Linear and nonlinear effects in luminescence decay kinetics in wide-gap scintillating materials

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Motivation

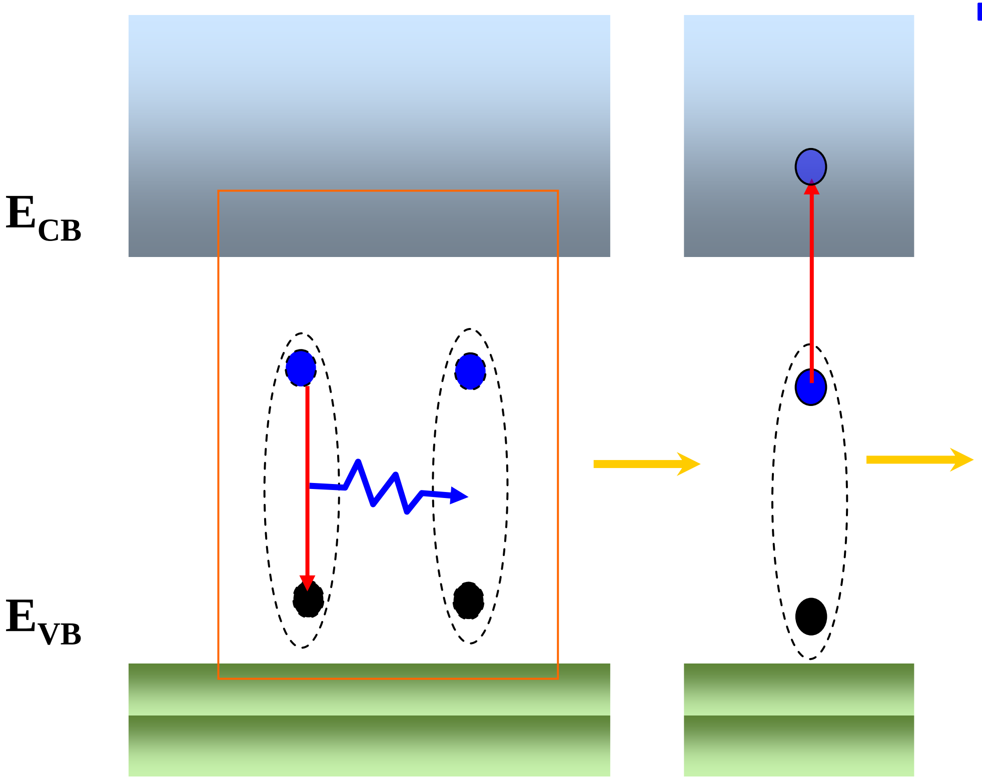
Decay kinetics of $CdWO_4$ under different excitations

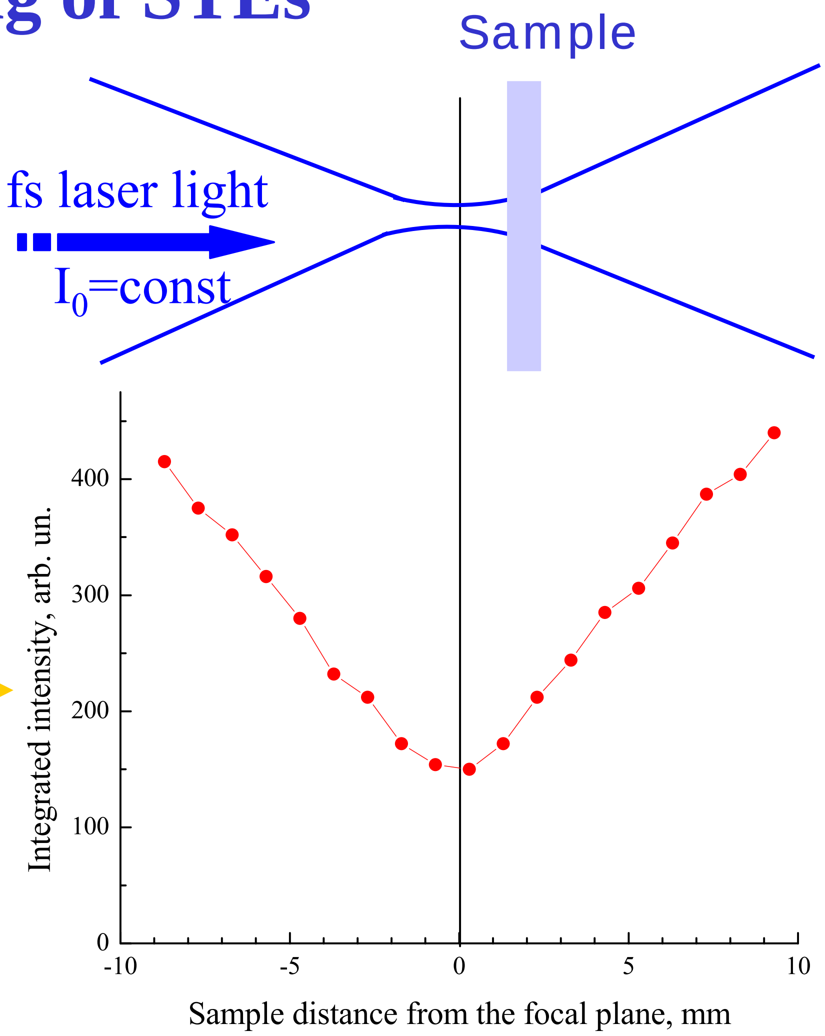
- 0.8 μs Gillette, R.H., 1950. Rev. Sci. Instrum. 21, p. 294
- 1.1 μs, 14.5 μs D. Kinloch et al., IEEE Trans. Nucl. Sci. 41, 752 (1994).
- 2 μs R. Deych et al., Proc. SCINT95, 1996, p. 36.
- 5 μs C.L. Melcher et al., IEEE Trans. Nucl. Sci. 36, 1188 (1989)
- 7.8 μs Beard, G.B. et al., 1962. J Appl. Phys.. 33, p. 144
- 9 μs B.C. Grabmaier. IEEE Trans. Nucl. Sci. 31, 372 (1984)
- 13-15 μs under optical excitation! Many papers.

Central idea:

The differences observed in the decay kinetics are due to the different densities of electronic excitations created in tracks of x-ray or γ quanta of different energies used in the studies of scintillation response. (?)

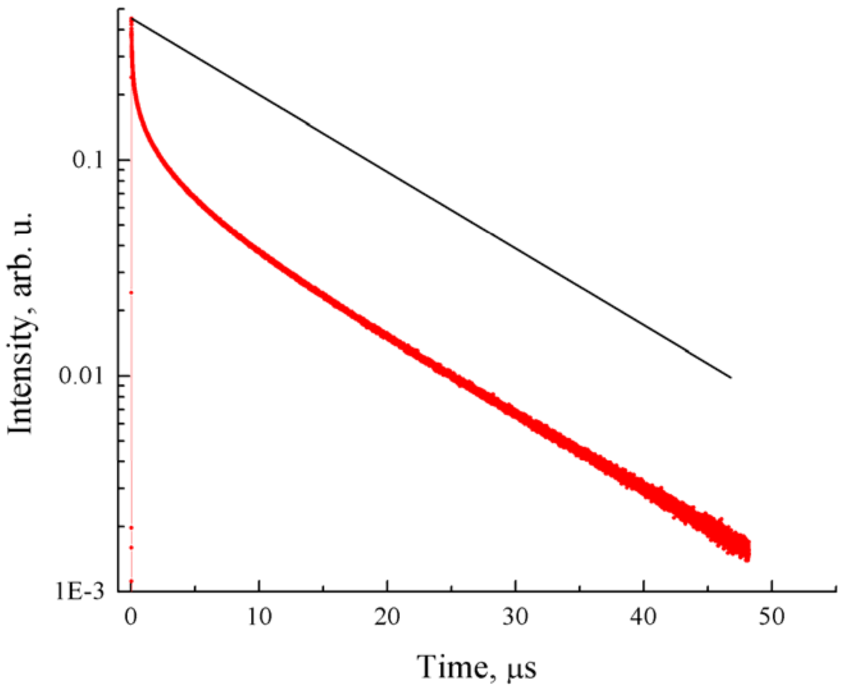
Frenkel excitons created at high densities. Self-quenching of STEs



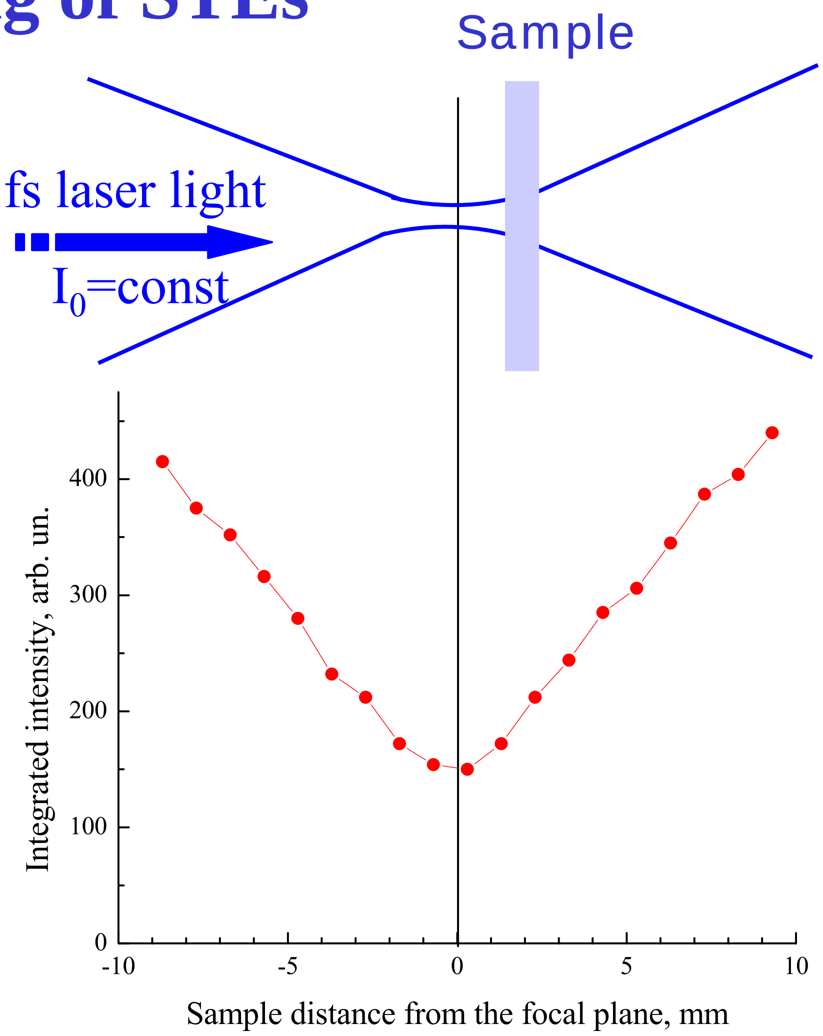


$CaWO_4$, E_{exc}=5 eV (247.5 nm), 80 fs pulse, 1 µJ pulse energy, 70 µm beam waist

Frenkel excitons created at high densities. Self-quenching of STEs



CdWO$_4$, E$_{exc}$=4.84 eV (256.4 nm), 80 fs pulse, 0.6 µJ pulse energy, 130 µm beam waist



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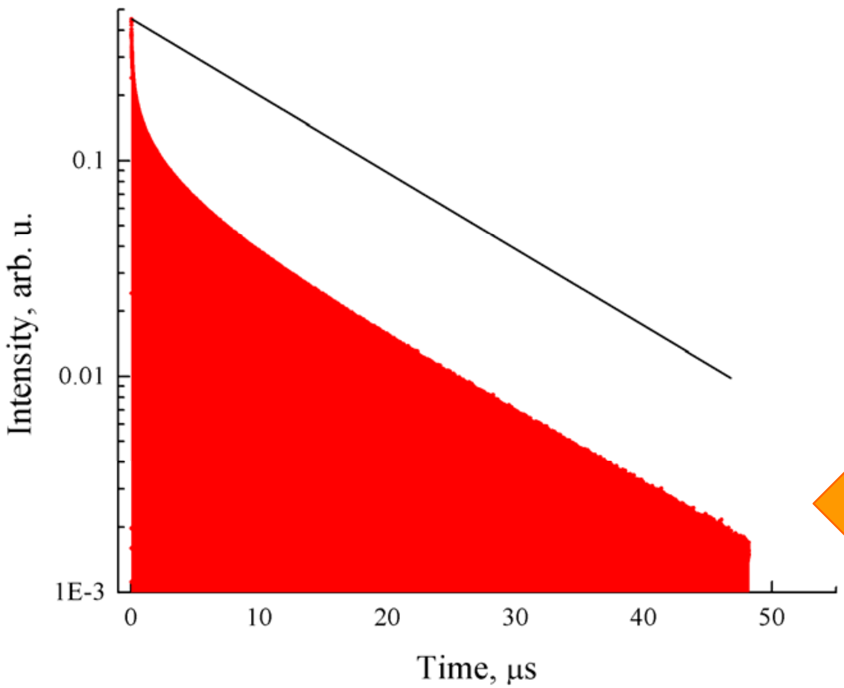

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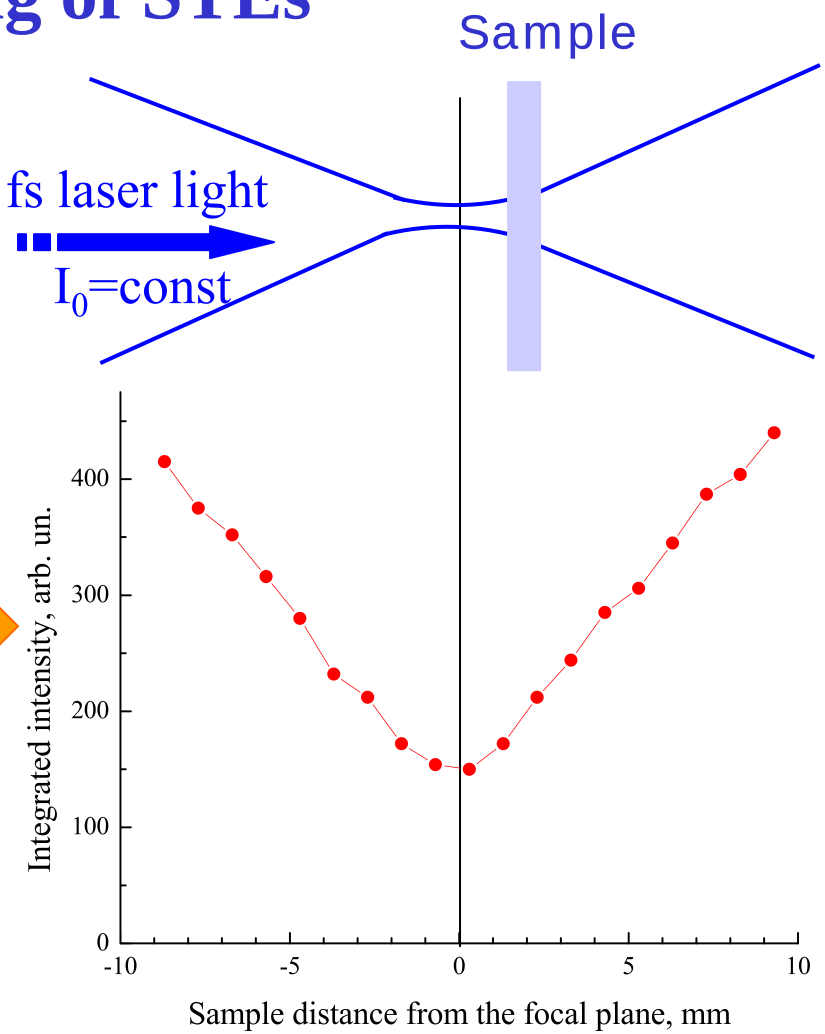


CaWO$_4$, E$_{exc}$=5 eV (247.5 nm), 80 fs pulse, 1 µJ pulse energy, 70 µm beam waist

Förster dipole-dipole energy transfer

M. Kirm et al, Phys. Rev. B **79** (2009) 233103

- Exciton concentration: $$\frac{\partial n(\mathbf{r},t)}{\partial t} = -\frac{n(\mathbf{r},t)}{\tau_r} - \gamma_{d-d}(t,\mathbf{r})\, n^2(\mathbf{r},t)$$
- Dipole-dipole energy transfer rate: $$\sim \frac{1}{\tau_r}\left(R_{d-d}/R\right)^6$$
- Dipole-dipole transfer radius: $$R_{d-d}^6 \propto \int \omega^{-4} F_{em}(\omega) F_{exc}(\omega)\, d\omega$$

$$I(t) = \frac{\sigma I_0}{\tau} e^{-t/\tau} \frac{-Li_2\left(-\frac{2}{3}\pi^2 R_{d-d}^3 N_{\max} erf\left(\sqrt{t\tau^{-1}}\right)\right)}{\frac{2}{3}\pi^2 R_{d-d}^3 N_{\max} erf\left(\sqrt{t\tau^{-1}}\right)}$$

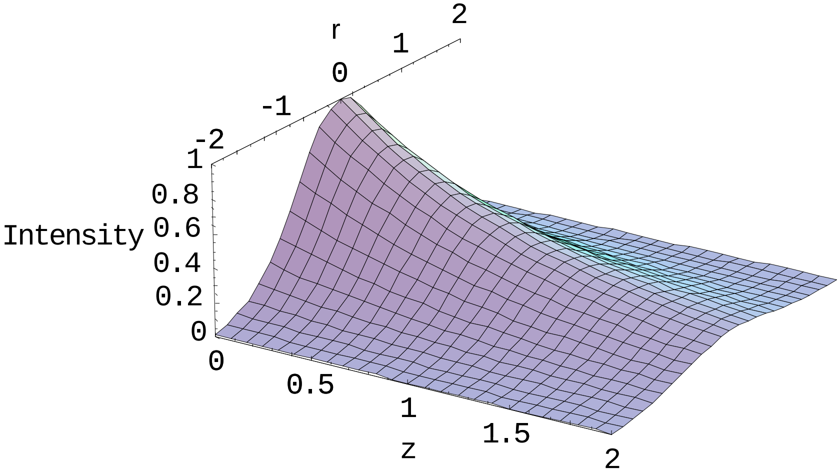
$$N_{\max} \equiv I_0 \frac{\sigma\alpha}{\pi a^2}$$

I_0 – number of photons in a pulse

α – absorption coefficient

σ – exciton yield

a – pulse radius



Experiments performed

•High-order harmonics generation (HHG): 23-32 eV, 10-15 fs

M. Kirm *et. al.*, Phys. Rev. B 79, 233103 (2009)

•Free electron laser (FEL): 89 eV, 25 fs

S. Vielhauer *et. al.*, Phys. Sol. State, 50, 1789 (2008)

Optical parametric amplifier (OPA, 240 - 2600 nm, 1-200 μJ/pulse, 100 fs,

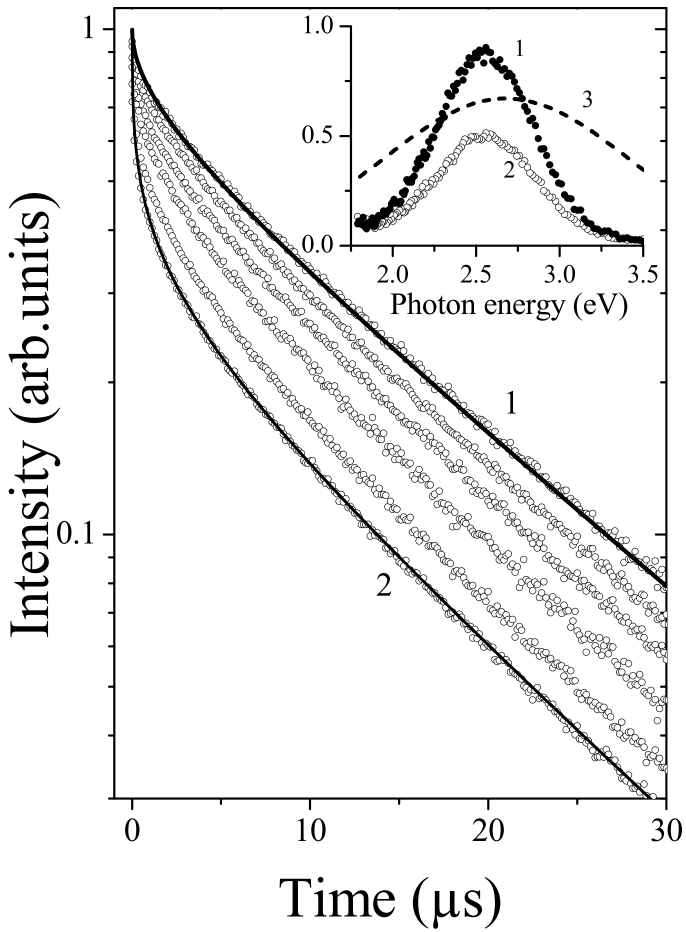
1 kHz (Laser Research Centre, Vilnius University)

V. Nagirnyi *et. al.*, IEEE Trans. Nucl. Sci. 57, 1182 (2010)

R. Laasner et al., under preparation.

Estimation of parameters

(High order harmonic generation, Saclay)



$$N_0^{max} = I_0 \frac{\alpha \sigma}{\pi a^2}$$

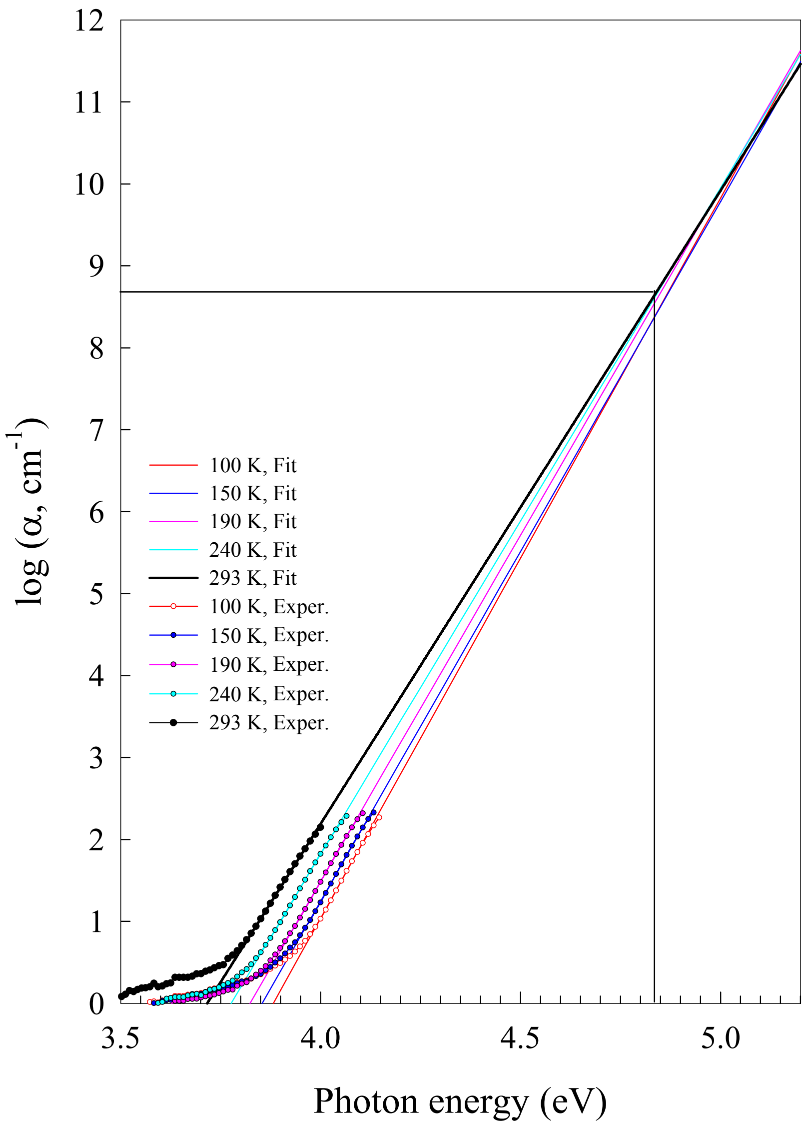
- α was taken 10^5 cm^{-1} for photon energy 23-32 eV, 15 fs
- σ = 2 - 3 for 23-32 eV ?
- a measured 70 µm
- N_0^{max} 2.5x10^{20} cm^{-3}
- **$R_{d\text{-}d}$ = 2.1 nm**

Lattice parameters:

***a*= 5.029 Å, *b*=5.859 Å, *c*=5.074 Å**

M. Kirm et al, Phys. Rev. B **79** (2009) 233103

Estimation of parameters 2

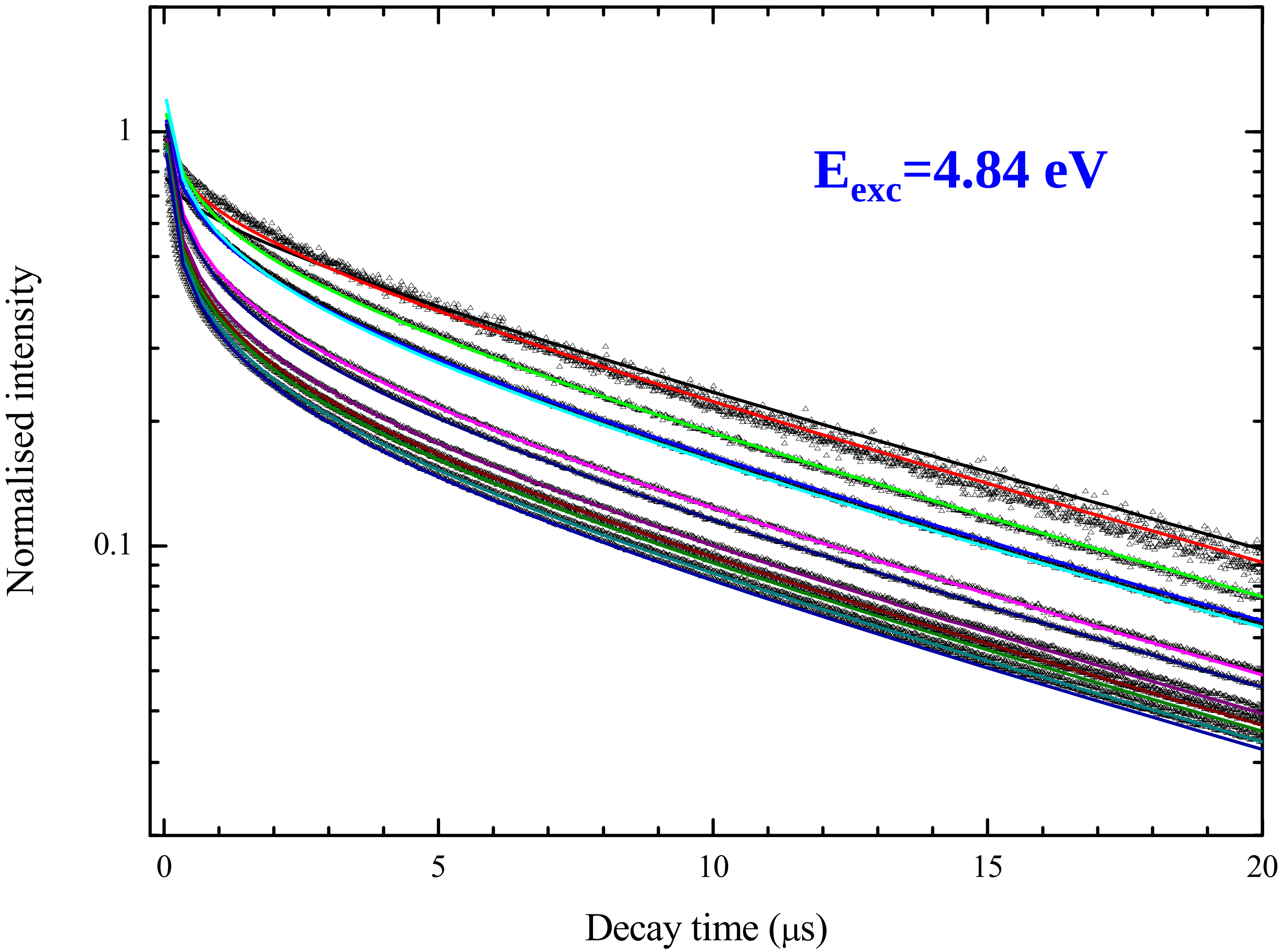


$$N_0^{max} = I_0 \frac{\alpha \sigma}{\pi a^2}$$

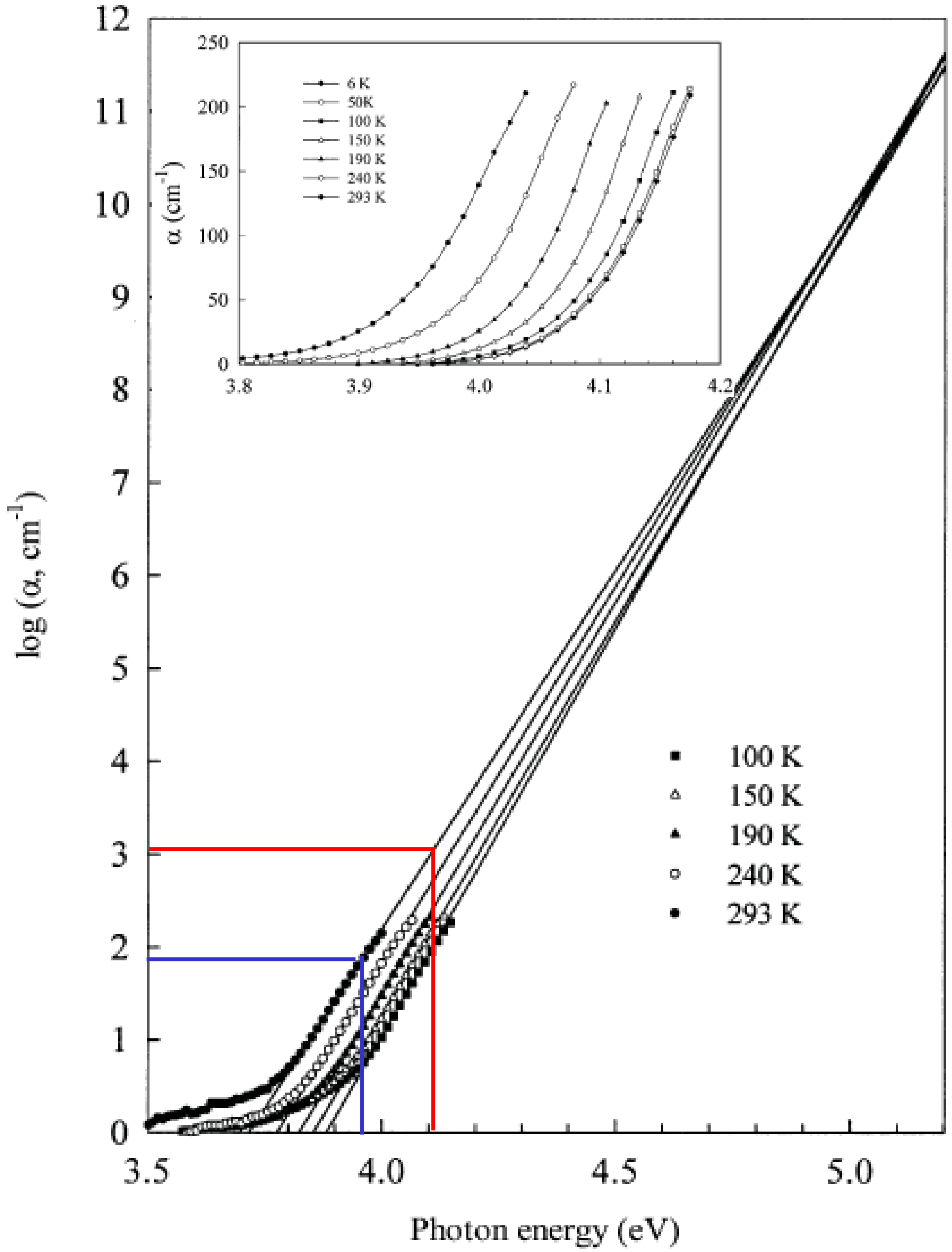
E_{exc}=4.84 eV, 100 fs

- $\sigma = 1$
- a measured 60 µm
- $\alpha = 10^6$ cm^{-1} ?
- ***$R_{d\text{-}d}$* = 3 nm**
- N_0^{max} 6x10^{21} cm^{-3}

Fitted curves for $CdWO_4$



$CdWO_4$ excitation in the Urbach tail region



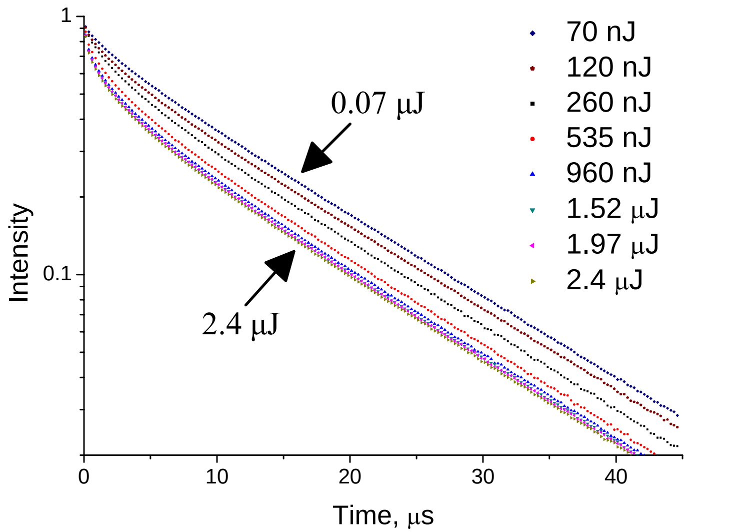
V. Nagirnyi et al., J. Lumin. **102**, 597 (2003)

313 nm (3.96 eV)

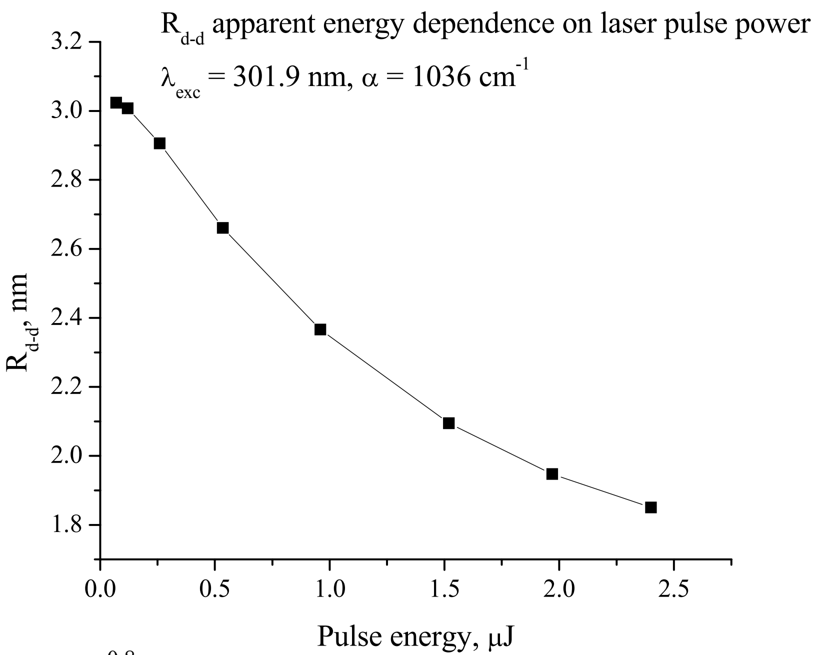
- α = 77.6 cm^{-1}
- σ = 1

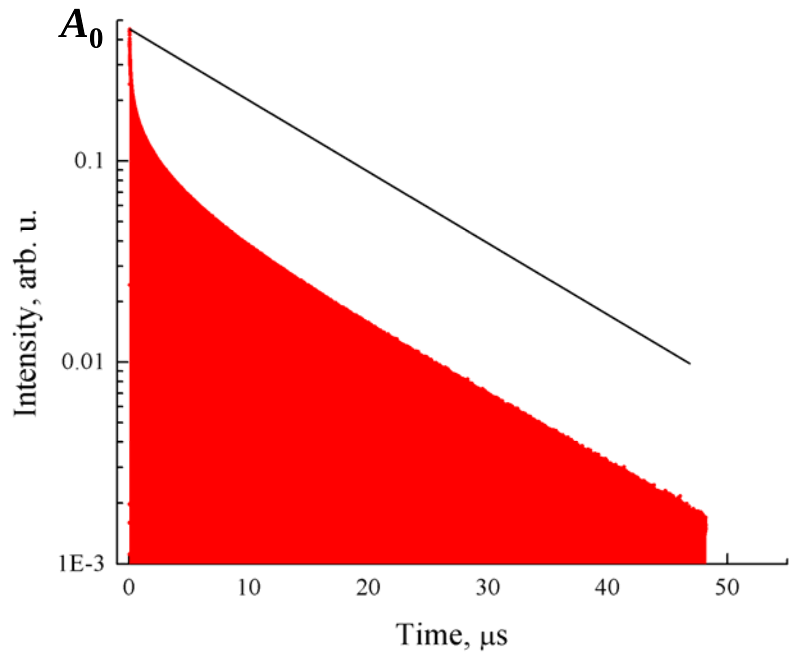
301.9 nm (4.11 eV)

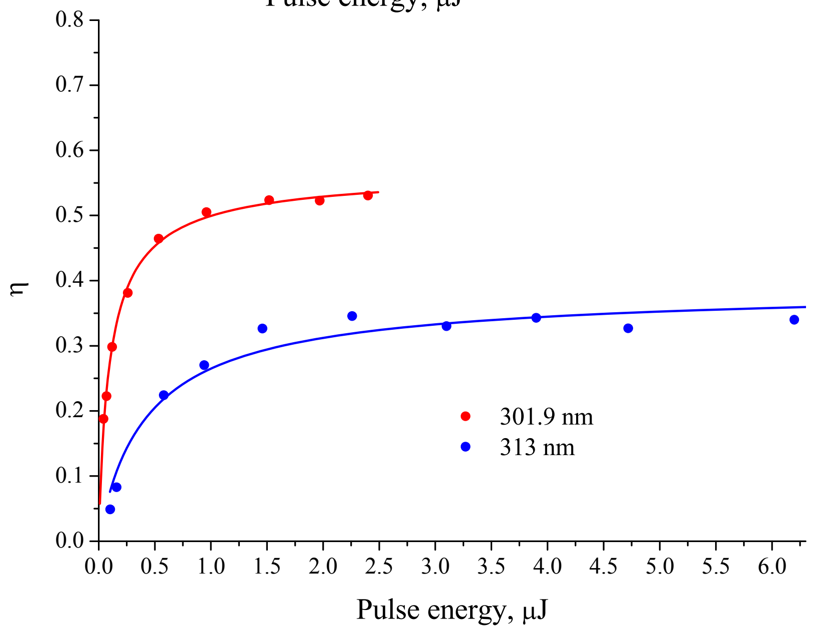
- α = 1036 cm^{-1}
- σ = 1



Problem

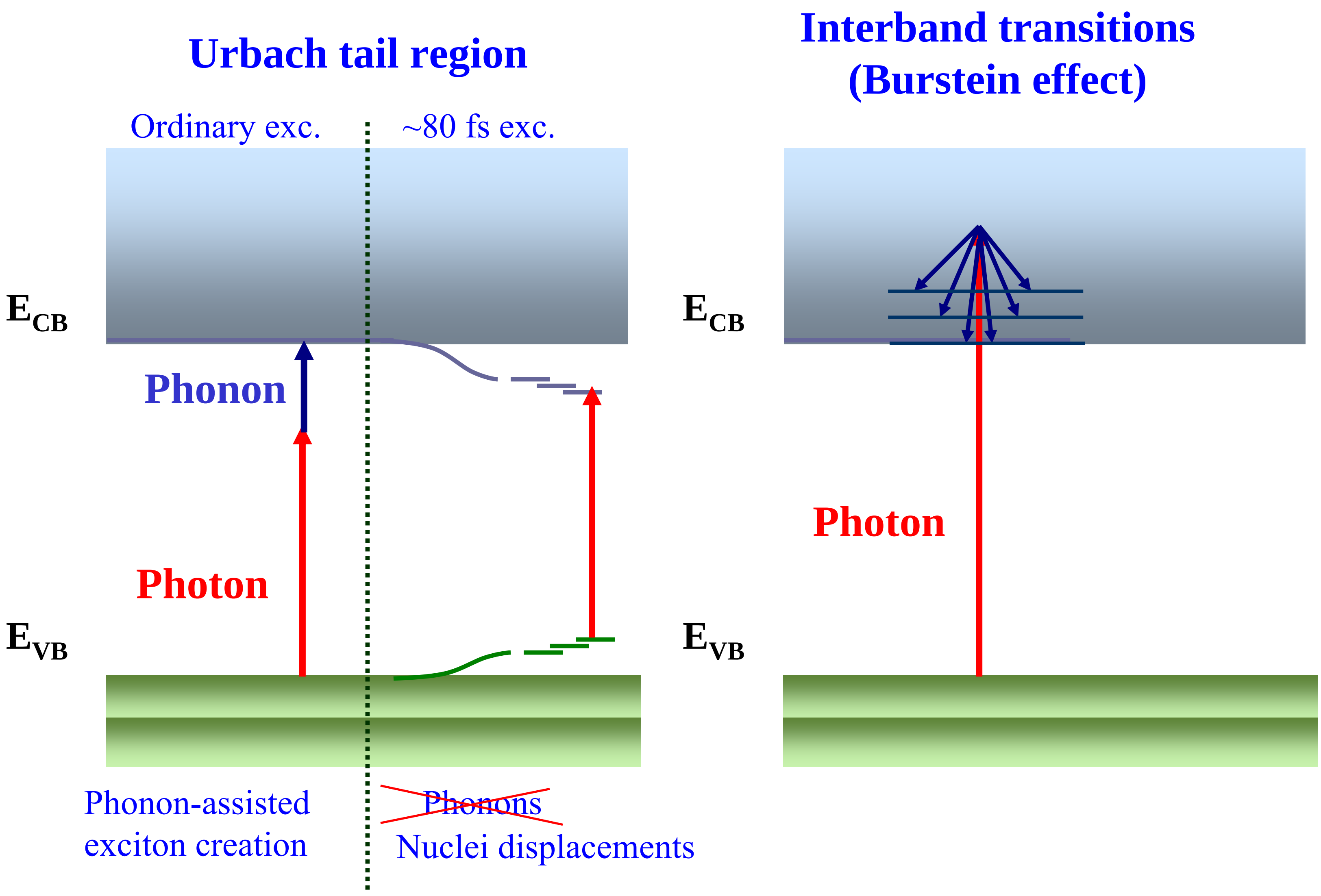






$$\eta = 1 - \frac{\int I_{exp}(t)\,dt}{A_0 \tau_r}$$

Reasons of the saturation of excitonic absorption



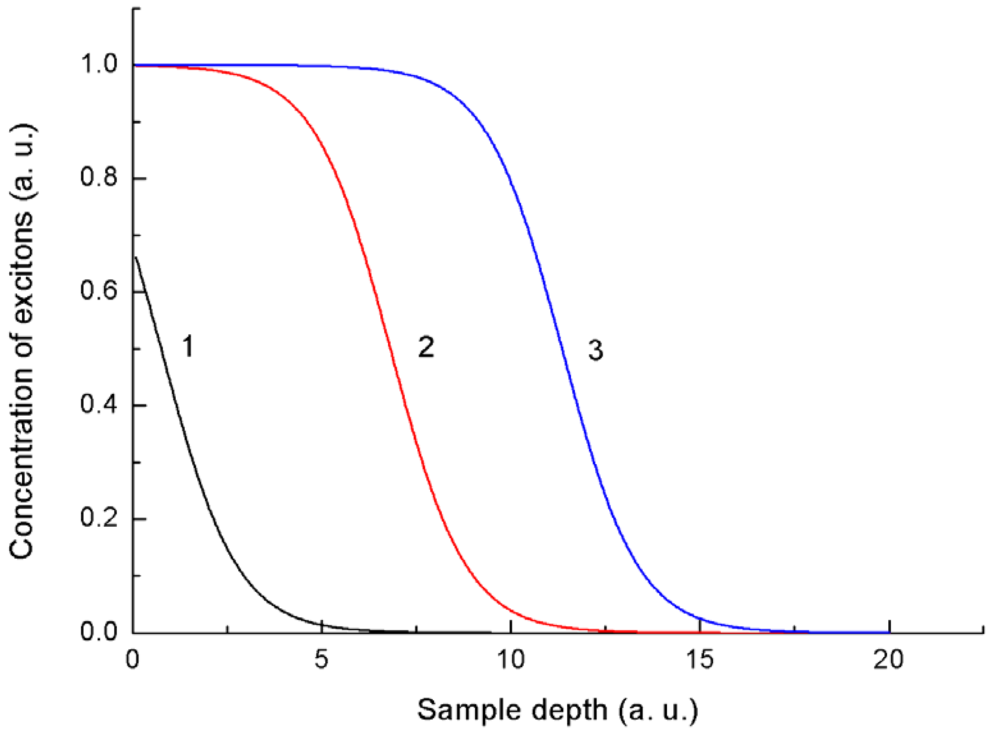
Modeling

80 fs pulses

Saturated absorption

$$\alpha = \alpha_{lin}\left(1 - n(\mathbf{r},t)/n_0\right)$$

n_0 – maximum possible concentration of excitations



$$I(t) = \frac{\pi a^2 n_0}{\tau\alpha} e^{-t/\tau} \int_0^{\frac{I_0\alpha}{\pi a^2 n_0}} \frac{\ln\left(e^x + \left(e^x - 1\right)\frac{2}{3}\pi^2 R_{d-d}^3 n_0 erf\left(\sqrt{t\tau^{-1}}\right)\right)}{x\left(1 + \frac{2}{3}\pi^2 R_{d-d}^3 n_0 erf\left(\sqrt{t\tau^{-1}}\right)\right)} dx$$

302 nm: $R_{d-d} = 3.7$ nm, $n_0 = 5.4 \times 10^{18}$ cm^{-3}

R_{d-d}=3.7 nm

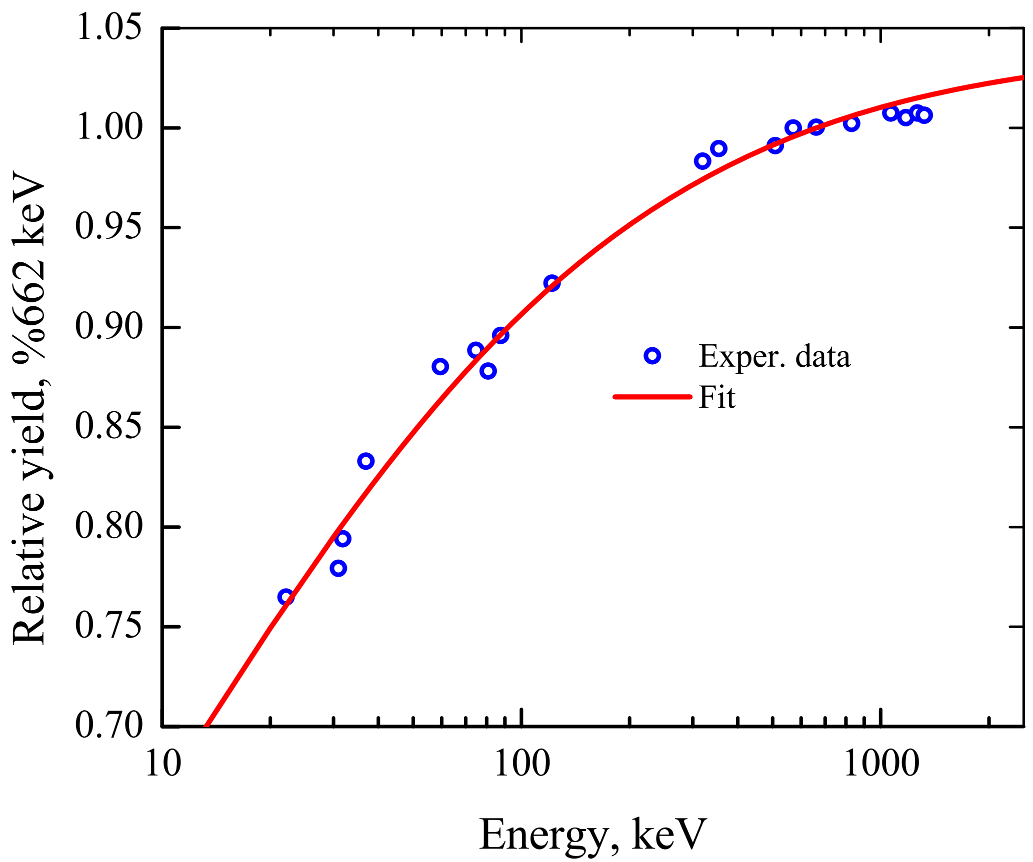
Modeling non-proportionality in terms of the Förster radius

$$Y(E_0) = \frac{1}{E_0}\int_0^{\infty}\frac{\eta e^{-t/\tau}}{\tau E_{eh} a(t)}\int_0^{E_0}\frac{\ln\left[1 + a(t)b(x)\right]}{b(x)}dxdt,$$

$$a(t) = \frac{2\pi\eta R_{d-d}^3}{3r^2 E_{eh}} erf\left(\sqrt{t/\tau}\right)$$

$$b(E) = \frac{e^4 \rho_e}{8\pi\varepsilon_0^2 E}\ln\left(1.164\frac{E + 0.81I}{I}\right).$$

Non-proportionality of $CdWO_4$ defined as the light yield relative to 662 keV.



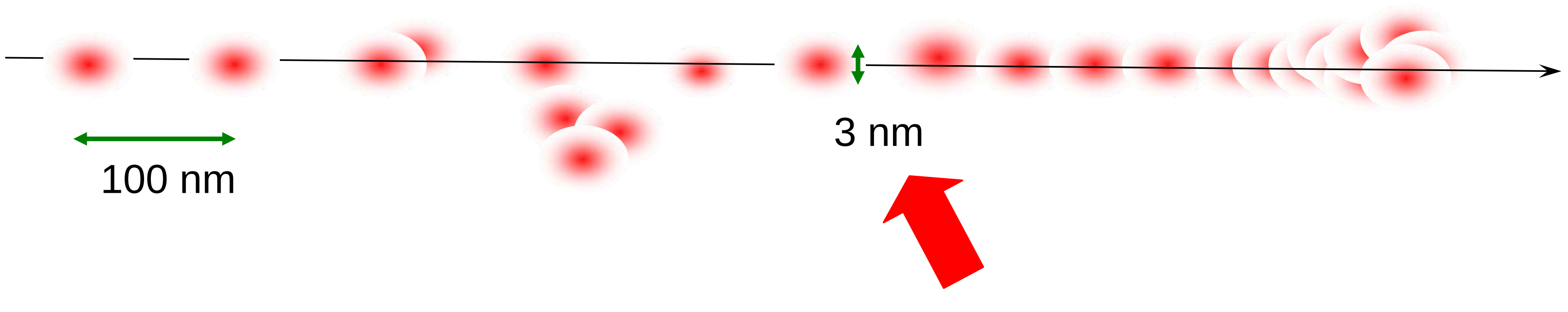
r_{tr} = 3.9 nm

Exper. Data -- W. Klamra, T. Szczesniak, M. Moszynski, et al., J. Instrum. **7**, P03011 (2012)

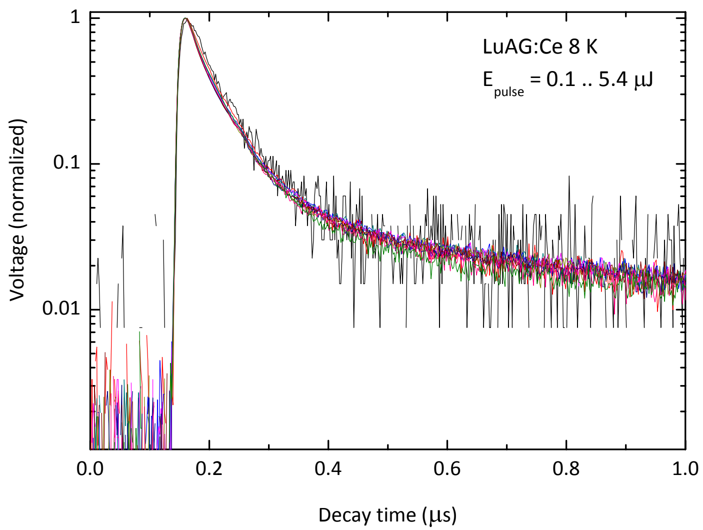
Track spatial and temporal structure

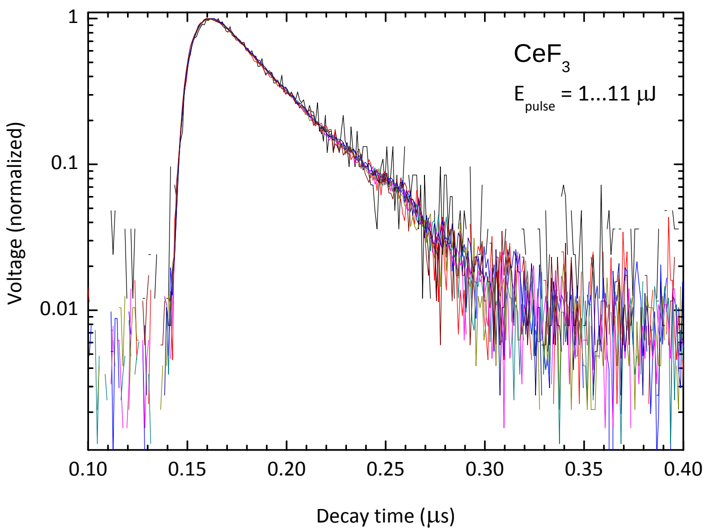
(A.N. Vasil'ev, SCINT'2009)

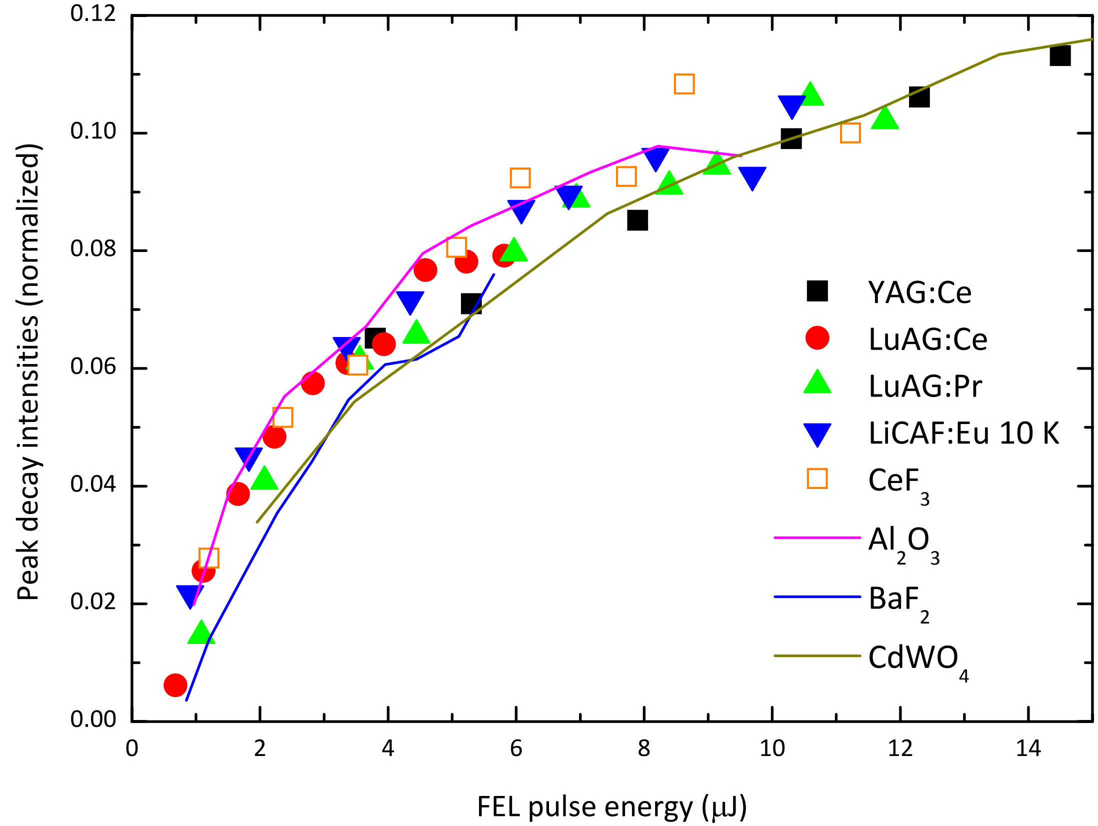
Initial electron track structure is defined by isolated and overlapped clusters of excitations with initial size of about 3 nm (just after initial recombination and thermalization of electrons and holes, ps time domain) and distances between clusters are about 1 to 100 nm.



RE activated scintillators







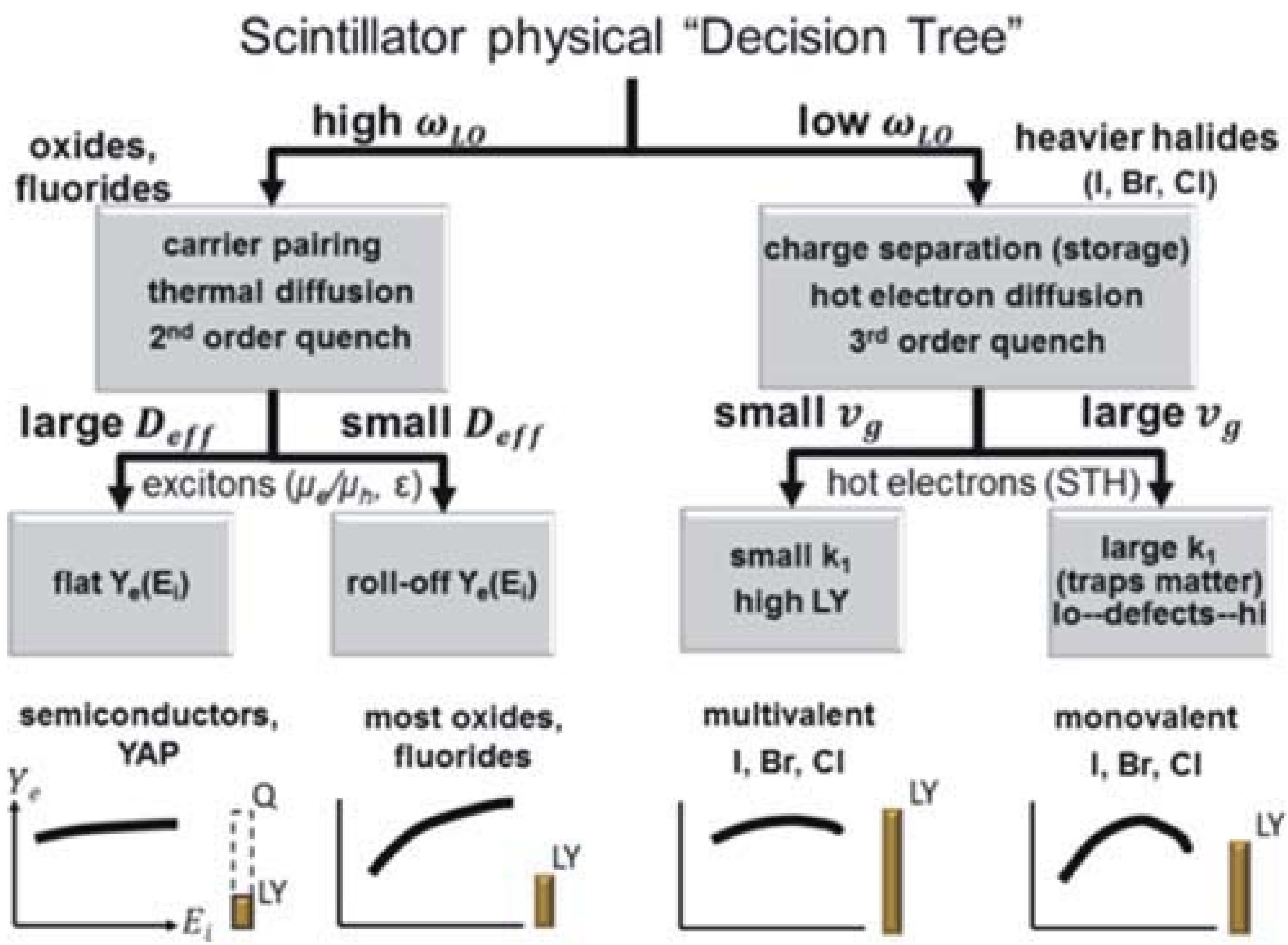
Theoretical analysis, further works

A. N. Vasil’ev, IEEE Trans. Nucl. Sci. 55, 1054 (2008).
G. Bizarri et al., J. Appl. Phys. 105, 044507 (2009).
G. Bizarri et al., J. Lumin. 129, 1790 (2009).
R. T. Williams et al., phys. stat. sol. (b) 248, 426 (2011).
W. W. Moses et al., IEEE Trans. Nucl. Sci. PP, 1 (2012).
Qi LI et al., J. Appl. Phys. 109, 123716 (2011)
Qi Li et al., P hys. Status Solidi RRL 6, No. 8, 346–348 (2012).

Main directions of studies (factors that influence proportionality of LY):

1. Charge carrier thermalization rate
2. Diffusion of charge carriers and excitons:
• group velocity of hot electrons
• mobility of thermalized charge carriers
• hole self-trapping
3. Quenching of luminescence
• linear – trapping at defects and impurities
• nonlinear – second order Förster, third order Auger

Nonproportionality in solids



Qi Li et al., Phys. Status Solidi RRL **6**, No. 8, 346–348 (2012).

To study

- Charge carrier relaxation (exciton formation)
- Charge carrier mobility (diffusion)
- Mutual interaction of electronic excitations
- Interaction of electronic excitations with impurities and defects, charge trapping

Two additional experiments

- High-density excitation; the study of interaction of electronic excitations (Saclay, Vilnius)
- Time-resolved interferometry; the study of thermalization and trapping dynamics of electronic excitations (Saclay)

Thank you for attention