Excitation dependence of photoluminescence transitions

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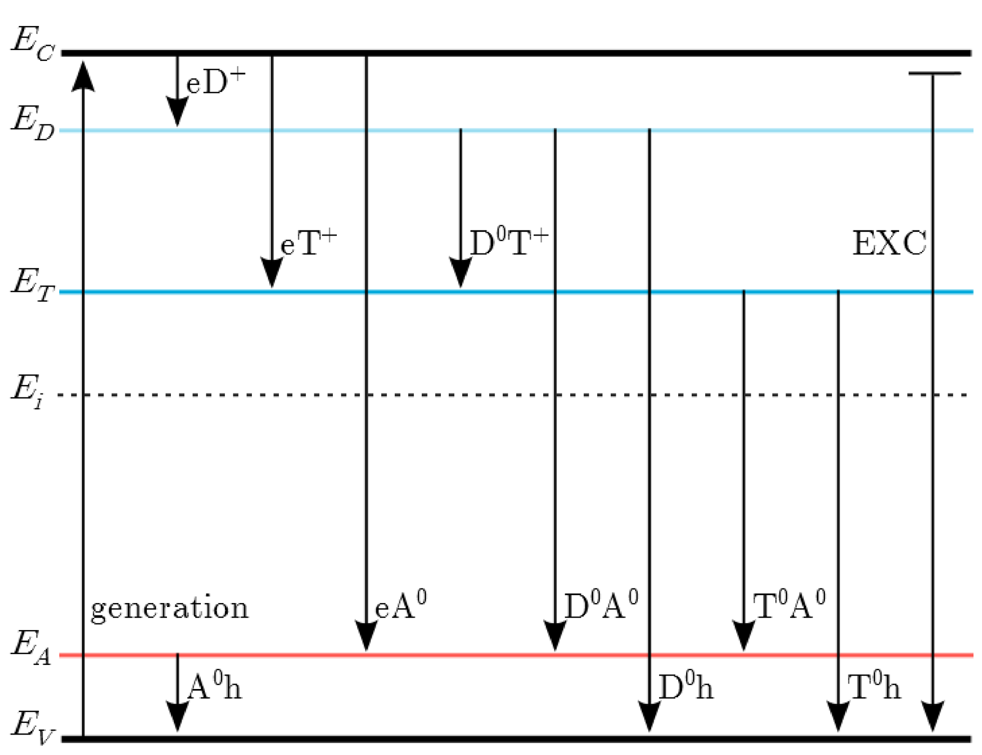
Motivation

1. excitation dependence often described with $I_{PL} \propto \phi^k$
⇒ Power-law exponent k: slope of linear fit in log-log-plot
⇒ fitting models for curved dependence of $I_{PL}(\phi)$ needed
2. excitation dependence often used to distinguish transitions [1]
EXC: $1 \leq k$ FB/DAP: $k \leq 1$
⇒ deviations from this behaviour observed in experiments
⇒ more models of k-values needed for further characterization

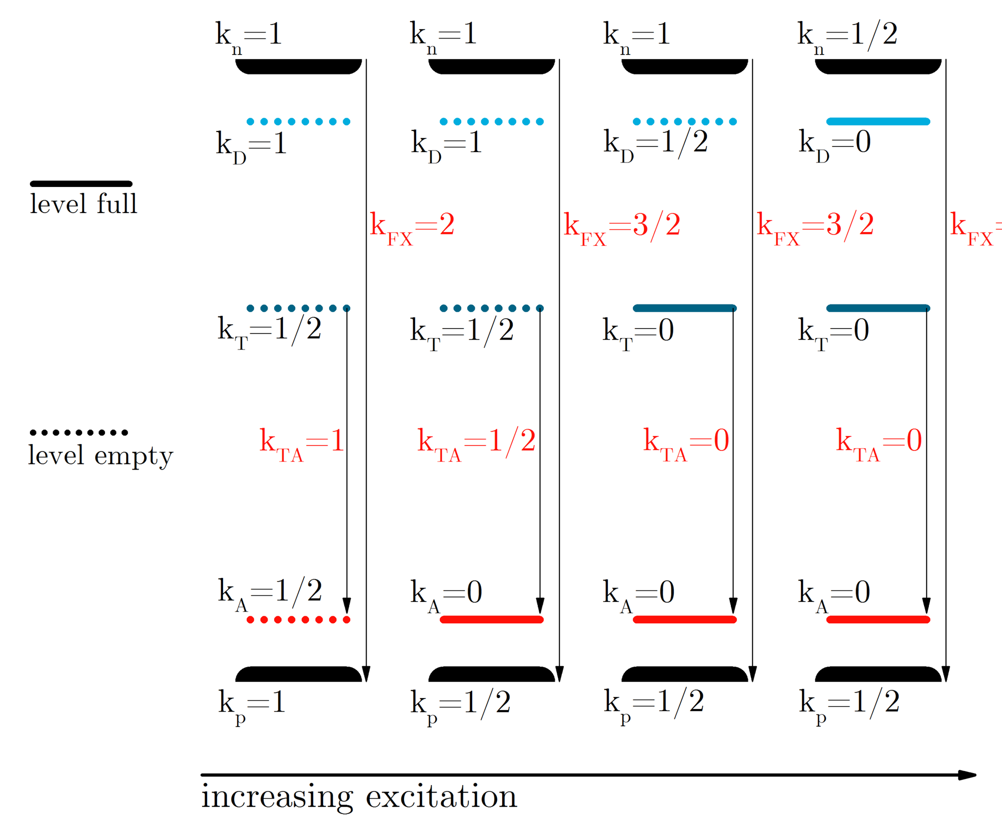
Photoluminescence transitions



- transitions eD$^+$, eT$^+$, D^{0}T$^+$, A^{0}h mostly non-radiative (low E)
- nearly no free carriers e/h at lowest temperatures/excitations

⇒ shallow- and deep defect-pair transitions are likely dominant

Power-law exponents



Power-law exponent k_i is sum of k-values from involved states

1. two states with no capture-states in between:
increasing excitation: k=1 → k=1/2 → k=0
2. two states with capture-state e.g. for electrons in between:
increasing excitation: k=3/2 → k=1 → k=1/2 → k=0

Samples

- epitaxially grown Cu-rich chalcopyrites: $CuInSe_2$ and $CuGaSe_2$
- high PL-intensity occurs from deep defects in $CuGaSe_2$
- observed free exciton emission in both samples
- no or negligible bound exciton emission (not discussed here)

Rate equations

- low temperatures ⇒ no thermal activation of defects
- for simplification no bound excitons taken into account
- one shallow donor N_D, shallow acceptor N_A, deep trap N_T

1. $\frac{dn}{dt} = c_\phi \phi - c_{nD} n (N_D - N_D^0) - c_{nT} n (N_T - N_T^0) - c_{nA} n N_A^0 - c_{np} n p = 0$
2. $\frac{dn_{FX}}{dt} = c_{np} n p - c_{FX} n_{FX} = 0$
3. $\frac{dN_D^0}{dt} = c_{nD} n (N_D - N_D^0) - c_{DT} N_D^0 (N_T - N_T^0) - c_{DA} N_D^0 N_A^0 - c_{Dp} N_D^0 p = 0$
4. $\frac{dN_T^0}{dt} = c_{nT} n (N_T - N_T^0) + c_{DT} N_D^0 (N_T - N_T^0) - c_{TA} N_T^0 N_A^0 - c_{Tp} N_T^0 p = 0$
5. $\frac{dN_A^0}{dt} = c_{Ap} (N_A - N_A^0) p - c_{DA} N_D^0 N_A^0 - c_{TA} N_T^0 N_A^0 - c_{nA} n N_A^0 = 0$
6. $n + N_A^- = p + N_D^+ + N_T^+$ charge neutrality

FX: $I_{FX} \propto np$

FB-D: $I_{FD} \propto N_D^0 p$ FB-T: $I_{FT} \propto N_D^0 p$ FB-A: $I_{FA} \propto n N_A^0$

DA-D: $I_{DA} \propto N_D^0 N_A^0$ DA-T: $I_{TA} \propto N_T^0 N_A^0$

Limits

free exciton	FX	$1 \leq k \leq 2$	no saturation of the bands
free-to-bound	FB	$\frac{1}{2} \leq k \leq 2$	> 1: deeper capture levels
donor-acceptor	DAP	$0 \leq k \leq 2$	> 1: deeper capture levels

Model function

- defect- or band-occupation known by Fermi-function $f(\phi)$

$$I_{PL} \propto f_1(\phi) f_2(\phi)$$

- exponential term $exp(\frac{E_i - F_i(\phi)}{k_B T})$ replaced by power-law $c_i \phi^{k_i}$

Recombination between two states:

1. No state gets fully occupied with excitation $E_{1/2} - F_{1/2}(\phi) \gg k_B T$

$$I_{PL} \propto \phi^{k_1+k_2} \propto \phi^k$$

2. One state gets fully occupied with excitation $E_1 - F_1(\phi) \approx k_B T$

$$I_{PL} \propto \frac{\phi^{k_1+k_2}}{1 + c_1 \phi^{k_1}}$$

3. Both states get fully occupied with excitation $E_{1/2} - F_{1/2}(\phi) \approx k_B T$

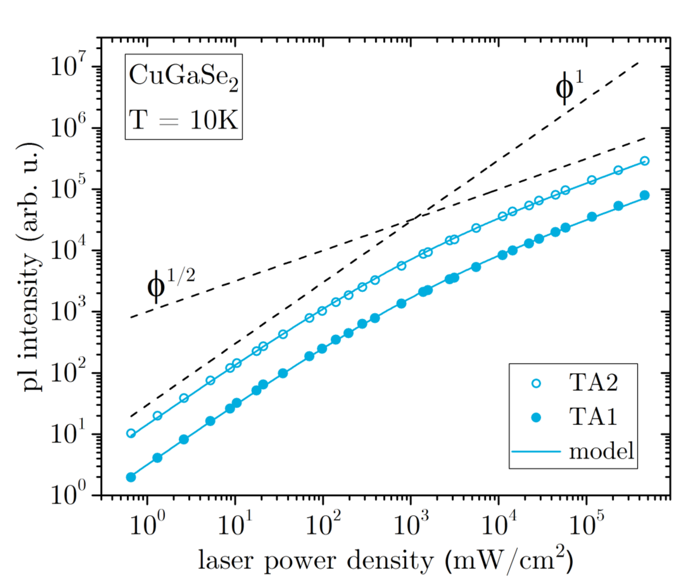
$$I_{PL} \propto \frac{\phi^{k_1+k_2}}{1 + c_1 \phi^{k_1} + c_2 \phi^{k_2} + c_1 c_2 \phi^{k_1+k_2}}$$

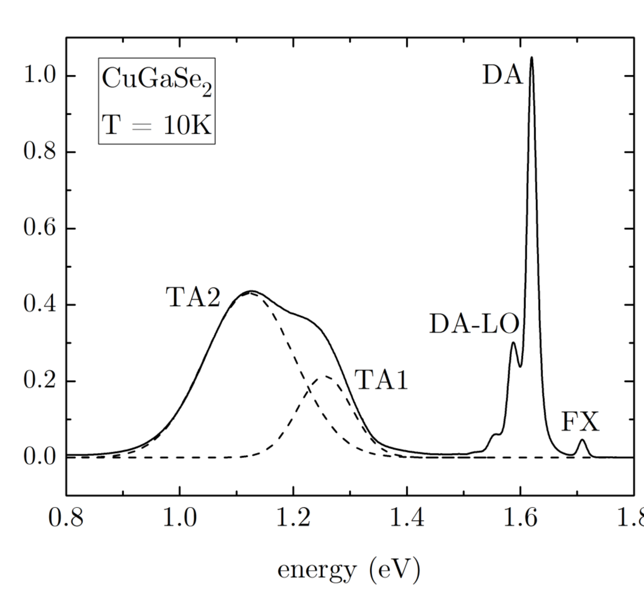
Summary

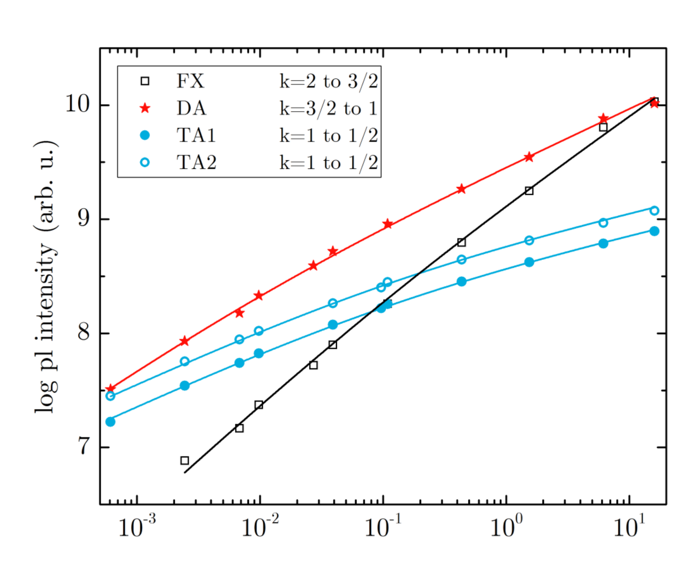
- excitation dependence more complicated than usually assumed
- most curved Power-laws described by straightforward fit-function

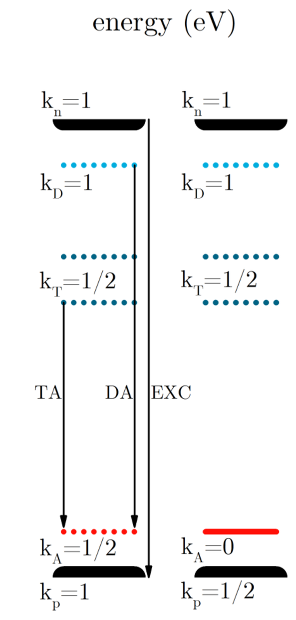
1. Power-law exponent k consists of multiples of 1/2
2. curved Power-laws due to saturation of one involved defect or due to saturation of one capture-state in between
⇒ resulting reduction of k by 1/2 ⇒ curved excitation dependence
3. k-value increases if lower capture-state is present (empty)
⇒ superlinear Power-law for donor-acceptor-pair transition

Examples: $CuGaSe_2$









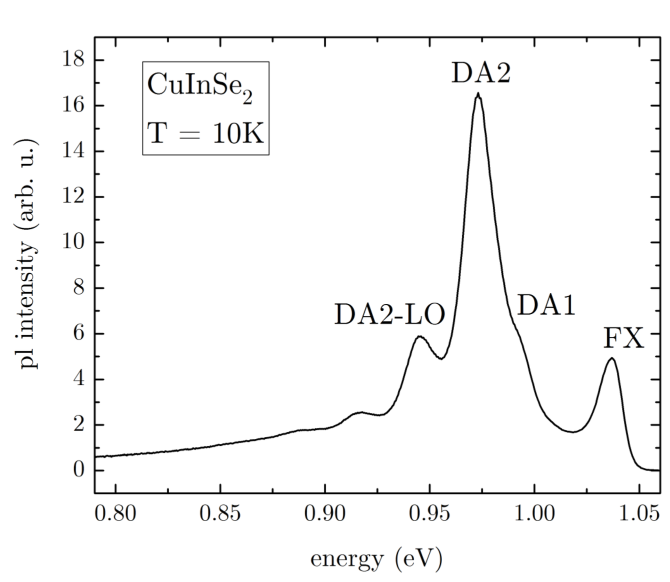
- excitaion dependencies can be fitted with case 2 and fixed k-values [2]

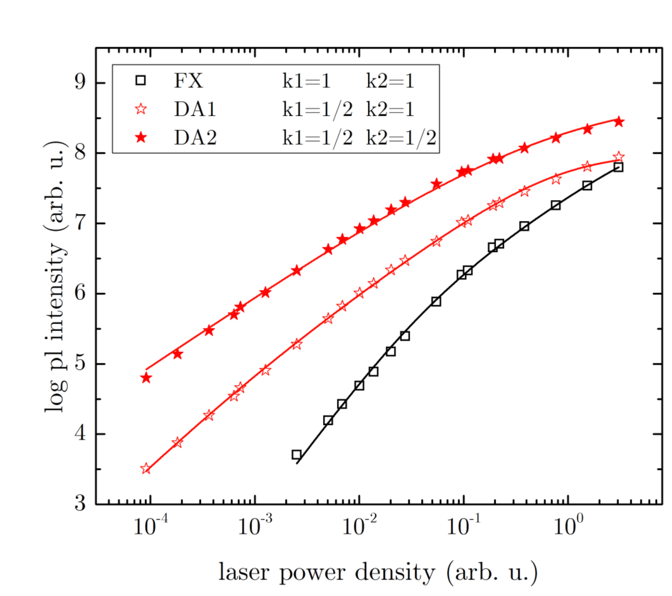
⇒just one defect gets saturated by excess carriers

- k-values of all transitions get reduced by 1/2 due to defect saturation
- excitation dependence of deep TA-transitions is identically

⇒known shallow acceptor gets saturated and not the deep trap levels [2]

Examples: $CuInSe_2$





- excitation dependence can just be fitted with case 3

⇒ two defect levels get saturated in the used excitation range

- dominant DA2-transition shows Power-law close to 1 for lowest used excitations

⇒no significant trapping of electrons from the donor-site by deep defects

[1] T. Schmidt et. al., Phys. Rev. B. 45(16), 8989 (1992)

[2] C. Spindler et. al., Appl. Phys. Lett. 109, 032105 (2016)

Acknowledgements:

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