a second one around 602 nm. While the intensity of the high energy line varies only slightly with excitation, the line at low energy increases strongly with increasing pump power. Further, with increasing carrier density, both lines shift toward the red, and a long low energy tail develops. In some of our thinnest samples, these two emissions merge to a single wide band.

Analysis and discussion

As already mentioned above, we attribute the two main luminescence emissions at high excitation densities to spontaneous direct and indirect zero–phonon recombinations. The spectral position of the two lines suggests this interpretation. We fitted our spectra with a similar theoretical model as already was employed for Ge [19] and GaAs [20]. For the luminescence intensities $I^d(\hbar\omega)$ and $I^i(\hbar\omega)$ coming from direct and indirect e-h recombinations, we write, respectively,

$$I^d(\hbar\omega) \propto \int d^3k \int d\varepsilon_e^d \int d\varepsilon_h \cdot A_e^d(E_e^d(k), \varepsilon_e^d) f_e^d(\varepsilon_e^d) \cdot A_h(E_h(k), \varepsilon_h) f_h(\varepsilon_h) \cdot \delta(\hbar\omega - \varepsilon_e^d - \varepsilon_h) \quad (1)$$

and

$$I^i(\hbar\omega) \propto \int d^3k_e^i \int d^3k_h \int d\varepsilon_e^i \int d\varepsilon_h \cdot A_e^i(E_e^i(k_e^i), \varepsilon_e^i) f_e^i(\varepsilon_e^i) \cdot A_h(E_h(k_h), \varepsilon_h) f_h(\varepsilon_h) \cdot \delta(\hbar\omega - \varepsilon_e^i - \varepsilon_h) \quad (2)$$

Here, ε_e^d, ε_e^i and ε_h are energies measured in the direct electron, indirect electron and hole valleys, respectively; A_e^d, A_e^i and A_h are the corresponding spectral weight functions, f_e^d, f_e^i and f_h are the corresponding Fermi functions; and

$$E_a(k_a) = E_a(0) + \frac{\hbar^2 k_a^2}{2m_a} \quad (3)$$

is the energy of a carrier of species a with wavevector k_a (which is measured starting from the extremum of the band a). For the evaluation of the widths of the reduced gaps and the spectral weight functons (i.e. approximately the real and imaginary part of the self-energy), we use the single-plasmon pole approximation [21] which has been introduced a long time ago already to calculate the dielectric constant of metals [22].

For the reductions ΔE_g^d and ΔE_g^i of the gaps in function of the carrier densities Thuselt [15] gave an analytical formula:

$$\Delta E_g^{d,i} = -\frac{d^{d,i} e^2}{\kappa_s} \sqrt{\frac{2m^* \omega_p}{\hbar}}. \quad (4)$$

Here the factors d^d or d^i depend very weakly on the mass ratio $m_e^{d,i}/m_h$, κ_s is the static dielectric constant and

$$\omega_p^2 = \frac{4\pi e^2}{\kappa_s} \sum_a \frac{n_a}{m_a} \quad (5)$$

is the plasma frequency which depends on the densities n_a of the different carrier species with masses m_a; for m^* (which determines the dispersion of the particle-hole excitations at large wavevectors) we take a weighted reciprocal mean of the

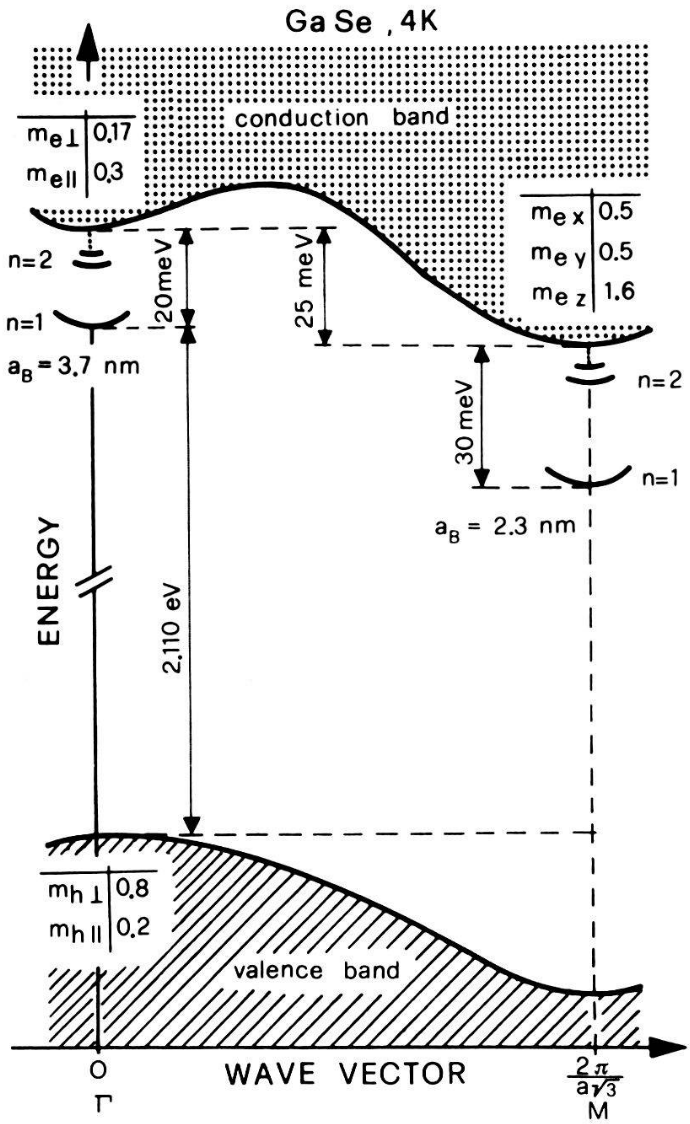

Figure 1
Simplified scheme of the highest valence band and the lowest conduction band in GaSe. Near the band extrema, the masses of the free carriers are given [24]. The approximate excitonic energies and the widths of the gaps are taken from [5] and [6] (see also [11] and [16]). a_B are the excitonic Bohr radii. The direct excitonic states form a hydrogenic series [9, 16], therefore the static dielectric constant $\kappa_s = 9.3$ has been chosen such as to reproduce, together with the reciprocally averaged masses, the direct excitonic Rydberg.

particle masses in our three component plasma:

$$\frac{1}{m^*} = \frac{\sum_a (n_a/m_a)}{\sum_a n_a} \tag{6}$$

Figure 2 shows the direct and indirect reduced gaps versus e-h pair density as predicted by equation (4).

We approximate the spectral weight functions A_e^d, A_e^i and A_h of the collision broadened single particle states by Lorentzians whose low energy tail is cut off at one plasmon energy below their central energy $E(k)$ [23]:

$$A(E(k), \varepsilon) = \frac{N \cdot \Delta \cdot \theta[\varepsilon - (E(k) - \hbar\omega_p)]}{(E(k) - \varepsilon)^2 + \Delta^2} \tag{7}$$

where N is a normalizing factor such as $\int A(E(k), \varepsilon)\, d\varepsilon = 1$ and θ denotes the unit-step function. For the width Δ we take the imaginary part of the self-energy as given by Haug and Tran Thoai [14]. Δ depends on the energy $E(k)$, the temperature T and the densities n_a; as for ΔE_g the plasma frequency is a most important parameter.

The band structure parameters are given in Fig. 1; unfortunately the parameters at the M point of the Brillouin zone are not very well known. Throughout the calculation, we replaced the anisotropic masses by appropriate spherical approximations. For the direct e-h recombinations – within the model of collision broadened single particle states – we assumed conservation of the wave vector, for the indirect zero–phonon recombinations we did of course not. Fitting parameters were the densities of direct and indirect electrons (the density of the holes is equal to the total electron density), the temperature assumed equal for all types of carriers, and the ratio of the transition probability for indirect recombinations to that of direct recombinations.

Results of our least square fits are shown in Figs 3 and 5 and in the table. The fits are excellent for the direct recombination radiation. The shape of the indirect recombination line seems to be slightly different from that predicted by our simple model which indeed neglects the effects due to the intervalley scattering processes responsible for the indirect zero phonon transitions. With the help of intensity, absorption coefficient and photon energy of the exciting laser, we extract a mean carrier lifetime of about 0.2 ns which is comparable to results reported earlier

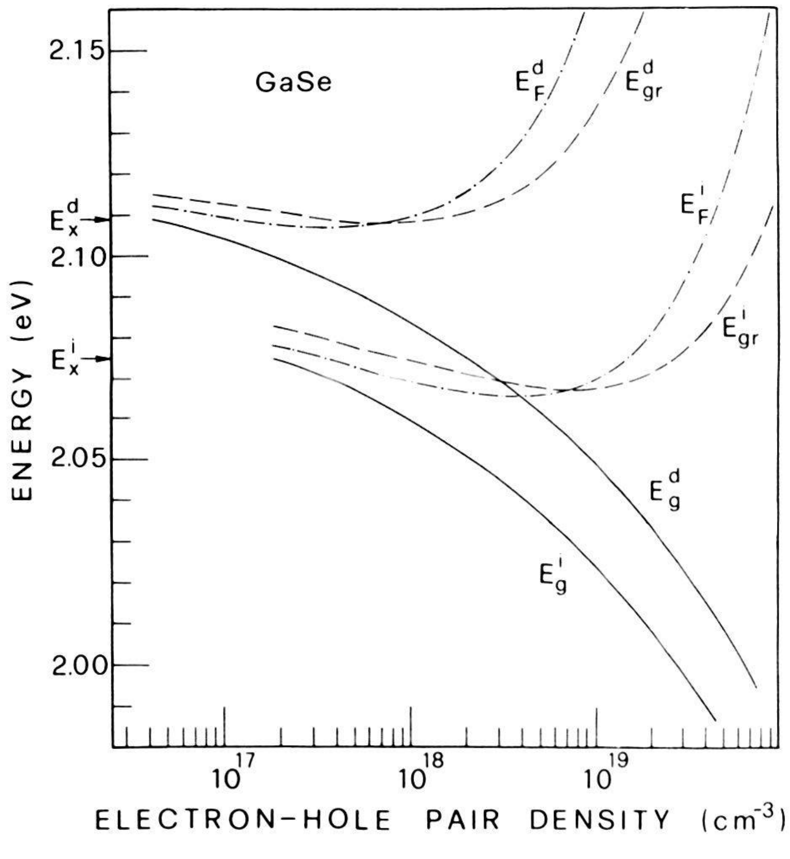

Figure 2
Properties of the electron-hole plasma in GaSe: reduced gaps (E_g^d and E_g^i), ground state energies (E_{gr}^d and E_{gr}^i) and Fermi energies (E_F^d and E_F^i) versus direct or indirect e-h pair density, calculated using the analytic expression of Thuselt [15]. E_x^d and E_x^i are the free exciton ground state energies.

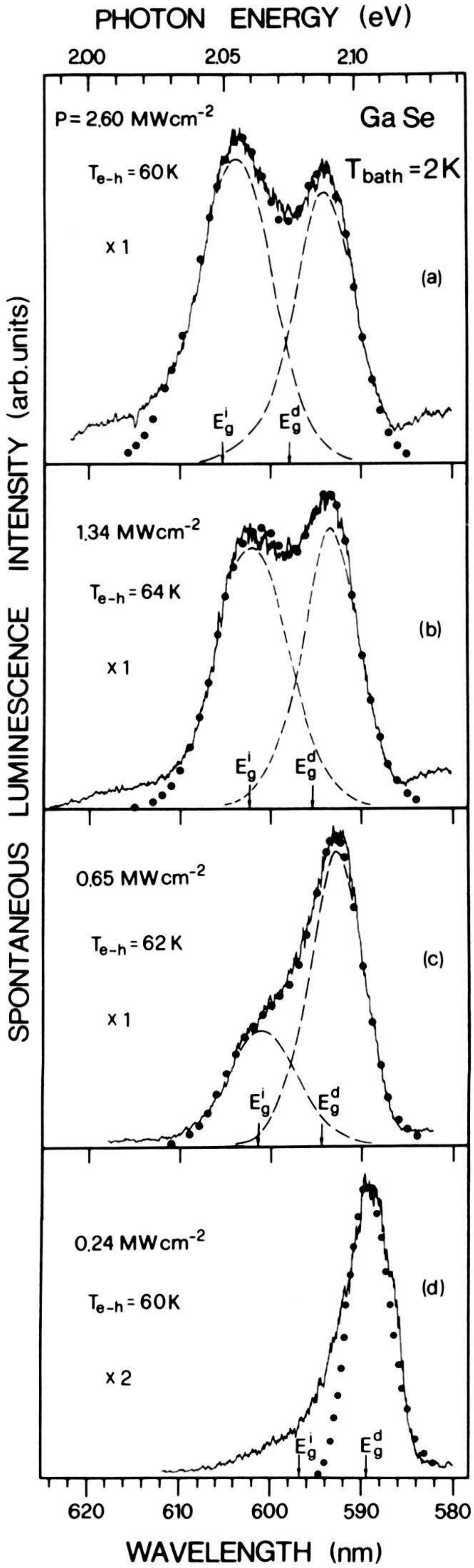

Figure 3
Luminescence spectra of GaSe at a bath temperature of 2 K and for the indicated excitation intensities. The dots are best fits as explained in the text, the extracted parameters are given in the table. Dashed lines represent the contributions from direct and indirect electron–hole recombinations alone. The shoulders appearing at energies below the indirect zero–phonon recombinations (mostly at higher excitations) are due to phonon assisted indirect recombinations. At highest energies there is luminescence coming from the laser dye. Since for spectrum nr (d) the e-h pair density is very close to the Mott value, the shown fit includes direct recombinations only.

Table

Results of the fit of the luminescence spectra of Figs 3 and 5 (*ned*: direct electron density, *nei*: indirect electron density, *Te*-h: carrier temperature, *Egd*: reduced direct gap, *Egi*: reduced indirect gap, *R*: ratio of (zero–phonon) indirect to direct transition probability, Δed, Δei, Δh: widths of the spectral functions of the single particle states in the e-h plasma at the band extrema, *EFed, EFei, EFh*: Fermi energies).

Spectrum nr	Excitation intensity	Carrier densities *ned*	Carrier densities *nei*	Temp *Te*-h	Renormalized gaps *Egd*	Renormalized gaps *Egi*	Width of single particle states at band extremum Δed	Δei	Δh
	$MW\,cm^{-2}$	$10^{17}\,cm^{-3}$	$10^{17}\,cm^{-3}$	K	eV	eV	meV	meV	meV
(*d*)	0.24	1.0	—	60	2.103	2.078	5.3	—	5.4
(*c*)	0.65	3.8	1.9	62	2.086	2.061	4.5	4.1	4.4
(*b*)	1.3	5.2	2.6	64	2.083	2.058	4.6	3.8	4.3
(*a*)	2.6	9.3	5.2	60	2.074	2.050	4.6	2.9	3.8
(*e*)	1.7	6.3	3.1	64	2.080	2.055	4.7	3.6	4.2
(*f*)	1.3	4.9	4.9	106	2.078	2.053	6.6	6.6	6.9

Spectrum nr	Max joint density of e-h pairs direct energy	direct	indirect energy	indirect	Fermi energies with respect to bottom of band *EFed*	*EFei*	*EFh*	Ratio of transition probab *R*
	eV	arb units	eV	arb units	meV	meV	meV	arb units
(*d*)	2.105	3.6*E*+17	—	—	3.8	—	1.6	—
(*c*)	2.091	4.7*E*+18	2.063	4.1*E*+14	9.4	0.8	5.0	4.5
(*b*)	2.089	6.9*E*+18	2.060	7.6*E*+14	11.5	1.0	6.2	8.4
(*a*)	2.087	1.6*E*+19	2.053	2.6*E*+15	16.9	1.5	9.2	6.7
(*e*)	2.089	8.9*E*+18	2.056	1.1*E*+15	13.1	1.1	7.0	7.5
(*f*)	2.084	3.4*E*+18	2.063	8.0*E*+14	11.0	1.5	7.1	2.5

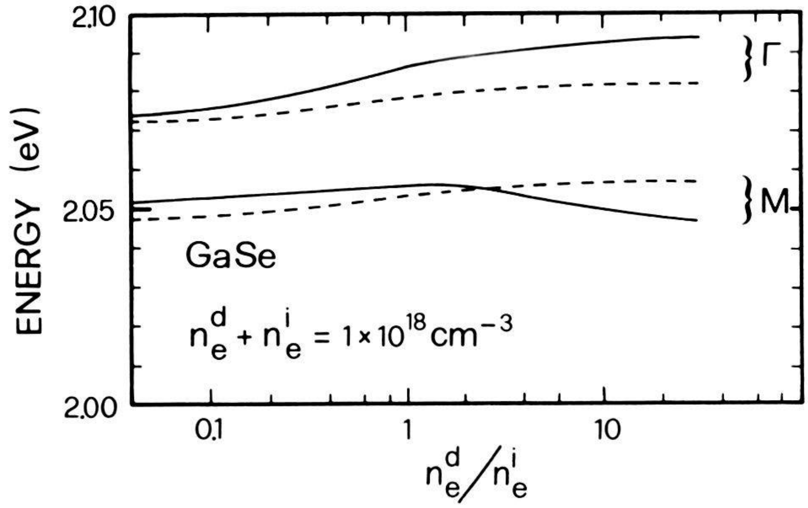

Figure 4

Calculated spectral positions of the luminescence peaks for direct (upper solid curve) and zero–phonon indirect (lower solid curve) e-h recombination versus ratio n_e^d/n_e^i of direct to indirect electron density. The total electron density $n_e^d + n_e^i = 10^{18}\,cm^{-3}$ is constant, and a carrier temperature of 50 K has been assumed. The reduced gaps (equation (4)) are also given (dashed curves).

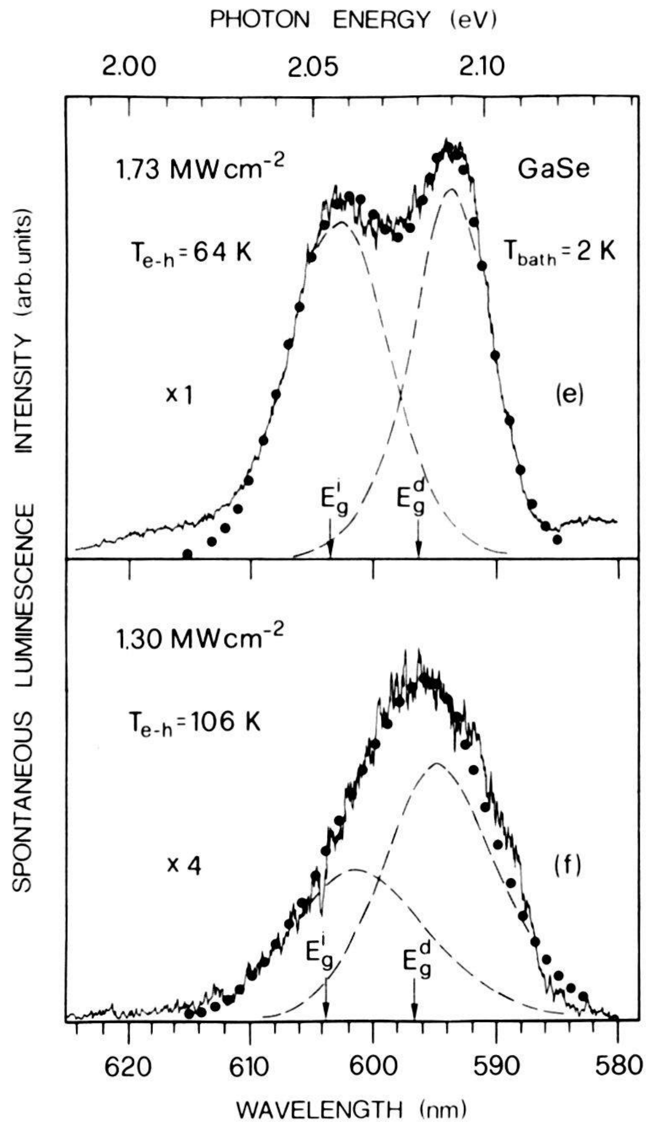

Figure 5
Luminescence spectra and their fits of two different GaSe samples at similar excitation intensities. The different symbols are the same as those in Fig. 3; for further parameters see the table.

[7, 12]. The carrier temperature seems to be practically independent on carrier density, but it varies from sample to sample. This indicates that extrinsic effects influence the plasma temperature more than non radiative Auger recombinations; weak extrinsic (?) luminescence around 589 nm on the high energy side of the spectra however might perturb the determination of the plasma temperature.

As mentioned above, in some of our thinnest samples we observe not two but only one single wide luminescence band. Assuming that the distribution of the electrons among the different conduction band minima at Γ and M is influenced by extrinsic effects (in GaSe in particular by stacking faults, and thin samples are easily damaged), the luminescence spectra become quite sample dependent. This is illustrated in Fig. 4 where the spectral position of the direct and indirect luminescence peaks versus the density ratio n_e^d/n_e^i has been plotted. An example of two quite different spectra is shown in Fig. 5, except for some (extrinsic ?) structure on the high energy side our model fits both spectra equally well.

Our model is somewhat unusual, because once the carrier densities are high enough the zero–phonon indirect recombinations at about 603 nm become highly probable, such as to allow even for moderate optical gain (up to about $100\,cm^{-1}$) [13]. For the special case of GaSe however, due to the vicinity of direct and indirect gaps, zero–phonon transitions are facilitated. Further, the density of lattice defects, in particular stacking faults, is quite high in GaSe [25, 11], in fact zero–phonon transitions have been observed [6]. Furthermore, other second order recombination processes such as direct–indirect electron scattering could also be involved, in a similar manner as for exciton–exciton recombination [7]. To our knowledge gain of the direct transitions has not yet been detected: in two beam experiments for practical reasons the polarization of the light is usually normal to the c-axis and therefore optical transitions are weakly allowed only [4]; in experiments where the light propagates perpendicularly to c the excited crystal volume is several tens of μm long [13] such as direct transitions which should have strong gain in this geometry saturate.

In *conclusion*, our three component plasma model which includes collision broadening of the single particle states accounts well for the experimentally observed luminescence spectra. As for the problem of stimulated emission, we have to note that optical gain in GaSe is only moderate at low temperatures [13]; in the framework of our model it is due to indirect zero–phonon recombinations. We did not try to interpret our spectra in terms of phonon assisted direct transitions, because shapes, intensity ratio and spectral position of the two luminescence bands depend strongly on excitation intensity. It would be interesting to have theoretical estimates of the different transition probabilities for the different e-h recombination processes occurring in highly excited GaSe.

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