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Manifestation of exciton-exciton interaction in scintillator response

Vitali Nagirnyi
Institute of Physics, University of Tartu
vetal@fi.tartu.ee

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Contributors:

Institute of Physics, University of Tartu, Estonia:
E. Feldbach, M. Kirm, A. Kotlov, R. Laasner, S. Vielhauer

Service des Photons Atomes et Molécules, CEA/Iramis, Gif sur Yvette, France:

M. De Grazia, B. Carré, H. Merdji

Laboratoire des Solides Irradiés, CEA-CNRS Ecole Polytechnique, Palaiseau, France:
S. Guizard, J. Gaudin, G. Geoffroy
Laboratoire CELIA, CNRS, CEA et Université de Bordeaux I, Talence, France:
N. Fedorov, P. Martin

Laboratoire de Physico-Chimie des Matériaux Luminescents, CNRS, UMR5620, Université Lyon 1, France:

A. Belsky

Laser Research Centre, Vilnius University, Vilnius, Lithuania:

R. Grigonis, V. Sirutkaitis

Institute for Scintillation Materials, NAS, Kahrkov, Ukraine:

L. Nagornaya, I. Tupitsyna -- crystal growth

Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Russia:

A. Vasil'ev

Outline

- Exciton-exciton interaction under XUV/X ray/γ ray excitation: difficulties of characterization
- Experiments with high-density UV/VUV excitation
- Methods of data treatment
- Conclusions

Scintillator nonproportional response

- Excitation density effects:
  Vasil'ev, IEEE Trans. Nucl. Sci. 55 (2008) 1054

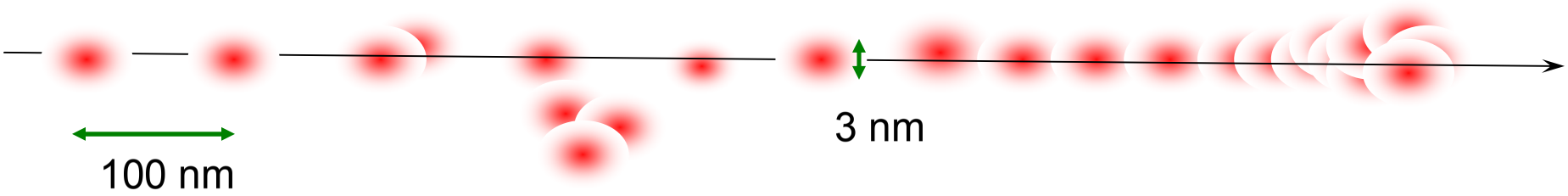
  •Luminescence excitation in the fundamental absorption region is intrinsically non-linear process

  •Luminescence non-linearity is displayed in decay kinetics

  • Luminescence yield depends on the density of initially created excitations, resulting in non-proportionality

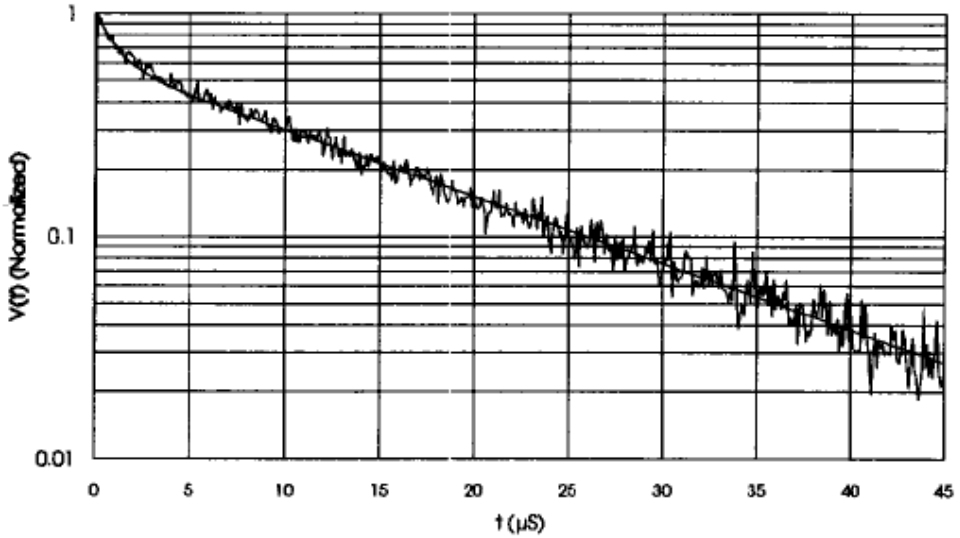
- Reason: **Initial electron track structure is defined by isolated and overlapped clusters of excitations with initial size of about 3 nm**

  Luminescence quenching mechanisms involved
  Method: comparison UV vs XUV/X rays



Decay kinetics of $CdWO_4$ excitonic emission under different excitations

- 0.8 μs Gillette, 1950. Rev. Sci. Instrum. 21, p. 294 **(γ rays)**
- 1.1 μs, 14.5 μs Kinloch et al., IEEE Trans. Nucl. Sci. 41, 752 (1994) **(γ rays)**
- 2 μs, 15 μs Deych et al., Proc. SCINT95, 1996, p. 36 **(γ rays)**
- 5 μs, 20 μs Melcher et al., IEEE Trans. Nucl. Sci. 36, 1188 (1989) **(X rays)**
- 7.8 μs Beard et al., 1962. J Appl. Phys.. 33, p. 144 **(α particles)**
- 9 μs Grabmaier. IEEE Trans. Nucl. Sci. 31, 372 (1984) **(X rays)**
- 13-15 μs under optical excitation! Many papers. **(UV photons)**



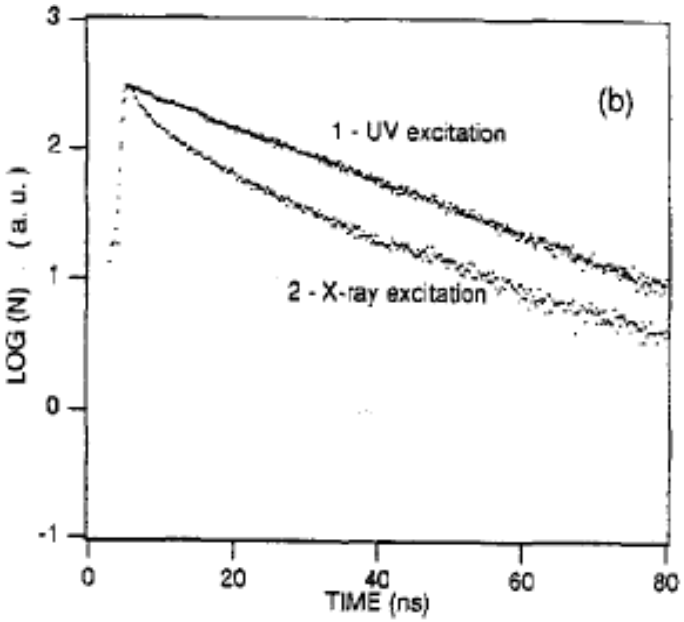
Kinloch et al., IEEE Trans. Nucl. Sci. **41**, 752 (1994)

10 microcurie Cs-137 source:
662 keV γ photons

Emission decay curves under XUV and X-ray excitation

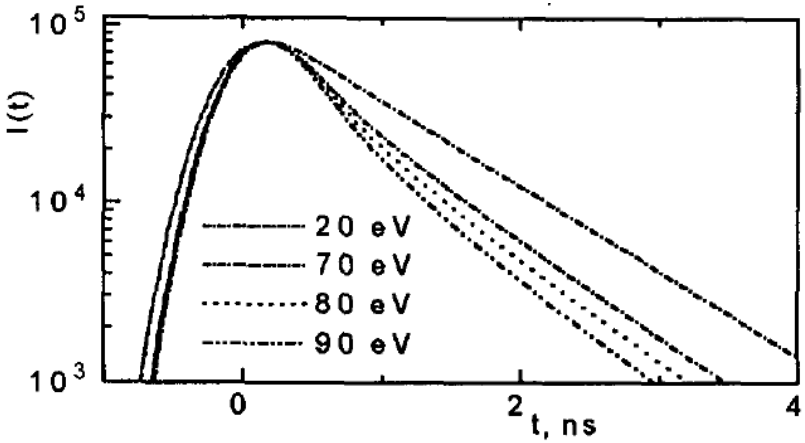
CeF_3

Pedrini, et al., Chem. Phys. Lett. 206 (1993) 470



BaF_2

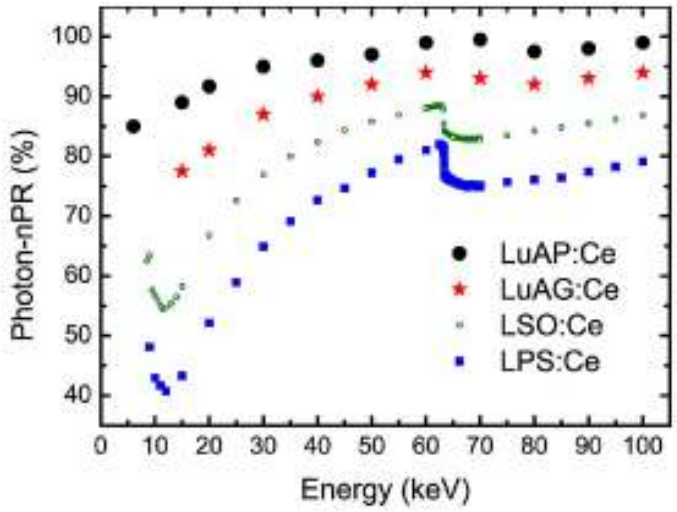
Belsky at al., J. Electr. Spectrosc. Rel. Phen. 79 (1996) 147



Crossluminescence(!?)

Difficulties with high-energy excitation

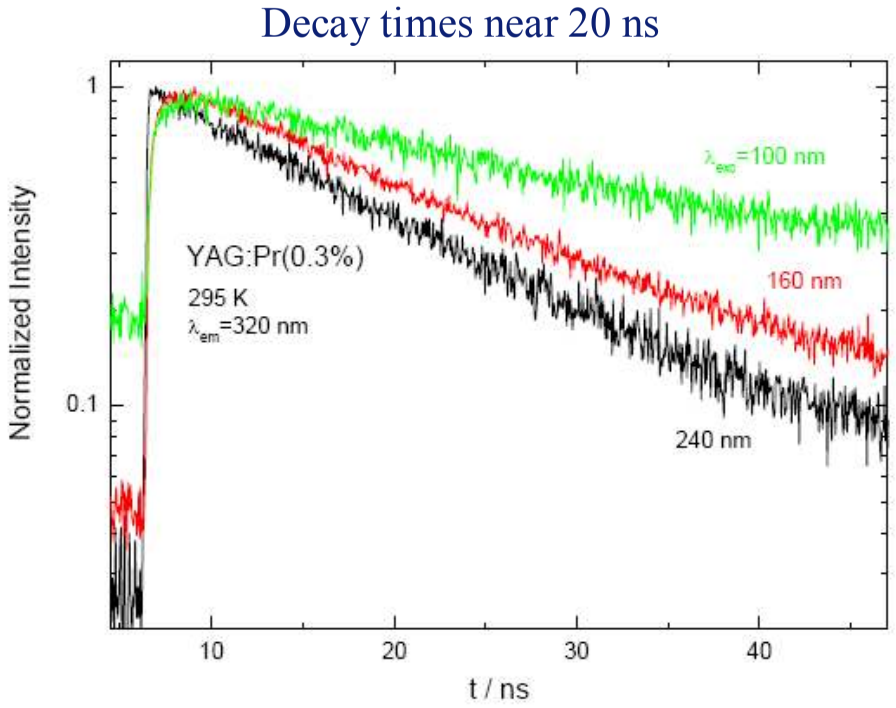
- Complex relaxation processes
- Radiation damage, colour defect creation
- Difficult to estimate number of excitations created per radiation photon
- Energy transfer from the host to a luminescence centre → additional slow components in emission decay
- Interaction of luminescence centre with transient defects → possible shortening of emission decay kinetics



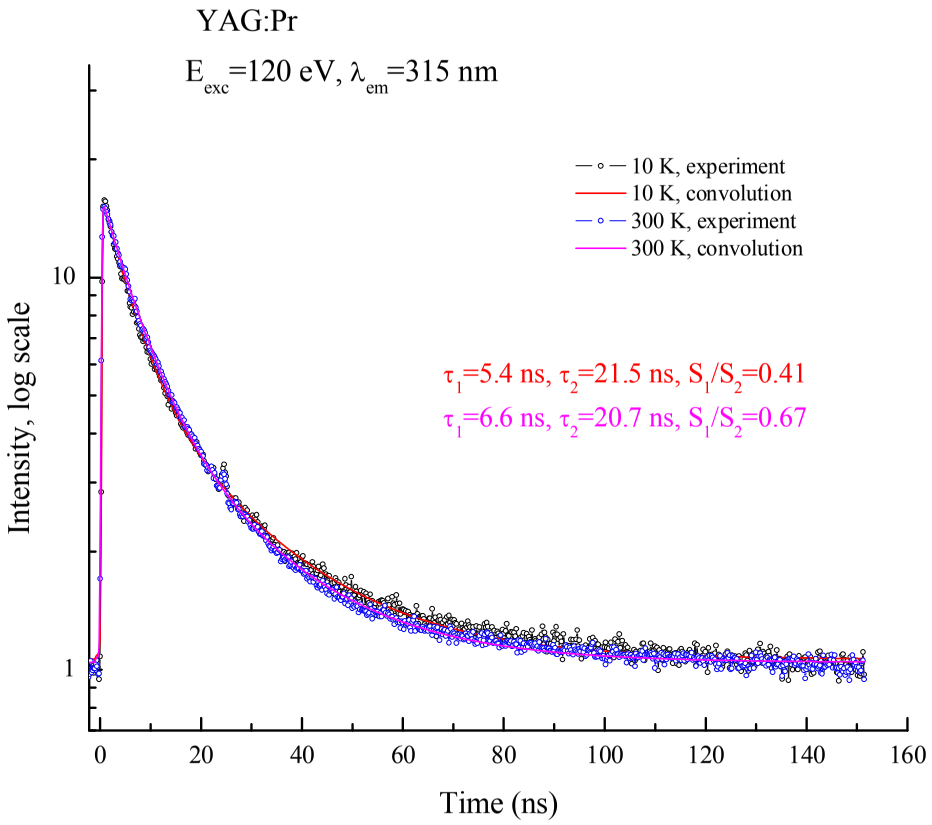
Khodyuk&Dorenbos, IEEE Trans. Nucl. Sci. 59 (2012) 3320

Interaction with transient defects: YAG:Pr^{3+}

Intrinsic f-d or low-energy excitation



High-energy XUV excitation



How to distinguish those changes in luminescence yield and decay kinetics under high-energy excitation, which are due to high excitation density?

Experiments in better controlled conditions.

Experiments performed

- **High-order harmonics generation (HHG): 23-32 eV, 10-15 fs**
- **Free electron laser (FEL): 89 eV, 25 fs**
- **Optical parametric amplifier (OPA, 240 - 2600 nm, 1-200 μJ/pulse, 100 fs, 1 kHz → We worked at 3.9 – 5.2 eV**
- **3rd harmonic of a Ti-sapphire laser, 4.66 eV, 80 fs**

Advantage: 1) laser → measurable pulse shape;

2) fs pulse → almost no heating

Crystals studied

- **Crystals with excitonic emission**
  $CdWO_4$, $ZnWO_4$, $CaWO_4$, $SrWO_4$, $PbWO_4$, CeF_3, BaF_2
- **Doped crystals with excitonic and impurity emission**
  YAG:Ce, LuAG:Ce, LuAG:Pr, LiCAF:Eu

Theory:
dipole-dipole energy transfer

•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: $$R_{d-d}^6 \propto \int \omega^{-4} F_{em}(\omega) F_{exc}(\omega) d\omega$$

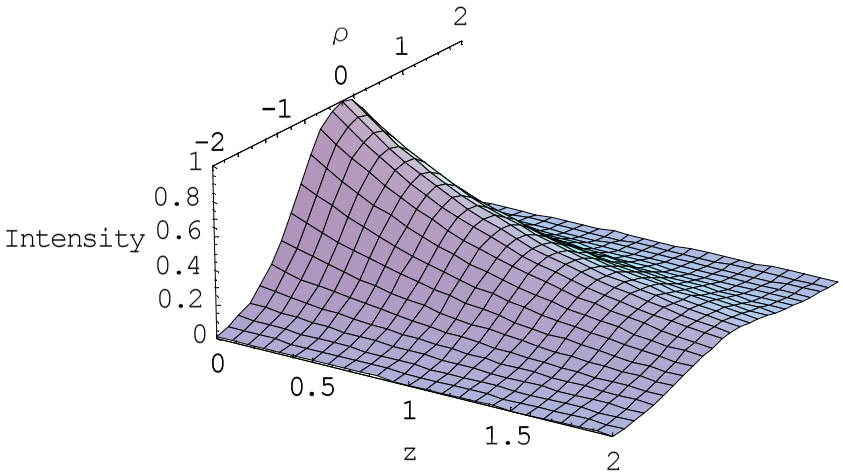
$$I(t) = \frac{\sigma I_0}{\tau} e^{-t/\tau} \frac{-Li_2\left(-\frac{2}{3}\pi^2 R_{d-d}^3 N_{\max} erf\left(\sqrt{t\tau^{-1}}\right)\right)}{\frac{2}{3}\pi^2 R_{d-d}^3 N_{\max} erf\left(\sqrt{t\tau^{-1}}\right)} \qquad N_{\max} \equiv I_0 \frac{\sigma\alpha}{\pi a^2}$$

I_0 – number of photons in a pulse

α – absorption coefficient

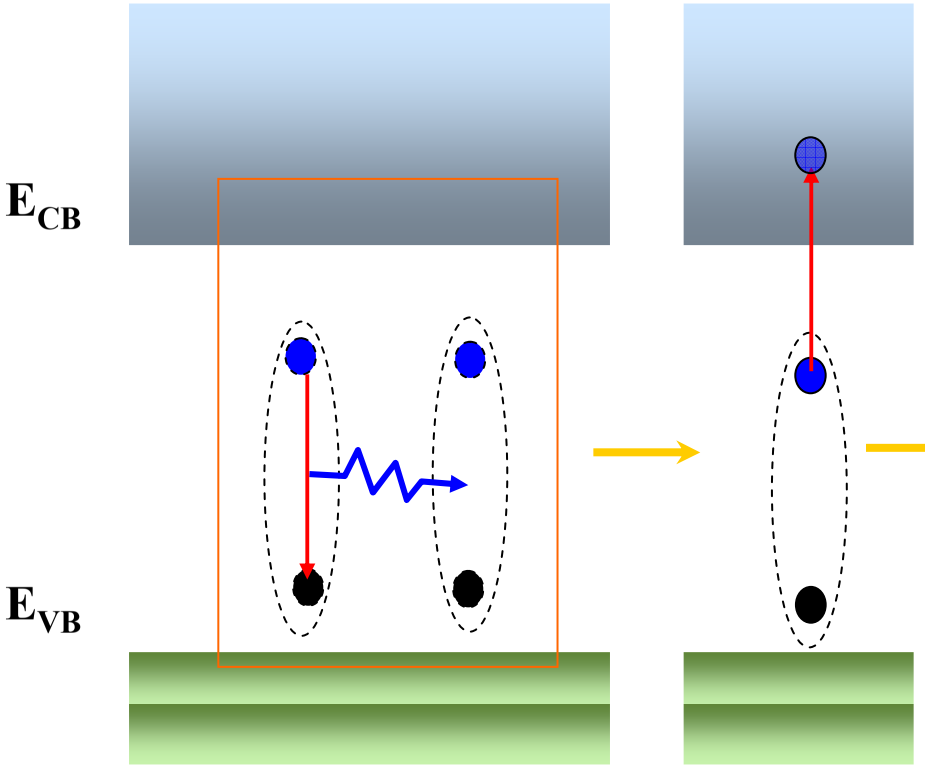
σ – exciton yield

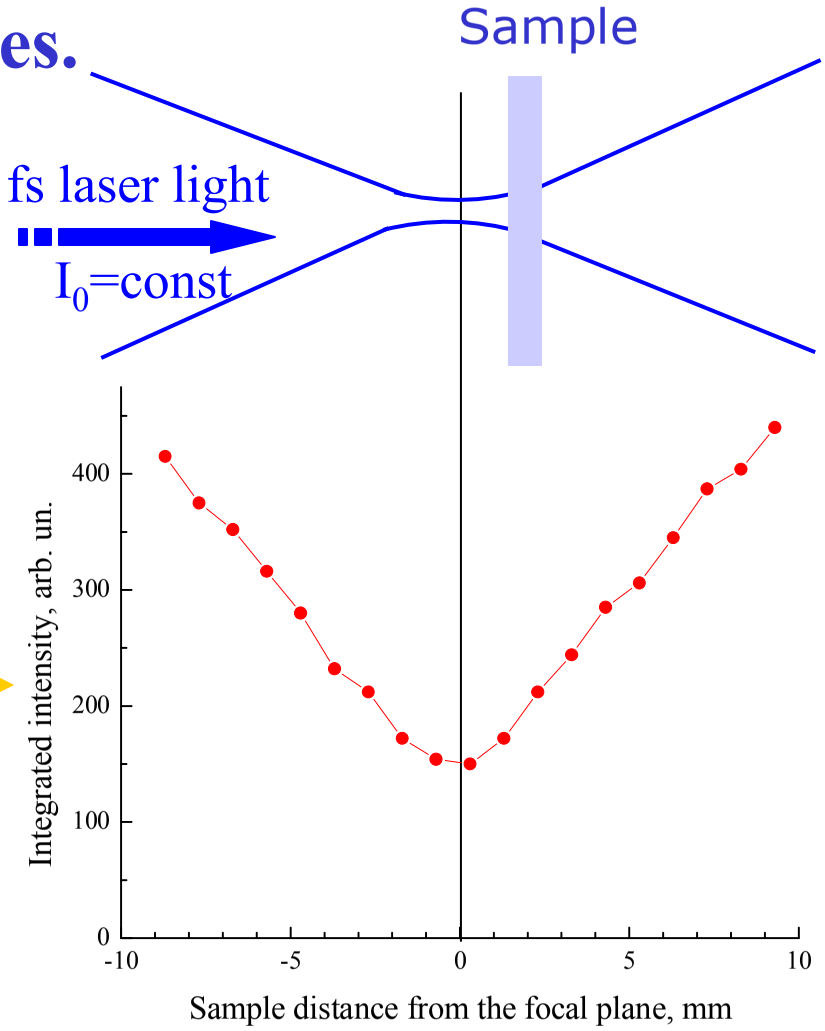
a – pulse radius



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

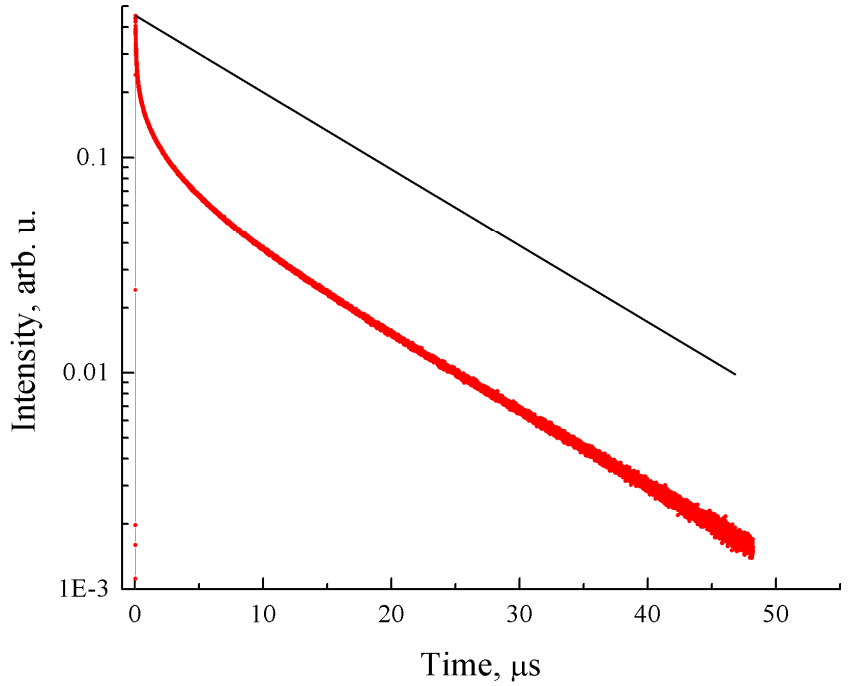
Excitons created at high densities. Self-quenching of STEs

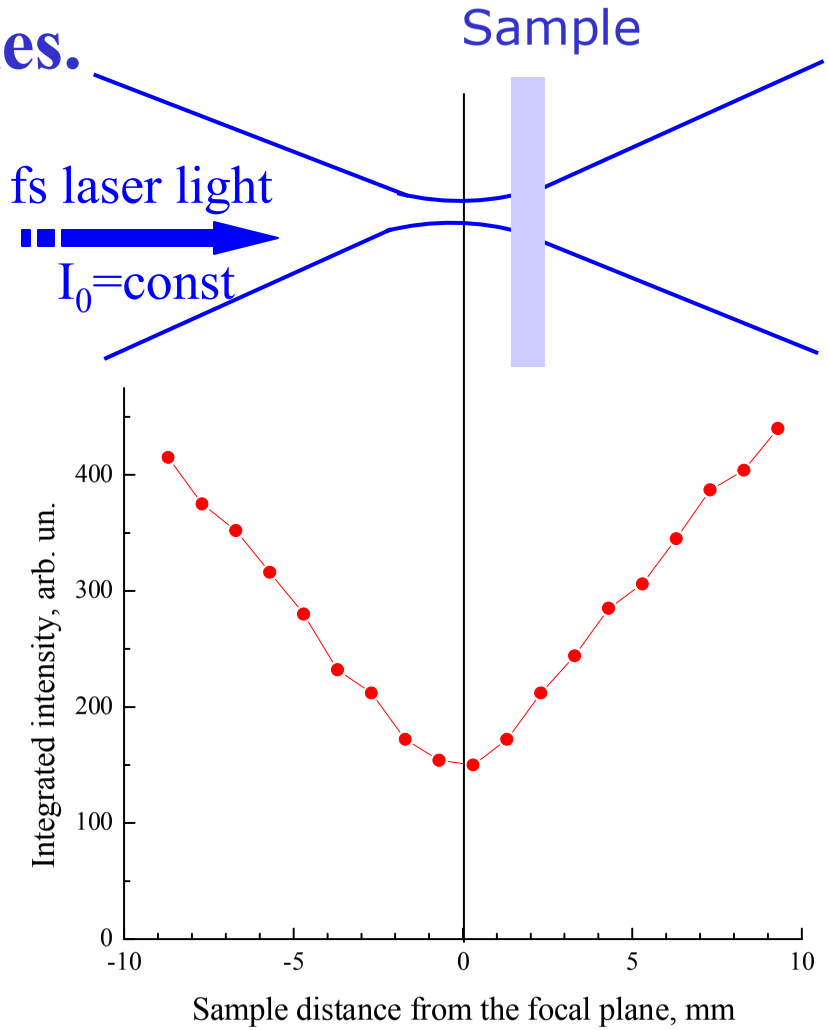




$CaWO_4$, E_{exc}=5 eV (247.5 nm), 80 fs pulse,
1 μJ pulse energy, 70 μm beam waist

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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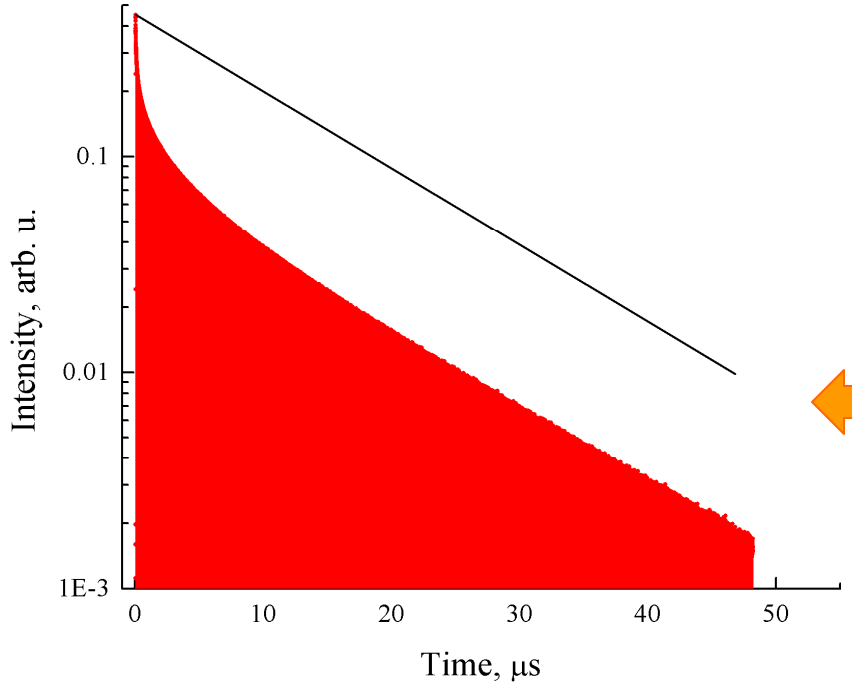
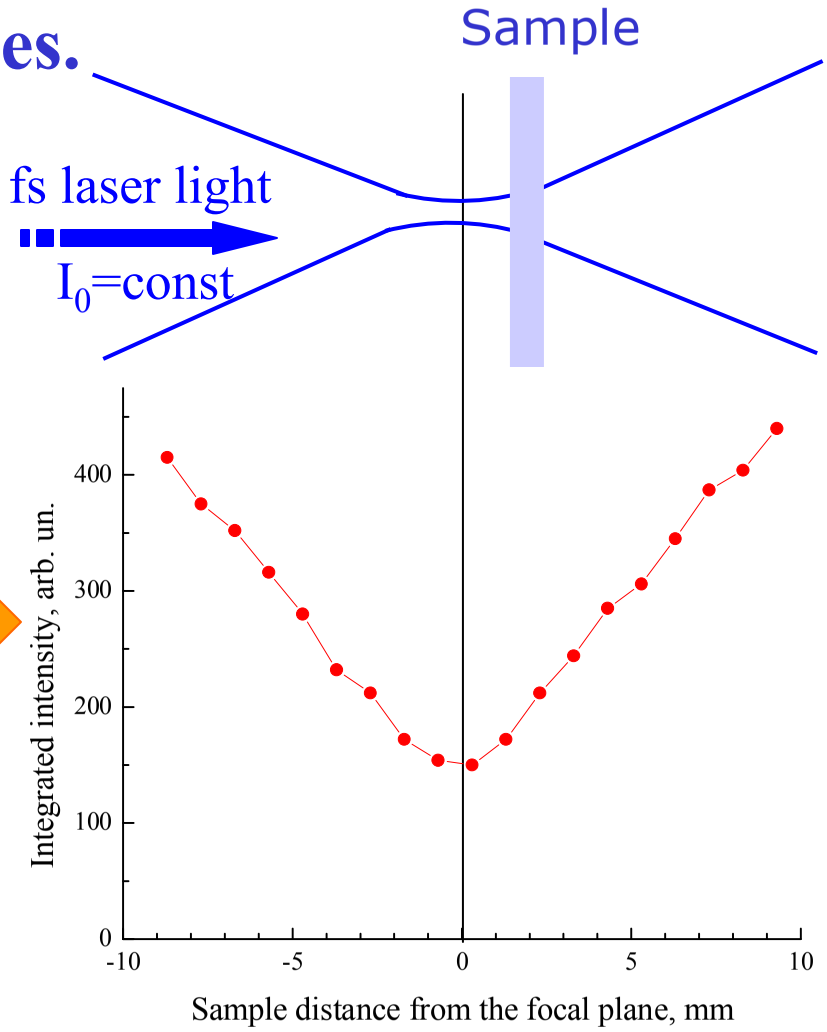
1 μJ pulse energy, 70 μm beam waist

Excitons created at high densities. Self-quenching of STEs





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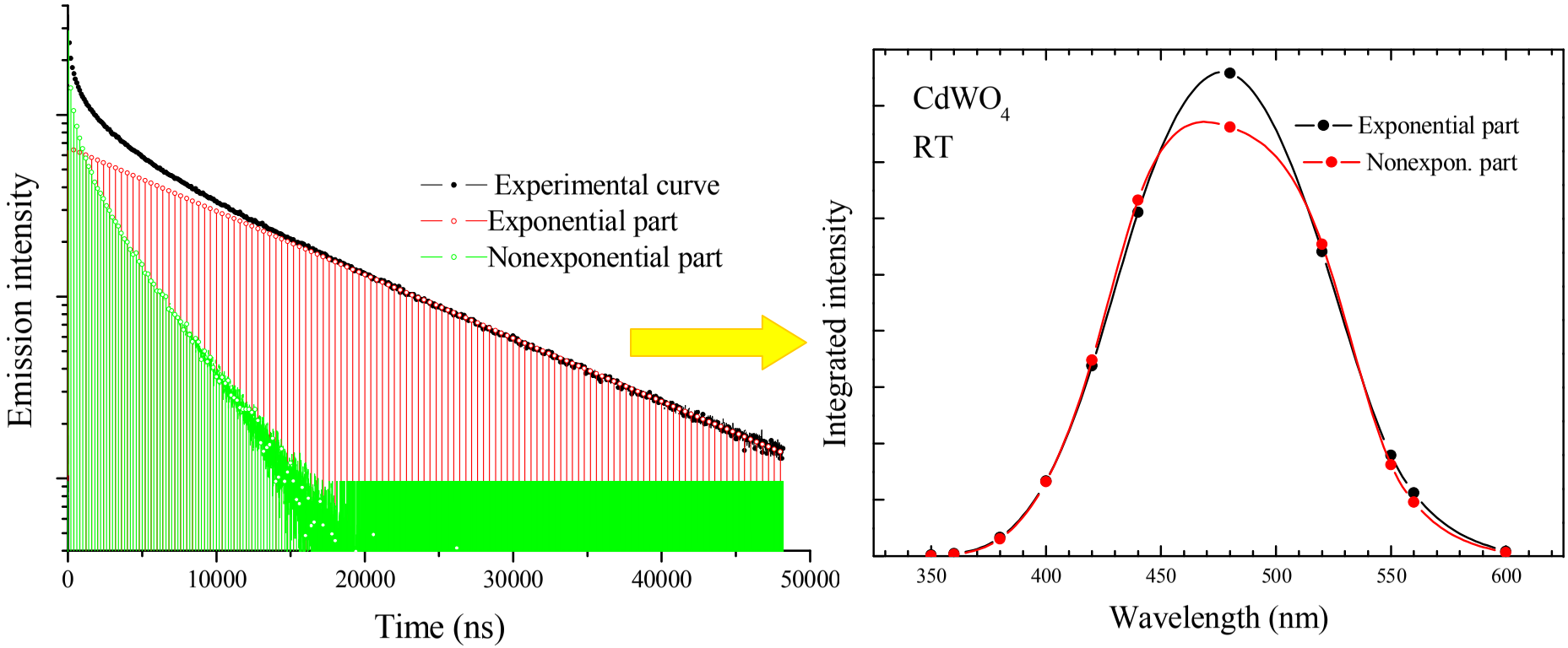
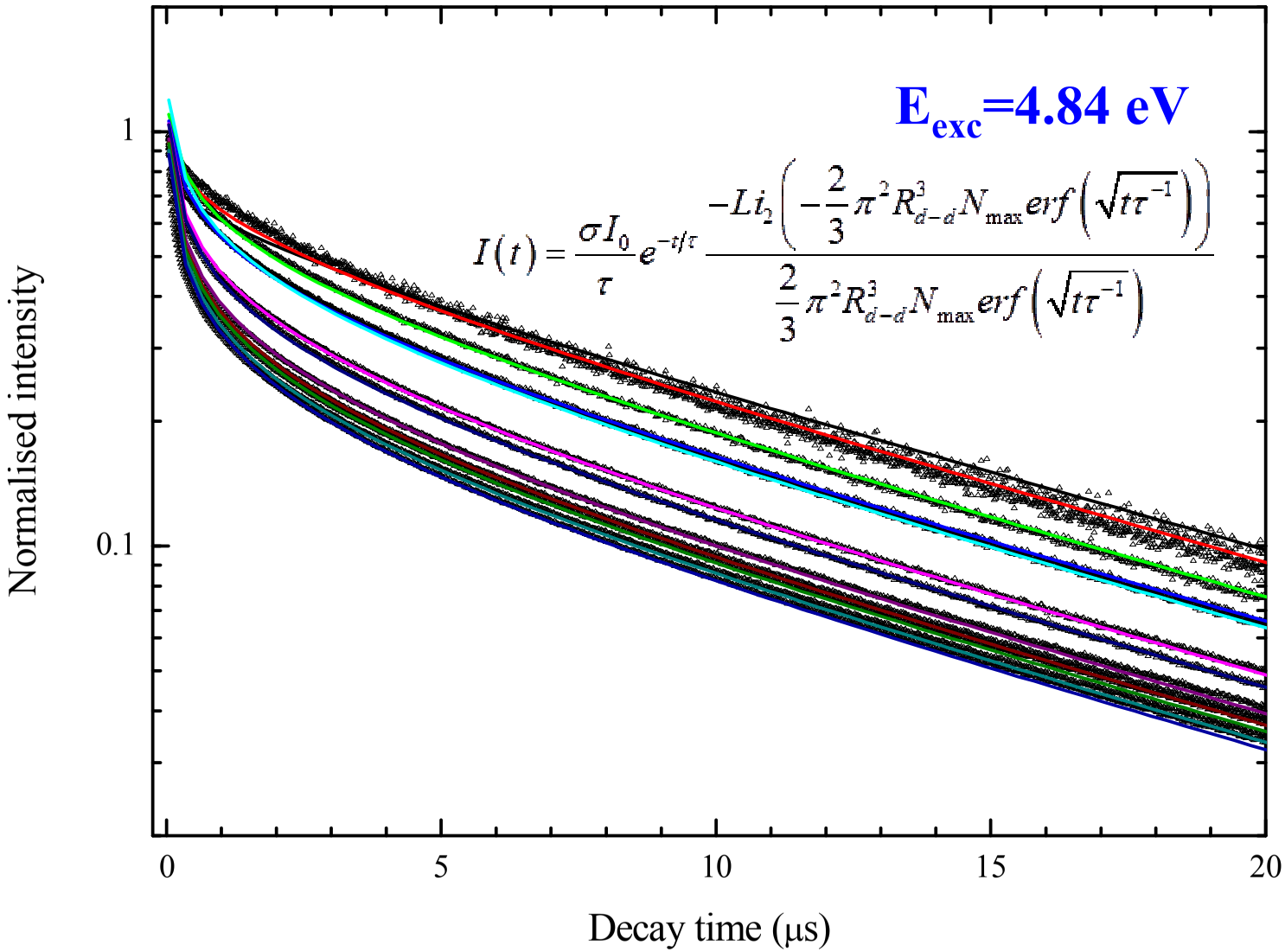
$CaWO_4$, E_{exc}=5 eV (247.5 nm), 80 fs pulse,
1 μJ pulse energy, 70 μm beam waist

The origin of nonexponential part



Radiative decay of **relaxed** Frenkel excitons

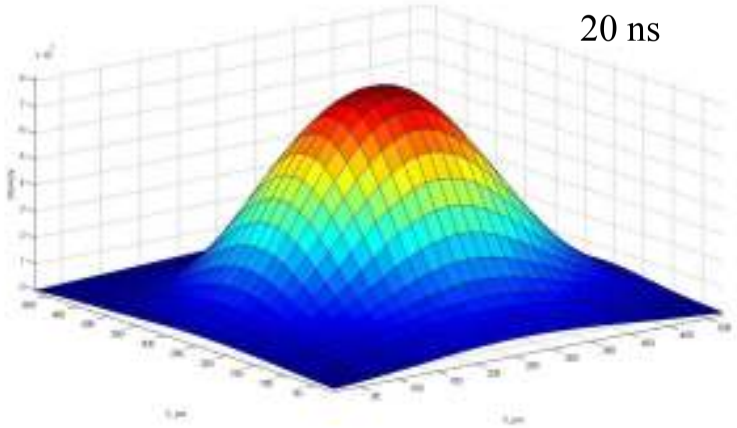
Fitted curves for the excitonic emission of $CdWO_4$



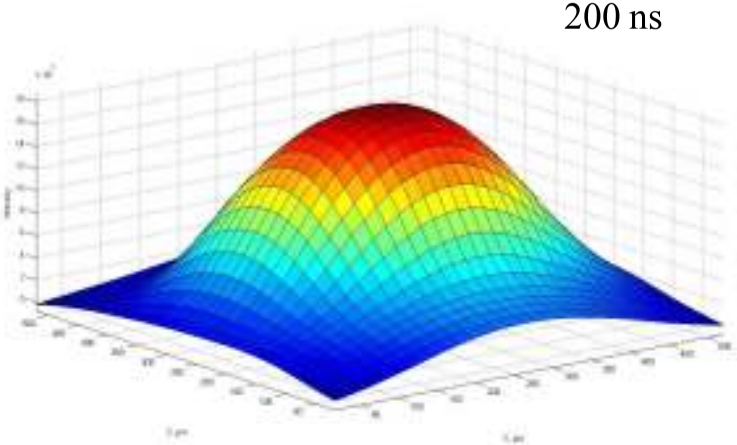
$R_{d\text{-}d}$=3.7 nm

Time-resolved images with i-CCD camera

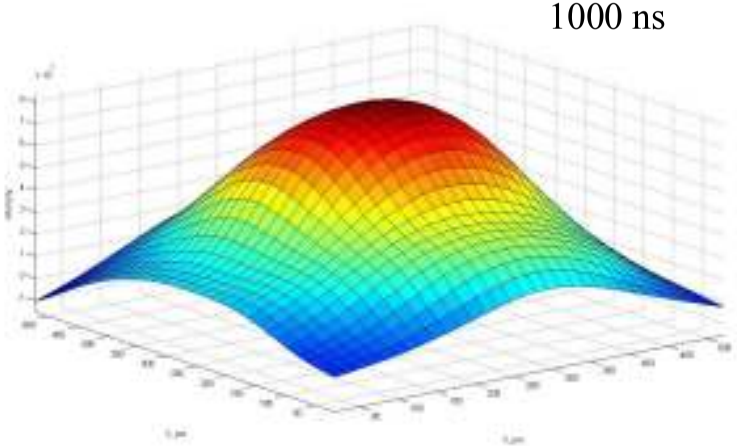
20 ns



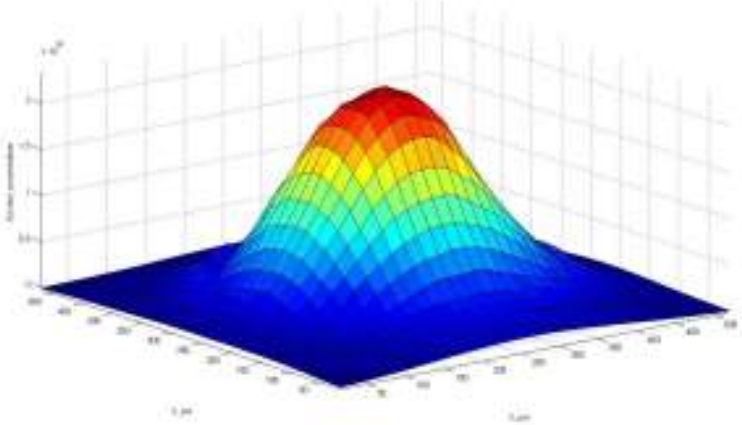
200 ns

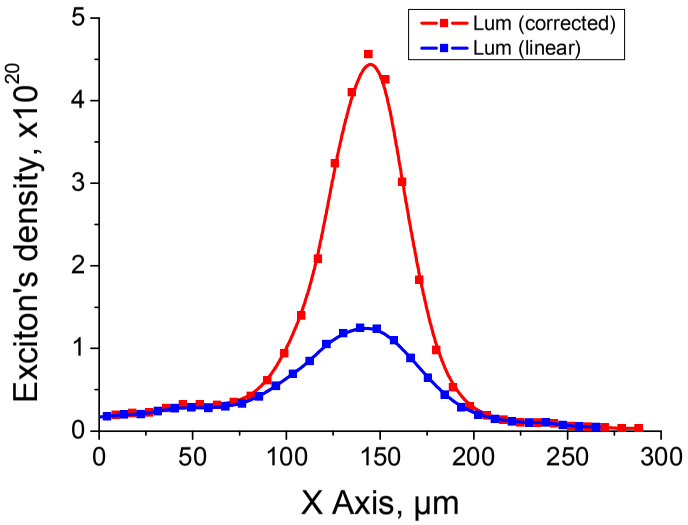


1000 ns

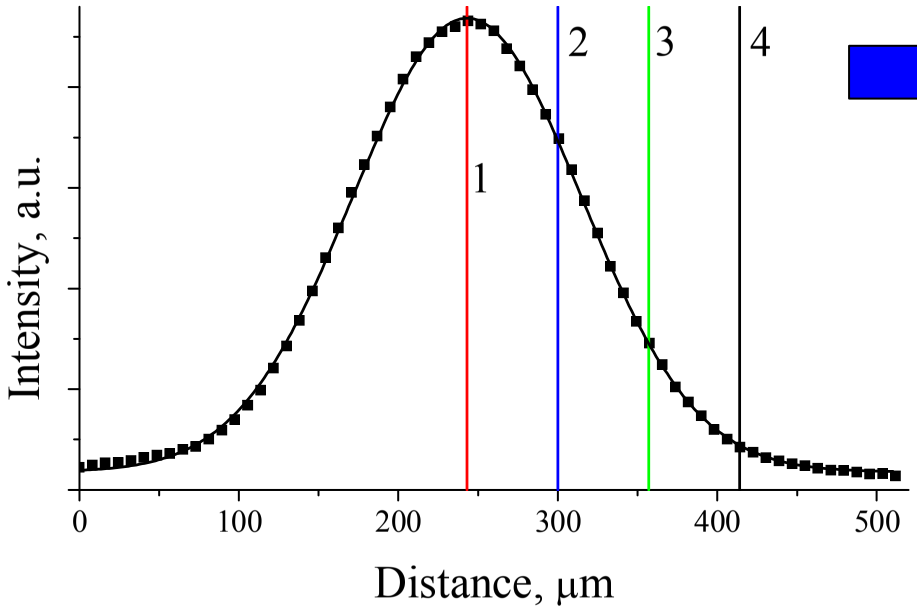


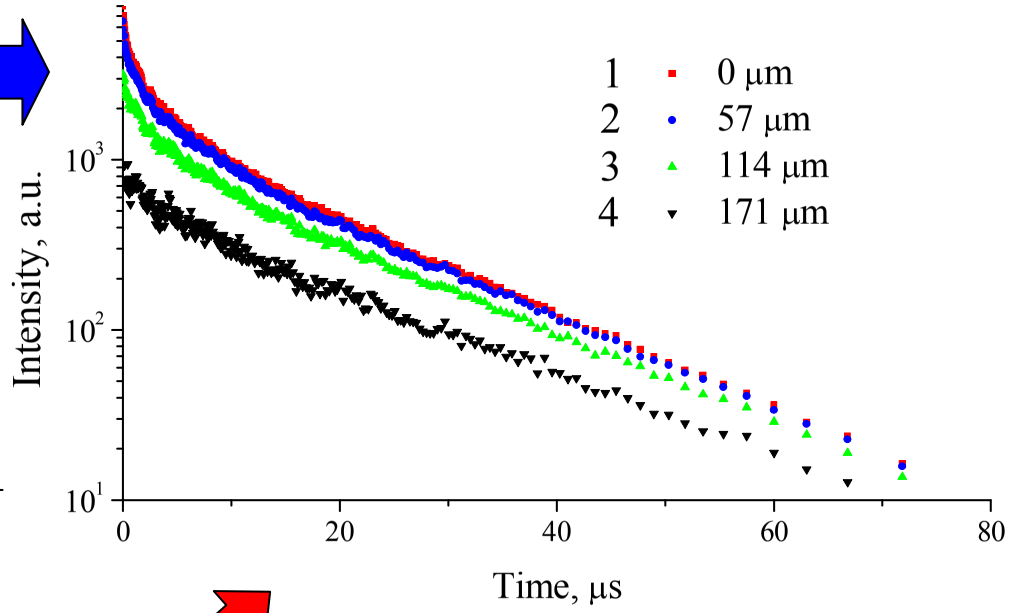
Initial distribution of excitons
(exciting beam profile)





$CdWO_4$ emission decay kinetics at different laser spot points

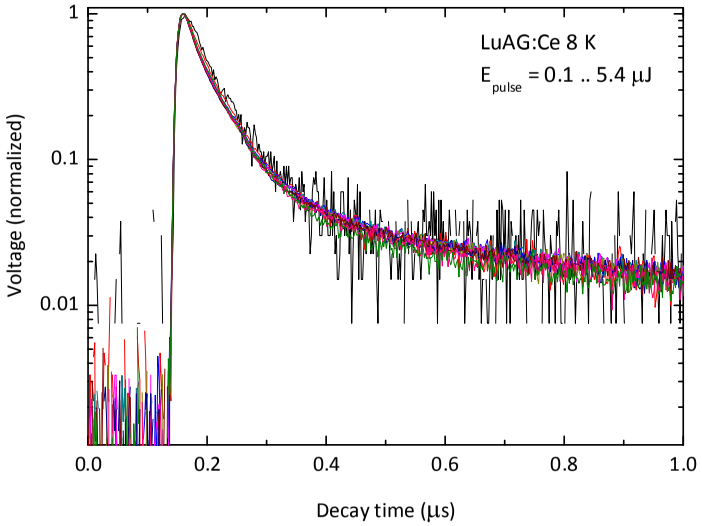


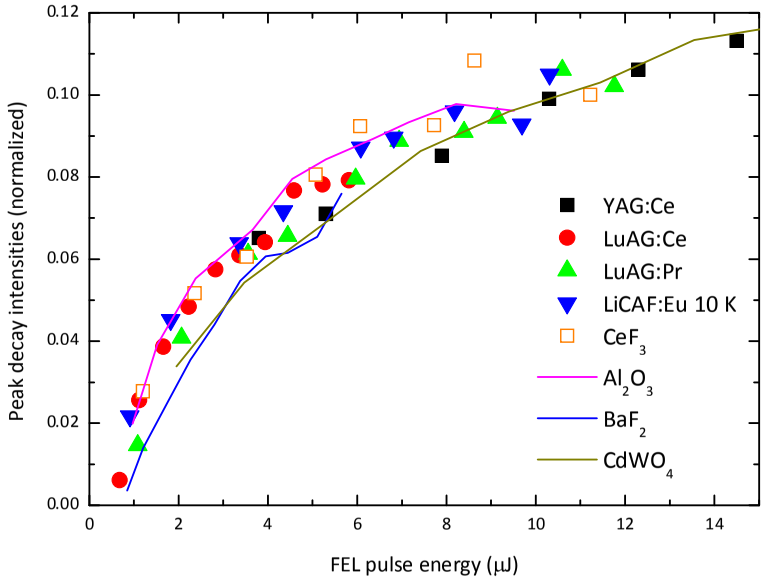


$$I(\rho,t) = \frac{\Delta S}{\tau\alpha} e^{-t/\tau} \times \frac{\ln\left[1 + \frac{2}{3}\pi^2 I_0 \frac{\sigma\alpha}{\pi a^2} e^{-\rho^2/a^2} R_{\text{d-d}}^3 \operatorname{erf}\left(\sqrt{t/\tau}\right)\right]}{\frac{2}{3}\pi^2 R_{\text{d-d}}^3 \operatorname{erf}\left(\sqrt{t/\tau}\right)},$$

RE activated scintillators

LuAG:Ce





- No changes in the shape of decay curves with pulse power – unlike intrinsic scintillators.
  (Similar observation in CsI:Tl, NaI:Tl -- Williams et al., phys. stat. sol. (b) **248** (2011) 426)
- Non-proportionality in luminescence yield:
  - almost not related to dopant concentration
  - starts well below activator saturation ($n_{exc} << n_{RE}$).
- **Model: quenching occurs in the precursor stage of activator luminescence.**

Empirical approach: from exciton-exciton interaction to activator luminescence quenching

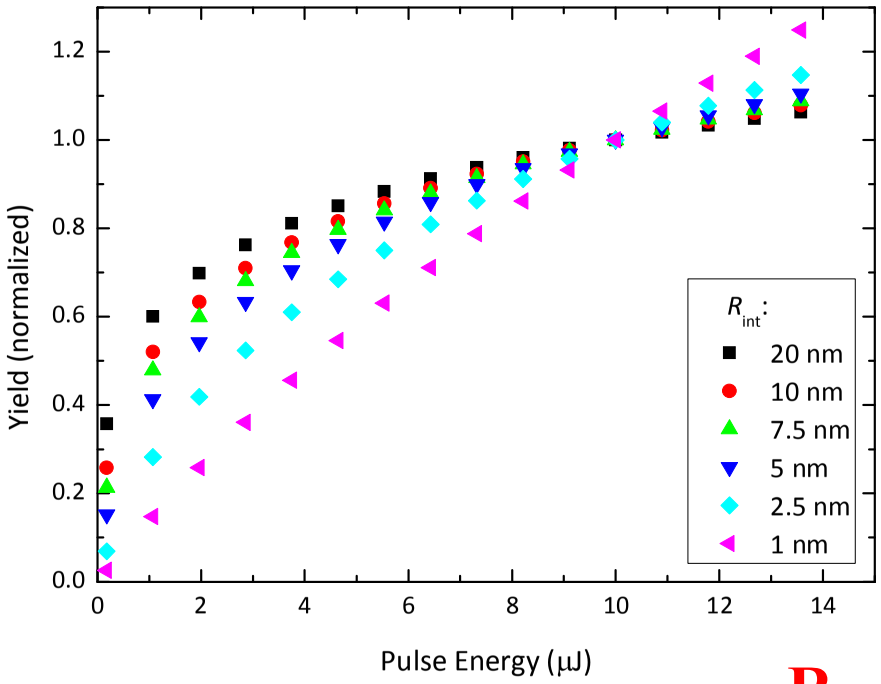
- Most simple scenario:
  - dipole-dipole interaction analog to intrinsic crystals with R_{int},
  - energy transfer to activator with constant rate (τ_{int}):

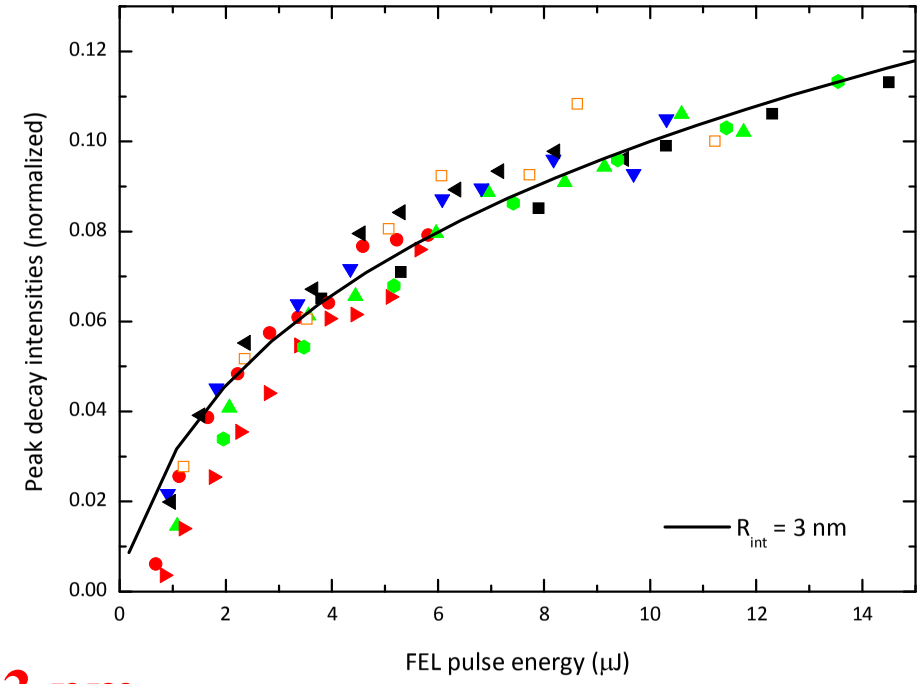
$$\frac{\partial n_{\text{int}}(\mathbf{r},t)}{\partial t} = -\frac{n_{\text{int}}(\mathbf{r},t)}{\tau_{\text{int}}} - \frac{1}{2}\gamma_{\text{int}}(t,\mathbf{r}) n_{\text{int}}{}^{2}(\mathbf{r},t)$$

  - Rate equation is equivalent to intrinsic case, luminescence yield can be calculated as

$$I_{tot} = \int_0^{\infty} dt \frac{\sigma I_0}{\tau_{\text{int}}} e^{-t/\tau_{\text{int}}} \frac{-\text{Li}_2\left(-2\pi^2 N_0^{\max} R_{\text{int}}^3 \text{erf}\left(\sqrt{t/\tau_{\text{int}}}\right)/3\right)}{2\pi^2 N_0^{\max} R_{\text{int}}^3 \text{erf}\left(\sqrt{t/\tau_{\text{int}}}\right)/3}.$$

Modeling the luminescence yield





R_{int}=3 nm

Main conclusion

The reason of nonlinear luminescence quenching and non-proportional response of the studied undoped and doped oxides and fluorides lies in the second order interaction – dipole-dipole interaction of excitons

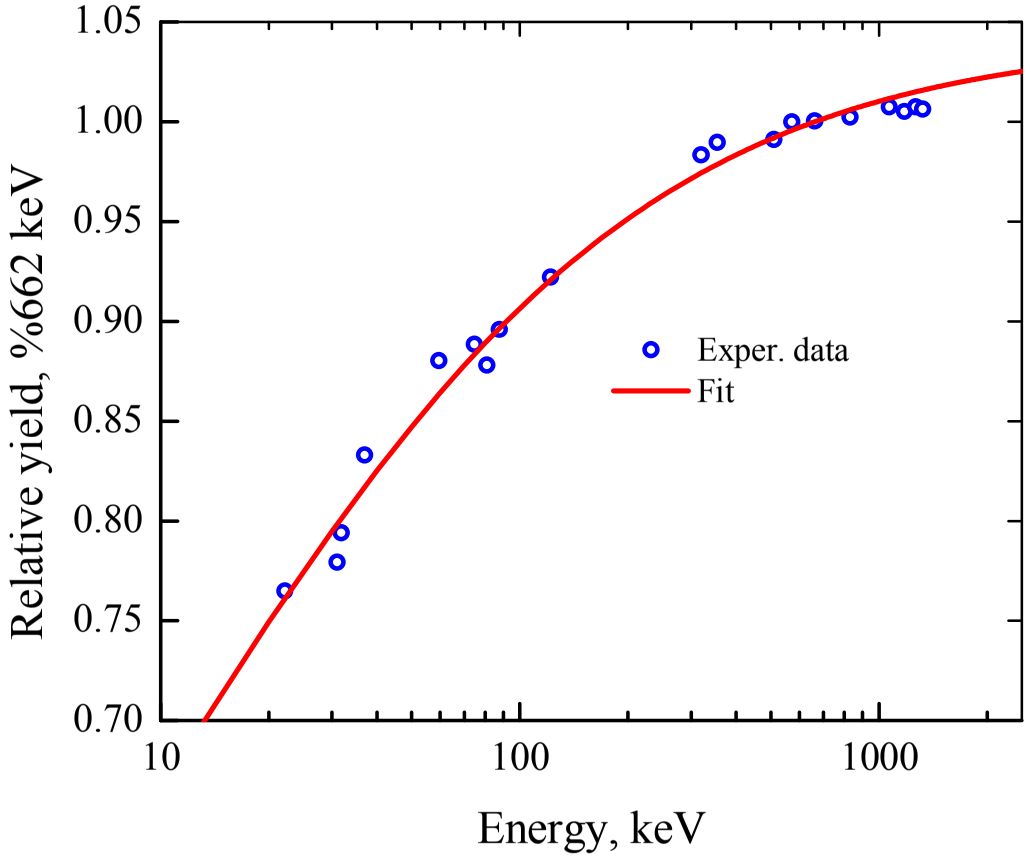
Modeling non-proportionality in terms of the dipole-dipole interaction radius

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

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

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

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



$r_{tr} = 3.9$ nm

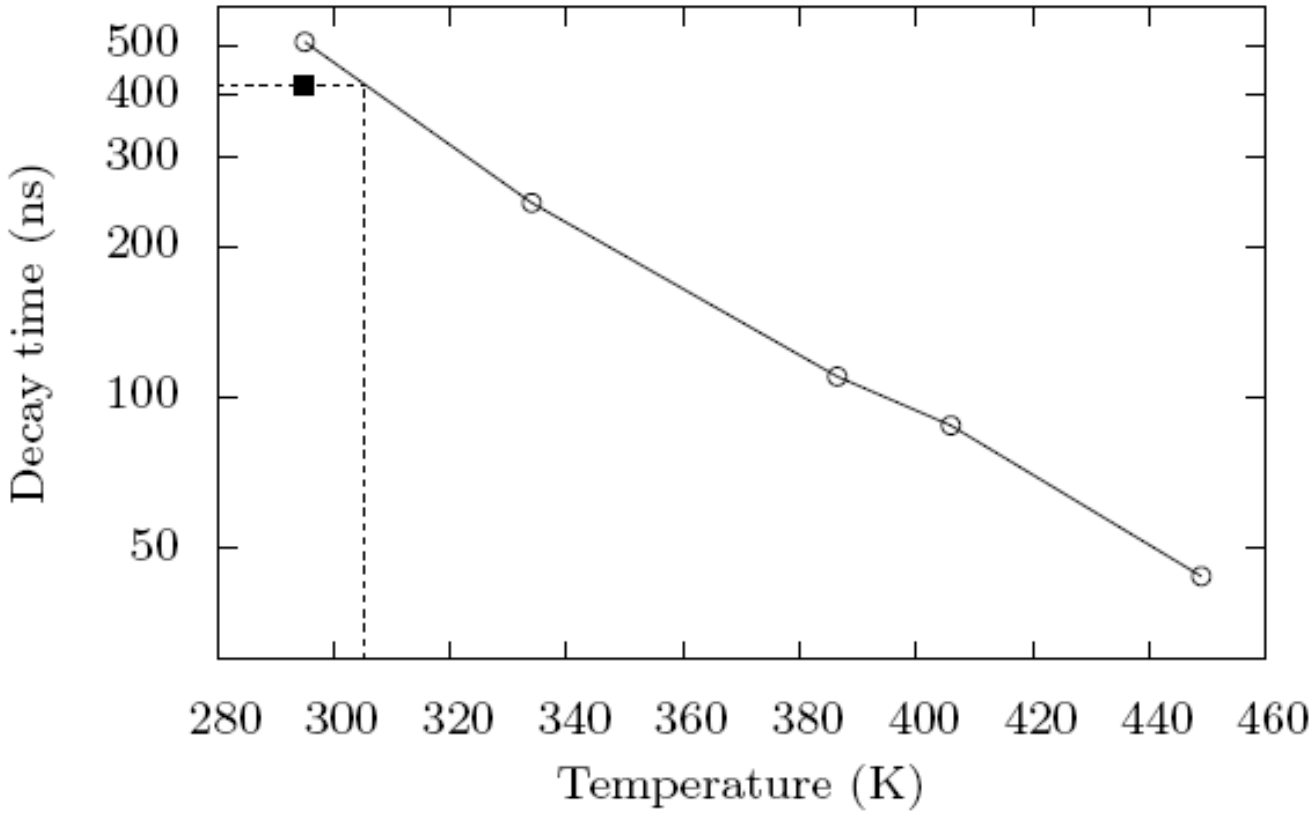
Exper. Data -- W. Klamra, T. Szczesniak, M. Moszynski, et al., J. Instrum. 7, P03011 (2012)

Conclusion

Modeling studies with UV/VUV pulsed excitation are useful for understanding scintillator non-proportionality problem

Thank you for your attention

Crystal heating with 100-fs pulses



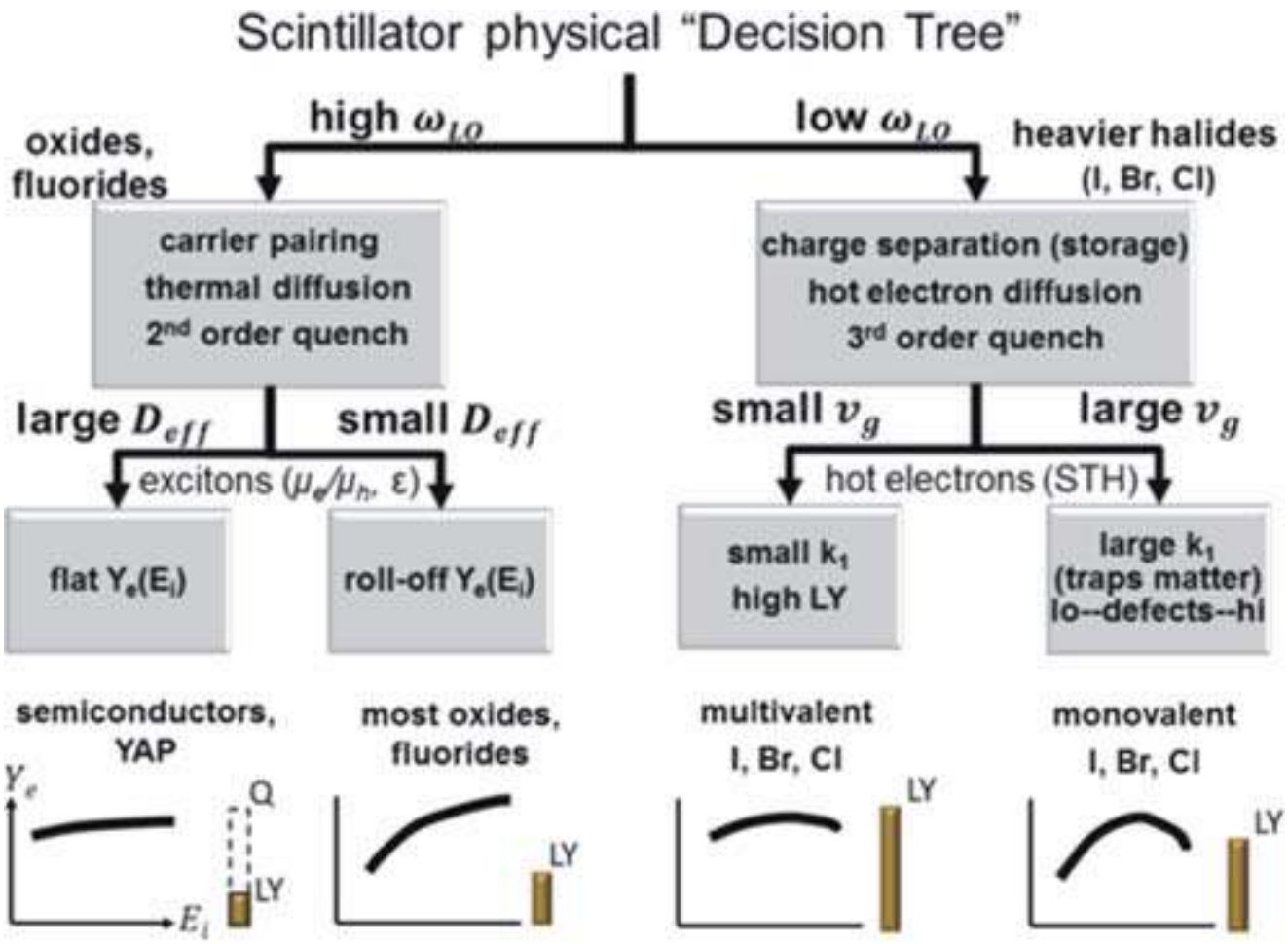
Theoretical analysis

A. N. Vasil'ev, IEEE Trans. Nucl. Sci. 55, 1054 (2008).
G. Bizarri et al., J. Appl. Phys. 105, 044507 (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).

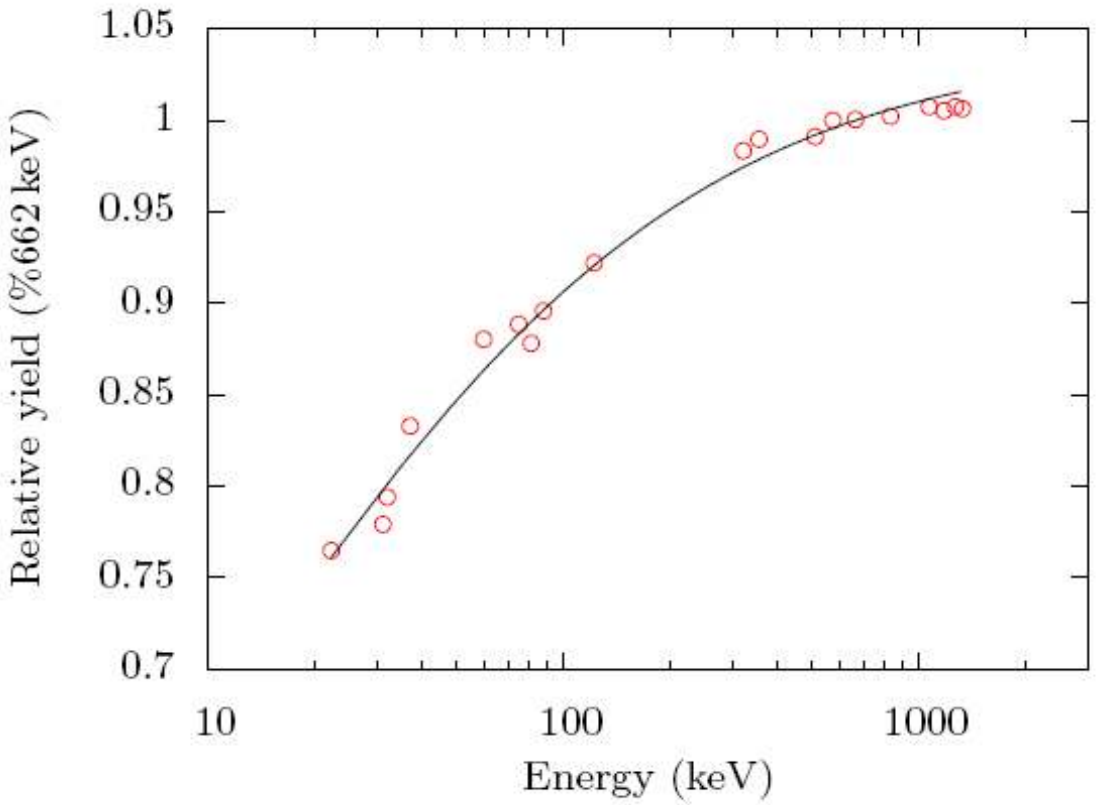
Main directions of studies (factors that influence proportionality of LY):

1. Charge carrier thermalization rate and path
2. Diffusion of charge carriers and excitons:
   - average 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

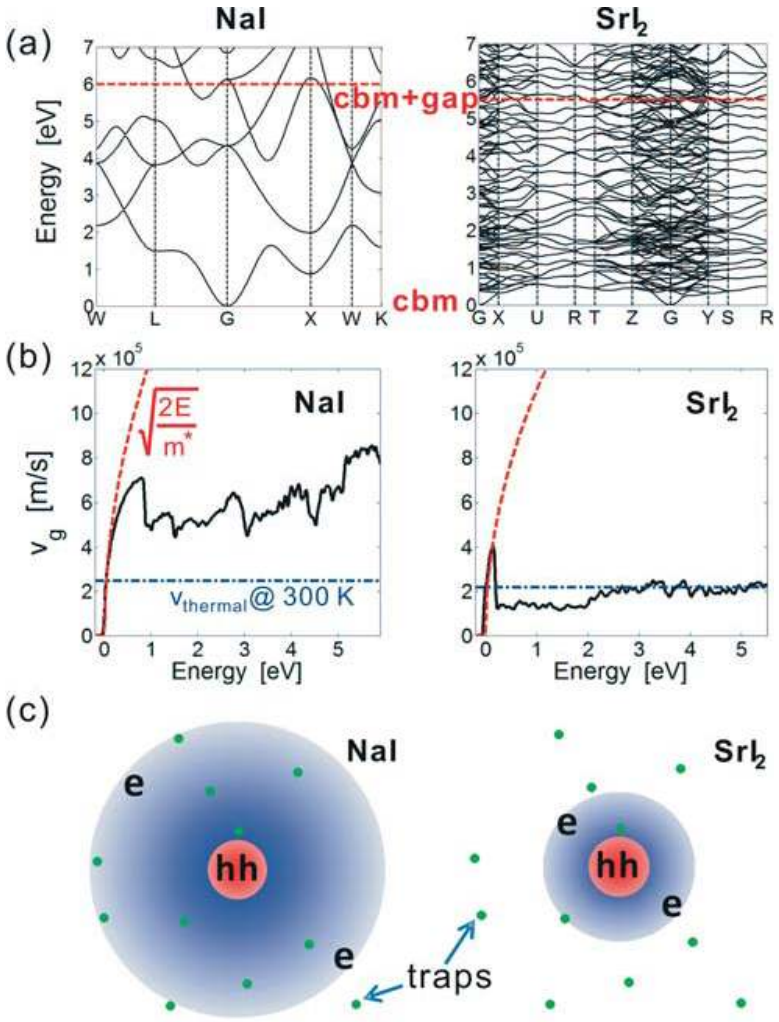
Nonproportionality in solids



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


1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
Relative yield (%662 keV)
10
100
1000
Energy (keV)

Group velosity of hot electrons



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

Non-proportional response of scintillators in visualization screens used in diagnostics of intense fs photon beams in VUV

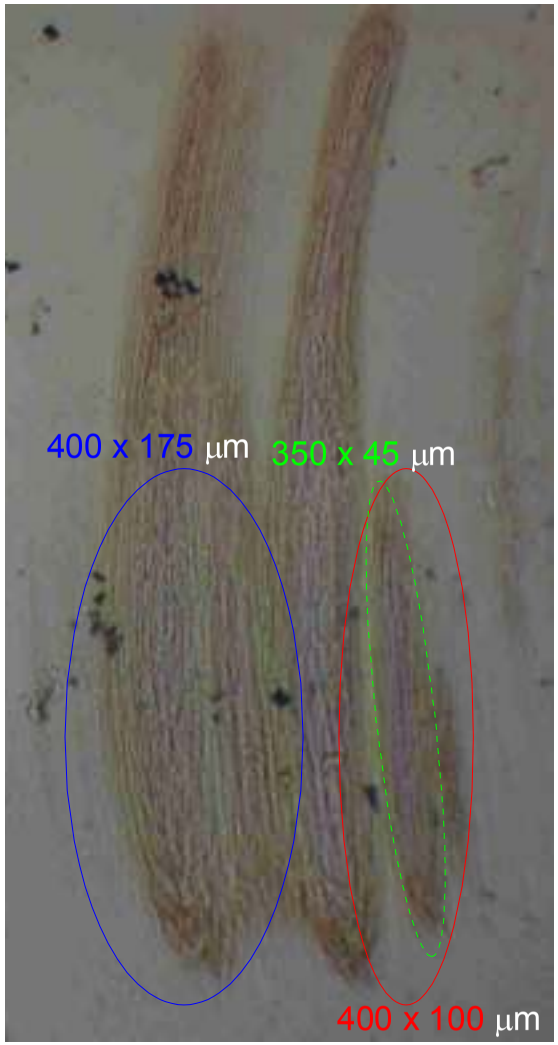
Free electron laser

FEL in VUV “FLASH” at DESY
260 m long laser

FLASH properties

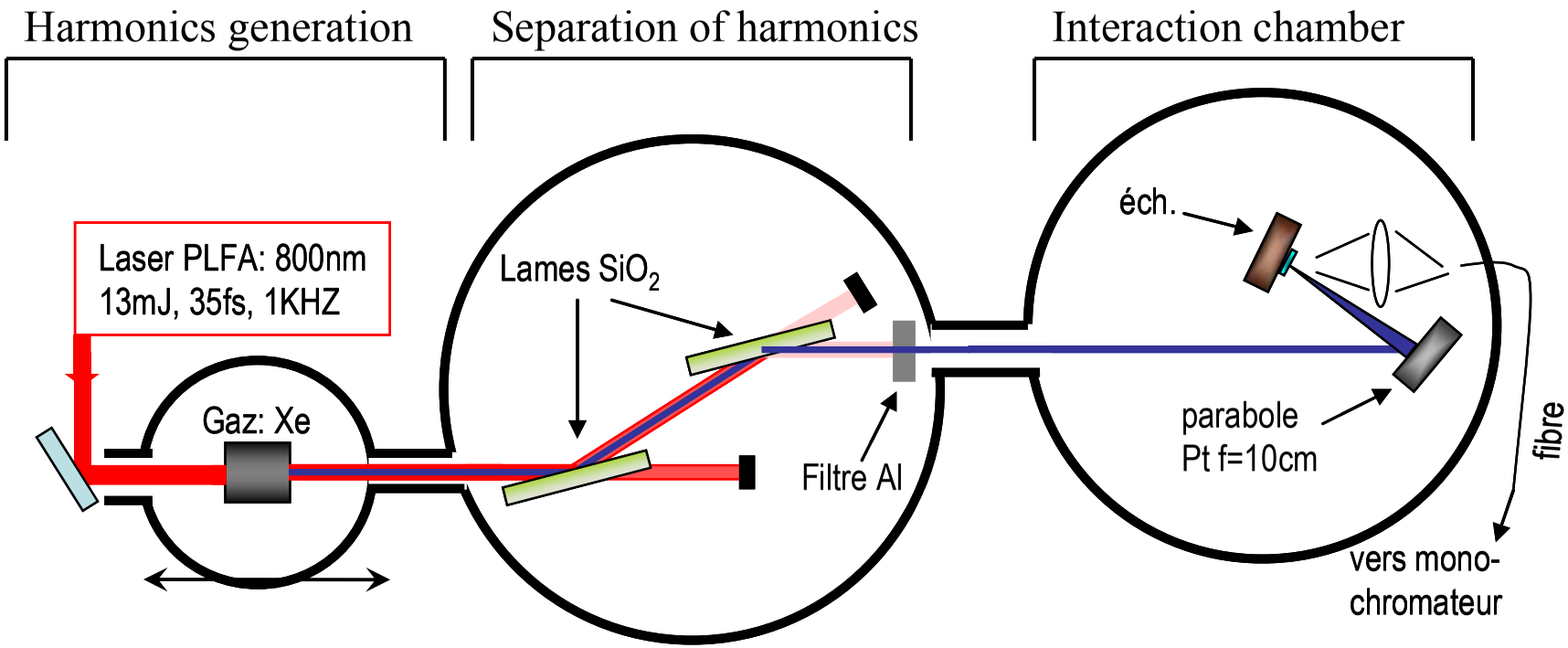
25 fs pulses
30 μJ pulse energy

up to $2*10^{12}$ photons per pulse
$\sim 10^{12}$ W/cm^2
Photon energy
up to 200 eV



- A comprehensive review of recent theoretical models:
  Moses et al., IEEE Trans. Nucl. Sci. 59 (2012) 2038.
- A systematic review of experimental data on photon nonproportional responce:
  Khodyuk&Dorenbos, IEEE Trans. Nucl. Sci. 59 (2012) 3320

Experiment. High-density VUV excitation



~1 nJ, 15 fs

density of excitations in the VUV (20- 30 eV) > **10^{20} cm^{-3}**

-Luminescence decay and spectra were measured

UV laser excitation of $CaWO_4$