Excitation-intensity dependence of shallow and deep-level photoluminescence transitions in semiconductors

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ABSTRACT

Photoluminescence characterization of semiconductors is a powerful tool for studying shallow and deep defects. Excitation-intensity-dependent measurements at low temperatures are typically analyzed to distinguish between exciton and defect related transitions. We have extended existing models based on rate equations to include the contribution of deep defects. Generally, it is observed that the photoluminescence intensity I_{PL} follows a power law $I_{PL} \propto \phi^k$ with the excitation intensity ϕ. We show that the exponent k takes on values of multiples of $1/2$. The values depend on the availability of additional recombination channels. Defect levels can saturate at high enough excitation intensities, leading to one or several crossover points from one power law behavior to another. Power law exponents different from $n/2$ can result from the transition region between two limiting cases of linear power laws. Model functions for the analytical description of these transitional excitation dependencies are derived and the analysis is applied to chalcopyrite thin films and to numerical data. The saturation effects of defects by excess carriers as well as the influence of deep recombination centers can be extracted with the help of the presented model, which extends existing theories.

I. INTRODUCTION

Excitation-dependent photoluminescence measurements are often used as a tool to distinguish excitons, free-to-bound or donor-acceptor-pair transitions in semiconductors.[1–22] The different transitions are generally identified by measuring the photoluminescence intensity in dependence of the laser power. For example, in Ref. 1, a description of the transitions with rate equations is given as well as numerical results and experimental measurements on CdTe. It is shown that the intensity of the photoluminescence transitions follows a power law behavior with $I_{PL} \propto \phi^k$ in simplified cases. The excitation power density ϕ is varied over several orders of magnitude. The power law exponent k is between 1 and 2 for free- or bound-exciton transitions and below 1 for free-to-bound or donor-acceptor pair transitions. This model is used in the literature to distinguish between excitonic and defect related transitions.[1–15] However, it has been shown that the attribution can be erroneous if deep levels are present as well.[17,19] For example, we will show in the following that, for certain cases, the PL intensity of a shallow donor-

acceptor pair transition can increase with a superlinear power law if deep recombination centers are present. Furthermore, it is often observed that the log-log plot of PL intensity vs excitation intensity is not linear. Several models exist for the analytical or numerical description of nonlinear log-log plots.[26] To detect this nonlinear behavior, it is very important to measure the excitation dependence over several orders of magnitude.

In the following, we derive a general model that combines limiting cases of low and high excitation regimes, and we describe the excitation dependence with a phenomenological fitting function. The model is applicable to cases with and without any number of deep defect levels. The motivation for the present study arises from the fact that, in the literature, including our own work, on discrete photoluminescence transitions at low temperatures, it is often taken for granted that a power law exponent between 1 and 2 indicates excitonic transition, whereas only an exponent smaller than 1 indicates a defect related transition.[1–15] In several publications with excitation-intensity-dependent photoluminescence measurements,

only single power law exponents are fitted to the experimental data.[5–15] From this, and based on the results in Ref. [1], different types of transitions are then discriminated from a power law exponent larger or smaller than 1.

We will show in the following that the conventional characterization does not hold in general when deeper luminescence transitions dominate. One needs to keep in mind that deep defect transitions might be present but not detected because they are outside the sensitivity range of the detector used. While exciton transitions always yield power law exponents above or equal to 1 (in accordance with Ref. [1]), defect related transitions, such as free-to-bound or donor-acceptor pair transitions, can also increase superlinearly with excitation and, therefore, could be falsely attributed to exciton transitions. Furthermore, our calculations and simulations indicate again that a large measurement range of excitation intensities is necessary.

If the power law exponents are measured for each unknown photoluminescence transition in the low and high excitation regimes, our model can yield a full overview of all involved transitions: a unique set of exponents leads to a unique set of observed transitions. It is possible to discriminate defect levels if only the exponents are known from the experiment. The results of Ref. [1] will be extended and a novel characterization method for defect studies is given. In general, nonlinear log-log plots are a result of the rate equations when changing more than 2 orders of magnitude of excitation intensity.

In Sec. II, a theoretical description of the rate equations is given for two situations with shallow or deep defects. A model function for nonlinear log-log plots is derived in Sec. III. For validation, the model is compared with numerical results and fitted to experimental data on chalcopyrite semiconductors in Sec. IV.

II. THEORETICAL EXCITATION DEPENDENCE

We consider a semiconductor with a shallow acceptor, a shallow donor, and an additional deep donorlike recombination center and the semiconductor emits excitonic luminescence at low temperatures. A schematic overview is given in Fig. 1. We make the following assumptions:

(i)   We consider an experiment with a continuous wave excitation and a steady state condition.

(ii) We assume a homogenous sample, where transport effects can be neglected.

(iii) We assume that at low temperature we can neglect thermally excited carriers; for example, only photogenerated electrons and holes are considered.

(iv) We assume that the transition coefficients are prefactors independent of the generation rate.

(v)   We neglect high excitation effects like Auger-recombination, Fermi-levels inside the bands, or stimulated emission.

(vi) Resonant defect absorption is not considered. This process is negligible for excitation energies far above the bandgap.

For typical low temperature PL experiments with laser excitation on semiconductors with a reasonable PL yield, these assumptions are likely to be fulfilled.

A. Rate equations and charge balance

In a photoluminescence experiment, electron hole pairs are generated at a rate G. This rate is proportional to the laser power density ϕ with a coefficient c_ϕ. Within 10^{-12} s, the excess carriers relax to the band edges[23] and are distributed according to a Fermi distribution with a temperature close to the temperature of the lattice.

After this process, transitions between the free carriers and defect levels will occur. An overview of possible transitions for the electrons is shown in Fig. 1 as an example. The rate of these transitions is proportional to the electron density in the upper state n_i and the hole density (empty states) in the lower state n_j with a transition coefficient c_{ij}.[24] These transition coefficients can cover radiative and nonradiative transitions. The rate equations are given for the free electron (hole) concentration n (p), the density of neutral donors (occupied by electrons) N_D^0, the density of neutral deep defects (occupied by electrons) N_S^0, and the density of neutral acceptors (occupied with holes) N_A^0. The corresponding constant total defect densities are written without the superscript for the charge state, for example, $N_i = N_i^0 + N_i^{+/-}$ for single charge levels,

$$\frac{dn}{dt} = \underbrace{c_\phi\, \phi}_{\text{generation}} - \underbrace{c_{nD}\, n(N_D - N_D^0)}_{\text{e-capture (eD}^+)} - \underbrace{c_{nS}\, n(N_S - N_S^0)}_{\text{e-capture (eS}^+)}$$
$$- \underbrace{c_{nA}\, nN_A^0}_{\text{FB}_A\,(\text{eA}^0)} - \underbrace{c_{np}\, np}_{\text{BB/FX}}, \tag{1}$$

$$\frac{dN_D^0}{dt} = \underbrace{c_{nD}\, n(N_D - N_D^0)}_{\text{e-capture (eD}^+)} - \underbrace{c_{DS}\, N_D^0(N_S - N_S^0)}_{\text{e-capture (D}^0\text{S}^+)}$$
$$- \underbrace{c_{DA}\, N_D^0 N_A^0}_{\text{DA (D}^0\text{A}^0)} - \underbrace{c_{Dp}\, N_D^0 p}_{\text{FB}_D\,(\text{D}^0\text{h})}, \tag{2}$$

$$\frac{dN_A^0}{dt} = \underbrace{c_{Ap}\, (N_A - N_A^0)p}_{\text{h-capture (A}^-\text{h})} - \underbrace{c_{DA}\, N_D^0 N_A^0}_{\text{DA (D}^0\text{A}^0)}$$
$$- \underbrace{c_{SA}\, N_S^0 N_A^0}_{\text{SA (S}^0\text{A}^0)} - \underbrace{c_{nA}\, nN_A^0}_{\text{FB}_A\,(\text{eA}^0)}, \tag{3}$$

$$\frac{dN_S^0}{dt} = \underbrace{c_{nS}\, n(N_S - N_S^0)}_{\text{e-capture (eS}^+)} + \underbrace{c_{DS}\, N_D^0(N_S - N_S^0)}_{\text{e-capture (D}^0\text{S}^0)}$$
$$- \underbrace{c_{SA}\, N_S^0 N_A^0}_{\text{SA (S}^0\text{A}^0)} - \underbrace{c_{Sp}\, N_S^0 p}_{\text{FB}_S\,(\text{S}^0\text{h})}. \tag{4}$$

Charge neutrality is given by

$$n + N_A^- = p + N_D^+ + N_S^+, \tag{5}$$

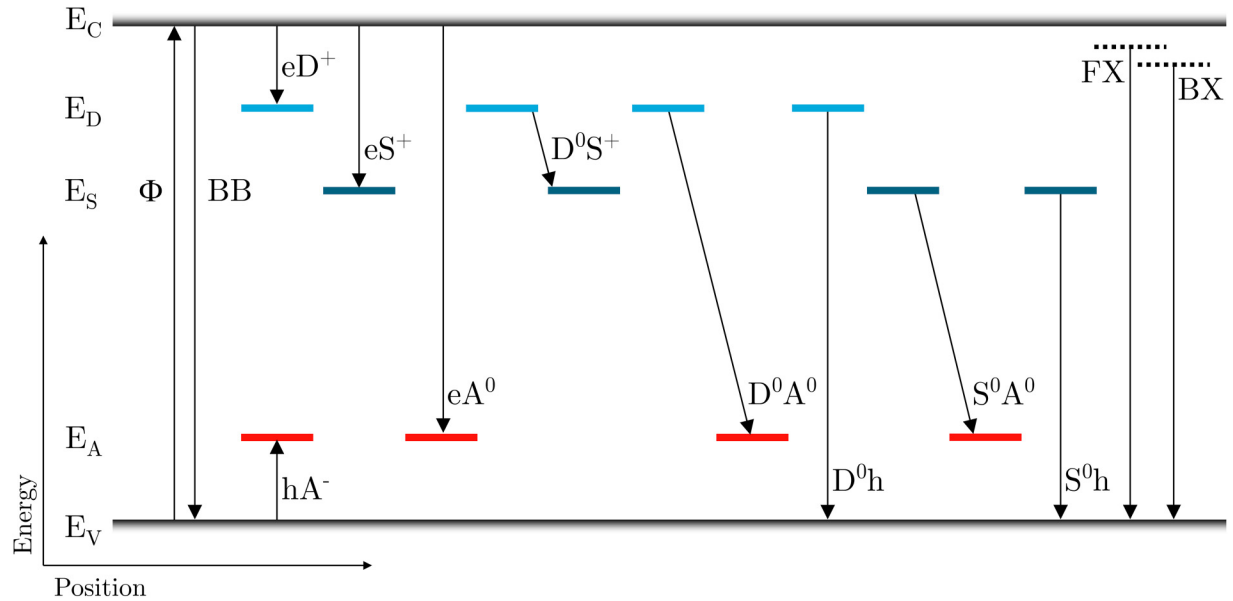assuming single charge levels for all defects.

FIG. 1. Band diagram of transitions in a semiconductor with a shallow donor level at E_D, a shallow acceptor level at E_A, and a deep donorlike level at E_S. Free (FX) and bound (BX) exciton transitions are given with reference to the band-to-band (BB) transition. The conduction band minimum is labeled with E_C and the valence band maximum with E_V.

Since we consider low temperatures, the band-to-band (BB) transition is dominated by the excitonic transition. Free- and bound-exciton transitions are labeled by FX and BX, respectively. Bound excitons are briefly discussed in the supplementary material (S2). If not stated otherwise, we will always refer to the recombination dynamics of free excitons when we discuss transitions involving excitons. Free excitons can be treated the same way as band-to-band transitions: both transitions are proportional to electron and hole concentrations in the band and we do not discuss the transition energies.

Obviously, the overall intensity of the free exciton and band-to-band transition are different, which can be accounted for by different prefactors c_{FX} and c_{BB}. At low temperatures where the thermal energy is below the exciton binding energy and the free carrier concentration is low, the band-to-band transition is unlikely and only the free exciton transition needs to be considered. Since we neglect thermal carrier generation at low temperatures, electron and hole densities are given by the photogenerated carriers only: Δn and Δp. For each state, the rate equations are given in Eqs. (1)–(4). The different terms are labeled with transitions from donor-to-acceptor (DA), deep-donor-to-acceptor (SA), and free-to-bound (FB) with the subscript of the involved defect levels. Since we assume steady state, the time derivative of the concentrations is zero, and the generation of carriers equals their recombination.

For each transition, we define the power law exponents by $k_i = \mathrm{d}\log(I_i)/\mathrm{d}\log(\phi)$. Because the rate of a transition depends linearly on the product of the charge densities of the two levels involved, the k-value of a transition is the sum of the k-values of

the two charge densities. The k-value of a charge density N_i^0 is defined as $k_i = \mathrm{d}\log(N_i^0)/\mathrm{d}\log(\phi)$. The recombination of a donor-acceptor pair, as an example, is proportional to the density of neutral donors and acceptors. In this case, the power law exponent k_{DA} is the sum of the exponents for each density with $k_D = \mathrm{d}\log(N_D^0)/\mathrm{d}\log(\phi)$ and $k_A = \mathrm{d}\log(N_A^0)/\mathrm{d}\log(\phi)$. Equations (6)–(11) give an overview of the link between these photoluminescence intensities, the carrier densities, and the power law exponents,[27]

$$I_{FX} \propto np \Rightarrow k_{FX} = k_n + k_p, \tag{6}$$

$$I_{FB_D} \propto N_D^0 p \Rightarrow k_{FB_D} = k_D + k_p, \tag{7}$$

$$I_{FB_S} \propto N_S^0 p \Rightarrow k_{FB_S} = k_S + k_p, \tag{8}$$

$$I_{FB_A} \propto n N_A^0 \Rightarrow k_{FB_A} = k_n + k_A, \tag{9}$$

$$I_{DA} \propto N_D^0 N_A^0 \Rightarrow k_{DA} = k_D + k_A, \tag{10}$$

$$I_{SA} \propto N_S^0 N_A^0 \Rightarrow k_{SA} = k_S + k_A. \tag{11}$$

In contrast to Ref. 1, we do not assume $n = p$. In certain cases, for example, when there is only one shallow acceptor level, the free electron concentration will be equal to the sum of concentrations of holes in the valence band and in the acceptor state.

Thus, the carrier densities n and p will be treated separately, as well as the corresponding power law exponents k_n and k_p.

In the following, we will discuss the power law exponents in low and high excitation conditions for two different cases: a semiconductor with one shallow donor and one shallow acceptor, and the case with a shallow donor/acceptor, each, and one deep recombination center. The cases with no defect level or with one shallow defect level can be found in the supplementary material (S1) for comparison.

B. Donor and acceptor: Compensated

In the compensated case, nearly all donors and acceptors are ionized at low temperatures with $N_D \approx N_D^+ \approx N_A \approx N_A^-$. There are no deep recombination centers in this example, so that $N_S = N_S^0 = 0$. In the dark, electrons from the donor sites compensate the holes from the acceptor sites.

For the lowest excitation, the free carrier concentration is negligible compared to the concentration of ionized defects. The neutral defect densities are negligible compared to ionized ones and the capture of electrons by the shallow donor level and the capture of holes by the shallow acceptor level dominate. In this case and under illumination, $p \ll N_A^0$ and Eq. (1) can be simplified to

$$c_\phi \, \phi \approx c_{nD} n N_D. \tag{12}$$

Because the fixed donor density N_D is independent of ϕ, it follows that the electron concentration n is proportional to ϕ. The charge balance provides $n = p$ and, therefore, the hole concentration p is also proportional to ϕ. The electron and the hole concentration both increase linear with excitation, which yields a power law exponent of $k_{n/p} = 1$. The corresponding power law exponent for the free exciton or band-to-band transition is 2 with $k_{FX} = k_n + k_p$. Equation (2) reduces to

$$c_{nD} n N_D \approx c_{DA} N_D^0 N_A^0. \tag{13}$$

The donor-acceptor pair transition increases proportionally to ϕ at low excitation, since $n \propto \phi$ from Eq. (12). Both the occupation of the donor with electrons N_D^0 and the occupation of the acceptor with holes N_A^0 increase only with $\phi^{1/2}$. The values are summarized in Table I.

If the compensation is not exact, e.g., if N_A is slightly lower than N_D, or if the capture cross sections of the defects are very different, one defect saturates first and the concentration of the neutral defect becomes independent of the excitation at intermediate excitation intensities. For example, if the acceptor defect saturates before the donor defect [see Table I, column (b)], the occupation of the donor defect with electrons can still increase and the power law exponents are $k_D = 1/2$ and $k_n = 1$. In this case, the hole capture into the acceptor can no longer increase, leading to $k_A = 0$ and $k_p = 1/2$. In comparison to the lower excitation case, the power law exponents k for the free exciton and the donor-acceptor pair transition k_{DA} are reduced by 1/2 in the intermediate excitation regime.

At highest excitation, all donors and acceptors are neutralized by photogenerated excess carriers and the last excitation

TABLE I. Power law exponents: Donor and acceptor.

Densities	Exponents	(a) $N_D^0 \ll N_D$ $N_A^0 \ll N_A$	(b) $N_D^0 \ll N_D$ $N_A^0 \approx N_A$	(c) $N_D^0 \approx N_D$ $N_A^0 \approx N_A$
n	k_n	1	1	1/2
p	k_p	1	1/2	1/2
N_D^0	k_D	1/2	1/2	0
N_A^0	k_A	1/2	0	0
Transitions		Low ϕ	Mid ϕ	High ϕ
FX	k_{FX}	2	3/2	1
FB_D	k_{FB_D}	3/2	1	1/2
FB_A	k_{FB_A}	3/2	1	1/2
DA	k_{DA}	1	1/2	0

regime in column (c) is reached, where the power law exponents decrease again by 1/2. Aside from bound excitons, k-values above 2 are not observed.[28] This is due to the fact that the free carrier concentrations in the bands cannot increase superlinearly with the excitation. They can only increase with a power law exponent of 1/2 or 1. For example, electrons can recombine with free holes as the dominant process ($k_n = 1/2$) or they get mostly captured by defects ($k_n = 1$).

C. Donor, acceptor, and deep level: Compensated

Here, we introduce an additional deep defect. We start the discussion with the lowest excitation intensities, so that $N_D^0 \ll N_D$, $N_A^0 \ll N_A$, $N_S^0 \ll N_S$, and $n, p \ll N_D, N_A, N_S$ is valid. We consider the compensated case.[29] If the defects are all compensated with $N_A \approx N_D + N_S$, Eq. (1) reduces at lowest excitation to

$$c_\phi \phi = n(c_{nD} N_D + c_{nS} N_S). \tag{14}$$

It follows that the free electron concentration is proportional to the excitation intensity and, therefore, increases with $k_n = 1$. The same argument holds for the free hole concentration and $k_p = 1$. The rate equation for the donor in Eq. (2) simplifies to

$$c_{nD} n N_D = N_D^0 (c_{DS} N_S + c_{DA} N_A^0 + c_{Dp} p). \tag{15}$$

If the density of the deep defect is high enough, so that the condition $c_{DS} N_S \gg c_{DA} N_A^0 + c_{Dp} p$ is valid, most of the electrons will fall into the deep defect before recombining with holes in the valence band or with holes from the acceptor site. In this case, the density of occupied shallow donors N_D^0 increases proportional to the electron concentration n and proportional to the excitation intensity ϕ with $k_D = 1$ [$n \propto \phi$ from Eq. (14) and $n \propto N_D^0$ from Eq. (15)]. The deep defect level captures most of the electrons which are first captured by the shallow donor. Because most of the holes are captured by the shallow acceptor at the same time, the deep SA transition will dominate the photoluminescence spectrum at lowest excitation. Thus, Eq. (4)

reduces to

$$c_{nS} n N_S = c_{SA} N_S^0 N_A^0. \tag{16}$$

The left side is proportional to the electron concentration n, which is proportional to ϕ from Eq. (14). Therefore, both densities N_S^0 and N_A^0 are proportional to $\phi^{1/2}$. There exists no further capture level between E_S and E_A, and the pair transition SA from the deep donorlike level into the shallow acceptor increases linearly with $k_{SA} = k_S + k_A = 1$.

Apart from this, the shallow DA-transition increases superlinearly, because $k_D = 1$ and $k_A = 1/2$ and, therefore, $k_{DA} = 3/2$. If one assumes a deep acceptorlike level instead of a deep donorlike level, the values of the power law exponents for k_n and k_p as well as for k_D and k_A are simply exchanged. It is important to mention that, in the literature, it is often assumed that the donor-acceptor pair transition yields power law exponents below or equal to 1 (Ref. 1 and literature citing this reference). This is only valid if no effective capture state (for example, an empty deep defect) exists between the two levels.

The value of k_D is reduced to $1/2$ at low excitation, if the deep donorlike defect does not exist or if it cannot capture more carriers (saturated or too low capture coefficient). In this case, the shallow donor-acceptor pair transition dominates the spectrum. An overview of all power law exponents k is given in Table II.

In this table, five different cases are considered for the defect saturation: from the case of lowest excitation (a) with nearly empty defect levels ($N_i^0 \ll N_i$) to the case of highest excitation (f) with full occupation of all defects ($N_i^0 \approx N_i$). The table is valid for a broad range of situations since the absence of one of the defects can be treated in the same way as the fully occupied case of this defect.

Furthermore, adding another deep recombination center does not change the results of Table II. The transition between two

highly localized levels (S_1 to S_2) is negligible. In this case, the same k-values for FB_{S_1} and FB_{S_2}, as well as for S_1A and S_2A, are the result. An experimental example for this is given in Fig. 3. Table II can also be used if the deep defects are acceptorlike ($N_S^{0/-1}$), but the values of k_n and k_p as well as k_D and k_A need to be exchanged.

In order to experimentally observe different cases of Table II, it is necessary to vary the excitation power over more than 3 orders of magnitude. Power law exponents larger than 1 generally result from empty capture levels between the two involved states. If one of the three levels becomes saturated by excess carriers (one of the two levels of the transition or the deeper level in between), the power law exponent observed at low excitation k_{low} is reduced by $1/2$ at high excitation with $k_{high} = k_{low} - 1/2$. Power law exponents of $1/2$ or smaller can only be observed if one defect level directly involved in the transition is saturated.

In Sec. III, a phenomenological fitting function is given, which can describe the full experimental curvature of excitation dependent photoluminescence intensities, including low and high excitation regimes with different power law exponents.

III. FITTING NONLINEAR LOG-LOG PLOTS

From the discussion above, it is clear that, in most cases, a simple power law will not be observed over a wide range of excitation intensities. In general, the excitation dependence of the photoluminescence in a log-log plot will have a curvature, resulting from the transition between two limiting power law exponents. In a simple case, only one crossover point exists and lies in between two different excitation regimes. In each excitation regime alone, the photoluminescence intensities increase according to a simple power law. The corresponding linear log-log plots can only be observed for excitation intensities far below or far above the crossover point. If the range of excitation allows us to fit the linear regimes in low and high excitation, the excitation intensity where both linear lines cross each other will be called crossover excitation ϕ_0.

TABLE II. Power law exponents: Donor, acceptor, and deep level.

	(a)	(b)	(c)	(d)	(e)	(f)
	$N_D^0 \ll N_D$ $N_S^0 \ll N_S$ $N_A^0 \ll N_A$	$N_D^0 \ll N_D$ $N_S^0 \approx N_S$ $N_A^0 \ll N_A$	$N_D^0 \ll N_D$ $N_S^0 \ll N_S$ $N_A^0 \approx N_A$	$N_D^0 \ll N_D$ $N_S^0 \approx N_S$ $N_A^0 \approx N_A$	$N_D^0 \approx N_D$ $N_S^0 \approx N_S$ $N_A^0 \ll N_A$	$N_D^0 \approx N_D$ $N_S^0 \approx N_S$ $N_A^0 \approx N_A$
k_n	1	1	1	1	1/2	1/2
k_p	1	1	1/2	1/2	1	1/2
k_D	1	1/2	1	1/2	0	0
k_A	1/2	1/2	0	0	1/2	0
k_S	1/2	0	1/2	0	0	0
	Low ϕ	…	…	…	…	High ϕ
k_{FX}	2	2	3/2	3/2	3/2	1
k_{FB_D}	2	3/2	3/2	1	1	1/2
k_{FB_A}	3/2	3/2	1	1	1	1/2
k_{FB_S}	3/2	1	1	1/2	1	1/2
k_{DA}	3/2	1	1	1/2	1/2	0
k_{SA}	1	1/2	1/2	0	1/2	0

In the present section, a fitting function for nonlinear log-log plots will be given. This fitting function can be used to quickly and easily estimate the crossover excitation and to get the limiting exponents k, even if only the curved transition region is measured. This can be the case if, for example, the experimental excitation range is not sufficient to resolve the linear regimes far below and far above ϕ_0. We have shown the case for two levels and with the saturation effects of only one level in Ref. 17. The fitting function was obtained by the multiplication of the carrier densities in the initial and the final state of the recombination path:

$$I_{PL} \propto n_1 n_2. \qquad (17)$$

For a donor-acceptor pair transition with no defect level in between, functions n_1 and n_2 are proportional to the occupation of the donor with electrons and the occupation of the acceptor with holes. We will take this example for a straightforward motivation of the fitting function. If under low excitation, the excess carrier density is far below the defect density, so that no saturation effects occur, a simple power law can describe n_i. On the other hand, at highest excitation when the occupation of a defect with excess carriers cannot increase any further, the power law behavior changes to a constant value. The crossover occurs in between with the crossover excitation ϕ_i. A fitting function which describes both excitation regimes for the donor occupation (power law exponent k_1) and the acceptor occupation (power law exponent k_2) in a donor-acceptor pair recombination is given by Eq. (18)

$$I_{PL} \propto \frac{\phi^{k_1}}{1+\left(\frac{\phi}{\phi_1}\right)^{k_1}} \frac{\phi^{k_2}}{1+\left(\frac{\phi}{\phi_2}\right)^{k_2}}, \qquad (18)$$

$$I_{PL} \propto \frac{\phi^{k_1+k_2}}{1+\left(\frac{\phi}{\phi_1}\right)^{k_1}+\left(\frac{\phi}{\phi_2}\right)^{k_2}+\left(\frac{\phi}{\phi_1}\right)^{k_1}\left(\frac{\phi}{\phi_2}\right)^{k_2}}. \qquad (19)$$

For low excitation with $\phi \ll \phi_1$, density n_1 (occupation of the donor with electrons) follows the power law ϕ^{k_1}. For high excitation with $\phi \gg \phi_1$, the term converges to the constant value $\phi_1^{k_1}$. The same holds true for the acceptor and k_2. The crossover excitations ϕ_i are linked to the defect densities which become saturated. Saturated in this case means that the occupation of the defect level with excess carriers is not increasing anymore with increasing excitation. A discussion for the saturation effects of the defect densities can be found in the supplementary material (S6). If all transition coefficients c_{ij} are equal, the defect population N_i^0 saturates for high excitation at $N_i/2$. On the other hand, if, for a shallow donor defect, the transition time for the free electron capture is much faster than the recombination of the captured electron with a free hole, the defect population N_i^0 saturates at the full defect concentration N_i.

Equation (19) has two different crossover excitations. However, the equation can be further simplified if only one of the two defects shows saturation effects in the range of excitation used. This is the case if one defect in the donor-acceptor pair transition has a much higher defect concentration. With $\phi_2 \to \infty$, the two

last terms in the denominator in Eq. (19) vanish and it follows:

$$I_{PL} \propto \frac{\phi^{k_1+k_2}}{1+\left(\frac{\phi}{\phi_1}\right)^{k_1}} = \frac{\phi^{k_{low}}}{1+\left(\frac{\phi}{\phi_0}\right)^{k_{low}-k_{high}}}. \qquad (20)$$

This equation can be used to fit a curved log-log plot with the crossover excitation at ϕ_0. It not only applies to a donor-acceptor pair transition but also to a free-to-bound or exciton transition where the values for k_{low} and k_{high} are different. For low excitation ($\phi \ll \phi_0$), the power law exponent converges to $k = k_{low}$. For high excitation ($\phi \gg \phi_0$), the 1 in the denominator can be neglected and the power law exponent converges to $k = k_{low} - (k_{low} - k_{high}) = k_{high}$. Equation (20) describes most experimental situations, where a nonlinear log-log plot is observed with only one crossover excitation ϕ_0. Equation (19), however, describes also situations where two crossover points in the log-log plot are observed.[30] Although Eq. (19) was motivated with a donor-acceptor pair transition, it can be easily extended to a free exciton transition as an example: the equation only needs to be multiplied with a single power law of $\phi^{1/2}$ for the free electron and one for the free hole concentration [see the supplementary material (S3)].

As an example, we assume one acceptor level at low temperatures. For the free exciton transition I_{FX}, the following values for the power law exponents k_{FX} have to be inserted into Eq. (20): $k_{low} = 3/2$ and $k_{high} = 1$. This condition corresponds to the last two columns in Table II. The photoluminescence intensity can be described in this example by

$$I_{FX} \propto \frac{\phi^{3/2}}{1+\left(\frac{\phi}{\phi_0}\right)^{1/2}}. \qquad (21)$$

For an arbitrary overall amplitude, the crossover excitation ϕ_0 is the only free fitting parameter in Eq. (21), which marks the crossover excitation in the nonlinear log-log plot. If in experiment the excitation intensity is only varied in a narrow range (for example, less than 3 orders of magnitude), close to the crossover excitation, any fit of a simple, linear power law would lead to k-values between 1 and 3/2.

Often observed single power laws with exponents different from $n/2$ could be a result of narrow excitation variations where the curvature is not clearly visible and an apparent straight line is assumed. We give an example in Sec. IV, where the fitting functions of Eqs. (19) and (20) are applied to numerical solutions of the rate equations and measurements on CuGaSe$_2$ thin films.

IV. VALIDATION OF THE MODEL

In this section, we will show that our model agrees well with numerical solutions of the rate equations, as well as experimental measurements on chalcopyrite thin films.

A. Fitting numerical solutions: Example with a shallow donor, a shallow acceptor, and a deep donor

In the following, we consider a semiconductor with a shallow donor, a shallow acceptor, and a deep donorlike level as given in

Table II. To minimize the number of possible crossover points in the excitation dependence and having a straightforward example for the influence of deep defects, we will again consider the compensated case with $N_D + N_S = N_A$. Analytical solutions of the rate equations can be found in supplementary material (S6).

In Fig. 2, numerical solutions of the rate equations are shown. Two different crossover excitations ϕ_1 and ϕ_2 can be seen. This leads to three different excitation regimes where the slope of the excitation dependent photoluminescence intensity can be different. For the selected parameters, the crossover excitation ϕ_1 is in between regime A, where the excess electron concentration n is much smaller than the deep donor concentration N_S, and regime B, where the excess electron concentration is much larger than the deep donor concentration. The first crossover results from saturation effects of the neutralized deep defect concentration N_S^0.

The second crossover excitation ϕ_2 from regime B to regime C results from saturation effects of the acceptor. The amount of neutralized defects N_A^0 is not further increased with higher excitation in regime C, far above ϕ_2. The same effect occurs for N_D^0 due to the compensation condition with $N_D \approx N_A$. The different power law exponents and excitation regimes can be compared with Table II and regimes A, B, and C can be attributed to cases (a), (b), and (f). The results of the numerical solutions confirm our descriptive arguments that led to the power law exponents in Table II.

Because there are two crossover excitations, the curves in Fig. 2 can be fitted with Eq. (19). The fitting function agrees well with the solutions of the rate equations. The power law exponents are given in the inset of the figure and confirm the model in
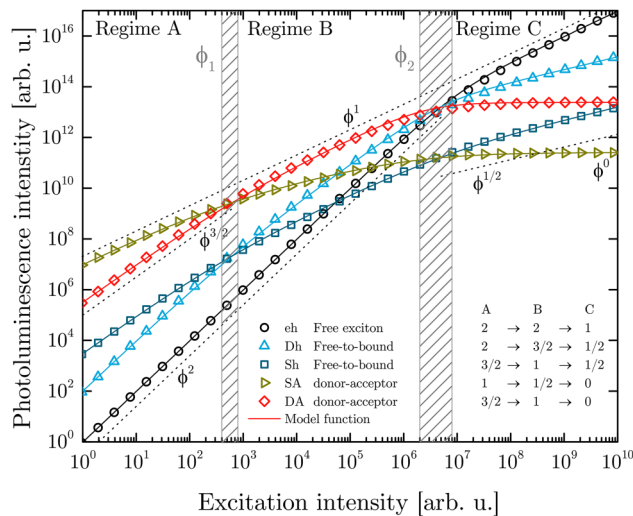
Table II. Some variation of the crossover intensities ϕ_i is expected because of differences in transition coefficients and the uncertainty of the fit. The variation of the fit is marked by the gray patterned boxes in the figure.

B. Fitting experimental data: CuGaSe$_2$ thin films

As the next step, we apply the theory to measurements and match the model functions from Sec. III to our experimental data. In Fig. 3, measurements on an epitaxial CuGaSe$_2$ thin film are given. It is the same sample and the same SA transitions as in Ref. 17. The photoluminescence intensity of several transitions is measured at low temperatures (10 K) with laser excitation variations over more than 5 orders of magnitude. The transitions, labeled with SA1 and SA2, are identical to the deep donor-acceptor pair transitions DDA1 and DDA2 in Ref. 17.

All curves in Fig. 3 can be well fitted with Eq. (20) because only one crossover excitation ϕ_0 occurs. The value of $k_{low} - k_{high}$ in Eq. (20) can be fixed to $1/2$ for all curves. Furthermore, the average crossover excitation ϕ_0 of all transitions is close to $1\,\text{W/cm}^2$ [see the supplementary material (S5)]. It can be concluded that the crossover excitation is the same for all transitions.

From the difference of $1/2$ for the power law exponents at low and high excitation, it can be concluded that only one defect saturates and causes the crossover. The saturation effect influences all transitions and is responsible for the nonlinear log-log plots. When
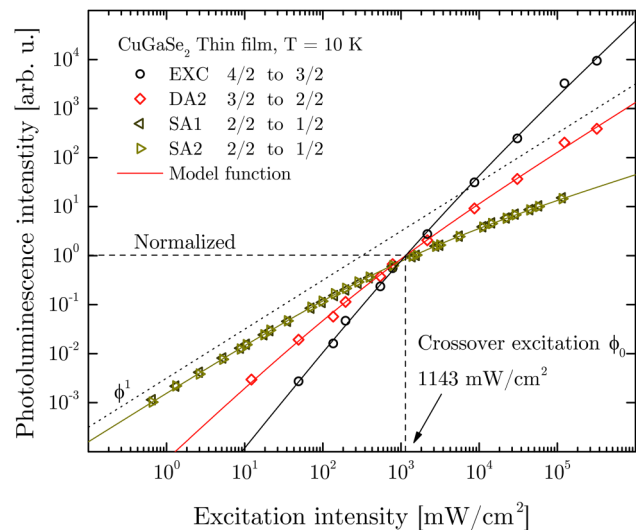

FIG. 2. Numerical solutions of the rate equations in Sec. II A for np (eh), $N_D^0 p$ (Dh), $N_S^0 p$ (Sh), $N_S^0 N_A^0$ (SA), $N_D^0 N_A^0$ (DA) with the constants $N_D = 10^{16}\,\text{cm}^{-3}$, $N_S = 10^{14}\,\text{cm}^{-3}$, $N_A = 1.01 \times 10^{16}\,\text{cm}^{-3}$, and $c_{ij} = 1$. Each curvature is fitted with the model function in Eq. (19) and slopes of constant power laws are shown with dotted lines. Variations of the crossover excitations as the fitting parameter are shown with the patterned boxes.

FIG. 3. Photoluminescence intensity of an exciton, donor-acceptor pair, and two deep donor-acceptor pair transitions for varying excitation intensities. Measurements are done on Cu-rich CuGaSe$_2$ thin films and at a temperature of $T = 10\,\text{K}$. Fits to Eq. (20) are shown by solid lines. The used fitting parameters are given in the supplementary material (S5). For better comparison of the slopes, all curves (arbitrary amplitude) are normalized to the photoluminescence intensity at the crossover excitation ϕ_0. An exemplary slope of a linear power law is shown with a dotted line. Power law exponents of low and high excitation regimes are given in the legend. The labeled SA transitions equal the DDA transitions in Ref. 17.

TABLE III. Limits of the power law exponents k with and without radiative contributions from a deep defect N_S.

	No N_S	With N_S
BX	1–5/2	1–3
FX	1–2	1–2
FB	1/2–1	1/2–3/2
DA	0–1	0–3/2
SA		0–1

comparing the fixed values of k_{low} and k_{high} (in the legend of Fig. 3) with Table II, the crossover from case (a) to case (c) is observed in low and high excitation. We can thus conclude, based on our model consideration, that the defect that saturates is the shallow acceptor.

This example also demonstrates that shallow donor-acceptor pair transitions (DA) can yield a power law exponent above 1, if deep recombination centers are present. The DA2 transition in CuGaSe$_2$ is well known in the literature.[7] In our study, the superlinearity is a result of the presence of deep defects. Our model describes well the excitation dependence of measured shallow defect transitions, as well as deep defect transitions.

A superlinear dependence of donor-acceptor pair transitions is not always only a result of deep defects. With increasing excitation, the overlap of the wavefunction from the donor and the acceptor increases, which can yield a much higher recombination probability and a superlinear increase of the photoluminescence intensity with increasing excitation.[25] This effect would, however, not lead to a power law. If the increasing overlap between donor and acceptor states is responsible for the superlinear behavior, then the transition coefficient itself becomes excitation dependent, which would result in an exponential behavior of the PL intensity on excitation.

V. CONCLUSION

We have presented a theoretical description of common cases of excitation-intensity-dependent photoluminescence measurements based on rate equations, as well as an extension of existing models now including the influence of deep defects. In contradiction to the previous conclusion that the donor-acceptor pair photoluminescence intensity increases with a power law exponent smaller or equal to 1, we have shown that a value of 3/2 can be observed if deep defects are present that interact with the free carriers and shallow donors or acceptors.

The nonlinear behavior of the PL intensity in a log-log plot vs excitation intensity results from a crossover from one single power law at low excitation to another single power law at high excitation. The crossover is triggered by the saturation of one of the defect levels participating in the radiative recombination or by the saturation of a deeper level that interacts with the two levels involved in the transition. In each excitation regime alone, far above, or far below the crossover excitation, the power law exponents can only be multiples of $1/2$. The limits are given in Table III. Measured curvatures can be described by a phenomenological fitting function

[Eqs. (19) and (20)], which consists of only one or two free parameters for the crossover excitations. The fitted parameters ϕ_i are linked to the defect saturation and can be used for the quantification of defect concentrations and, therefore, of semiconductor quality.

SUPPLEMENTARY MATERIAL

See the supplementary material for further theoretical cases of semiconductors in which no defect or only one defect can be found (S1), as well as comments on bound excitons (S2), an extended fitting function (S3), another fitting example with numerical results from the literature (S4), used fitting parameters (S5), and a short discussion for the transition coefficients and possible analytical solutions of the rate equations (S6).

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[26]In Refs. 1 and 2, the influence of deep defects is not included, whereas, in Ref. 19, only one defect level deep in the gap is assumed (no recombination from shallow levels). Although Klasens[16] gave a large overview of possible recombination orders for the intensity-dependent photoconductance and luminesecence of semiconductors, we will give a more applied overview by focusing on the most common transitions in low temperature photoluminescence and by direct comparison to experimental data.

[27]Transitions over small energy differences like the electron-capture into the shallow donor and the hole capture into the shallow acceptor are often nonradiative or usually not measured in standard photoluminescence experiments. The electron-capture by the deep defect level can be radiative but is in many cases outside the energy range of conventional experiments.

[28]An exception are bound excitons, where the PL intensity is proportional to n, p, and $N_{D/A}^0$. Thus, their k-value can be above 2.

[29]The compensated case is more accessible for the understanding of the general model. If the donors and acceptors are not compensated, all of the 3 given defects can lead to 3 different crossover excitations, and, for each excitation regime, the power law exponents have to be discussed for 6 possible transitions (exciton, 3 free-to-bound, and 2 donor-acceptor pair transitions). Nevertheless, the uncompensated case can be understood from the more accessible compensated case, too. As an example, if the semiconductor has only one donor and acceptor level without compensation, the whole model can often be reduced to the case of only one level considered (the one which has a much higher defect concentration and, therefore, leads to a much higher amount of neutral defects in the dark).

[30]It is also possible that no saturation effects of defects are observed in the experiment. In this case, no discrimination between low and high excitation regimes exists with $\phi_1, \phi_2 \gg \phi$ in Eq. (19) and a single power law is the result, $I_{PL} \propto \phi^{k_1+k_2} = \phi^k$.