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Nonlinearities in the impurity related photoluminescence response in semiconductors

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(17. VIII. 1984)

In honor of Emanuel Mooser's 60th birthday

Abstract. After reviewing some nonlinear photoluminescence processes for impurity related emission in semiconductors, we analyse experiments performed on the bound exciton luminescence in AgBr:I at various concentrations of iodine. We show that the fit to the nonlinear response yields information on rate constants and non-radiative loss mechanisms difficult to obtain otherwise. Some difficulties inherent to these measurements will be discussed.

1. Introduction

In this paper, we are concerned with processes which lead to nonlinearities in the photoluminescence response of impurities in semiconductors. We consider briefly:

- 1) Saturation phenomena in donor-acceptor pair spectra,
- 2) Excitons bound to isoelectronic traps exhibiting a nonlinear photoluminescence response when a second recombination channel via the decay of bound excitonic molecules becomes important,
- 3) Nonradiative recombination via an Auger-process.

However, it is surprising to realise that the most obvious mechanism leading to a nonlinear response of impurity related luminescence – namely

- 4) Optical saturation due to the finite number of impurity atoms – has to the best of our knowledge been treated never thoroughly in the literature, although effects of this type have been mentioned in Refs. 1 and 8. We shall be concerned with this process for the most part of this paper. We have selected the radiative recombination of excitons bound to iodine impurities in AgBr, because the radiative recombination is well known and characterised at both low impurity concentrations [2] and as a function of concentration [3]. Moreover we know that in all of our samples except for the least doped iodine is the dominant impurity. The result of our analysis is information on the rate for the formation of bound excitons and for the nonradiative loss mechanism.

All examples discussed in this paper show that the conceptually simple measurement of the excitation dependence of photoluminescence intensity – if performed with some care – yields rather detailed information on the processes involved.

2. Saturation in donor-acceptor-pair spectra

By their very nature donor-acceptor pair spectra (DAP spectra) show a nonlinear photoluminescence response which can be explained qualitatively as follows: assuming for simplicity of argument an equal concentration of donors and acceptors, the spatial distribution of DAP with various separations r can be calculated [4]. If the concentration is not too large pairs of shorter separation can be treated as unperturbed by all others.

After excitation at low temperatures electrons and holes are captured by the impurities. The number of recombination transitions per unit time of donor electrons with acceptor holes will depend on the density of pairs at each separation r and on the overlap of their wavefunctions. The energy of the light quantum emitted by the recombination is given by [4]

$$\hbar\omega = E_G - E_A - E_D + \frac{e^2}{\epsilon r}, \quad (1)$$

where ϵ is the static dielectric function, E_G the energy gap and E_D and E_A are the donor and acceptor ionisation energies respectively. At high excitation densities the recombination channels with low transition probabilities (large DAP separations) will be nearly all “filled” and an increasing number of recombination transitions will move to pairs with shorter separations. The reason for this shift is that the set of those pairs with the highest recombination velocity will also have the largest relative number of unoccupied members. This behaviour is demonstrated qualitatively in Fig. 1 (taken from Ref. 4) for the resolved pair lines and the unresolved intensity. In the following we consider the unresolved part of the spectrum. Since with increasing excitation a deformation of the spectral distribution is produced it is appropriate to consider the change in intensity of a particular emission energy as function of the excitation density. This calculation has been performed by Zacks and Halperin [5] yielding the equation

$$J = D \frac{(\hbar\omega_m - \hbar\omega_\infty)^3}{\hbar\omega_B - \hbar\omega_\infty - 2\hbar\omega_m} \exp \left\{ -\frac{2(\hbar\omega_B - \hbar\omega_\infty)}{\hbar\omega_m - \hbar\omega_\infty} \right\}, \quad (2)$$

which gives the excitation intensity J necessary to observe the maximum of the unresolved pair emission at the energy $\hbar\omega_m$. D , $\hbar\omega_B$ and $\hbar\omega_\infty$ are treated as fitting parameters. D is a factor of normalisation, $\hbar\omega_\infty$ the photon energy in the limit $r \rightarrow \infty$ (compare equation (1)) and $\hbar\omega_B$ is related to the Bohr radius R_B of the shallower of the two impurities by

$$\frac{e^2}{\epsilon R_B} = \hbar\omega_\infty - \hbar\omega_B. \quad (3)$$

The fits give values for $E_G - E_A - E_D$ and the Bohr radius which agree to a few percent with the values obtained from an extrapolation of the spectral positions of

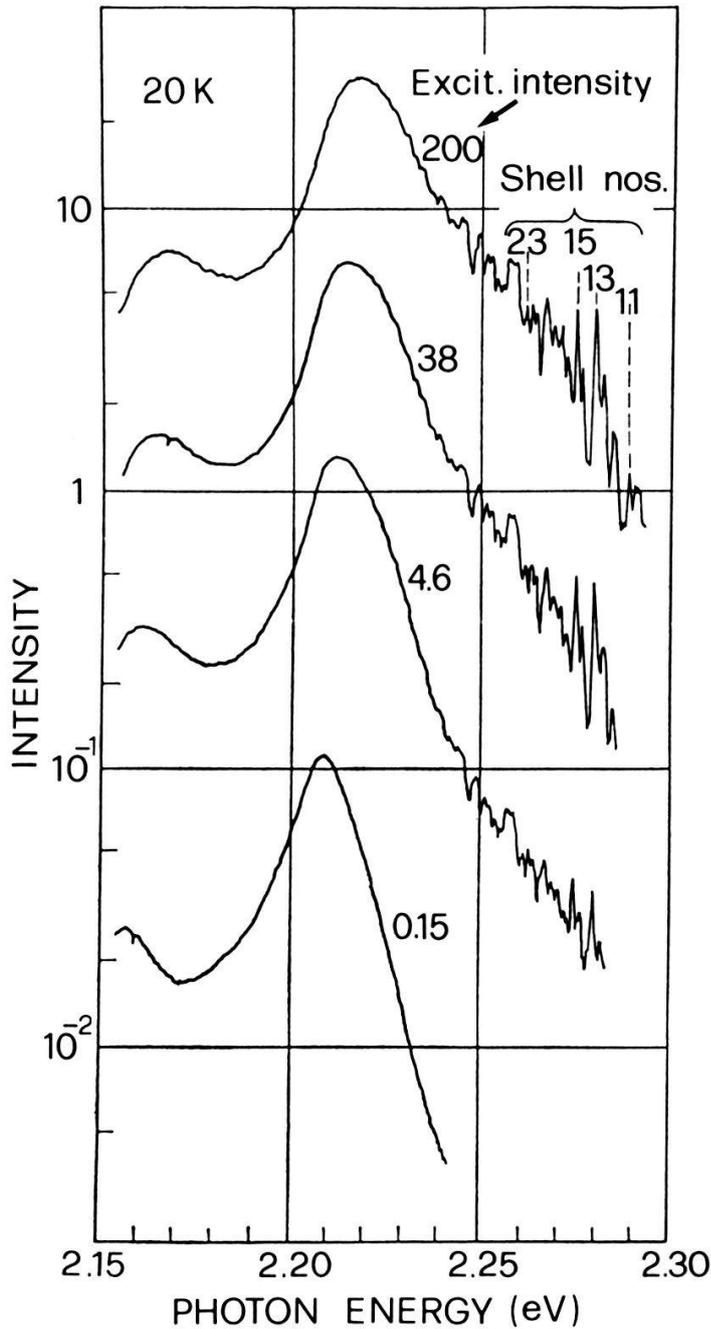


Figure 1 Donor Acceptor Pair Spectra in the system GaP:S, C at different excitation intensities, from Ref. 4.

the resolved pair lines according to equation (1) and from infra-red absorption measurements [5].

3. Nonlinear response due to competition between exciton and biexciton recombination

The isoelectronic trap nitrogen in GaP not only binds one exciton but also – at higher excitation densities – an excitonic molecule or biexciton [6]. The same process has been reported recently for AgBr:I [7]. Although in both

examples a similar excitation dependence of the exciton luminescence is to be expected [8] we confine ourselves for our discussion to the case of GaP:N [6]. According to recent investigations [8] the case of AgBr:I appears to be more complicated which may be related to the value of the ratio of the bound exciton localisation energy to the free exciton binding energy, which is <1 in GaP: but >1 in AgBr:I.

Figure 2 [9] shows the measured dependence of the luminescence intensity vs. excitation density for the exciton and for the biexciton recombination. The nitrogen bound exciton in GaP is known to be only weakly localised. We therefore expect the recombination process in a reasonable approximation to be effective mass-like and independent of the presence of the binding nitrogen impurity. We therefore apply the reaction kinetics developed for free exciton and free exciton molecule decay [10]. The rate equations are the following:

$$\begin{aligned}\frac{dn_1}{dt} &= aJ - kn_1 - Bn_1^2 + Cn_2, \\ \frac{dn_2}{dt} &= \frac{1}{2}Bn_1^2 - Cn_2 - k'n_2.\end{aligned}\tag{4}$$

n_1 and n_2 are the concentrations of excitons and biexcitons respectively. kn_1 is the radiative exciton decay, Bn_1^2 is the formation of biexcitons from excitons, Cn_2 describes the formation of excitons due to the dissociation of biexcitons. $k'n_2$ is the decay of biexcitons which can be monitored via a radiative process, and finally J is the excitation density, such that aJ is the exciton generation rate. Equations (4) have as solutions in the stationary case

$$\begin{aligned}n_1 &= P \left[\left(\frac{J}{J_0} + 1 \right)^{1/2} - 1 \right], & J_0 &= \frac{k^2(C + k')}{2a(C + 2k')}, \\ n_2 &= Q \left[\left(\frac{J}{J_0} + 1 \right)^{1/2} - 1 \right]^2,\end{aligned}$$

with the asymptotic behaviour

$$\begin{aligned}\frac{J}{J_0} \ll 1: & \quad n_1 = \frac{1}{2}P \frac{J}{J_0}, & n_2 &= \frac{Q}{4} \left(\frac{J}{J_0} \right)^2, \\ \frac{J}{J_0} \gg 1: & \quad n_1 = P \left(\frac{J}{J_0} \right)^{1/2}, & n_2 &= Q \frac{J}{J_0}.\end{aligned}$$

P and Q are combinations of the rate constants from equation (4) which shall not be discussed any further. With a detailed fit of equation (6) to the data [9] as shown in Fig. 2, it becomes clear that in the low excitation limit the slopes of value 1 and 2 are asymptotic values which will never be reached experimentally; a fact which was not realised in Ref. 6. The high excitation limits are masked by an excitation related increase of the sample temperature which can be measured by the temperature sensitive ratio of the A -line to the B -line.¹⁾ At high temperatures, as known from different experiments, the A -line intensity shows an additional increase due to the temperature rise whereas the B -lines emitted by

¹⁾ The A -line is the dipole-allowed zero phonon ($|\Delta J| = 1$) component of the zero phonon line, the B -line the dipole-forbidden ($|\Delta J| = 2$) component; in GaP:N $E_A - E_B \approx 1$ meV and the two components are well resolved.

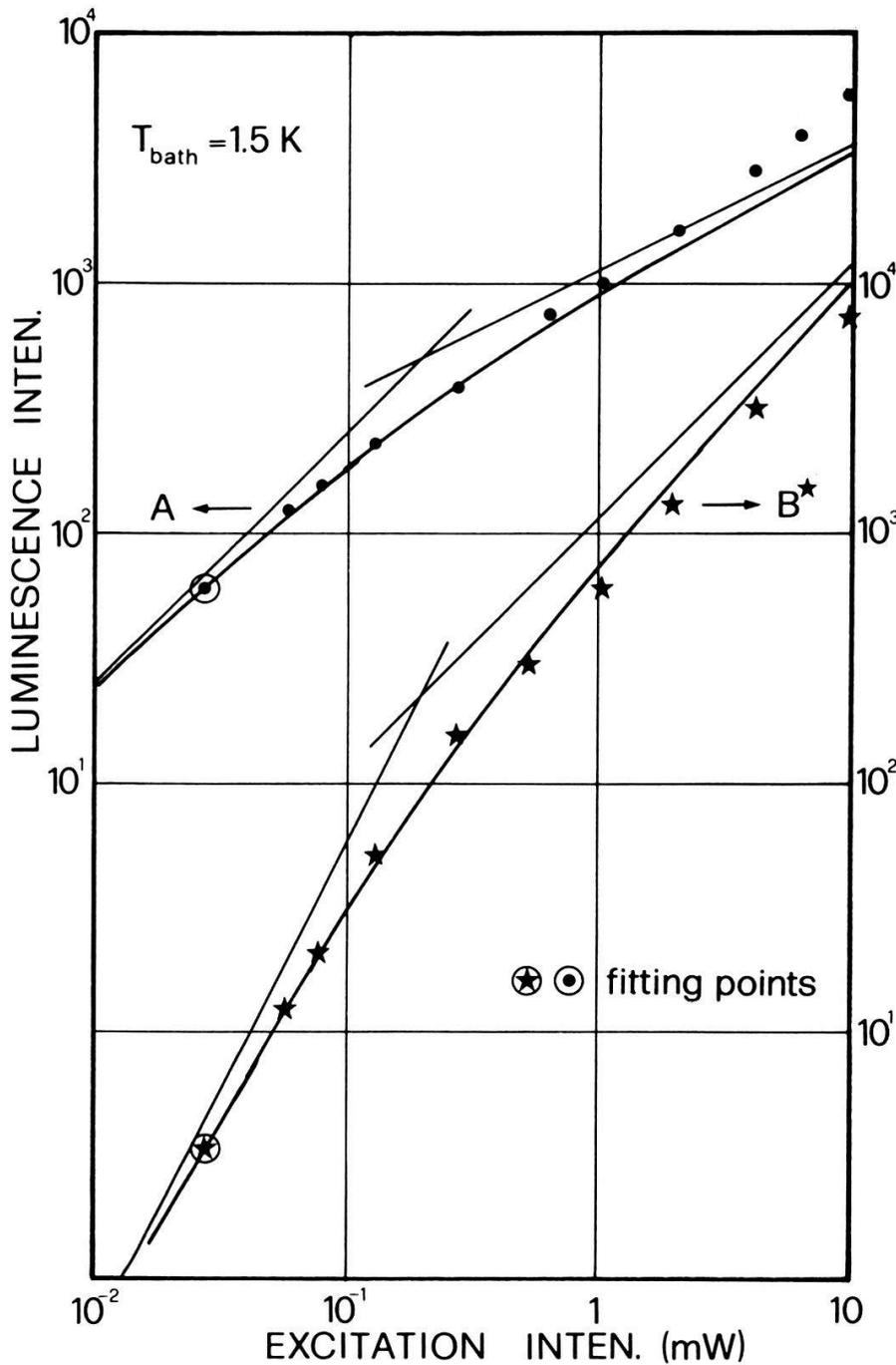


Figure 2
 Bound exciton and bound biexciton luminescence intensity in GaP:N as a function of excitation intensity. A fit to the solutions equation (5) of the rate equations is shown. Note that the two pairs of asymptotes intersect at the same excitation intensity. Parameter values: $J_0 = 0.05$ mW, $P = 249$, $Q = 58.5$.

the bound exciton molecules are relatively reduced in intensity. This behaviour is well represented in Fig. 2, including the onset of the deviations which occur about the temperature increase deduced from the intensity ratio of the A- and B-line [9].

The fit shown in Fig. 2 provides us with two pieces of information:

- a) the photoluminescence response due to the decay of an exciton (or biexciton) bound to the isoelectronic trap is inherently nonlinear.

- b) above about 1 mW excitation intensity (a value which depends in detail on the amount of focussing of the laser beam and on the sample geometry) the temperature of the sample begins to rise above the temperature of the bath.

4. Auger effect

The Auger effect is known to be an important nonradiative recombination process for electron hole pairs in semiconductors. There are a number of review papers [11, 12, 13, 4], and some more recent publications [14], which treat this subject in some detail. Although the Auger effect is inherently nonlinear in the concentration of the charge carriers, whether this nonlinearity can be actually be observed depends on a number of details. This holds in particular for impurity related recombinations. We shall limit our discussion to mentioning briefly two observations.

The lifetime of excitons bound to neutral donors or acceptors is determined by the Auger-recombination as has first been pointed out for the host GaP in 1966 [15]. This model was later confirmed quantitatively for bound excitons in Si [16]. In the system of excitons bound to neutral donors or acceptors the bound exciton has a third carrier present in its close vicinity by definition and an Auger process is always possible while its importance is given by the branching ratio for the transitions involved.

This is drastically different in the case of excitons bound to isoelectronic traps. However, even here an Auger process may become important due to the presence of a second (donor or acceptor like) impurity as has been found with the impurity band Auger effect (IBA effect) [11]. It is because of this effect that the control of unwanted impurities is important for the measurements which will be presented in the next paragraph. In both cases, however, the nonlinearity in the photoluminescence response has not been the major concern. It has been partially replaced by a dependence on doping. It is interesting to realise that it has been shown for Si that the relevant Auger coefficients are the same whether electrons and holes are generated by high doping or high excitation [17].

5. Optical saturation due to the finite number of impurities

In this section, we report on measurements performed on iodine doped AgBr in the concentration range of $4 \cdot 10^{14} \text{ cm}^{-3}$ to $2 \cdot 10^{18} \text{ cm}^{-3}$. Upon excitation of the crystal with energies above the absorption edge at low temperatures excitons bound to iodine impurities are formed and their recombination radiation is detected. The spectra observed have already been published in Refs. 2 and 3 and will therefore not be shown here. We add the remark that the slight difference in the spectral shape between the figures of Refs. 2 and 3 is due to a difference in spectral response of the equipment used and disappears after correcting for the spectral response.

In these measurements we found that the detection of the integral spectrum leads to the same result as the measurement of only a part of the spectrum resolved in energy.

Finally, it should be mentioned that our measurements may be considered as one of the simplest examples of quantitative spectroscopy.

5.1. *Experimental*

The samples were cut, polished and etched in a 2N- $\text{Na}_2\text{S}_2\text{O}_3$ solution for about 5 minutes. After a heat treatment as described in Ref. 2, the samples were etched again. The heat treatment has been found to be essential to assure the observability of a well behaved spectrum for the least doped samples. Above a concentration of 10^{16} cm^{-3} iodine the spectral shape is hardly influenced at all by strains introduced during the cooling procedure or by prolonged illumination at low temperatures. Small differences in geometrical shape and surface finish could not completely be avoided and therefore a comparison of the absolute magnitudes of the luminescence intensities of different samples is not directly possible. A sample dependent intensity factor enters the fitting procedure.

The samples were immersed in pumped liquid helium kept at 2.0 K. For the excitation we have used the UV-radiation ($\approx 3.5 \text{ eV}$) of an argon ion laser whose intensity has been stabilised. For the measurements the intensity was varied with calibrated filters. The use of 3.5 eV excitation has the important consequence that the absorption, i.e. the penetration depth or the excited volume respectively is independent of the doping since at this energy the intrinsic absorption dominates. It will also have as a drawback a strong inhomogeneity of the excitation which will be discussed in Appendix 2.

5.2. *Results*

Figure 3 shows the raw data clearly displaying a nonlinearity which is the more pronounced the lower the iodine concentration. Also interesting is the behaviour of the data for the two most strongly doped samples. They can be matched to within experimental accuracy by a slight scaling of the respective luminescence intensities. Since the iodine doping of these samples varies by a factor of ten we argue that the residual nonlinearity must have a reason different from optical saturation. Independent measurements, as explained in Appendix 1, have shown that for UV excitation intensities from an argon laser up to 30 mW the increase of the sample temperature at a bath temperature of 1.0–1.5 K is insignificant (about 0.1 K).²⁾ With increasing excitation density, however, a measurable increase of the sample temperature of several Kelvin degrees has been observed. This temperature increase reduces not only the zero phonon intensity but also the intensity of the LO-phonon replica as can be seen from Ref. 2. We believe that the rise of the sample temperature is the reason for the observed nonlinearity of the two most strongly doped samples.*) In order to account for this temperature effect, we have corrected all our measurements for excitations above 30 mW by a factor defined so that the corrected values of the two most strongly doped samples lie on the straight line corresponding to no optical saturation effects. The experimental curves corrected as described are then fitted to the solution of kinetic equations to be discussed in the next subsection.

²⁾ The difference between this excitation threshold and the lower one mentioned in paragraph 3 is probably due to the difference in focalisation and sample geometry.

*) Note added in proof: Recent measurements with a chopped light source have confirmed this interpretation.

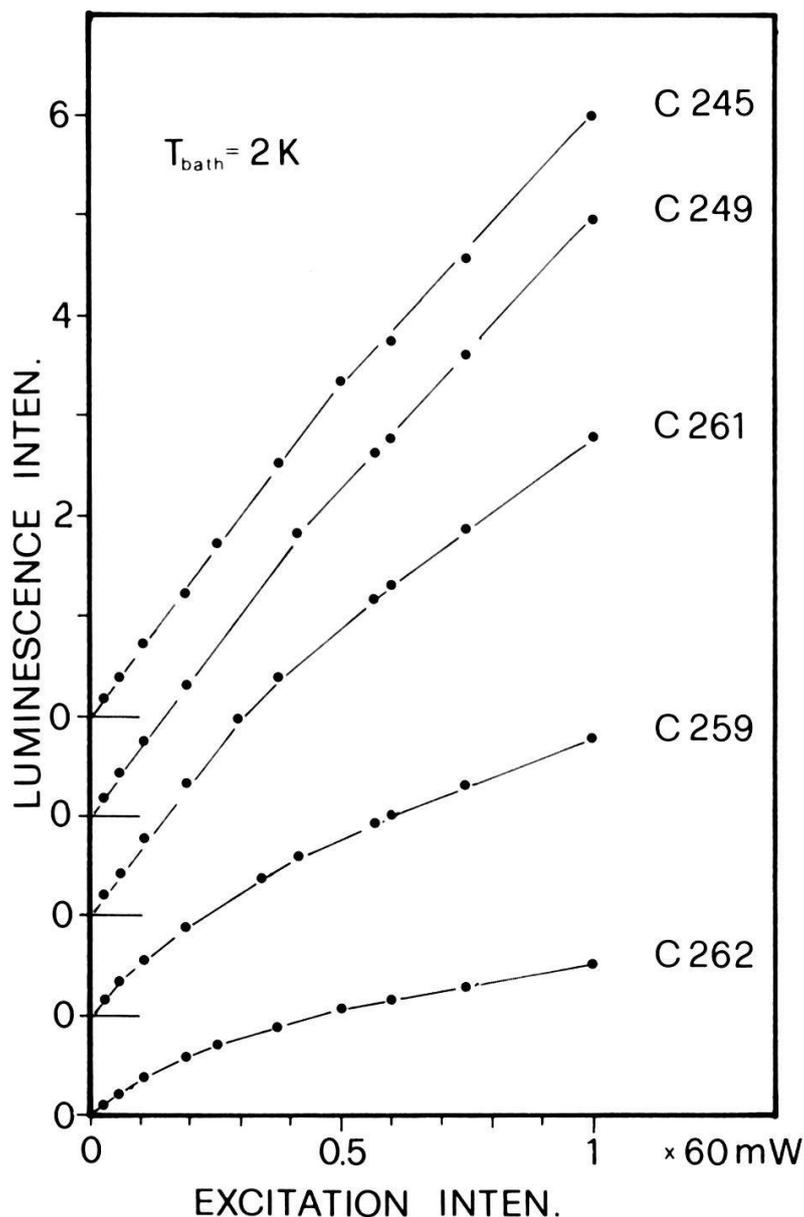


Figure 3
Integrated iodine luminescence intensity (arbitr. units) in the system AgBr:I as a function of excitation intensity. The points correspond to the raw experimental data. The lines connecting the points are guides to the eye.

5.3. Kinetic equations

To explain the concentration related nonlinear photoluminescence response, we propose the following model. While the radiative recombination of bound excitons (n) is assumed to have 100% efficiency and is characterised by a radiative life-time τ , the formation of bound excitons from electron-hole pairs (\tilde{n}) will be the result of two competing processes: the loss of electron-hole pairs described by τ_0 and the formation of bound excitons equal to $A(N-n)$ with N the concentration of iodine impurities. The resulting rate equations are:*)

*) Note added in proof: Due to the much weaker excitation in our case as compared to Ref. [8] we have neglected any biexciton contribution.

$$\begin{aligned} \frac{d\tilde{n}}{dt} &= g - \frac{\tilde{n}}{\tau_0} - \tilde{n}A(N - n), \\ \frac{dn}{dt} &= \tilde{n}A(N - n) - \frac{n}{\tau}, \end{aligned} \tag{6}$$

where g describes the generation of electron-hole pairs by the excitation. The solutions of equation (6) in the steady state are:

$$\begin{aligned} n &= \frac{N}{2} \frac{1}{x} \left(1 - \frac{\tau g}{N} x \right) \left[1 - \left\{ 1 - 4 \frac{\tau g}{N} x^2 \frac{1}{\left(1 + \frac{\tau g}{N} x \right)^2} \right\}^{1/2} \right], \\ \tilde{n} &= \frac{\tau_0}{\tau} (g\tau - n). \end{aligned} \tag{7}$$

It should be noted that $n \rightarrow N$ in the limit of infinitely strong excitation.

The quantity which we fit to the experimental data is the luminescence intensity defined as

$$I_L = B \frac{n}{\tau} \tag{8}$$

with B depending on sample shape, surface quality, light collection, etc. In our discussion, we shall not consider this quantity any more.

The fit to the data is performed by adjusting the two parameters

$$x = \frac{A\tau_0 N}{1 + A\tau_0 N}, \quad \gamma = \frac{BN}{2\tau}. \tag{9}$$

Since in the majority of the cases an expansion of the solution equation (7) was not possible, we have used the exact solution throughout.

Into the fitting procedure enter the following quantities whose values are known experimentally

$$\tau = 18\mu\text{s}, \quad N, \quad g_{\text{max}} = 1.35 \cdot 10^{21} \text{ cm}^{-3} \text{ s}^{-1}.$$

The radiative lifetime has been taken from experiment [18], [19], which gave a value independent of iodine concentration, N , at about 4 K.

N is either known from chemical analysis or from the amount of iodine added to the melt, compare Table 1.

The maximum e-h pair generation rate g_{max} is calculated for a photon density corresponding to 60 mW on a light spot of 2 mm diameter. The energy of the photons being ≈ 3.5 eV. The penetration depth of the light at that energy is about 25 μm . The value of g is then changed by filters with known transmission.

5.4. Discussion

The quality of the fit is satisfactory as can be judged from Fig. 4. In Table 1, we collect the numerical results. The trend in the combination $A\tau_0 N^3$) of rate constants determined from the fit is significant, although the values for the two most strongly doped samples need some discussion.

³⁾ As it will turn out shortly below $A\tau_0 N = \tau_0/\tau^*$ is the branching ratio of loss processes for electron hole pairs.

Table 1

Sample	$N \text{ cm}^{-3}$	$\frac{g_{\max} T}{N}$	γ	x	$A\tau_0 N$	$A\tau_0 \text{ cm}^3$	$n \text{ cm}^{-3}$	$\bar{n} \text{ cm}^{-3}$	$\tau^* = (AN)^{-1} \text{ sec}$	$\tau_{\text{total}} = \tau_0 \frac{1}{1 + A\tau_0 N} \text{ sec}$
C262	$4.3 \cdot 10^{14}$	$5.65 \cdot 10^1$	$4.71 \cdot 10^{-1}$	$3.04 \cdot 10^{-2}$	$3.14 \cdot 10^{-2}$	$7.3 \cdot 10^{-17}$	$3.14 \cdot 10^{14}$	$2.06 \cdot 10^{13}$	$8.3 \cdot 10^{-7}$	$1.6 \cdot 10^{-8}$
C259	$4.3 \cdot 10^{15}$	5.65	1.56	$1.31 \cdot 10^{-1}$	$1.51 \cdot 10^{-1}$	$3.5 \cdot 10^{-17}$	$1.93 \cdot 10^{15}$	$1.93 \cdot 10^{13}$	$8.3 \cdot 10^{-8}$	$1.3 \cdot 10^{-8}$
C261	$2.1 \cdot 10^{16}$	1.16	2.44	$2.86 \cdot 10^{-1}$	$4.0 \cdot 10^{-1}$	$1.9 \cdot 10^{-17}$	$5.5 \cdot 10^{15}$	$1.62 \cdot 10^{13}$	$1.7 \cdot 10^{-8}$	$8.2 \cdot 10^{-9}$
C249	$2.1 \cdot 10^{17}$	$1.16 \cdot 10^{-1}$	3.95	$0.95 < x \leq 1$	≥ 19	$9 \cdot 10^{-17}$	$2.4 \cdot 10^{16}$	$2.6 \cdot 10^{11}$	$1.7 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$
C245	$2.1 \cdot 10^{18}$	$1.16 \cdot 10^{-2}$	$3.80 \cdot 10^1$	$0.95 < x \leq 1$	≥ 19	$0.9 \cdot 10^{-17}$	$2.4 \cdot 10^{16}$	$2.6 \cdot 10^{11}$	$1.7 \cdot 10^{-10}$	$1.7 \cdot 10^{-10}$

The last two columns are calculated using the values of equation (12) and (13).

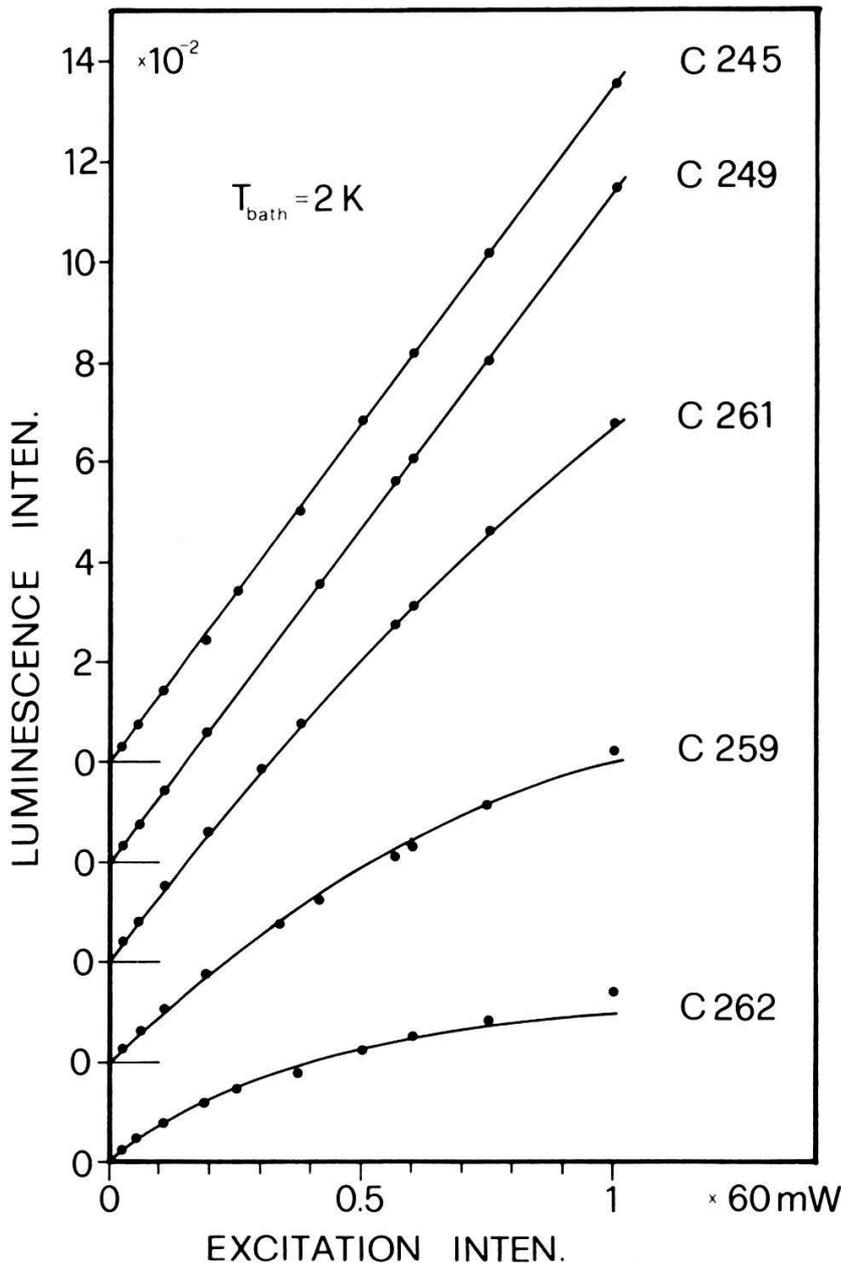


Figure 4
 Integrated iodine luminescence intensity (arbitr. units) in the system AgBr:I as a function of excitation intensity. Fit of the corrected data to equation (8). Per sample there are two fitting points.

First we have to realise that I_L depends linearly on the excitation density only as an asymptotic behaviour. In the limit of a linear dependence the parameter x would go to one and $A\tau_0 N$ to infinity. With the temperature correction applied we have lost the possibility to obtain a more realistic value of $A\tau_0 N$ for the two most strongly doped samples. We therefore have estimated the precision with which we can determine the value $x = 1$ and deduce from this a value for a lower bound of $A\tau_0 N$.

Taking the evidence for all samples together, we obtain a systematic variation of $A\tau_0 N$ with N such that $A\tau_0$ is of the order of 10^{-17} cm^{-3} with the mean value $4.5 \times 10^{-17} \text{ cm}^{-3}$.

It is immediately clear that A has to be related to the absorption cross-

section α/N with the absorption coefficient α by [20]

$$A \approx \frac{\alpha}{N} C_{gr} \quad (10a)$$

where C_{gr} is the group velocity of light. Since the wavelength of interest here is still above the absorption edge we approximate equation (10a) by

$$A \approx \frac{\alpha}{N} \frac{C_{ph}}{n_{stat}}. \quad (10b)$$

Now C_{ph} stands for the phase velocity of light in vacuum and n_{stat} (≈ 3.25) [21] for the static index of refraction. The process corresponding to the formation of bound excitons is the absorption related to the iodine impurity at energies of the indirect band gap (~ 2.7 eV). It has been shown experimentally in Ref. 22 that the absorption cross section at this energy is independent of N and has the value of

$$\frac{\alpha(E = 2,69 \text{ eV})}{N} \approx 3 \cdot 10^{-19} \text{ cm}^2. \quad (11)$$

With equations (10b) and (11), we obtain

$$A = 2.8 \cdot 10^{-19} \text{ cm}^3 \text{ s}^{-1}. \quad (12)$$

This value for A has two interesting consequences:

- 1) $(AN)^{-1}$ equals the effective time constant τ^* for the formation of bound excitons and is given in Table 1. Obviously for relatively pure samples ($N \sim 2 \cdot 10^{16} \text{ cm}^{-3}$ and lower) this time constant is at least 17 ns. This value corresponds well to the remark to be found in Ref. 8 that excitation by pulses of 10 ns fails to excite the iodine bound spectrum. It has to be remarked, however, that τ^* larger than the excitation pulse length is a necessary but not a sufficient condition. In addition a strongly nonlinear second recombination path is necessary.
- 2) The combination of equation (12) with the mean value of $A\tau_0$ yields

$$\tau_0 = 1.6 \cdot 10^{-8} \text{ s} \quad (13)$$

This value of τ_0 means that an electron-hole pair generated in AgBr containing about 10^{16} cm^{-3} iodine has about the same probability to form an iodine bound exciton or to recombine via some (radiationless) "loss" mechanism. The low temperature (~ 1.7 K) mobility of electrons is slightly higher than that of holes, however, both have at least $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [23]. This yields at liquid helium temperatures a carrier diffusion coefficient of $D \approx 25 \text{ cm}^2 \text{ s}^{-1}$. With this value of D and the total free carrier loss described by τ_0 and $(AN)^{-1}$ we calculate a diffusion length between $1.4 \mu\text{m}$ and $6 \mu\text{m}$ which agrees by order of magnitude with the diffusion length derived from cyclotron resonance measurements [23].

5.5. Conclusions

Analysing the optical saturation of various AgBr samples containing different amounts of iodine, we have arrived at numerical values for rate constants. These values are in substantial agreement with a number of different observations. In

particular:

The independence of $A\tau_0$ from the iodine concentration deduced from our measurements is well confirmed by the measured absorption cross sections.

The loss mechanism for electron-hole pairs described by τ_0 is important. While the actual value of τ_0 is certainly sample dependent, in order of magnitude it compares well with other measurements.

Since we have used cw excitation our data are limited by sample heating effects at higher excitation densities. However, at least to some degree, this limitation might be circumvented by introducing a low duty cycle, quasi, cw, pulsed excitation.

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- Eastman-Kodak Co., Rochester, USA	C 261
- Laboratory of Photoprocessing, Bulg. Acad. Sci., Sofia, Bulgaria	C 259
- Dept. Physics Astronom. Univ. North-Carolina, Chapel-Hill, USA	C 262

Appendix 1: Sample temperature

Some time ago tests have been performed employing the measurement of the intensity ratio of Stokes and anti-Stokes lines of a AgBr TA-phonon in Brillouin scattering.⁴⁾ The ratio of the Stokes to anti-Stokes intensity yields directly the temperature of the scattering volume, which is determined by the focus of the 5145 Å laser line on or close to the sample surface.

At a bath temperature of 1.1 K the sample temperature has already risen to about 2.5 to 2.9 K due to the laser beam intensity necessary for the Brillouin scattering to be detectable. Simultaneous excitation with cw UV light created a negligible (~0.1 K) further increase up to 30 mW UV laser power. For cw powers above 30 mW an additional increase in sample temperature is observed. This is intirely consistent with our present observation. Only for more than 30 mW power have the most strongly doped samples shown the behaviour described.

Appendix 2: Influence of inhomogeneous excitation

Any optical excitation for which the radiation is totally absorbed within a fraction of the thickness of the sample represents a strongly inhomogeneous excitation. The effect of such inhomogeneous excitations has been discussed in

⁴⁾ In cooperation with J. R. Sandercock, Lab. RCA Ltd. CH-8048 Zürich (1976).

Ref. 24, and a general method was given to correct for this effect. This method involves an integration which in the general case leads to nontractable integrals; but which for power laws introduces just the power as a correction factor in the denominator: A dependence

$$I_L = 2\gamma(zx - z^2x^2(1-2x)), \quad z = \frac{\tau g}{N} \quad (14a)$$

is corrected to

$$I_L = 2\gamma(zx - \frac{1}{2}z^2x^2(1-2x)). \quad (14b)$$

In the fit of equation (8) to the experimental data we have not taken into account this correction; nevertheless we have obtained a very good fit. The reason for this is twofold:

- a) The diffusion of carriers generated will to some degree reduce the inhomogeneity of the excitation, although in view of the numerical values for the reciprocal absorption coefficient and the diffusion lengths involved this reduction will not be a major effect.
- b) Equation (14a) is the result of an expansion of equation (7) up to terms of second order and has been used to estimate the effect of the correction introduced into equation (14b). It turns out that a slight readjustment of the fitting parameter x ($\sim 5-10\%$) will compensate the correction factor. Since the effect of this readjustment on the rate constants is not of importance we can safely state that in our experiments and analysis we are not sensitive to effects related to the inhomogeneity of the excitation.

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