LUMINESCENCE. SPECTROSCOPIE DE DÉFAUTS IILASER TRANSITIONS IN DIRECT GAP SEMICONDUCTORS

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LASER TRANSITIONS IN DIRECT GAP SEMICONDUCTORS

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Résumé. — On fait la récapitulation des transitions laser impliquant des porteurs libres, des excitons et des états liés dans les semiconducteurs à gap direct. Les problèmes des transitions bande à bande et des interactions des excitons à haut niveau d'excitation sont discutés conjointement avec des résultats expérimentaux récents sur l'effet laser dans du GaAs de haute pureté.

Abstract — The laser transitions involving free carriers, excitons, and bound states in direct gap semiconductors are reviewed. The problems of band-to-band transitions and exciton-interactions at high excitation level are discussed in connection with recent experimental results of lasing in high purity GaAs.

1. **Introduction.** — The most widely studied semiconductor laser materials are the direct gap II-VI, III-V, and IV-VI compounds. The by far largest number of publications deals with highly doped GaAs and its application in injection laser structures [1].

Although stimulated emission has been observed for indirect gap semiconductors too (GaP [2], GaAsP [3], GaInP [4]), no practical laser structures have been built from these materials.

This article reviews laser transitions in direct gap III-V compounds, predominantly GaAs, and in some II-VI compounds. No reference to the work on narrow gap lasers (IV-VI compounds) and to new groups of laser materials like II-IV-V or I-III-VI compounds is made.

The present situation for GaAs, the most widely studied laser material, is as follows : The *spontaneous radiative transitions* are in general very well understood. In particular, the recombination in highly doped materials, e. g. band-to-band as well as band-to-acceptor transition involving tail states, has been well studied several years ago. The luminescence of high purity GaAs was studied only recently, and processes like various free-to-bound transitions, donor-acceptor pairs, free and bound excitons have reached a high level of understanding [5], [6]. The *gain processes*, on the other hand, have been studied extensively only for the high doping case. In high purity materials, the laser emission is associated with a number of new phenomena occurring at high excitation level. These include many-body effects and Auger-interactions, which in many instances are still not understood sufficiently well. This paper will discuss in particular recent results on these transitions in high purity materials. The study of laser transitions in this case is intimately connected with interaction phenomena at high excitation level in general.

2. **Experimental.** — An experimental study of the laser gain should always start with an examination of the spontaneous radiative processes. In fact, if the quantum efficiency (η), the photon energy ($h\nu$), and the line width ($\Delta\nu$) of the spontaneous processes are known, the gain (g) can be determined from the following general relation, which holds for $T = 0$ [7]

$$g = \frac{c^2 I_{exc} \eta}{8 \pi e n^2 \Delta\nu d} \qquad (1)$$

(I_{exc} = excitation level, d = width of active layer).

An actual study of the stimulated processes can be made by 1) investigating a laser oscillator and 2) by investigating an amplifier. In the first case the threshold relation can be used to study the gain and loss in semiconductors.

Threshold for oscillations is reached, when the total gain equals the total losses

$$g(h\nu)\, L = \alpha(h\nu)\, L + \ln (1/R) \qquad (2)$$

($\alpha(h\nu)$ = internal losses, R = reflection coefficient at the laser ends, L = laser length).

Most experimental investigations are based on the model of uniform active and passive layers, which is not quite true in reality. In general, the gain (and the losses) will be complex functions of energy, excitation level and spatial coordinates of the active layer.

In the second case, the study of amplifiers, gain measurements as a function of energy and excitation level are particularly easy [8]. Amplification of light over a path of length (L) leads to an intensity I

$$I = \frac{I_s}{(g - \alpha)} (e^{(g-\alpha)L} - 1) \qquad (3)$$

(I_s = spontaneous emission).

If non-radiative processes are included in a microscopic gain model, the following dependence between intensity and length is obtained [8] :

$$(g - \alpha)\, L = \ln (bI + 1) + aI \qquad (4)$$

(b = parameter connected with the spontaneous emission intensity, a = parameter describing the gain saturation $a \sim 1/I_{sat}$, I_{sat} = saturation intensity).

A study of intensity as a function of excitation

TABLE I

Laser transitions in direct gap materials

Radiative transition	Description, comments	Materials, references
I. Band-to-Band	High doping level : Impurity tail states involved Low doping level : Gap-shrinkage effects	Most highly doped III-V, II-VI, IV-VI, etc. compounds [1] GaAs, InP [42], [46], [50]
II. Conduction band-acceptor	Common laser transition in p-type GaAs, InP, and in most homo-structure injection lasers	GaAs, InP [1]
III. Bound exciton Bound exciton-LO	Low temperature ; narrow spontaneous line width, gain limited by number of binding centers	ZnO [13], CdS [14], CdSe [14] CdS [15]
IV. Free exciton-LO (X, LO)	Photon-like state reached by scattering with : LO-phonons : $X_{n=1} + \mathrm{LO} \rightarrow h\nu$	CdS [17], [18], [19], ZnO [13], CdSe [13], [24]
Exciton-electron (X, e)	electrons (holes) : $X_{n=1} + \mathrm{e}(h) \rightarrow h\nu + \mathrm{e}(h)_{\mathrm{hot}}$	CdS [17], GaAs [46], CdSe [24]
Exciton-exciton (X, X)	excitons : $X_{n=1} + X_{n=1} \rightarrow h\nu + X_{n=\infty}$	CdS [17], GaN [23], CdSe [24], GaSe [25], GaAs [26], [46], InP [47], ZnO [30]
V. Excitonic-molecules	$\mathrm{EM} \rightarrow X_{n=1} + h\nu$	CuCl [35]

length gives information about the gain as a function of energy and excitation intensity, and also about its saturation behaviour.

In the case of amplifiers, too, gain variations and refractive index variations perpendicular to the amplified beam should be taken in principal into account. These vary in a complex manner with the excitation level and contribute to phenomena like gain saturation which, until now, are not well understood.

3. **Review of laser transitions.** — A summary of different laser transitions reported for direct gap semiconductors is given in table I.

3.1 BAND-TO-BAND TRANSITIONS. — The band-to-band transition, that is the recombination of electrons in the conduction band with holes in the valence band, can be described by Fermi-statistics for the two separate Fermi-systems. With F_n and F_p denoting the two quasi-Fermi levels, stimulated emission is obtained, if

$$F_n - F_p > h\nu \quad \text{(Laser energy)} . \qquad (5)$$

This transition and the band-acceptor transition are the only observed stimulated processes in highly doped III-V semiconductors. Their quantitative description is complicated by the fact, that impurity states mix with band states giving rise to « tails », which modify the density of states functions describing the gain [9], [10].

Furthermore, it was found that recombination in highly doped GaAs takes place without k-selection rules [11] which is not surprising considering the participation of impurity states. The application of k-selection rules has a pronounced effect on the lineshape of spontaneous and stimulated recombination processes. This is discussed in detail later in this paper in connection with experimental results on GaAs (compare Fig. 11). As a point of practical interest, introduction of k-selection rules also alters the temperature dependence of the laser threshold. This is demonstrated in figure 1, where the theoretical dependence of the threshold current density on the

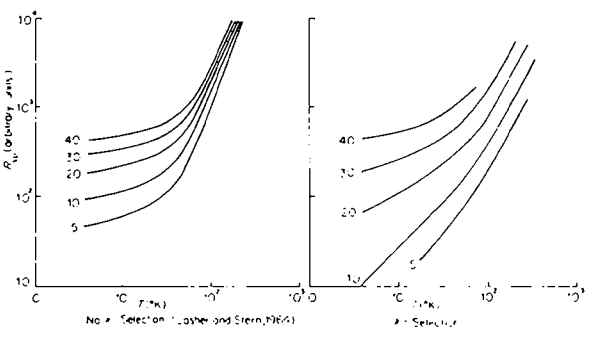

FIG. 1. — Temperature dependence of threshold current density (expressed through R_{spon}) assuming k-selection [12] or no k-selection rules [11] Labelling parameters give the values of $C^{-1}\, r_{\mathrm{stim}}(E)$ in cm^{-1} (gain in active region).

temperature for the two cases, k-selection rules [12] and no k-selection rules [11] has been plotted. Parabolic density of states have been assumed in the calculation. Inclusion of tail states changes the dependence of the laser threshold on temperature appreciably [10], [11].

3.2 BAND-ACCEPTOR TRANSITIONS. — These transitions are in principal similar to the band-to-band transitions as long as shallow acceptors are involved. The gain of the band-acceptor transition is very small in high purity materials and increases with acceptor concentration [48], [49]. At high acceptor concentration, the situation becomes more complex because of the formation of impurity tails [9], [10], and the transition may become a band-to-band (or « tail-to-tail ») transition [57].

3.3 BOUND EXCITONS. — The very narrow spontaneous line width of the bound exciton should give rise to a large gain if one considers eq. (1). On the other hand, since bound excitons are usually seen in fairly pure materials, one should also consider that a small number of binding centers implies a small gain. Stimulated emission due to the radiative recombination of bound excitons has been observed in II-VI compounds [13], [14]. In one case, stimulated emission for the LO phonon satellite of the bound exciton has been reported [15]. In GaAs, sharp bound exciton lines are only seen at impurity concentrations too low for a reasonable gain. This should be true for all semiconductors with very small effective electron masses (i. e. small exciton and donor binding energies).

The binding energy of the exciton to the center determines the temperature range in which laser emission can be observed.

3.4 LASER TRANSITIONS INVOLVING FREE EXCITONS. — The decay of the free exciton is complicated by the fact, that the exciton coupling to the photon (i. e. the polariton) has to be considered. This implies that a third particle (e. g. phonon, electron, exciton) is needed to scatter the exciton to a photon-like state on the polariton curve. This type of interaction process only can lead to stimulated emission [16]. Furthermore, the absorption losses (predominantly penetration losses due to penetration of the electromagnetic wave into passive adjacent layers) are small, because the scattering process shifts the emission away from the absorption edge.

Exciton interaction with LO-*phonons* (X, LO) are likely to be favoured in the more polar semiconductors. Stimulated emission for this recombination mechanism was reported for II-VI compounds [17], [18], [19]. The (X, LO) transition is very weak in III-V compounds [20]. In CdS even two LO-phonon assisted free exciton decay (X, 2 LO) has been associated with stimulated emission [18]. Recently, excitonic recombination with emission of two TO-phonons has been made responsible for laser emission in GaSe [21].

Exciton-electron scattering (X, e). — The required scattering of the exciton to a photon like state can be also achieved by collision with a free electron or hole [17]. This Auger-type interaction is depicted in figure 2 which shows the momentum and energy transfer in the two seperate dispersion relations for an electron and exciton-polariton. A high concentration of eleotrons (or holes) *and* excitons clearly favours this interaction. (Note that the previous case of (X, LO) scattering is not an Auger-type interaction : The recombination rate depends only on the concentration of excitons.)

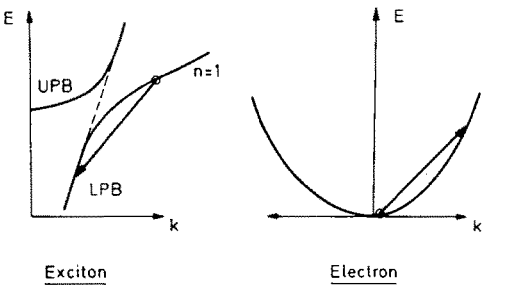

FIG. 2. — Dispersion curves for an exciton-polariton and a free electron. An exciton-electron scattering process with energy and k-conservation is indicated by the arrows.

Exciton-exciton scattering (X, X). — Figure 3 shows the dispersion relation for several exciton-states

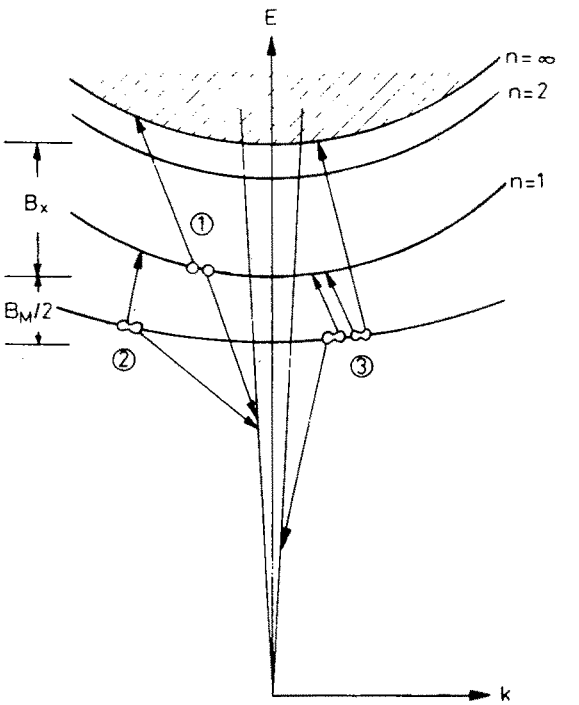

FIG. 3. — Dispersion relations for the $n = 1$, $n = 2$ and $n = \infty$ exciton states, the excitonic molecule, and the photon. Polariton effects have been neglected. The following recombination processes are depicted schematically : 1) exciton-exciton interaction, 2) excitonic-molecule decay (photon and $n = 1$ exciton are final states), and 3) molecule-molecule interaction (final states : photon, two $n = 1$ exciton, one free electron-hole pair). The direction of the arrows has to be consistent with k- and energy conservation.

($n = 1$, $n = 2$, $n = \infty$) and for the exciton molecule (EM) together with the dispersion relation for the photon near $k \sim 0$. The polariton effects as shown in figure 2 have been omitted. Exciton-exciton scattering refers to process No. 1 in figure 3. In this process, one exciton is scattered into the continuum states (free electron-hole pair), for which the minimum energy transfer of the exciton binding energy (B_X) is necessary. The maximum energy of the (X, X)-emission line should be therefore

$$h\nu_{max} \sim E_g - 2\,B_x \quad (E_g = \text{band gap energy}).$$

Emission lines attributed to this process have been claimed in a number of semiconductors [17], [18], [22]-[27]. Scattering into higher lying states of the continuum can lead to a « red-shift » of the emission line [28]. Scattering into the $n = 2$ exciton state can also occur [29], [30]. Which of the two processes (X, X) or (X, e) prevails depends on the density of free excitons and free carriers. At low excitation levels (small free carrier concentration), exciton-exciton scattering will usually dominate. With increasing excitation, exciton-free electron (hole) interactions will take over, to some part because an increasing number of free electron-hole pairs are generated in the exciton-exciton interaction.

Excitonic molecule recombination. — Although the excitonic molecule theoretically exists for all semiconductors ($0 < m_n/m_h < 1$) [31], it has experimentally been found only in very few cases: CuCl [32], CdSe [33], CdS [33], [34].

In figure 3, the dispersion relation for the molecule, without polariton effects, shows one of the possible radiative recombination paths (No. 2 in Fig. 3) for the molecule, leading to a photon and a $n = 1$ exciton. For this process, stimulated emission has been reported in CuCl [35]. Different recombination paths having the $n = 2$ or $n = \infty$ exciton as final state are obviously other possibilities to be considered, but in these cases no laser transitions have been seen so far.

Even more complicated is the situation of molecule-molecule scattering [34], [36], for which one possibility (reaction No. 3) is included in figure 3. A choice of different final states leads to different emission lines [34]. Recently, a Bose-Einstein condensation of excitonic molecules has been reported for CdSe and CdS [37]. It will be an interesting task for the future to investigate whether coherent laser emission is possible from this condensed Bose-Einstein system.

4. **Experimental results.** — The excitonic interaction processes described in the previous section have been mainly investigated in the II-VI compounds, in particular in CdS, CdSe and ZnO (compare Table I). In these compounds exciton binding energies are fairly large and polar interactions are strong, which means that (X, LO)-, (X, 2 LO)-, (X, X)- and (X, e)-emission peaks can be clearly resolved. An example is given in figure 4, which shows emission spectra of CdS at different excitation levels. CdS was in fact the first material where the various excitonic laser processes were investigated (Benoit à la Guillaume) [17].

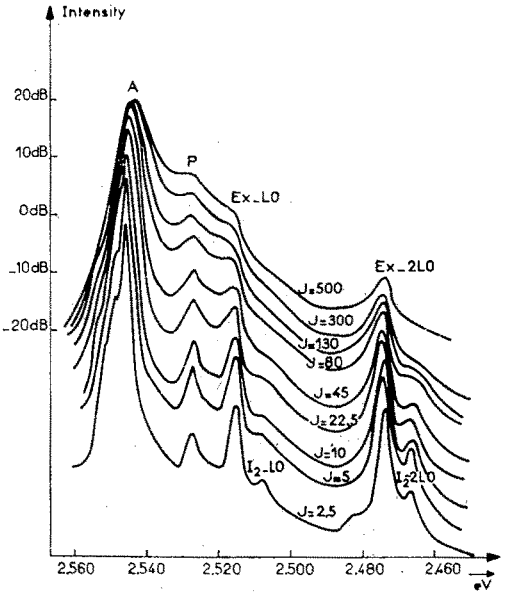

FIG. 4. — Spectrum of spontaneous emission of high purity CdS at about 10 K as a function of excitation intensity [17]. The various free- and bound excitonic recombination processes are described in the text. The exciton-polariton emission (A) includes exciton-electron interactions at high excitation level. P corresponds to exciton-exciton interaction, I_2 denotes a bound exciton.

In the direct gap III-V compounds, the excitonic interaction processes are much more difficult to study, because the small effective electron masses lead to small binding energies of excitons (and donors). Instead, the band-to-band transition is mostly favoured and easy to investigate. In the following section, recent experiments concerning gain processes in GaAs as the best known representative for direct gap III-V compounds are described. Recent experimental work for II-VI compounds was reviewed by Bille [38] earlier this year.

4.1 LUMINESCENCE AT LOW EXCITATION LEVELS : III-V COMPOUNDS. — Excitonic emission lines in GaAs can be observed only at low impurity concentration, low excitation level and low temperature. A typical luminescence spectrum of high purity GaAs is shown in figure 5 ; results for InP are quite similar. The highest energy emission is attributed to the free exciton. It often consists of two weak emission lines (1.515 7 eV and 1.514 6 eV), whose detailed shape has to be explained by the exciton-polariton model [39], and/or experimental conditions like surface transmission [40], [41].

The free exciton decay usually has a very weak phonon-satellite [20] (compare Fig. 6), which, contrary

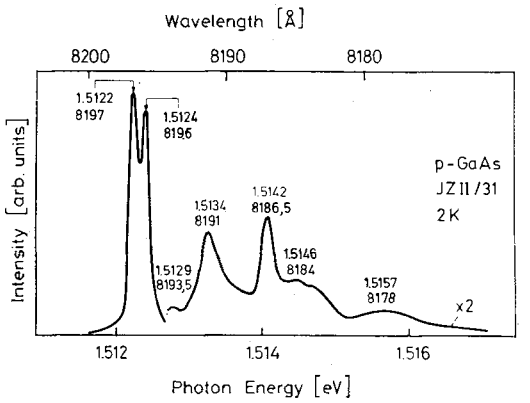

FIG. 5. — Spectrum of spontaneous emission of high purity p-type GaAs ($N_A - N_D = 3 \times 10^{13}$ cm^{-3}) [47] at low excitation level.

to the II-VI compounds, does not exhibit gain at high pumping levels. Bound excitons can be seen as very sharp emission lines, and binding centers can be identified as neutral donors (D^0, X), ionized donors (D^+, X) (?), and neutral acceptors (A^0, X). The recent extensive literature [5], [6] on these bound excitons will not be reviewed here, however, it seems noteworthy that stimulated emission has never been observed in bound exciton lines in GaAs and InP. Further transitions at still lower energy (not shown in Fig. 5) include donor-acceptor pair transitions (D^0, A^0), conduction band-acceptor transitions (e, A^0), the LO-phonon satellite of the (A^0, X)-bound exciton and further lines like « two-hole-transitions », which are of minor importance for the topic of this paper. In highly doped GaAs, all the near-edge excitonic luminescence lines merge into a broad band-to-band emission, whose halfwidth increases with doping level. As a second emission band the band-to-acceptor transition remains at high doping levels.

4.2 LUMINESCENCE AT HIGH EXCITATION LEVEL : III-V COMPOUNDS. — At high excitation levels, the appearance of the emission spectra changes significantly [26], [42]-[47], and a typical experimental result is shown in figure 6. Three emission processes become important : 1) The band-to-band transition at a reduced band gap (line B) [42], [46], [47] ; 2) exciton-exciton- [26], [45], [46], [47] and exciton-electron-scattering [46], [47] and 3) free electron-acceptor transitions. All of these transitions are capable of stimulated emission. Two of them (Nos. 2 and 3), however, are seen only under special conditions : excitonic contributions to the gain have been observed only in p-type GaAs of extreme purity ($N_A - N_D = 10^{14}$ cm^{-3}) [46], [47]. The band-acceptor transition lases only at sufficiently high acceptor-concentration [48], [49]. The strongest gain process in direct gap III-V compounds is always the band-to-band transition. In figure 7 a spectral gain profile (of the unsaturable gain component) for high purity GaAs at low temperature is shown [46]. The maximum of the band-to-band gain (curve B in Fig. 7) occurs about 10 meV below the gap and reaches a magnitude of typically $g \sim 1\,000$ cm^{-1} [45], [46]. The excitonic gain process (curve A in Fig. 7) is more than ten times weaker. At

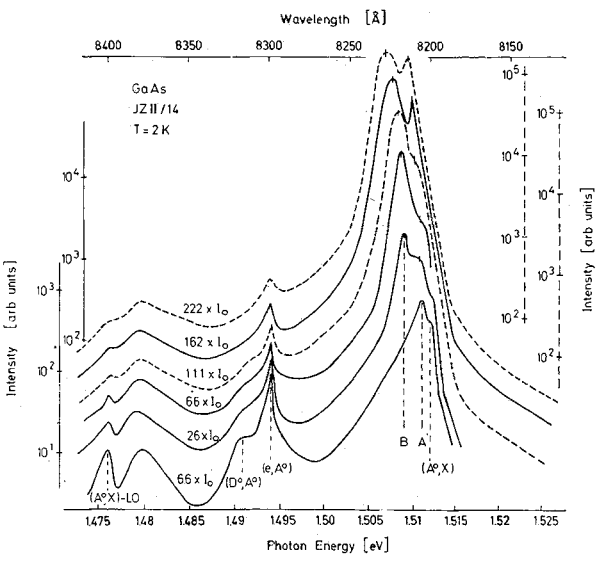

FIG. 6. — Emission spectrum of high purity p-GaAs at several high excitation levels [47]. I_0 corresponds to a power density of 4.5 kW/cm^2 of a nitrogen-pump laser. Intensities are plotted in logarithmitic scale.

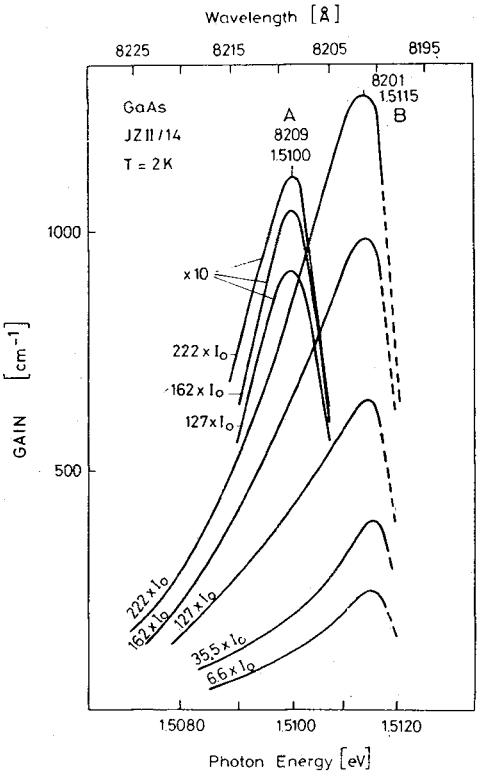

FIG. 7. — Gain spectra of p-GaAs for different excitation levels [46]. The gain spectra are determined from amplification experiments using eq. (4) (compare section 2). Saturation of the gain is not included in this diagram (compare Fig. 10). I_0 corresponds to a power density of 4.5 kW/cm^2.

high temperature or high doping level, the band-to-band or band-to-acceptor gain is the only existing gain mechanism.

For the consideration of the gain mechanism in semiconductors it appears essential to take gain spectra of the type of figure 7. Emission spectra may shift considerably with excitation [8], [43], [45], [47], because of unavoidable amplification at high excitation level. This and saturation phenomena of the gain can lead to considerable distortions of the emission spectra and false informations about laser processes [8], [46], [50]. For instance, the unsaturable component of the gain spectra of high purity GaAs, as depicted in figure 7, are independent of excitation intensity, whereas the actual band-to-band emission and the emission due to excitonic recombination processes (Fig. 6) shift considerably to lower energy.

Similar shifts of stimulated emission to lower energy, or a successive « turn-on » of lower energetic laser lines have been found in CdS [18] and other II-VI compounds. Variation of gain and absorption with excitation level have been made responsible for it [8], [18], [46], [50], [51].

4.3 BAND-TO-BAND LASER-TRANSITIONS IN GaAs. — The stimulated emission rates for band-to-band transitions have been extensively studied in highly doped GaAs [1]. Experimental results can be well described theoretically if the following assumptions are made :

1) No k-selection rules are applied [11] ; 2) Density-of-states functions incorporating tail states are used [9], [10].

Calculations using k-selection rules [12] lead to unsatisfactory agreement with the experimental data on spectral shape of spontaneous and stimulated emission, and temperature dependence of the threshold. The absence of k-selection rules has been usually assumed to be a consequence of the presence of the large number of impurities. Obviously, these arguments cannot be applied to high purity materials. Therefore, a quantitative analysis of the band-to-band gain without the influence of impurities is of great interest.

A theoretical analysis of the low temperature gain spectrum [11], [12] is shown for high purity GaAs [47] in figure 8. In this figure, the gain (expressed by the stimulated emission rate) is plotted as a function of the energy (relative to the band gap). The theoretically determined gain profiles (solid lines) have quite different shapes depending on whether k-selection rules or no k-selection rules are applied. The experimental points can be fitted only by the latter case : no k-selection rules should be used to describe the gain profile.

This result seems at first sight surprising. However, one should keep in mind, that k-selection should apply to single particle recombination. At the high excitation level where gain is observed, many-body interactions in a dense electron-hole plasma occur, leading to a significant shift of the energy gap apart from the before mentioned absence of k-selection rules.

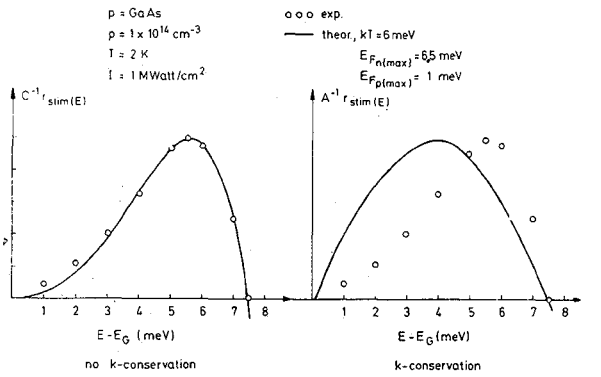

FIG. 8. — Energy dependence of the stimulated emission rate $C^{-1}\, r_{stim}$ (proportional to the gain) for the band-to-band transition at low temperature. Energies are taken relative to the band gap. Experimental results are designated by circles, theoretical curves by solid lines. The two theoretical curves correspond to the cases of application [12] or omission [11] of k-selection rules. In addition, they also take into account a gain decrease from the surface into the bulk [47].

The « gap shrinkage effect » has been observed already a number of years ago [42]. A quantitative theoretical understanding has been approached only recently [52]-[56].

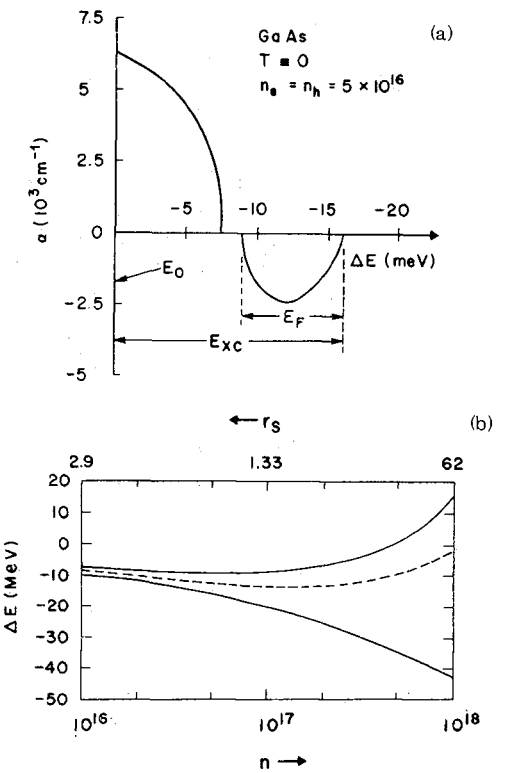

FIG. 9. — Theoretical results for the energy dependence of the absorption constant (Fig. 9a) and for the energy gap change (ΔE) with carrier concentration (Fig. 9b). The optical absorption $\alpha(E)$ was computed for intrinsic GaAs (5×10^{16} cm^{-3} holes and electrons excited) [52], [53]. Negative absorption corresponds to positive gain. Exchange energies and screened Coulomb-potentials are taken into account.

Essentially, the theoretical work takes exchange energies (through Hartree-Fock type calculations), correlation energies, and screening of Coulomb-potentials in dense electron-hole plasmas into account. To demonstrate the effects of high carrier concentration on the band gap and gain, figure 9 shall serve as a representative theoretical result [52], [53] : In the lower part (Fig. 9*b*), the change of the energy gap (lowest curve) with increasing carrier concentration demonstrates that shifts in the order of 10-20 meV are easily conceivable at carrier concentrations of 10^{16}-10^{17} cm^{-3}. Simultaneous with a gap shrinkage, band-filling takes place : The upper solid line in figure 9*b* shows the shift of the quasi-Fermi level. The dashed line depicts the shift of the gain-peak with carrier concentration. In the upper part (Fig. 9*a*), the gain-loss profile at a fixed carrier concentration ($n_e = n_h = 5 \times 10^{16}$ cm^{-3}) has been drawn (negative absorption corresponds to positive gain). Qualitative agreement with the experimentally determined band-to-band gain (Fig. 7) is reached, even if exchange energies only and screened Coulomb potentials are taken into account. The most recent theoretical work on GaAs also includes correlation effects [54], [56]. The problems which are least understood in the low temperature band-to-band gain are saturation effects. They can be investigated experimentally in the manner described in section 2 [8] applying eq. (4). A typical experimental result is depicted in figure 10 for the case of GaAs [47]. The dashed line depicts the unsaturated gain component as a function of energy (compare Fig. 7). The solid line shows the variation of the saturation parameter (parameter « a » of eq. (4)) with energy. Gain saturation is strongest on the high energy side of the gain spectrum and drops very rapidly towards lower energy. This saturation behaviour seems to be universally present in many materials [8], and may find a general explanation in case of laser transitions in Fermi-systems [50]. Definitely more experimental as well as theoretical work is desired to reach a satisfactory understanding of the energy dependence of the gain saturation.

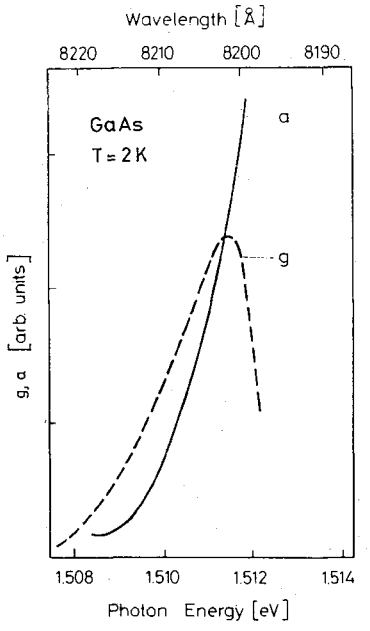

FIG. 10. — Gain (g) and saturation parameter (a) versus photon energy for p-GaAs [47]. Both are determined from amplification experiments and defined through eq. (4). Excitation intensity : 1 MW/cm².

4.4 EXCITONIC GAIN PROCESSES IN GaAs. — As already mentioned, the (X, LO)-, (X, e)- and (X, X)-contributions to the gain can be studied very conveniently in II-VI compounds [17], [18], [19], [22], [24]. In this section, we confine the discussion to new experimental results for the case of GaAs. The recent observation of excitonic interactions in high purity epitaxial GaAs layers [26], [46] have raised the question whether they participate in gain processes. The presence of excitonic gain at very low temperature has been pointed out already in figure 7 (gain-curve A). The excitonic gain is very weak (typically 100 cm^{-1}) and is observed only at low temperature [46]. A detailed spectral analysis of emission due to excitonic interactions is discussed in figure 11 [47], where an

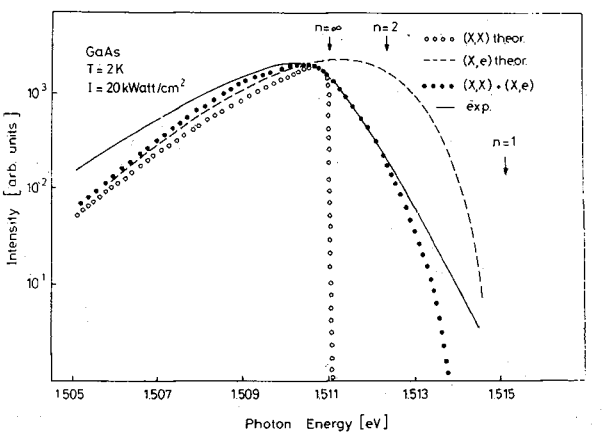

FIG. 11. — Comparison of the measured spontaneous emission of the excitonic scattering process (solid line) with various calculated curves [47]. The curve for (X, X)-scattering (open circles) is computed from reference [17], the curve for (X, e)-scattering from reference [58]. No fit of the high energy side is obtained by either (X, X)- or (X, e)-scattering, but only by a combination of the two (full circles).

experimental spectrum is compared with theoretical spectra for (X, X)- [17] and (X, e) [58] -interactions. The emission due to (X, X)-interaction should exhibit a sharp cut-off at $E_g - 2\,B_x$ (1.511 eV in GaAs). This cut-off is not seen in the experimental data. The low energy part of the spectrum can be fitted equally well by (X, X)-, and (X, e)-interactions. In order to fit the high energy side, one has to assume simultaneous presence of both scattering processes [47]. It seems certain that the (X, X)-process should gradually convert into the (X, e)-process when the excitation

level is increased [17]. At very low excitation level (X, X)-scattering dominates and (unresolved) bound-exciton luminescence may appear on its high energy side [26].

4.5 TEMPERATURE EFFECTS. — Exciton emission and exciton-interaction effects in II-VI compounds are not limited to very low temperatures, as expected because of the large exciton binding energies. Figure 12 gives results for CdS [38], [59] : The peak energies of spontaneous and stimulated emission lines are plotted as a function of temperature. At high temperature, the

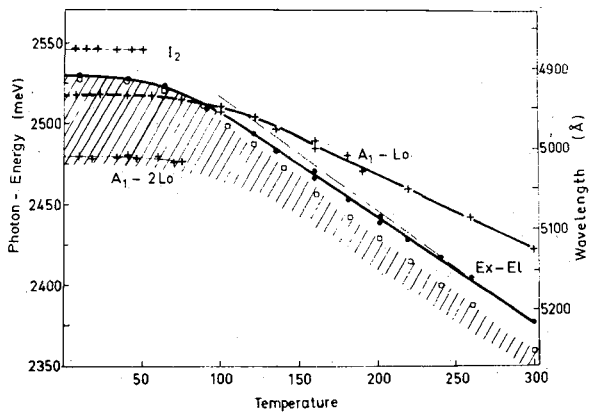

FIG. 12. — Temperature dependence of the peak energies of spontaneous and stimulated emission lines in CdS [38]. In the dashed region, laser modes of steadily decreasing energy are oscillating with increasing excitation [59]. The highest energy laser mode observed, is denoted by an open square. Other notations A_1 = free exciton, I_2 = bound exciton, $E_X - E_1$ = (X, e)-interaction.

LO-phonon satellite of the free exciton and emission due to exciton-electron scattering prevails. Stimulated emission is observed on the low energy side of the emission due to exciton-electron scattering [59]. Similar results have been found for CdSe [24], where the exciton-exciton interaction leads to stimulated emission up to temperatures of 70 K, and exciton-electron collisions to lasing at higher temperatures. In high purity GaAs,

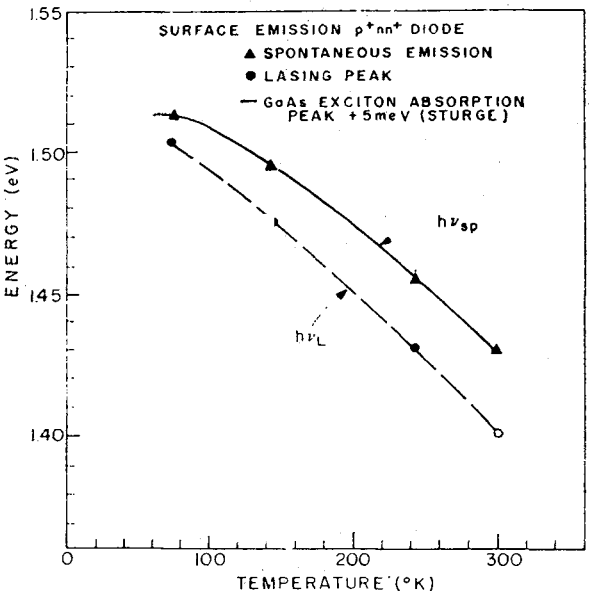

FIG. 13. — Temperature dependence of the spontaneous emission peak ($h\nu_{sp}$) and of the lasing photon energy ($h\nu_L$) for a p^+nn^+-laser structure [44]. The variation of the band gap energy with temperature is also shown (solid line).

the excitonic emission including (X, X)- and (X, e)-interactions disappears rapidly when the temperature is raised. Above 40 K, only the band-to-band transition remains and gives rise to laser action at high excitation level [44], [46]. The laser emission at high temperature is observed 10-30 meV below the low level spontaneous peak or below the band gap [44]. This is demonstrated in figure 13. Let us remember that at low temperatures a reduction of the energy gap due to many-body interaction was made responsible for the energy shift of the band-to-band emission. At high temperature, the reduced band gap can exhibit additional tail states which are quite analogical to impurity tail states [55], [56]. These tail states become more pronounced with increasing temperature and can explain the experimentally observed large shift up to 30 meV [44].

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DISCUSSION

C. BENOIT A LA GUILLAUME. — The problem of knowing whether k-selection rule has to be used or not may depend not only on the density n but also on the temperature. Also some « tailing » due to the high carrier density may occur.

M. PILKUHN. — I agree that the situation concerning k-selection rules may depend on temperature. Experimentally the question whether k-selection rules should be used at high temperature has not been clearly answered so far. In the case of GaAs there are indications that k-selection is in fact needed at room temperature and not too high excitation level [49]. « Tailing » at high temperature has been assumed [55], [56] and the large energy shift of the band-to-band emission in GaAs [44] has been interpreted in this way. At low temperature, tailing effects are small.