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Optical Properties of Highly Excited Crystals

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Recently, the optical properties of highly excited crystals have been intensively studied.

New emission bands have been observed in many materials. They are related to new recombination mechanisms as excitonic molecule recombination (CuCl), exciton-exciton collision recombination (CdS) or electron-hole drops recombination (Ge). We will leave this last subject out of this talk. It has seen considerable developments recently and should be a subject by itself.

The excitonic absorption has also been studied in highly excited crystals. Interesting informations on the behaviour of excitons, when high concentration of excitons and carriers are created, have also been obtained.

A. Emission of Light in Highly Excited Crystals

1. Excitons

Excitons play an important role in the radiative desexcitation of a crystal at low intensities of excitation.

Even, if a crystal is excited in its band to band absorption, the hot carriers created are very rapidly thermalized ($10^{-10} - 10^{-12}$ sec) [1] and form free excitons [2, 3]. These free excitons may recombine:

    a) non radiatively (Auger process)

    b) radiatively

— by a direct process which gives the free excitonic emission. This resonant line is strongly reabsorbed.

$$\text{Exciton} \rightarrow \text{photon}$$
$$hv = E_g - E_x \tag{1}$$

E_g is the band gap energy and E_x the binding energy of the exciton.

— by an indirect process with simultaneous emission of one or more longitudinal optical phonons. This emission is very weakly reabsorbed [4].

$$\text{Exciton} \rightarrow \text{photon} + \text{phonon}$$
$$hv = E_g - E_x - \hbar\omega_{LO} \tag{2}$$

$\hbar\omega_{LO}$ is the LO phonon energy.

The excitons may also be trapped by impurities centers: neutral or ionized acceptors or donors. The binding energy E_D of excitons to these centers is usually small. This recombination will therefore be important only at very low temperatures. These bound excitons will recombine [5, 6, 7]:

    a) non radiatively (Auger process)

    b) radiatively

— by a direct process.

$$\text{bound exciton} \rightarrow \text{photon}$$
$$h\nu = E_g - E_x - E_D \tag{3}$$

— by an indirect process.

$$\text{bound exciton} \rightarrow \text{photon} + \text{phonon}$$
$$h\nu = E_g - E_x - E_D - \hbar\omega_{L0} \tag{4}$$
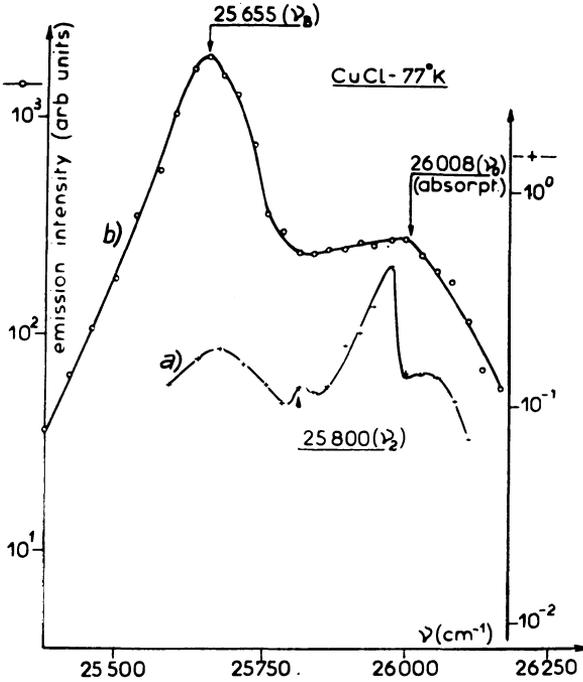
Fig. 1. Luminescence spectrum of CuCl at 77°K for two intensities of UV laser light excitation
a) $7 \cdot 10^{21}$ photons/cm² . s, b) 10^{25} photons/cm² . s

The luminescence of lower states will predominate, especially at low temperatures.

When the crystal is highly excited, new emission phenomena are observed.

2. Excitonic molecule

Under intense light excitation, a new emission line has been observed in CuCl as shown in Fig. 1. This emission peak has been identified as an excitonic molecule (EM) recombination radiation [8, 9, 10, 11].

2.1. Energy balance

The assumed recombination mechanism is an Auger process where one of the exciton of the molecule is scattered into the $n = 1$ state of the free exciton while the other one is scattered into a photon-like state as shown in Fig. 2. The energy balance is:

$$\text{EM} \rightarrow \text{photon} + \text{exciton}$$
$$h\nu_B = E_g - E_x - E_B - E_x^K - E_B^K \tag{5}$$

where $h\nu_B$ is the energy of the emitted photon, E_B the binding energy of the EM, E_X^K the kinetic energy of the exciton, E_B^K the kinetic energy of the excitonic molecule.

The emitted photon is shifted down in energy from the absorption line corresponding to the first exciton state by the binding energy of the molecule for molecules with small wave vectors. For molecules with large wave vectors, the photon will have lower energies due to the difference in the dispersion curves of the molecule and the free exciton.

The experimental value obtained for the EM binding energy in CuCl was about 44 meV.[*] It was interesting to compare this value with theoretical estimations.

Sharma [12] has given the variation of $E_B/E_X(1+\sigma)$ with the ratio σ of the electron and hole effective masses. Knowing the value of σ and E_X from Ringeissen's studies of the excitonic absorption in CuCl [13]

$$\sigma = 0.02$$
$$E_X \simeq 190 \text{ meV}$$

we were able to deduce a theoretical value of E_B equal to 47 meV.

Figure 2. Dispersion curves of the exciton, excitonic molecule and photon

Wehner, later on, has discussed the dependence of E_B on σ [14]. Although his results do not agree with Sharma's ones for large value of σ, he has found very similar results for values of σ close to zero.

$$E_B/E_X(1 + \sigma) = 0.346 - 0.764 \sqrt{\sigma} \qquad (6)$$

which gives $E_B \simeq 46$ meV.

Further calculations have been done by several authors [15, 16, 17]. They all agree for small values of σ.

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[*] Two emission lines have been observed at liquid helium temperature. They may be due to the recombination of excitonic molecules towards ortho and para excitonic states [9].

2.2. Kinetic model

The intensity dependence of the new emission line ν_B has been studied. As shown in Fig. 3, at low intensities of excitation the intensity of emission varies as the power 1.7 of the excitation intensity, then, after a smooth change, as the power 0.8 at high intensities of excitation. The variation of intensity of the resonant excitonic emission ν_0 has also been measured as seen in Fig. 3. This line varies linearly with the excitation intensity.

The intensity dependence of the EM emission can be easily understood in terms of probability of collision of two excitons and of formation of a molecule. At low exciton densities, the probability is proportional to the square of the exciton density, and hence to the square of the excitation intensity. At high exciton densities, the time required for the formation of a molecule becomes short compared to the lifetime of the exciton; an equilibrium is established where the rate of molecule formation is proportional to the excitation intensity. Not as easily explained is the overall linear dependence of the exciton emission intensity.

Fig. 3. *Variation of the intensity of EM and X emission bands versus the UV light intensity at 77°K*

A kinetic of excitons and EM recombinations has been given by Knox and alii [18]. They assume that all electron and hole pairs are forming excitons. They distinguish in this population of excitons two different groups: the optical excitons with a wave vector $\vec{\kappa} = 0$ (density n_x^0) and the thermal excitons ($\vec{\kappa} \neq 0$) (density n_x^1). The biexcitons (density n_B) are assumed to be formed primarily from the large pool of thermal excitons.

The kinetic equations are the following:

$$\frac{dn_x^o}{dt} = A_o i - \frac{n_x^o}{\tau_o} - kn_x^o + k'n_x^1 \qquad (7)$$

$$\frac{dn_x^1}{dt} = A_1 i + kn_x^o - k'n_x^1 - k''n_x^1 - B(n_x^1)^2 + Cn_B \qquad (8)$$

$$\frac{dn_B}{dt} = \frac{1}{2} B(n_x^1)^2 - Cn_B - k'''n_B \qquad (9)$$

$A_o i$ and $A_1 i$ are the rates of creation of optical and thermal excitons. (i is the excitation intensity).

$1/\tau_o$ is the radiative decay rate of optical excitons.

k and k' are the rates of thermalization of optical excitons and the reverse.

k'' is the rate of radiationless decay or dissociation of thermal excitons; k''' is the rate of non radiative decay of biexcitons.

B is the bimolecular collision coefficient.

C is the recombination coefficient of biexcitons.

k' is assumed to be negligible, the density of optical exciton states being much smaller than that of the thermal excitons.

k''' is also assumed to be negligible. The principal decay mechanism of biexcitons is assumed to be radiative, the binding energy of the biexciton being large, the thermal dissociation of the molecule is unlikely and the molecule cannot be dissociated on impurities.

In the steady state conditions:

$$n_x^o = \frac{A_o \tau_o i}{1 + k\tau_o} \qquad (10)$$

$$n_x^1 = \frac{k''}{B} \left[\sqrt{\frac{i}{i_o} + 1} - 1 \right] \qquad (11)$$

$$n_B = \frac{(k'')^2}{2BC} \left[\sqrt{\frac{i}{i_o} + 1} - 1 \right]^2 \qquad (12)$$

$$i_o = \frac{(k'')^2}{2B} \left[\frac{1 + k\tau_o}{A_1 + k\tau_o(A_o + A_1)} \right] \qquad (13)$$

The intensity of the ν_B line will be proportional to n_B. At low intensities $i \ll i_o$, a square dependence on the excitation intensity is expected. When $i \gg i_o$, a linear dependence is obtained. A smooth change between these two regions is expected.

The intensity of the resonant excitonic line is proportional to n_x^o, thus at all intensities of excitation, a linear dependence is predicted.

Two remarks are necessary:

α) Benoît à la Guillaume and alii have explained a similar behaviour of the intensity dependence of exciton and biexciton luminescences in Ge by a simple model

[19]. They have considered the populations of excitons and biexcitons introducing in their kinetic equations a term for biexciton-exciton collisions.

β) The preceding kinetics does not consider explicitly the existence of radiative and non radiative traps. They may be important, if one considers the low efficiency of the observed luminescence in CuCl.

2.3. Stimulated emission

The excitonic molecule recombination plays an important part in the stimulated emission as shown by Shaklee and alii [20].

The crystals of CuCl are hygroscopic and soft, it was therefore difficult to make an optical cavity and observe a real laser action. However, Shaklee and alii were able to measure the gain by the technique shown in Fig. 4. A rectangular beam of a nitrogen laser of 20 μm width and of variable length (0 — 100 μm) was focused on the surface of the sample near the edge. The light coming out of the excited region is dispersed by a monochromator and detected by a photomultiplier.
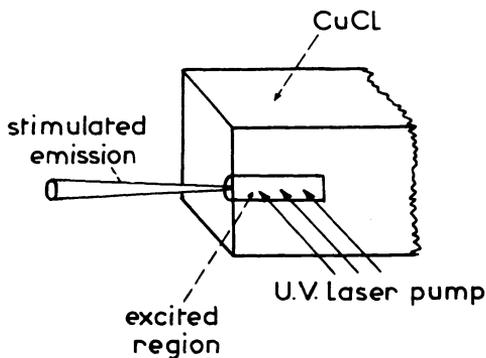
This light has the following intensity dependence on the length of excitation l:

$$I = I_S [\exp(gl) - 1]/g \qquad (14)$$

where I_S is the spontaneous emission intensity, g the optical gain (total gain

Fig. 4. Geometry used by Shaklee and alii for the measurement of high-intensity photoluminescence spectra of CuCl

— loss). The exponential dependence of I on l is an indication of gain.

Fig. 5 gives the EM emission intensity in CuCl as a function of the excitaation length for four different pump powers. These curves show a linear behaviour for short excitation lengths in a semilog-plot, giving direct indication of a stimulated emission. Peak gains of 10^4 cm^{-1} have been obtained by Shaklee and alii for 2×10^7 W/cm^2 pump power, two times larger than in GaAs in the same conditions. A saturation is observed when all excited EM participate to the process.

The large optical gain of the stimulated EM recombination process in CuCl is related to the large binding energy of the molecule as explained by Shaklee and alii [20]. The stimulated emission occurs in a low-loss region of the spectrum. The principal decay mechanism of the excitonic molecule is probably radiative as explained previously. All the molecules can participate to the process: The momentum of the molecule is transmitted to the remaining exciton in the assumed Auger recombination process.

2.4. Conclusion

At high excitation intensities, the EM should play an important role in radiative recombinations in semiconductors.

In fact, in many materials, new emission lines may be due to EM recombinations. In Si and Ge, a new emission peak observed at very low temperatures has first been explained as a EM recombination radiation, then as electron-hole drops recombinations but the EM explanation is not yet entirely discounted [21, 26]. In Cu_2O,
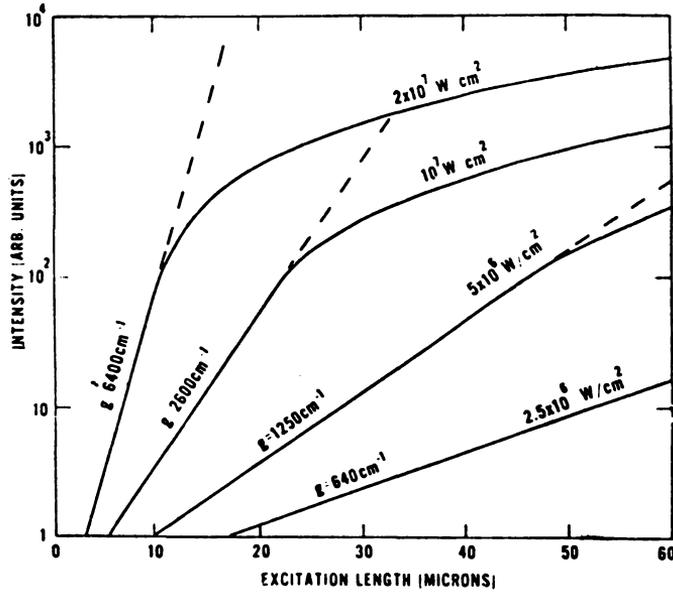
Fig. 5. EM emission intensity as a function of excitation length for four different pump powers. The gain g, as obtained from the linear portion of each curve on this semilog plot, is given for each pump power.
(According to Shaklee and alii)

Gross and alii have obtained a hydrogenoid series of emission lines well explained by a EM recombination [27, 28]. In GaP, Dean and alii have obtained new emission lines interpreted as the recombination of EM bound to a defect [29]. The complex Zeeman splitting predicted by this model agrees in detail with the experiments.

One question arises: Should the excitonic molecule be stable in all crystals? After the work of Sharma excluding the existence of excitonic molecule for materials with $0.2 < \sigma < 0.4$, new results by Hanamura [17] have shown that the EM is stable for all values of σ. However, as we will see now in II-IV compounds for instance, no evidence of EM has been obtained. Instead, a recombination mechanism, where two excitons collide, explained quite well the observed emission.*)

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*) At the last semiconductors conference in Warsaw, J. Bille and alii seem to have observed in CdSe excitonic molecules and even at higher excitations electron-hole drops.

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It must be noted that the EM binding energy calculation might not be applicable to II-VI compounds because of the anisotropy of the effective masses, as pointed out by Hanamura [17].

3. Exciton-exciton collision

Indeed, a new emission line M appears under intense laser light or electron beam excitation in some II-VI crystals like CdS, CdSe, ZnO, as shown for CdS in Fig. 6.
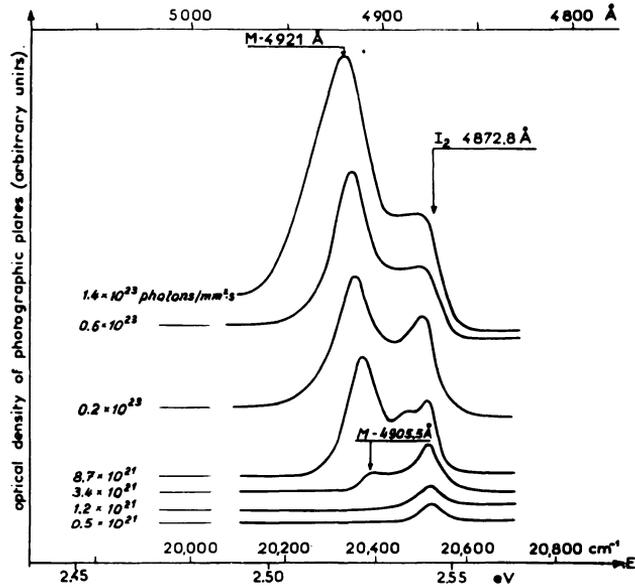
Fig. 6. Emission spectra of a thick sample of CdS for increasing ultraviolet light excitations at 4,2°K

This emission peak has however been identified as an exciton-exciton collision recombination radiation.

3.1. Energy balance

The peak position is shifted from the free exciton recombination line A by about the binding energy of the exciton. The recombination process involved is an exciton-exciton interaction in which one of the excitons scatters into a dissociation state while the other one scatters into a photon-like state as suggested by Benoît à la Guillaume and alii [30, 31], Fig. 7.

The energy balance is simply:

$$\text{Two excitons} \rightarrow \text{photon} + \text{electron-hole pair}$$

$$h\nu_M = E_g - 2E_x - E_{e,h}^K \tag{15}$$

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where $h\nu_M$ is the energy of the emitted photon, $E_{e,h}^K$ the kinetic energy of the unbound pair of electron and hole created during the collision, the excitonic kinetic energy is neglected.

At relatively low excitation intensities, the bands are empty and the kinetic energies of electrons and holes can be neglected.
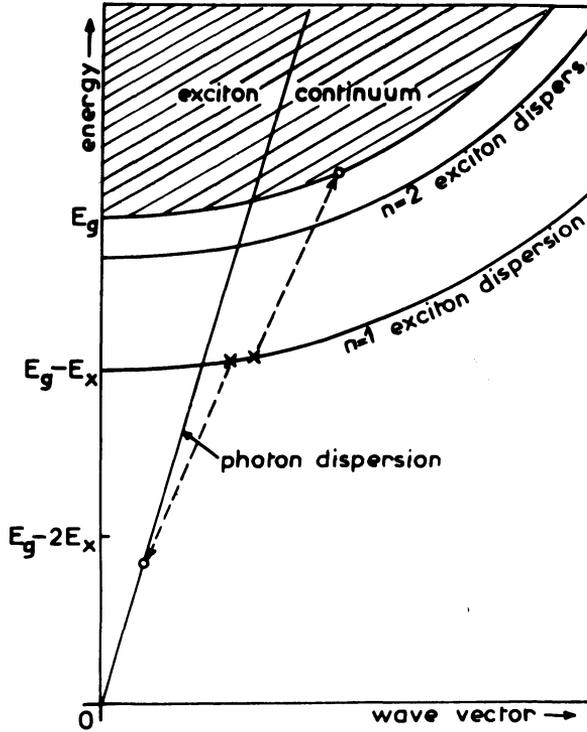
Figure 7. Dispersion curves of excitons and photons

At high intensities, however, a high density of free carriers is created as shown by Goto and Langer [42] in absorption studies. When the exciton-exciton recombination takes place, the unbound pairs created in the process must have higher energies, the kinetic energy $E_{e,h}^K$ can no more be neglected. A shift of the recombination line M towards lower energies is expected:

$$h\Delta\nu = - E_{e,h}^K \qquad (16)$$

This shift was indeed observed in CdS [32] as shown on Fig. 8.

If we take elliptical bands with one extremum only, the band filling effect suggested above gives a calculated line shift equal to:

$$h\Delta\nu = \left[\frac{1}{m_e^*} + \frac{1}{m_h^*}\right] \frac{\hbar^2}{2} \pi^2 \left(\frac{3}{8\pi}\right)^{2/3} n^{2/3} \qquad (17)$$

where m_e^*, m_h^* are the mean values of hole and electron effective masses, n is the number of free carriers per unit volume.

n in the steady state depends on the square-root of the absorbed photon flux i, therefore the line shift is proportional to $i^{1/3}$. This theoretical dependence drawn in solid line in Fig. 8 is in good agreement with the experimental points.

Theoretical evaluations of this shift have also been made and give reasonable values.
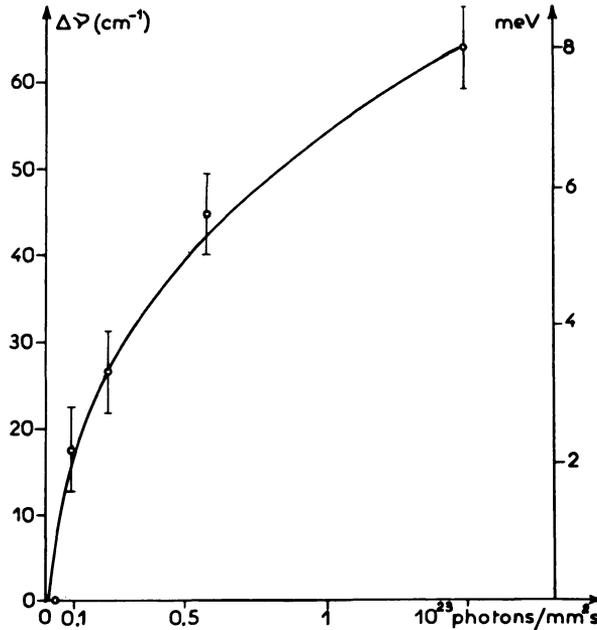
Fig. 8. Shift of the M emission line versus the intensity of UV photons at 4,2°K. We have taken for origin of the shift the position of the M line at the lowest excitation intensity. o experimental points, — theoretical curve

3.2. Kinetic model

A kinetic model of the recombination processes in CdS has been given by Magde and Mahr [33]. They assume that all electron-hole pairs created by light absorption form free excitons. In order to explain the low overall quantum efficiency of luminescence in even good crystals, they also suppose that an efficient excitonic trap exists that makes excitons decay non radiatively and rapidly*).

The excitons may be trapped with a rate constant k_{NR} by these traps of concentration N_{NR}, n_{NR} of these being occupied. The excitons may also be trapped with

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*) Another model has also been considered by Magde and Mahr [33], where only a small fraction of electron-hole pairs created form excitons, explaining the low quantum efficiency of luminescence. This model gives a less realistic result for the bimolecular exciton-exciton interaction coefficient.

a rate constant k_R by traps of concentration N_R, n_R of these being occupied. These trapped excitons deexcite radiatively with a rate constant k_0 giving rise to the I_1 and I_2 bound-exciton lines. The free exciton will also be scattered by another free exciton with a rate constant B and by an exciton bound to traps with rate constants B' and B''.

Let n_x be the free exciton concentration:

$$\frac{dn_x}{dt} = Ai - k_R(N_R - n_R)\, n_x - k_{NR}(N_{NR} - n_{NR})\, n_x - \qquad (18)$$
$$- Bn_x^2 - B'n_R n_x - B''n_{NR} n_x$$

Ai is the rate of absorption of photons in $cm^{-3} \times s^{-1}$, hence the rate of creation of free excitons.

The rate of change of radiative traps concentration is given by:

$$\frac{dn_R}{dt} = k_R(N_R - n_R)\, n_x - B'n_R n_x - k_0 n_R \qquad (19)$$

The steady state solutions of the kinetic equations are:

$$n_x = Ai/(k_R N_R + k_{NR} N_{NR}) \qquad (20)$$

and:
$$n_R = \frac{N_R \times Ai}{[(k_R N_R + k_{NR} N_{NR})\,(k_0/k_R) + Ai]} \qquad (21)$$

The luminescence intensity due to trapped excitons (emission lines I_1 and I_2) is given by the rate of emission of the corresponding I_1, I_2 photons:

$$\frac{dN_{I_1, I_2}}{dt} = \alpha k_0 n_R = \frac{\alpha \times Ai}{[(k_R N_R + k_{NR} N_{NR})/k_R N_R] + (Ai/k_0 N_R)} \qquad (22)$$

where α is the fraction of the traps which deexcite radiatively.

A linear variation of the luminescence intensity, with the excitation intensity i, is expected at low values of i, a saturation for large values of i, when all the traps are occupied. This behaviour has been observed [34].

The luminescence intensity of the line M due to exciton-exciton interaction is given by:

$$\frac{dN_M}{dt} = \beta B n_x^2 = \frac{\beta B \times (Ai)^2}{(k_R N_R + k_{NR} N_{NR})^2} \qquad (23)$$

where β is the fraction of exciton-exciton interactions which gives a luminescence.

A quadratic dependence of the emission M on excitation intensity i is expected and has been observed as shown in Fig. 10.

Henry and Nassau reported measurements of the lifetime of the I_1 and I_2 bound excitons in CdS, the trapping time of a free exciton at I_1 and I_2 traps and a luminescence efficiency of these traps $\cong 1$ [35]. Knowing the intensity of excitation

i which saturates the I_1 and I_2 traps, Magde and Mahr were able to deduce the exciton-exciton rate constant [33] in CdS:

$$\beta B \cong 3 \times 10^{-13} \text{ cm}^{+3} \times \text{s}^{-1}$$

The interaction of free excitons with bound excitons is also possible and an emission band similar to the M band should be observed. Its position is shifted from the M emission line by the binding energy of excitons to (I_1, I_2) traps. Its intensity proportional to $n_R n_x$ first grows quadratically with i, and after the saturation of the (I_1, I_2) traps linearly with i. Its intensity should be much lower than the M band anyway (10^{-3}).

3.3. Stimulated emission

The exciton-exciton collision recombination plays an important part in the stimulated emission of CdS crystals as first shown by Benoît à la Guillaume and alii [30].

Shaklee and alii have used the previously described technique to measure the gain in the exciton-exciton process [36]. Fig. 9 shows the variation of the light output with the increasing length of the excited region for different pump intensities. The solid line corresponds to the fitting of the light intensity equation with the experimental points when the exponential factor is large enough, a region of linear variation is observed on the semi-logarithm plot and the gain can be deduced from the slope of the curves. Values of 160 cm^{-1} have been obtained for pump intensities of 12 MW/cm^2. A saturation is observed when all the excitons participate to the process.

Fig. 10 shows on a logarithm plot the variation of the M emission line intensity versus the pump intensity. The square dependence of the spontaneous emis-

Fig. 9. Variation of the light output with the length of excited region for indicated pump intensities.
(According to Shaklee and alii)
o experimental points, — theoretical curve

sion intensity is observed at low excitation intensities. At higher pump intensities, the stimulated emission starts to increase exponentially, the characteristic breakdown is observed on the curve.

At low pumps, in many crystals, the emission line due to the recombination of an exciton with the simultaneous creation of a longitudinal phonon is first stimulated as shown in Fig. 10. But the gain of this process varies linearly with the pump intensity. On the contrary, the exciton-exciton recombination gain varies quadraticcally with the excitation intensity, it will become large enough to leave the exciton-exciton process as the main stimulated process in the crystal at high intensities.

A different behaviour of the stimulated emission is observed in a direction nonparallel to the surface of the sample. The exciton-exciton emission line is saturated in this direction but the emission of other lines is stimulated. The stimulated emission jumps from one line to another of longer wavelength when the UV excitation increases. The processes involved in the lasing are assumed to be: a bound exciton recombination to excited states of donors, an exciton-bound exciton interaction recombination and finally, a simultaneous emission of photons and LO phonons.
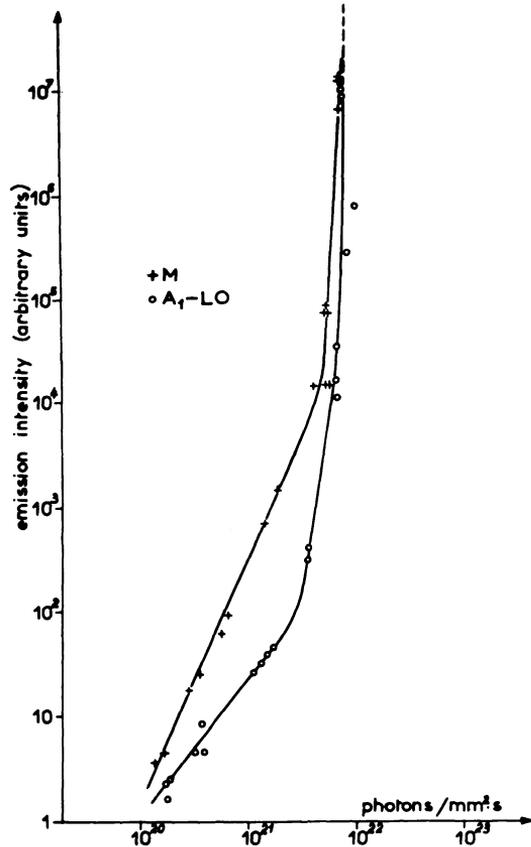
Fig. 10. Variation of the intensity of the M and A-LO emission lines with the UV laser light intensity at 4,2°K

3.4. Conclusion

In many crystals, instead of the EM recombination an exciton-exciton collision recombination is observed. The II-VI compounds like CdS, CdSe, ZnO, show such a behaviour as observed by Magde and Mahr [31]. The EM seems to be instable in this kind of crystals.

What happens to these excitons at very high intensities of excitation? Is there a possibility of condensation of these excitons, or of formation of electron-hole drops? It is interesting to mention here the study by Leheny and alii [37] of the spontaneous

emission line due to the recombination of the free exciton with simultaneous emission of two L0 phonons.

They have shown that this line varies linearly with the excitation intensity till intensity pumps of the order of 10 MW/cm^2 as shown in Fig 11. The exciton-exciton interaction do not influence significantly the dynamics of excitons. No evidence of an excitonic condensate is given.
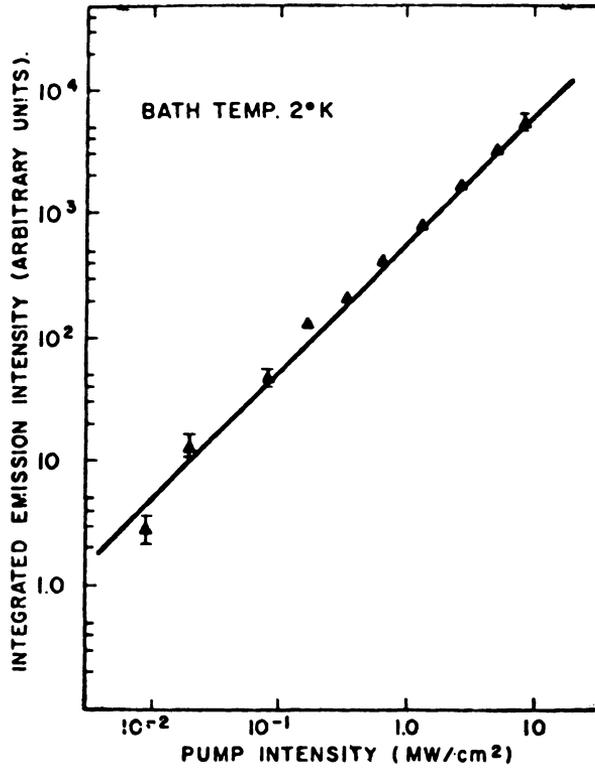
Fig. 11. *Variation of the integrated emission due to A-2L0 recombination process versus the UV pump intensity. (According to R. F. Leheny and alii)*

They have also studied the line shape, in Fig. 12. They have applied the theory of Segall and Mahan for phonon-assisted free exciton recombination [38] which gives the following luminescence intensity:

$$I(E) \approx (E - E_0)^{1/2} \exp (E_0 - E)/kT \qquad \text{for } E \geq E_0 \qquad (24)$$
$$I(E) = 0 \qquad \text{for } E < E_0$$

where E is the photon energy

$$E_0 = E_g - E_x - 2\hbar\omega_{L0}$$

T is the equilibrium temperature of the system.

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To fit the experimental spectra over the entire range of pumps investigated, they had to introduce an effective excitonic temperature T_x different from the lattice temperature. This rise of temperature was the only response of the system to increasing excitation intensity.

Similar conclusions will be obtained by absorption studies.
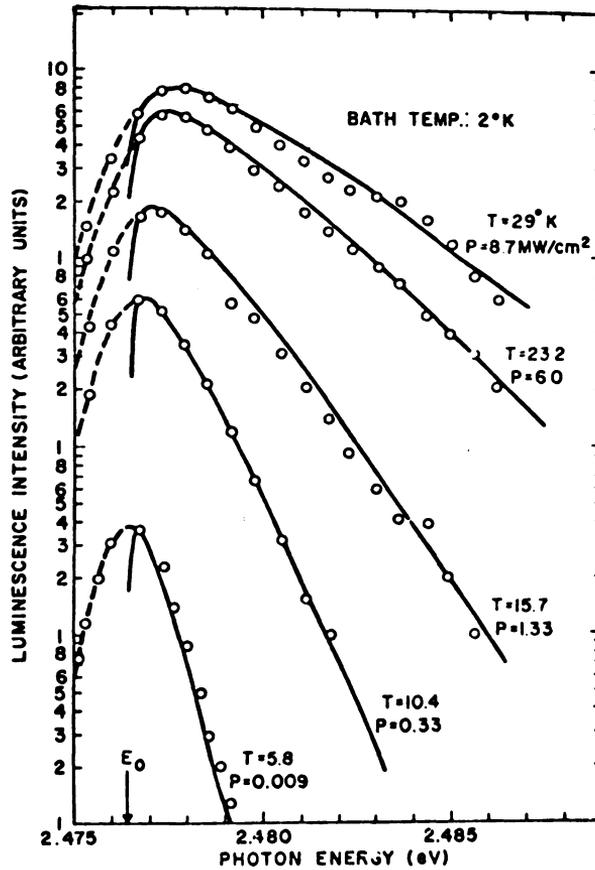
Fig. 12. Emission line shape for the A-2L0 phonon-assisted recombination of free excitons in CdS. The solid lines correspond to theoretical curves. The dashed curve indicates how the emission falls off for $E < E_0$ (According to R. F. Leheny and alii)

B. Absorption of Light in Highly Excited Crystals

New effects related to the creation of high concentrations of excitons and (or) carriers have also been observed by the study of the excitonic absorption spectrum of crystals during their excitation by a powerful light source.

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1. Excitons

In the absorption spectrum of semiconductors, the continuum of absorption due to band to band transitions is followed on the low energy part of the spectrum by a series of absorption lines due to excitonic transitions [39, 41].

The exciton energies are given by:

$$E = E_g - \frac{E_x}{n^2} + E_x^K \qquad (25)$$

where E_g, E_x have already been defined, E_x^K is the excitonic kinetic energy.

$$E_x^K = \frac{\hbar^2 \vec{K}^2}{2M}$$

where $\vec{K}$ is the exciton wave vector, M is the total excitonic mass ($M = m_e^* + m_h^*$).

When excitons are created by photons, the transitions from the ground state of the crystal to the excitonic states are vertical ($\vec{K} = 0$, $\Delta \vec{K} = 0$). In the absorption spectrum, a series of sharp lines are therefore observed at the following energies:

$$\hbar\omega = E_g - \frac{E_x}{n^2} \qquad (26)$$

These excitonic transitions have been studied in highly excited crystals (CdS, CuCl). As we will see, different phenomena have been observed with these two different materials.

2. Excitonic absorption in highly excited CdS

This study has been made by Goto and Langer [42]. The crystals of CdS were excited at 2°K by a powerful nitrogen laser. The decrease of the transmitted light of a Xe flashlamp was measured at a given wavelength as a function of time with a sampling oscilloscope. The induced absorption appears to have at any wavelength two distinct time components.

The slow one has a decay time of the order of 10 μs for CdS platelets of about 6 μ thickness. The magnitude of this induced absorption and its time constant vary with the crystal thickness. This absorption is probably due to an increase of the crystal temperature. The induced absorption coefficient of the slow component is shown on the upper part in Fig. 13. When the excitation intensity increases, the A excitonic line broadens and shifts towards lower energies as expected when the crystal temperature increases.

The time dependence of the fast component is undistinguishable from that of the laser pulse. The magnitude of this fast component and its time constant do not depend on the crystal thickness. The central part of the figure shows the induced optical density of the fast component in the region of the A excitonic line, the lower part of the figure shows the induced absorption constant in the excited region of 10^{-5} cm thickness. An absorption continuum which is larger near the absorption edge and tails off towards lower energies can be seen. In the immediate vicinity of the A

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line, the induced background can be considered as wavelength independent. The shape of the absorption line, however, changes with the increasing excitation, resembling one of the curves derived by Fano for the case of interference of an autoionized state with a continuum of states [43].
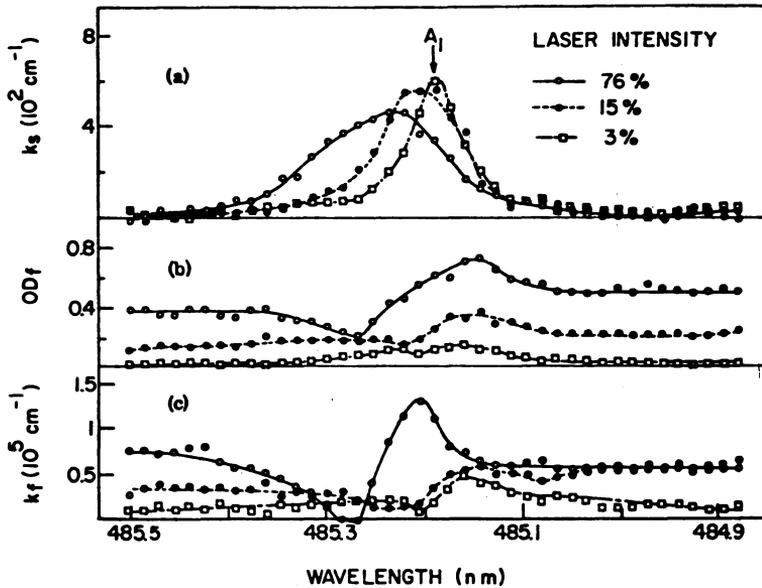
Fig. 13. In the vicinity of the A exciton, the upper section shows the induced absorption coefficient corresponding to the large time constant effect (slow component). The center section shows the optical density associated with the fast time constant effect. The lower section of the figure shows the induced absorption constant in the excited region of 10^{-5} cm thickness. (According to T. Goto and alii)

This fast absorption continuum on the low energy side of the A line cannot be explained by exciton-phonon transitions or by the creation of excitons with non-zero kinetic energies. It may however be due to free carriers absorption with an interference between these transitions and the excitonic transitions.

The binding energy of the exciton is not appreciably changed. We have obtained similar conclusions in studying the reflection anomalies corresponding to the A exciton line. The observation, already mentioned of the A — 2L0 emission line by Leheny and alii [37] leads also to similar results. The exciton seems not to be drastically perturbed in this high concentration of carriers and (or) excitons.

3. Excitonic absorption in highly excited CuCl

Very different results have been obtained in the study of the absorption spectrum of copper chloride crystals at different temperatures (77°K and 4.2°K) in the same conditions of strong ultraviolet excitation of the crystals.

We became interested in this problem in studying the free excitonic emission

line X of CuCl at low temperatures (Fig. 1). At low levels of UV light excitation, this emission line is partly reabsorbed in the crystal in the first excitonic absorption peak. But, at high excitation levels, the minimum due to the reabsorption disappears. The possibility of a shift of the absorption line was then considered. The absorption of highly excited crystals was therefore investigated [44].

3.1. Experimental set-up

The experimental set-up-used to study the absorption of thin samples of CuCl $(0,4$ to $1\,\mu)$ during the high intensity laser light excitation is shown in Fig. 14.

The second harmonic of the light of a Q-switched ruby laser provides a high intensity beam of UV light.

One-half of this beam is semi-focused on the rear of the sample and excites our crystal in the band to band absorption. A cell of variable thickness filled with CrO_4K_2 is used to vary the light intensity.

The other half of the beam is focused on a cell filled with a scintillator. The emission of
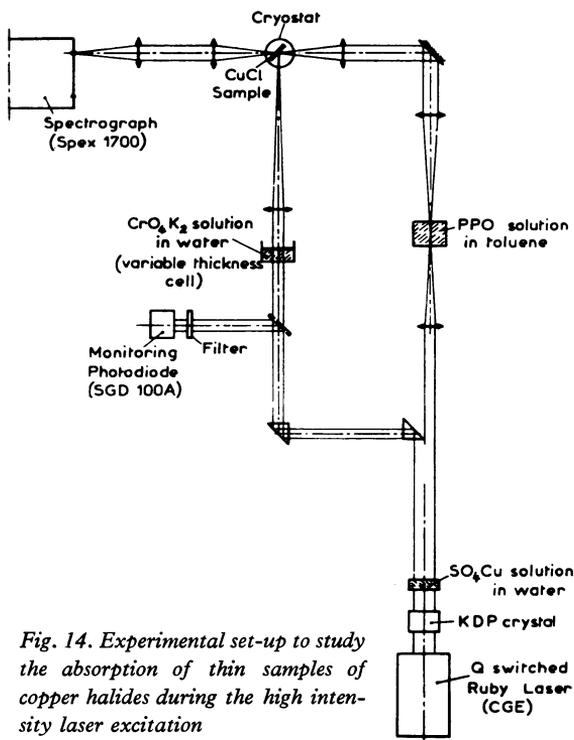
Fig. 14. Experimental set-up to study the absorption of thin samples of copper halides during the high intensity laser excitation

this scintillator is then used as a probe beam to record photographically the absorption spectrum of our sample through a spectrograph Spex. The time coincidence of the ultraviolet excitation and of the probe beam was very well achieved, the fluorescence decay time of the scintillator emission being 1.4 ns.

3.2. Experimental results

With this ultra-fast spectroscopy set-up we were able to study photographically the excitonic absorption spectrum during the UV laser light excitation.

Fig. 15 shows the excitonic spectra obtained for different intensities of the ultraviolet light at liquid helium temperature for a sample of CuCl $(0,5\,\mu$ thickness). A change of the excitonic spectrum can be seen, as the ultraviolet light intensity increases. The excitonic lines are shifted towards the high energy part of the spectrum, while their intensity is decreasing. At the same time, the absorption con-

tinuum is moving towards the low energy part of the spectrum. The spectrophotographic method used did not allow us to make quantitative measurements of the absorption changes.

However, the shift of the first line of the first excitonic series has been measured versus the flux density of ultraviolet photons at both liquid nitrogen and liquid helium temperatures. The experimental points obtained are shown in Fig. 16 for these two temperatures. The curves drawn represent a square-root dependence of the shift with the impinging photon flux. The agreement with the experimental points is reasonably good.
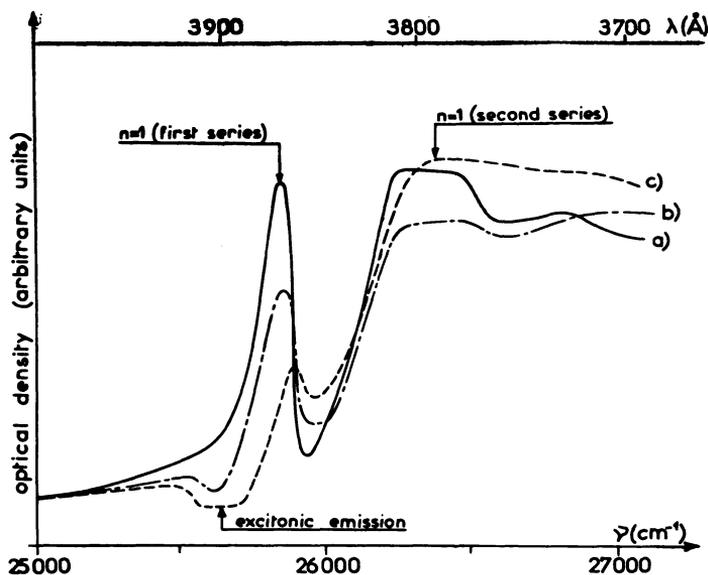
Fig. 15. Absorption spectra of a thin sample of CuCl. a) without UV light
b) $0,3 . 10^{24}$ UV photons/ cm^2 . c) $0,3 . 10^{25}$ UV photons/cm^2 . s

At 77°K, the shift reaches a maximum value of 50 cm^{-1} for a flux density of ultraviolet photons of about 10^{25} photons/cm^2 . s. At these high values, a saturation effect seems to appear which does not fit in with the square-root dependence. The maximum value of the ultraviolet light corresponds to the damaging intensity threshold of the samples.

At 4°K, the shift of the first absorption line towards the high energy part of the spectrum is more rapid than at 77°K. The maximum shift value obtained (65 cm^{-1}) corresponds to the maximum flux density of ultraviolet photons for which a measurement of the position of the absorption line is still possible, the line disappearing in the absorption continuum, as can be shown in Fig. 15.

It was interesting to study comparatively the behaviour of other excitonic lines.

We thus measured the shift of the first absorption line of the second excitonic series. It was difficult to have a very precise measurement, this line being very wide. We could nevertheless show that this line is shifted towards the high energy part of the spectrum as the first line of the first excitonic series. But we could not follow this shift for very high values of the excitation light, the line disappearing very rapidly in the absorption continuum. For the same reason, we did not study higher order lines of these excitonic series.
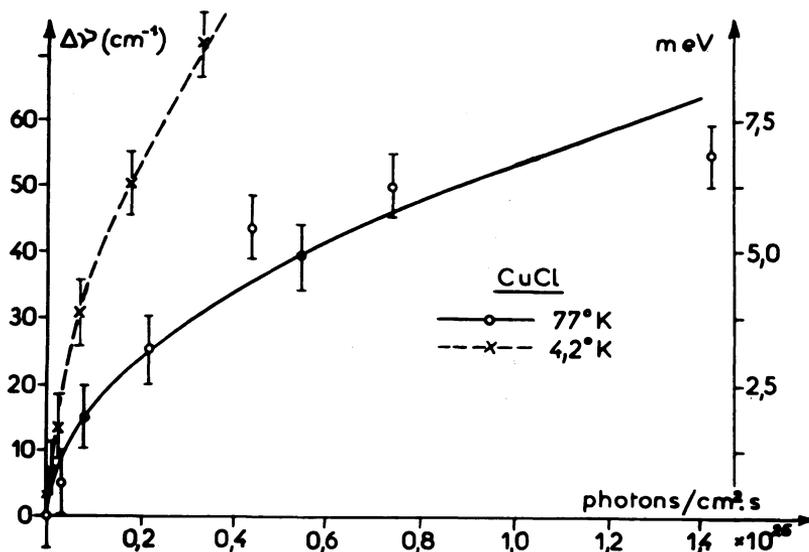
Fig. 16. Frequency shift of the first excitonic absorption line of CuCl versus the intensity of UV photons at liquid helium and nitrogen temperatures
o, x experimental points at 77°K and 4,2°K respectively
— — — — square-root dependence on light intensity at 77°K and 4,2°K

Many samples have been similarly studied. We have obtained for all these samples exactly the same qualitative behaviour. The shift was more or less rapid, depending on the observed sample, but was always following a square-root dependence with the ultraviolet excitation intensity. The maximum value of this shift could also be 20 to 30 per cent lower than the preceding value.

A similar shift of the first exciton absorption line in other copper halides (CuBr and CuI) has also been observed when the samples were excited by the same intense UV light.

On the contrary, the emission lines are not shifted when the excitation intensity increases. This fact enabled us to rule out the possibility of a global heating of our sample when highly excited. The observed change of the excitonic absorption spectrum is not due to an increase of the temperature of the sample.

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3.3. Discussion

Due to the strong light excitation, a great number of electrons and holes is created. They will rapidly thermalize to the extrema of the bands. When these electrons and holes are not forming very rapidly excitons, a non-equilibrium situation in which the excited electrons occupy the bottom of the conduction band has been assumed by Haken [44]. When an exciton is then created by absorption of a photon, its wave function cannot be formed out of all the conduction band states because it must be orthogonal to the occupied states (Pauli Principle). The binding energy of an exciton has been calculated by a variational principle when the states of the partly filled conduction band have been projected out. The following energy shift of the 1S exciton energy towards the higher energies has been obtained:

$$\Delta E_{1S} = 32 \, \pi a_x^3 E_x n \tag{27}$$

where E_x is the unchanged binding energy of the exciton
  a_x is the radius of the exciton in the ground state
  n is the free carriers concentration.

The dependence of the observed absorption peak shift, as a function of the intensity of the impinging light, can now be explained. This may be done by studying the rate equation for the electron density $\dot{n}$:

$$\frac{dn}{dt} = Ai - \gamma n^2 \tag{28}$$

The first term gives the creation of electrons (or holes) by the absorbed photon flux i, A being the absorption coefficient. The second term describes the recombination of two carriers with the recombination rate γ. Using realistic parameters A, i and γ, one finds that under the present experimental conditions, the steady state is reached very rapidly in the first phase of the pump process. Thus, one may solve equation (28) under the assumption that the time variation of n may be neglected. We thus find that n depends on the square-root of i:

$$n = [(A/\gamma)i]^{1/2} \tag{29}$$

Inserting reasonable values for the constants, namely:

$$A = 10^5 \, \text{cm}^{-1}$$
$$\gamma = 3 \cdot 10^{-7} \, \text{cm}^3 \cdot \text{s}^{-1}$$
$$i = 10^{25} \, \text{photons/cm}^2 \cdot \text{s}$$

we obtain an electron density $n = 1.7 \times 10^{18} \, \text{cm}^{-3}$. Introducing this value in the theoretical expression of the line shift, taking $E_x = 190$ meV and $a_x = 7$ Å for CuCl, a shift of the exciton absorption line of 86 cm^{-1} is expected, therefore of the same order of magnitude as the experimental shift.

Furthermore, the shift depends linearly on the carrier concentration n, thus

in square-root of the light intensity i. Such a square-root dependence is drawn in Fig. 16. The fit with the experimental points is reasonably good.

The excitonic absorption spectrum observed corresponds to the creation of new excitons in this non-equilibrium situation. On the contrary, when the exciton recombines on account of the selection rules $\Delta\vec{\kappa} = 0$ and $\vec{\kappa} = 0$ ($\vec{\kappa}$ being the exciton wavevector) the "optical" excitons only will participate in this recombination. These excitons are formed of all the states so that their binding energy is not changed. The exciton emission line will not be shifted as observed experimentally.

It must be emphasized that the above arguments remain valid if the electrons and holes form partly or completely excitons. In this case however the numerical value of the constant in the above formula changes.

The elementary excitation energy necessary to create a new exciton in a high density of excitons has also been calculated by Hanamura [46, 47] and by Keldysh and Kozlov [48].

These two theories, almost equivalent, predict a shift of the 1S exciton level which is given by the following formula:

$$\Delta E = f\, a_x^3 E_x n_x \tag{30}$$

where n_x is the exciton concentration and f a numerical factor of the order of 9π for Hanamura and of the unity for Keldysh and Kozlov.

These theories predict a shift of the exciton level of the order of magnitude of the experimental one, if all electron-hole pairs are forming excitons. The square-root dependence of the shift on the excitation intensity i can also be deduced from excitons and biexcitons rate equations. However, these theories predict that the emission and absorption involve the same energy level. The emission band should then be shifted towards higher energies as the absorption band. This is in contradiction with the experiment. In these theories, Bose condensation and superfluidity of excitons are supposed. One is tempted to conclude that the experiment is in contradiction with Bose condensation of excitons.

3.4. Conclusion

The drastic changes in the excitonic absorption spectrum of highly excited CuCl can be explained by a high non-equilibrium concentration of carriers and (or) excitons. The excitons are still there, no condensation has been observed, however the exciton energy is altered.

C. General Conclusion

In conclusion, new phenomena have been observed in highly excited crystals, showing the great interest of this new field of research.

New emission bands due to excitonic molecule recombination as in CuCl, to exciton-exciton collision recombination as in CdS, or to electron and hole drops as in Ge and Si, have been obtained with intense excitation of the crystals.

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New effects related to the presence of high concentrations of excitons and (or) carriers have been observed. A "red" shift of the exciton-exciton emission band in CdS is explained by a filling of the conduction and valence bands. A new absorption due to free carriers transitions is induced in highly excited CdS crystals. These transitions interfere with the excitonic transitions. The excitonic absorption is strongly modified in highly excited CuCl samples. A "blue" shift of the exciton absorption peak is observed and explained by a high non-equilibrium concentration of carriers and (or) excitons. However, the excitons still appear to remain a viable excitation in both crystals, no condensation has been observed in these experimental conditions.

There is however no doubt that the surface of this field of research has only been scratched out. Many new interesting phenomena are still to be discovered.

Acknowledgments

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