

Kinetics of Excitons in CdS at Temperature*

Douglas Magde and Herbert Mahr

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

(Received 13 July 1970)

New experimental results of photoluminescence of CdS at He temperatures suggest two alternative models for the fate of an exciton in CdS. The models, presented below, include exciton-exciton interaction and explain in a self-consistent way all known experimental facts. One model assumes that the low over-all luminescent efficiency of CdS at low temperatures is due to the existence of a large concentration of nonradiative traps; it predicts a rate constant of $3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ for the trapping of excitons at traps giving rise to bound exciton luminescence, and a rate constant of $3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ for exciton-exciton interaction which gives rise to luminescence. The alternative model assumes that the over-all loss in excitation is caused by the process of formation of excitons from electron-hole pairs. It uses only known radiative traps, and predicts a rate constant for exciton-exciton interaction of $5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$ and a rate constant for trapping of excitons at radiative traps of $3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$.

I. INTRODUCTION

At helium temperatures the photoluminescence of CdS normally consists of a series of sharp lines near the band edge (the most prominent I_1 and I_2 being associated with bound-exciton decay), and a series of broad green bands at lower photon energies. Recently, it has been found^{1,2} that under intense illumination in the range $1-100 \text{ kW cm}^{-2}$ an additional luminescence feature M appears, the sharp bound exciton lines I_1 and I_2 "saturate" and the broad green bands are not visible at all. Figure 1 shows the relevant experimental results.

The additional luminescence feature M appears under conditions which should favor high concentrations of free excitons. It appears in three substances: CdS, CdSe, and ZnO, and its position is shifted in each case from the free-exciton energy by about an exciton binding energy. It was therefore proposed that the additional luminescence is due to an exciton-exciton interaction in which one exciton, gaining energy, scatters into a higher excited exciton state and the other exciton, losing energy, becomes "photonlike."

In the meantime Henry and Nassau³ reported the first reliable measurements of the lifetimes of the I_1 and I_2 bound exciton lines in CdS. Also measured were the times it takes a free exciton to get trapped ("trapping time") at I_1 or I_2 sites. In addition, it was suggested that the I_1 and I_2 excitons decay predominantly by luminescence, i. e., their luminescence efficiency was almost 1. This is surprising in view of the low over-all luminescent efficiency of CdS at He temperatures.⁴ These measurements were performed at low-intensity levels.

Taken together, these new data suggest two different kinetic models for the fate of free excitons in "good" quality CdS at He temperatures. Both models are self-consistent, in that they explain all presently known experimental data. They cover

the low-intensity excitation level as well as the onset of exciton-exciton interaction at laser excitation levels. Finally, the models predict values for the rate constant of free-exciton trapping at I_1 , I_2 type traps and the rate constant for exciton-exciton interaction. The predicted values of the rate constant for exciton-exciton interaction differ substantially for both models.

The kinetic models to be described neglect completely the well-known "green emission." This emission is not observed at high levels of excitation by pulsed lasers and, in fact, is not expected for the reason that the centers involved occur in concentrations of order $10^{15}-10^{16} \text{ cm}^{-3}$ and decay⁵ with the relatively long lifetime 10^{-7} sec . Hence, these centers are rapidly saturated and represent a negligible decay channel for excitation rates in excess of $R = 10^{24} \text{ photons cm}^{-3} \text{ sec}^{-1}$, an intensity 2 orders of magnitude lower than used in the laser experiments.² Even at low excitation levels, the green emission is only approximately comparable in intensity to the I_1 and I_2 emission.

II. KINETIC MODEL A

This model contains two crucial assumptions which must be tested by further analysis and experiment: One is the assumption that all electron-hole pairs, created by the absorption of light, form free excitons first. Second is the postulate that there exists an efficient exciton trap which dominates exciton trapping and which makes the excitons decay nonradiatively and rapidly. This hypothesis is introduced initially to explain the known over-all luminescence efficiency⁴ of even "good" CdS platelets. Once introduced it leads also to plausible values for all other parameters.

The model assumes, then, that each absorbed photon leads to the creation of a free exciton in a time short compared to the lifetime or trapping

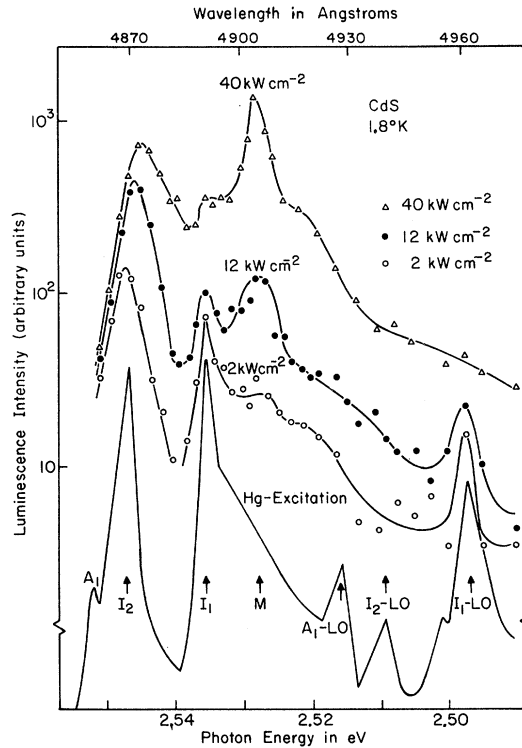


FIG. 1. Luminescence spectra of CdS for intense laser illumination. Band M becomes prominent at higher excitation levels. The lowest curve shows, on a displaced intensity scale, the continuously recorded, conventional photoluminescence. [See Douglas Magde and Herbert Mahr, *Phys. Rev. Letters* **24**, 890 (1970).]

time of excitons. The free exciton can undergo four major processes as shown in Fig. 2. The exciton may be trapped, with rate constant k_{NR} by traps of concentration N_{NR} ; n_{NR} of these are occupied. These traps deexcite the exciton without radiation. The exciton may be trapped by traps of the kind which give rise to I_1 and I_2 bound-exciton lines. Let the rate constant be k_R and the total concentration N_R ; n_R of these are occupied. Finally, we must allow for exciton-exciton interaction. A free exciton may scatter (inelastically) from another free exciton with a rate constant k_{ff} . Let n_f be the free-exciton concentration. Free excitons may interact with excitons bound to radiative traps with a rate constant k_{ft} . Free excitons may also interact with excitons bound to nonradiative traps, rate constant k'_{ft} .

The rate of change of exciton concentration is then given by

$$\frac{dn_f}{dt} = R - k_R(N_R - n_R)n_f - k_{NR}(N_{NR} - n_{NR})n_f - k_{ff}n_f^2 - k_{ft}n_Rn_f - k'_{ft}n_{NR}n_f. \quad (1)$$

R is the rate of absorption of photons in $\text{cm}^{-3}\text{sec}^{-1}$, which by assumption is the rate at which free excitons

are created.

Trapped excitons may decay with rate constant k_0 emitting luminescent radiation (lines I_1 , I_2) with efficiency α . The fraction $1 - \alpha$ of trapped excitons n_R may decay nonradiatively, most likely through an Auger process.³ The rate of change of the concentration of "radiative" traps is then given by

$$\frac{dn_R}{dt} = k_R(N_R - n_R)n_f - k_{ft}n_Rn_f - k_0n_R. \quad (2)$$

Exciton-exciton interaction (Fig. 2) may lead to a scattering process in which one exciton is scattered into a higher excited exciton state, whereas the other one is scattered to lower energy. The lower-energy exciton is photonlike, and will leave the crystal as a luminescence photon (band M ; Fig. 1). Exciton-exciton interaction may also lead to nonradiative deexcitation of one exciton; the other exciton gains the energy of the first and is excited high into the continuum (Auger process). Let the ratio of luminescent (M band) to the total exciton-exciton scattering be β .

Finally, in Fig. 2, occupied traps may scatter free excitons. In one type of process, similar to the one which gives rise to band M , the trapped exciton is raised to a higher excited state or ionized state, whereas the free exciton is scattered to a photonlike, lower-energy exciton state. This lower-energy exciton leaves the crystal as a "luminescent" photon. Another possible process is the deexcitation of the free exciton and the excitation of the trapped exciton high into the continuum (Auger process).

Under the conditions of the experiments quoted above^{2,3} the excitation time was longer than the

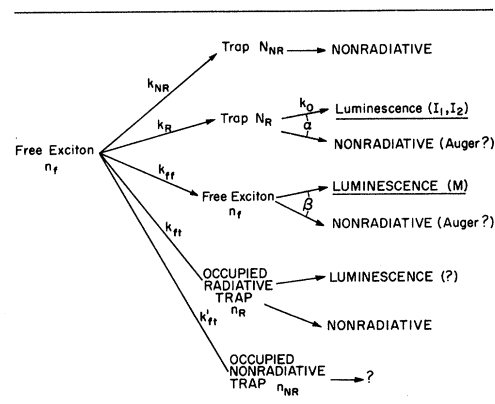


FIG. 2. The fate of free excitons: schematic display of possible interaction of free excitons with unoccupied traps, other free excitons and trapped excitons (occupied traps). Rate constants (k) and concentrations (N , n) are as indicated. Also indicated are possible deexcitation mechanisms, their rate constants (k_0), and the fraction of radiative deexcitation (α , β).

trapping or radiative decay time of excitons. We shall therefore look for steady-state solutions, i. e.,

$$\frac{dn_f}{dt} = \frac{dn_R}{dt} = 0.$$

In solving the rate equations it was assumed that the nonradiative traps are not saturated under the conditions of the laser experiments, i. e., $N_{NR} \gg n_{NR}$. It was also assumed that the interaction of free excitons with excitons bound to traps could be neglected compared to the trapping of free excitons at traps ($k_{NR} N_R \gg k_{ft} n_R, k_{ft}' n_{NR}$). In addition, it was assumed that $k_R \gg k_{ft}$. A discussion of the possible implications of these assumptions and a derivation of a solution to the rate equations without these assumptions is given in Appendix A.

Solutions of the rate equations for steady-state condition leads then to

$$\frac{R}{N_R k_0} = \frac{k_R N_R + k_{NR} N_{NR}}{k_R N_R} \frac{x}{1-x} - \left(1-x - \frac{k_{ff} k_0}{k_R N_R k_R}\right) \left(\frac{x}{1-x}\right)^2 \quad (3)$$

and

$$n_f = \frac{k_0}{k_R} \frac{x}{1-x}; \quad x = \frac{n_R}{N_R}. \quad (4)$$

As long as

$$\frac{k_R N_R + k_{NR} N_{NR}}{k_R N_R} > \frac{x}{1-x}$$

and

$$\frac{k_{ff} k_0}{k_R N_R k_R} \approx 1,$$

the second term in (3) can be neglected. Appendix B shows that, for the experimental conditions of the laser experiments of Ref. 2, the second term is actually small. In this case,

$$\frac{R}{N_R k_0} = \frac{k_R N_R + k_{NR} N_{NR}}{k_R N_R} \frac{x}{1-x}, \quad (5)$$

$$n_f = R / (k_R N_R + k_{NR} N_{NR}), \quad (6)$$

and

$$n_R = N_R R / [(k_R N_R + k_{NR} N_{NR}) (k_0/k_R) + R]. \quad (7)$$

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

$$\begin{aligned} \frac{dN_{I_1, I_2}}{dt} &= \alpha k_0 n_R \\ &= \alpha \frac{R}{(k_R N_R + k_{NR} N_{NR}) / k_R N_R + R / k_0 N_R}. \end{aligned} \quad (8)$$

The luminescence observed in band M due to exciton-exciton interaction, that is, the rate of emission of M -band photons, is given by

$$\frac{dN_M}{dt} = \beta k_{ff} n_f^2 = \beta k_{ff} \frac{R^2}{(k_R N_R + k_{NR} N_{NR})^2}. \quad (9)$$

α and β are the fraction of radiative deexcitation of traps and of exciton-exciton interactions which produce luminescence, respectively.

Equation (8) predicts a linear rise of luminescent intensity with excitation intensity (R) at low values of excitation, and saturation of luminescence emission at high values of R with a value of $(dN_{I_1, I_2}/dt)_{\text{saturation}} = \alpha/k_0 N_R$.

Equation (9) predicts a quadratic dependence of luminescence emitted into band M on incident intensity R .

III. NUMERICAL VALUES FOR MODEL A

Values obtained by Henry and Nassau³ for "good" platelets of CdS are $k_R N_R + k_{NR} N_{NR} \approx 10^9 \text{ sec}^{-1}$; $k_0 \approx 10^9 \text{ sec}^{-1}$; $\alpha \approx 1$. These values are accurate to within a factor of 2 for both I_1 and I_2 . From the laser work² (Fig. 1), it is observed that saturation of trapped exciton luminescence and the appearance of M -band luminescence both set in at about 30-kW/cm² incident laser intensity. Using an absorption constant of $\kappa = 10^{25} \text{ cm}^{-1}$ and a reflection loss of 50%, we calculate the absorbed rate of photons per volume as $R = \frac{1}{2} I_0 \kappa / \hbar \omega$ or $R = 3 \times 10^{27} \text{ cm}^{-3} \text{ sec}^{-1}$ for $I_0 = 30 \text{ kW/cm}^2$.

Saturation of trapped exciton luminescence is predicted by Eq. (7) to set in when $(k_R N_R + k_{NR} N_{NR}) / k_R N_R = R / k_0 N_R$ or $R = (k_0 / k_R) (k_R N_R + k_{NR} N_{NR})$; for $R = 3 \times 10^{27} \text{ cm}^{-3} \text{ sec}^{-1}$ we get for the unknown $k_R = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$.

The over-all quantum efficiency for bound-exciton emission (I_1 and I_2 line) is $\eta = (\text{photons emitted into } I_1, I_2) / (\text{photons absorbed}) = (dN_{I_1, I_2}/dt) / R$. From (8) we get at low-excitation levels below saturation

$$\eta = \frac{dN_{I_1, I_2}}{dt} / R = \alpha \frac{k_R N_R}{k_R N_R + k_{NR} N_{NR}}. \quad (10)$$

If $N_R = 3 \times 10^{15} \text{ cm}^{-3}$ [this is an estimate from the linewidth of luminescence fine structure in the I lines (not resolved in Fig. 1) in comparison with the work of Thomas and Hopfield⁶] and $\alpha \approx 1$, $k_R = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, $k_R N_R + k_{NR} N_{NR} = 10^9 \text{ sec}^{-1}$, then

$$\eta = \frac{k_R N_R}{k_R N_R + k_{NR} N_{NR}} \approx 10^{-3}. \quad (11)$$

Previously, the low over-all efficiency of edge luminescence in CdS at 1.8 °K was explained as being due to a nonradiative deexcitation (Auger ef-

fect) of the trapped exciton. The new experimental results of Henry and Nassau,³ suggesting $\alpha \approx 1$, rule out this possibility. It was with this discrepancy in mind that the present model was constructed.

Band *M* becomes "comparable" to the I_2 and I_1 bands (see Fig. 1) in the neighborhood of an incident intensity of 30 kW/cm² or $R = 3 \times 10^{27}$ cm⁻¹ sec⁻¹. From Eq. (6) we calculate an exciton density of $n_f \approx 3 \times 10^{18}$ cm⁻³.

Knowledge of the particular free-exciton concentration which leads to equal contributions to the luminescence by *M* and (I_1, I_2) emission, allows us to calculate the rate constant k_{ff} . From Eqs. (8) and (9) we get

$$\alpha k_0 n_R = \beta k_{ff} n_f^2 \quad (12)$$

or

$$\frac{\alpha k_R N_R R}{2(k_R N_R + k_{NR} N_{NR})} = \beta k_{ff} \frac{R^2}{(k_R N_R + k_{NR} N_{NR})^2},$$

or with Eq. (6),

$$\beta k_{ff} = \alpha k_R N_R / n_f. \quad (13)$$

With

$$N_R = 3 \times 10^{15} \text{ cm}^{-3}, \quad k_R = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1};$$

$$n_f = 3 \times 10^{18} \text{ cm}^{-3}; \quad \alpha = 1$$

we get

$$\beta k_{ff} \approx 3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}. \quad (14)$$

The interaction of free excitons with radiative traps (I_1, I_2 type) ought to produce a luminescent band similar to band *M*.⁷ Such a band might actually be present in the laser work² (see Fig. 1) at an energy shifted by the exciton binding energy from the I_2 line. Because of its proportionality to $n_R n_f$, this luminescent band should grow quadratically with *R* first [see Eqs. (6) and (7)] and then near saturation of the bound-exciton lines it should proceed to rise proportional to *R*. It should be most favorable to observe this band near saturation because it might overtake linear bound-exciton features and still be comparable to the *M* band. The curves for 12 and 40 kW/cm² of Fig. 1 show possibly this band although its assignment to trapped free-exciton interaction is far from unique. Compared to $k_{ff} n_f^2$, the term $k_{ff} n_R n_f$ contains an extra factor $k_R N_R / k_0 \approx 10^{-3}$; so other things being equal, this band should be considerably smaller than band *M*.

IV. KINETIC MODEL B

A crucial assumption of the model was that electron-hole pairs created by absorption of light would form free excitons. The over-all loss of excitation, measured as a low over-all quantum efficiency of

luminescence in CdS at He temperatures, is then blamed on nonradiative traps.

Alternatively, one might be tempted to assume that the loss of excitation takes place while electron-hole pairs form excitons. Let us now assume that only a fraction $R'/R = 10^{-3}$ of electron-hole pairs form free excitons and that no nonradiative traps are present ($N_{NR} = 0$).

Equation (3) would now read

$$\frac{R'}{N_R k_0} = \frac{x}{1-x} - \left(1-x - \frac{k_{ff} k_0}{k_R k_R N_R}\right) \left(\frac{x}{1-x}\right)^2. \quad (3')$$

As long as

$$\left(1-x - \frac{k_{ff} k_0}{k_R k_R N_R}\right) \left(\frac{x}{1-x}\right) < 1$$

(for numerical values see Appendix C), we may neglect the term quadratic in $x/(1-x)$ and get simply

$$\frac{R'}{N_R k_0} = \frac{x}{1-x} \frac{k_R}{k_0} n_f \quad \text{or} \quad n_f = \frac{R'}{N_R k_R}. \quad (4')$$

Near saturation ($I_0 \approx 30$ kW/cm² or $R = 3 \times 10^{27}$ cm⁻³ sec⁻¹) we get

$$n_f = (3 \times 10^{24}) / 10^9 \approx 3 \times 10^{15} \text{ cm}^{-3},$$

a very low concentration indeed. It does, however, agree with the assumption that $N_R = 3 \times 10^{15}$ cm⁻³ radiative traps are nearly filled at 30 kW/cm². The low free-exciton concentration does, however, lead to a very large rate constant for exciton-exciton interaction. Again assuming that

$$\left(1-x - \frac{k_{ff} k_0}{k_R k_R N_R}\right) \frac{x}{1-x} < 1,$$

we get from Eqs. (8) and (9) for $I_0 = 30$ kW/cm² ($R = 3 \times 10^{27}$ cm⁻³ sec⁻¹)

$$\alpha k_0 n_R = \beta k_{ff} n_f^2 \quad \text{with} \quad n_R = R' N_R / N_R k_0 + R'$$

and

$$n_f = R' / N_R k_R$$

or

$$\beta k_{ff} = (N_R k_R)^2 / 2R' = 5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}. \quad (5')$$

This seems like a tremendously large bimolecular rate for exciton-exciton scattering into the suggested radiative mode (band *M*).

The rate constant of trapping of free excitons at I_1, I_2 type traps is now given by

$$k_R = k_R N_R / N_R = 3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}. \quad (6')$$

V. CONCLUSIONS

The values of the rate constants of model B appear rather large, in particular, the bimolecular rate of exciton-exciton interaction. In the process

proposed for exciton-exciton scattering it might seem that the scattering of an exciton from an excitonlike to a photonlike form would result in very small transition probabilities. On the other hand, Hopfield⁸ pointed out that although the excitation spectrum of exciton polaritons becomes photonlike very rapidly, away from the exciton resonance, the wave function remains excitonlike for very much longer. In the energy region of photons of band M ($\hbar\omega_M$), 80% of the wave function of the exciton polariton is still excitonlike. However, preliminary calculations by Buttner⁹ of the bimolecular exciton-exciton interaction rate suggest that even with an excitonlike wave function around $\hbar\omega_M$ the values are closer to the ones proposed by model A.

There are experimental tests which could distinguish between models A and B. In model A the vast reservoir of nonradiative traps would determine the lifetime of the free excitons to be constant long after the onset of exciton-exciton scattering. Conversely, in model B exciton-exciton interaction

would rapidly decrease the free-exciton lifetime. If model A describes the real behavior of excitons, free excitons would start to be "tightly packed" at a concentration of $4.5 \times 10^{19} \text{ cm}^{-3}$ (for an exciton "radius" of 28 Å). Given a lifetime of free excitons of $\approx 10^{-9}$ sec, such a concentration would be reached at about 400-kW/cm² incident light intensity. Interesting changes could be expected near or below such excitation levels. On the other hand, given model B with its prediction of $R'/R = 10^{-3}$ efficiency for exciton formation, we could not expect to see any effects of "exciton crowding" before reaching excitation levels in excess of 400 MW/cm². Crystals tend to be destroyed at these levels.

ACKNOWLEDGMENTS

The authors would like to thank Dr. C. H. Henry for comments on the impurity content of "good quality" CdS. We would also like to thank Dr. H. Buttner for transmitting preliminary results of calculations of the exciton-exciton interaction.

APPENDIX A

From Eqs. (1) and (2), it follows that

$$\frac{R}{N_R k_0} = \frac{k_{NR}(N_{NR} - n_{NR}) + k_R N_R + k_{ft} n_R + k'_{ft} n_{NR}}{k_R N_R} \frac{x}{1 - [(k_R + k_{ft})/k_R] x} - \left(1 - \frac{k_R + k_{ft}}{k_R} x - \frac{k_{ft} k_0}{N_R k_R k_R}\right) \left(\frac{x}{1 - (k_R + k_{ft})/k_R}\right)^2 \quad (\text{A1})$$

and

$$n_f = \frac{k_0}{k_R} \left(\frac{x}{1 - [(k_R + k_{ft})/k_R] x}\right); \quad x = \frac{n_R}{N_R} \quad (\text{A2})$$

If we can neglect the quadratic term in (A1) we get

$$\frac{R}{N_R k_0} = \frac{k_{NR}(N_{NR} - n_{NR}) + k_R N_R + k_{ft} n_R + k'_{ft} n_{NR}}{k_R N_R} \frac{x}{1 - [(k_R + k_{ft})/k_R] x}, \quad (\text{A3})$$

$$n_f = \frac{R}{k_{NR}(N_{NR} - n_{NR}) + k_R n_R + k_{ft} n_R + k'_{ft} n_{NR}}, \quad (\text{A4})$$

$$n_R = \frac{N_R k_R}{k_R + k_{ft}} \frac{R}{[k_0/(k_R + k_{ft})] [k_{NR}(N_{NR} - n_{NR}) + k_R N_R + k_{ft} n_R + k'_{ft} n_{NR}] + R}. \quad (\text{A5})$$

I_1 and I_2 luminescence is given by

$$\frac{dN_{I_1, I_2}}{dt} = \alpha k_0 n_R = \alpha k_0 \frac{N_R k_R}{k_R + k_{ft}} \frac{R}{[k_0/(k_R + k_{ft})] [k_{NR}(N_{NR} - n_{NR}) + k_R N_R + k_{ft} n_R + k'_{ft} n_{NR}] + R}, \quad (\text{A6})$$

and M -band luminescence by

$$\frac{dN_M}{dt} = \beta k_{ft} n_f^2 = \beta k_{ft} \frac{R^2}{[k_{NR}(N_{NR} - n_{NR}) + k_R N_R + k_{ft} n_R + k'_{ft} n_{NR}]^2}. \quad (\text{A7})$$

The bound-exciton luminescence (I_1, I_2) predicted by (A6) is linear in excitation intensity (R) as long as $N_{NR} \gg n_{NR}$ and $k_{NR}N_{NR} \gg k_{ft}n_{NR}, k'_{ft}n_{NR}$. The first condition of nonsaturation of nonradiative traps depends on the concentration N_{NR} of such traps as well as on the deexcitation time for excitons getting trapped at such sites. If k_{NR} is comparable to $k_R = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, then from a measured value for $k_R N_R + k_{NR} N_{NR}$ of 10^9 sec^{-1} at low excitation levels,³ we get

$$N_{NR} = 10^9 / (3 \times 10^{-10}) \approx 3 \times 10^{18} / \text{cm}^3.$$

With an estimated lifetime for excitons in such non-radiative traps of $\tau_{NR} = 10^{-10} - 10^{-11} \text{ sec}$ and a rate of creation approximately equal to R , we get $n_{NR} \approx \tau_{NR} R$, which at $R = 3 \times 10^{27} \text{ cm}^3 \text{ sec}^{-1}$ gives $n_{NR} \approx 3 \times 10^{17} - 3 \times 10^{16} \text{ cm}^{-3}$. We would then just about escape trap saturation near the highest levels of laser excitation used in Ref. 2. If saturation of traps is reached, however, before saturation of I_1, I_2 luminescence sets in (at 30 kW/cm^2 in the experiments), then the luminescence intensity should rise steeper than linearly with incident intensity. On the other hand, should saturation of traps occur after saturation of luminescence due to the filling of radiative traps, then saturation is approached more quickly. None of these features is observed in the experiments of Fig. 1.

The condition $k_{NR}N_{NR} \gg k_{ft}n_{NR}$ is most likely fulfilled. Because $N_{NR} \gg N_R \gg n_{NR}$ ($N_{NR} \approx 3 \times 10^{18} \text{ cm}^{-3}$, $N_R \approx 3 \times 10^{15} \text{ cm}^{-3}$) and probably the interaction constant k_{ft} for the interaction of free excitons with excitons trapped at I_1, I_2 sites is not much larger than k_{NR} , the rate constant for trapping of free excitons at trapping sites, we are justified in neglect-

ing $k_{ft}n_{NR}$. It is more difficult to estimate the importance of the term $k'_{ft}n_{NR}$. If $n_{NR} \ll N_{NR}$ throughout the regime of measurements, then it is probably justifiable to neglect $k'_{ft}n_{NR}$ compared to $k_{NR}N_{NR}$.

APPENDIX B

It was assumed before [Eq. (3)] that $k_{ff}k_0/k_R N_R k_R \approx 1$. With $k_{ff} = 3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$; $k_R N_R = 10^6 \text{ sec}^{-1}$; $k_R = 3 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$; $k_0 = 10^9 \text{ sec}^{-1}$ we get

$$k_{ff}k_0/k_R N_R k_R \approx 1. \quad (\text{B1})$$

Thus up to

$$\frac{1}{10} [(k_R N_R + k_{NR} N_{NR}) / k_R N_R] \approx x / (1-x)$$

we can neglect the second term in Eq. (3) with a 10% error. From Eq. (5) this happens when

$$R / N_R k_0 = \frac{1}{10} [(k_R N_R + k_{NR} N_{NR}) / k_R N_R]^2 \approx 10^5, \\ R = 3 \times 10^{29} \text{ cm}^{-3} \text{ sec}^{-1}; I_0 = 3 \text{ MW/cm}^2 \text{ incident laser intensity. This is well above the laser intensities used for the laser work.}^2$$

APPENDIX C

Let us check on the validity of neglecting the second term in (3')

$$\frac{k_{ff}k_0}{k_R N_R k_R} = \frac{5 \times 10^{-7} 10^9}{3 \times 10^{-7} 10^9} \approx 1,$$

$$x / (1-x) = (k_R / k_0) n_f = [(3 \times 10^{-7}) / 10^9] 3 \times 10^{15} \approx 1.$$

Although near saturation, we are not quite justified by this estimate to neglect the quadratic term, its consideration would not change the order-of-magnitude values obtained for n_f and βk_{ff} .

*Work supported by the Office of Naval Research under contract No. NONR-401(47), Technical Report No. 33, and by the Advanced Research Projects Agency through the Materials Science Center at Cornell University, MSC Report No. 1395.

¹C. Benoit la Guillaume, J. M. Debever, and F. Salvan, in *Proceedings of the International Conference on II-VI Semiconducting Compounds*, 1967 (Benjamin, New York, 1967), p. 669.

²Douglas Magde and Herbert Mahr, *Phys. Rev. Letters* **24**, 890 (1970).

³C. H. Henry and K. Nassau, *Phys. Rev. B* **1**, 1628 (1970).

⁴D. G. Thomas and J. J. Hopfield, *J. Appl. Phys.* **33**, 3243 (1962).

⁵D. G. Thomas, R. Dingle, and J. D. Cuthbert, in *Proceedings of the International Conference on II-VI Semiconducting Compounds*, 1967 (Benjamin, New York, 1967), p. 863.

⁶D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **175**, 1021 (1968).

⁷K. Era and D. W. Langer claim to have seen luminescence from the I_1 bound-exciton-free-exciton interaction in CdS [*Bull. Am. Phys. Soc.* **15**, 349 (1970)].

⁸J. J. Hopfield, *Phys. Rev.* **182**, 945 (1969).

⁹H. Buttner (private communication).