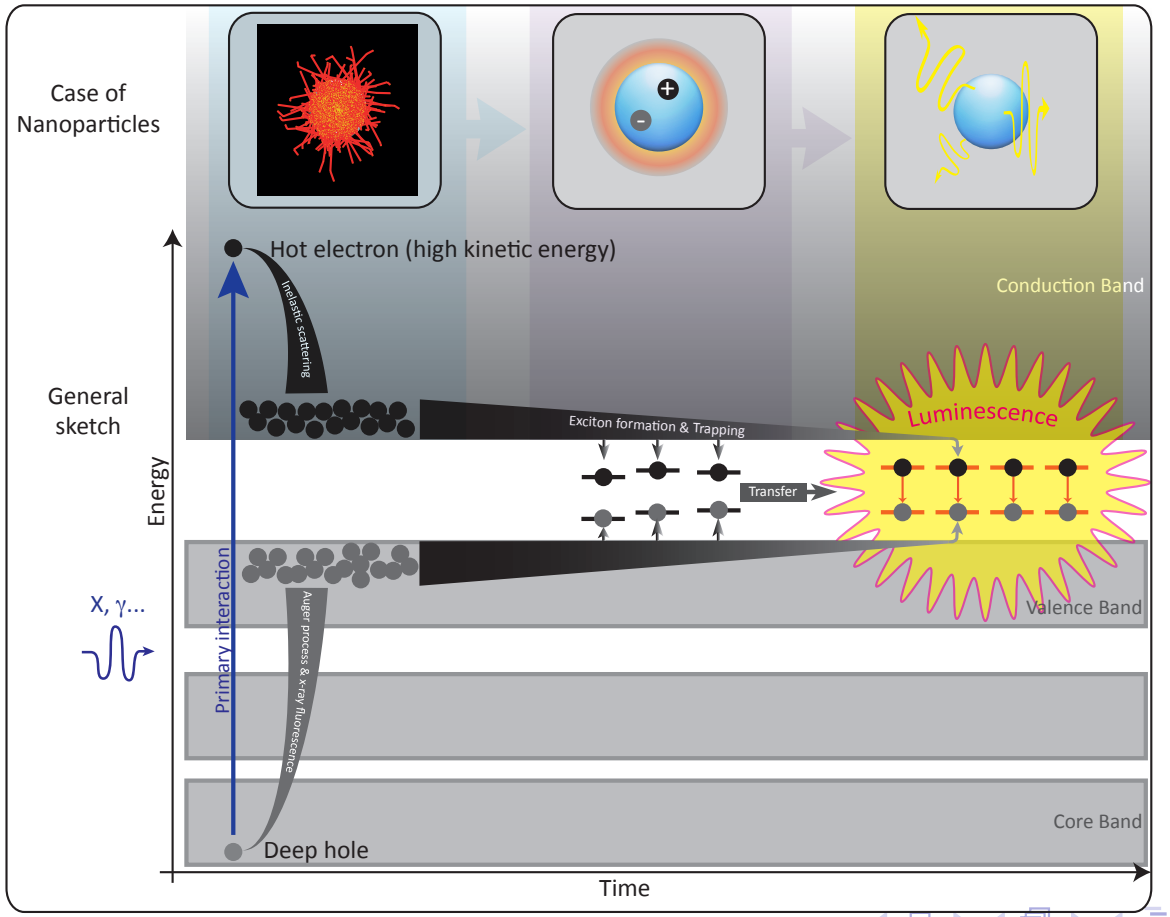
Scintillation mechanisms

from fast electron to light emission

A crude description: $n_{photon} = \beta . E_\gamma \times S \times Q$

- β: conversion yield into relaxed electron-hole pairs
- S transfer yield from relaxed electron-hole pair to the activator
- Q: luminescence quantum yield



Solid description: discrete states & localized states

We need to complete the Energy diagram: Excitons

- Energy bands diagram: semi-continuum of delocalized states
- An excited state is: electron in the conduction band and hole in the valence/core band
- The electron-hole pair can be correlated or not
- When correlated, it can form excitons

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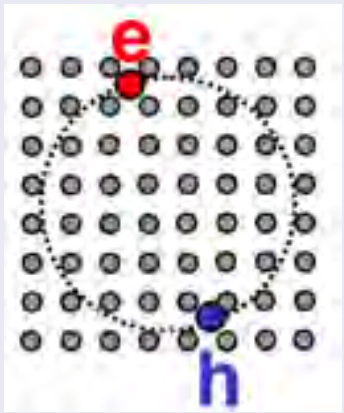
We need to complete the Energy diagram: Defects

- The crystal can contain defects: unwanted and wanted
- A defect brings its own set of energy level to the scheme: spatially localized, but a large number of defects
- unwanted defects $\rightarrow$ traps, parasitic luminescence, quenching centers
- wanted defects $\rightarrow$ desired luminescence, trap engineering (photostimulated x-ray imaging, dosimetry)

Brief description of Excitons: 2 extreme cases

Wannier-Mott excitons



- Weakly bound exciton - binding energy $\simeq$ 10 meV
- Hydrogen like model: effective mass of e & h; ϵ_r...
- Common in inorganic semi conductor (AsGa, CdS...)
- Can migrate $\rightarrow$ wavevector $\rightarrow$ dispersion curve

Text book: M.Fox, Optical properties of Solids, Oxford Master Series

Brief description of Excitons: 2 extreme cases

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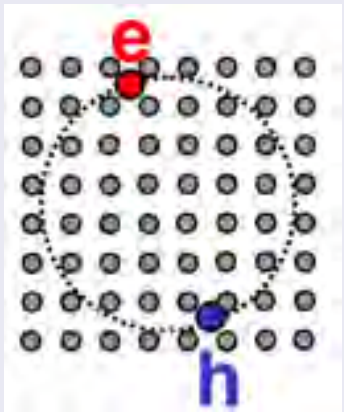

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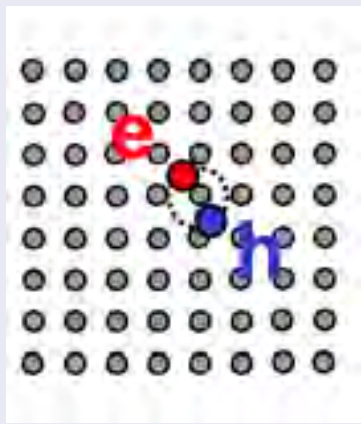
Frenkel excitons



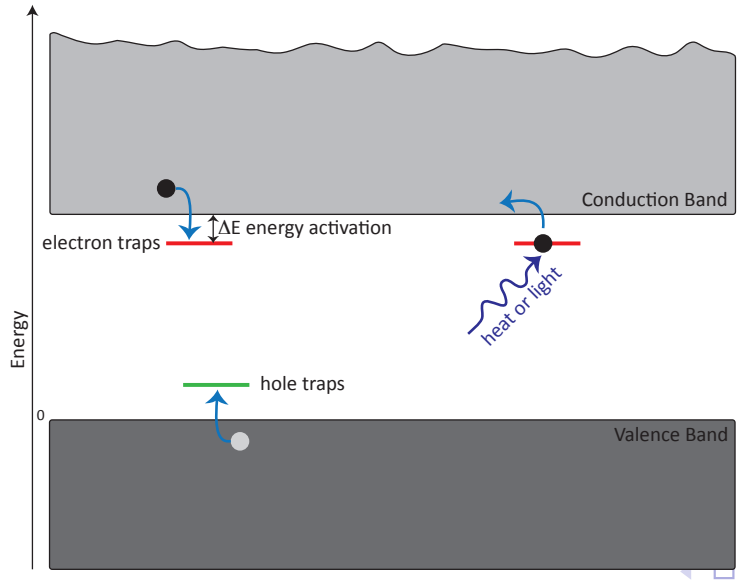
- Tightly bound exciton - binding energy $\simeq$ 0.1 - 1eV
- Transfer of excited state model using Bloch wave function $\rightarrow$ dispersion curves
- Common in insulators (rare gas crystals, alkali halides, organics crystals)

Text book: M.Fox, Optical properties of Solids, Oxford Master Series

Solid description: discrete states & localized states

Traps (We need to complete the Energy diagram)

- Displaced ions, vacancies, impurities... can be electron or hole traps
- It induces valence change. The reverse process (detrapping) may occur with energy input: heat or light
- With light $\rightarrow$ photostimulation (x-ray imaging)
- With heat $\rightarrow$ thermostimulation (thermoluminescence if it leads to emission of photons) (used in dosimetry) It brings some discrete levels in the Gap

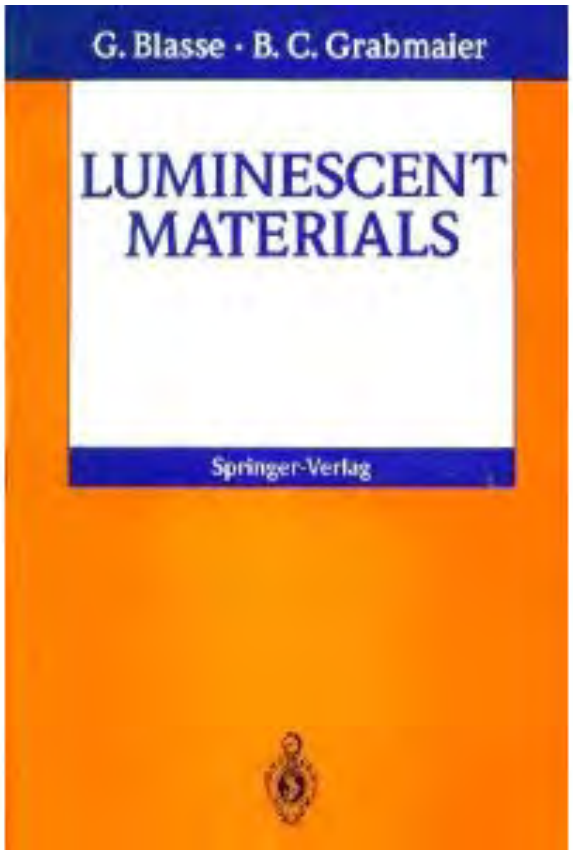


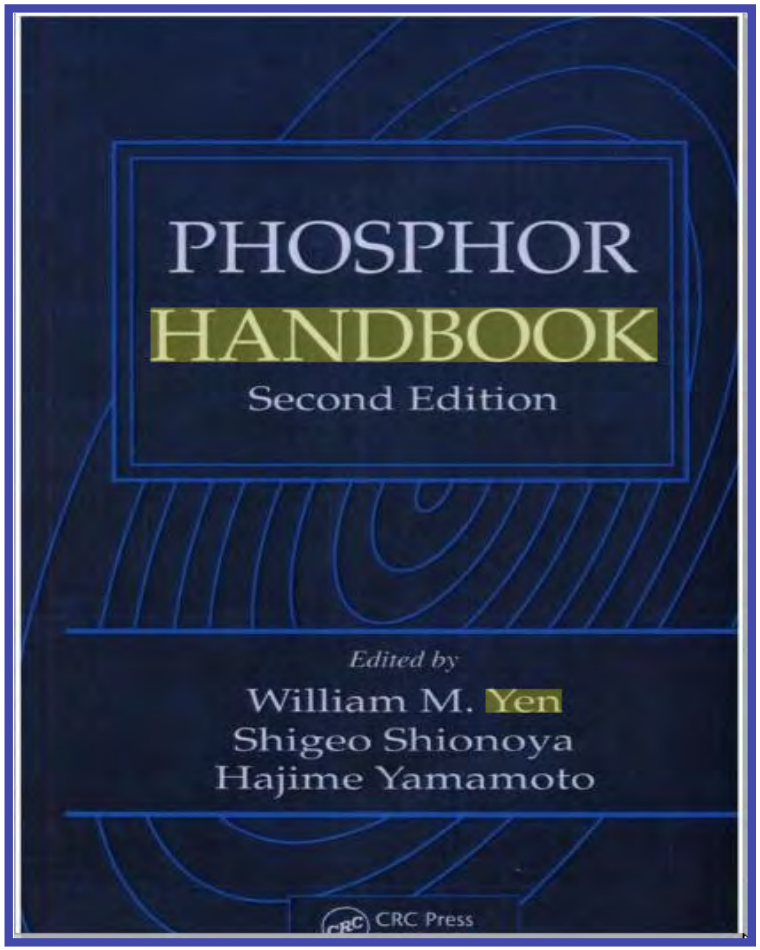
Solid description: discrete states & localized states

Activators (We need to complete the Energy diagram)

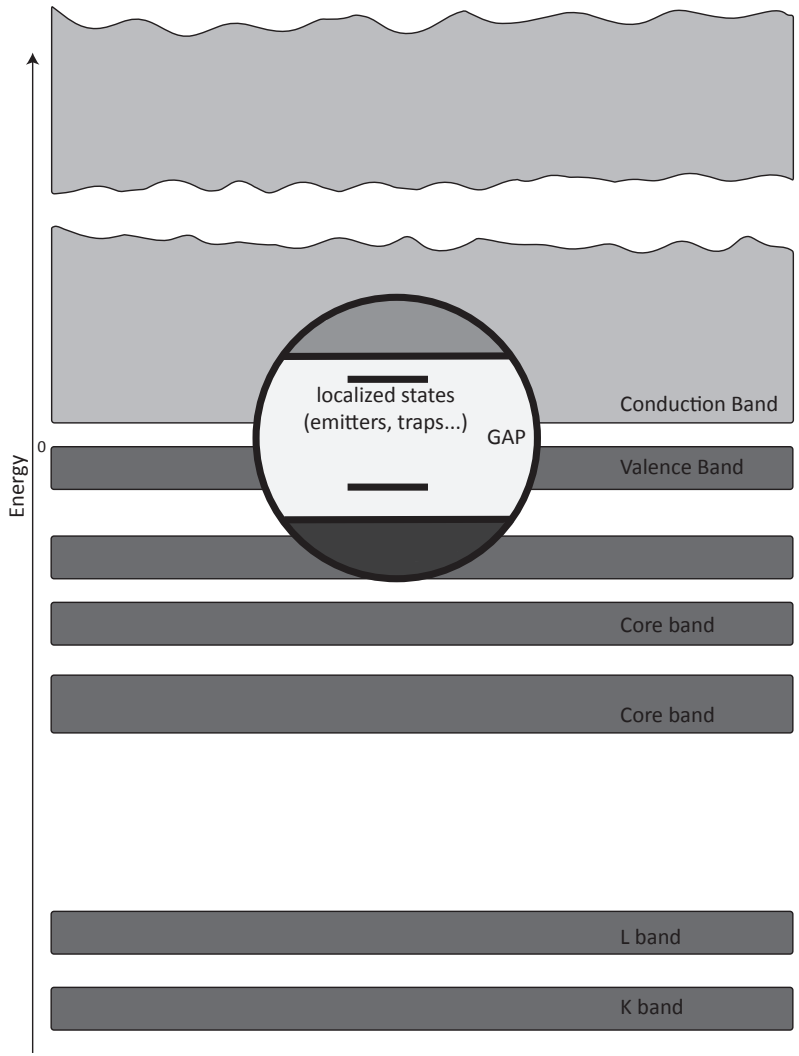
- Materials are generally doped to "tune" the luminescence properties
- From a chemical point of view: the dopant has to be compatible with the host
- $\rightarrow$ Charge and volume compatibility for substitution
- More flexible for interstitial positions
- Each activator has its own set of energy levels
- Positioning these levels depends on the interaction strength with the host

Some essential Books on Luminescent centers





Full Energy description of the solid (Energy "levels")



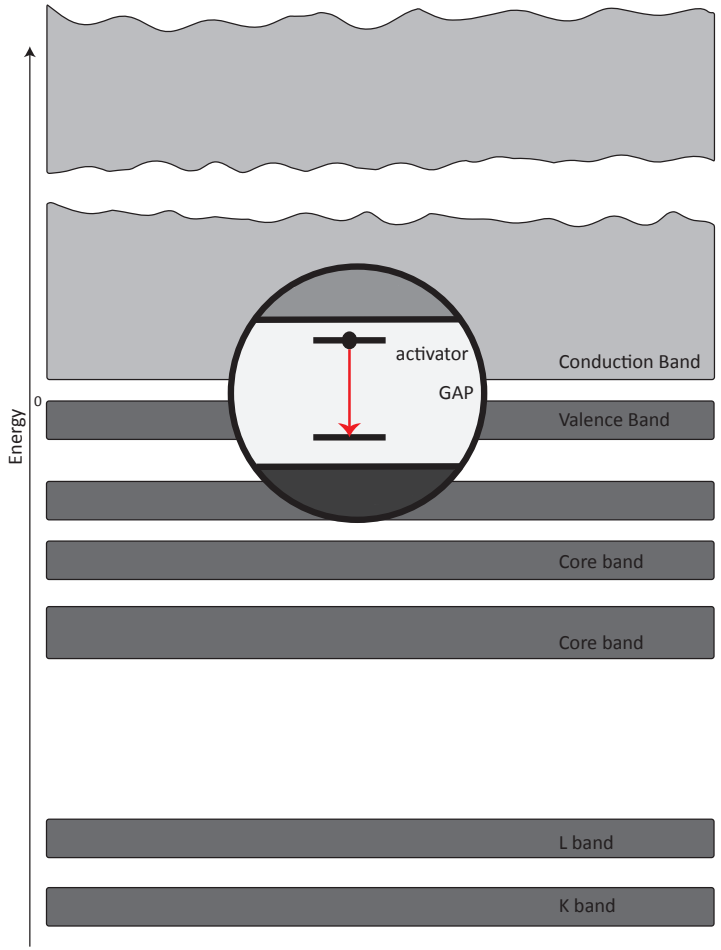
Luminescence: Last stage of the scintillation process

Timing

- Slow luminescence → Slow scintillator
- Fast luminescence → Fast or Slow scintillator

Light yield

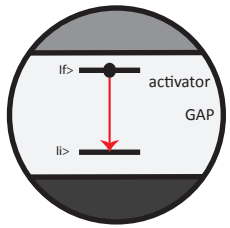
- Selection rules
- Electron phonon interactions
- → Temperature dependance
- Concentration quenching
- Energy tranfers to traps
- ...



Luminescence: timing & light yield

decay time

- about the timing properties
- Population: $n(t)$ in the excited state.
- $dn = -n(t) W_{rad} dt$ (W_{rad}: spontaneous emission rate)
- $\rightarrow n(t) = n_0 e^{-W_{rad} t} = n_0 e^{-\frac{t}{\tau}}$
- $\rightarrow$ weak probability = slow decay



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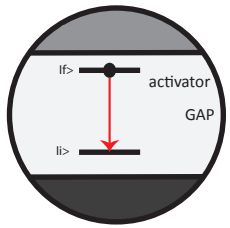


spontaneous emission rate

- Fermi Golden's rule: $W_{rad} = \frac{2\pi}{3\hbar}\rho(\omega_{if})|\mathcal{E}_{loc}|^2|\mu_{if}|^2$
- $\rho(\omega_{if})$: density of field oscillators at frequency
- $\mathcal{E}_{loc}$:local field at the position of the emitting center
- μ_{if}:transition dipole moment between $Ii>$ and $If>$
- As a result, τ depends on the selection rules, λ and on n

Luminescence: timing & light yield→ Cartoon model

- $n(t)$ = volume of wine
- decay time = time to make the barrel empty
- W_{rad} = diameter of the tap
- Light yield = Volume of drunk wine

Luminescence: timing & light yield → Cartoon model

High W_{rad} → fast

Middle W_{rad}

Low W_{rad} → slow

but the luminescence yield is the same: 100%

(As example Eu^{3+} is very efficient despite the transition is forbidden $f \rightarrow f$)

Luminescence: timing & light yield→ Cartoon model

A hole in the barrel

Luminescence: timing & light yield→ Cartoon model

non-radiative processes

- $\rightarrow W_{nr}$
- $dn = -n(t)(W_{rad} + W_{nr})dt$
- $n(t) = n_0 e^{-(W_{rad}+W_{nr})t} = n_0 e^{-\frac{t}{\tau}}$
- $\rightarrow \tau \searrow$ but the yield $\searrow$

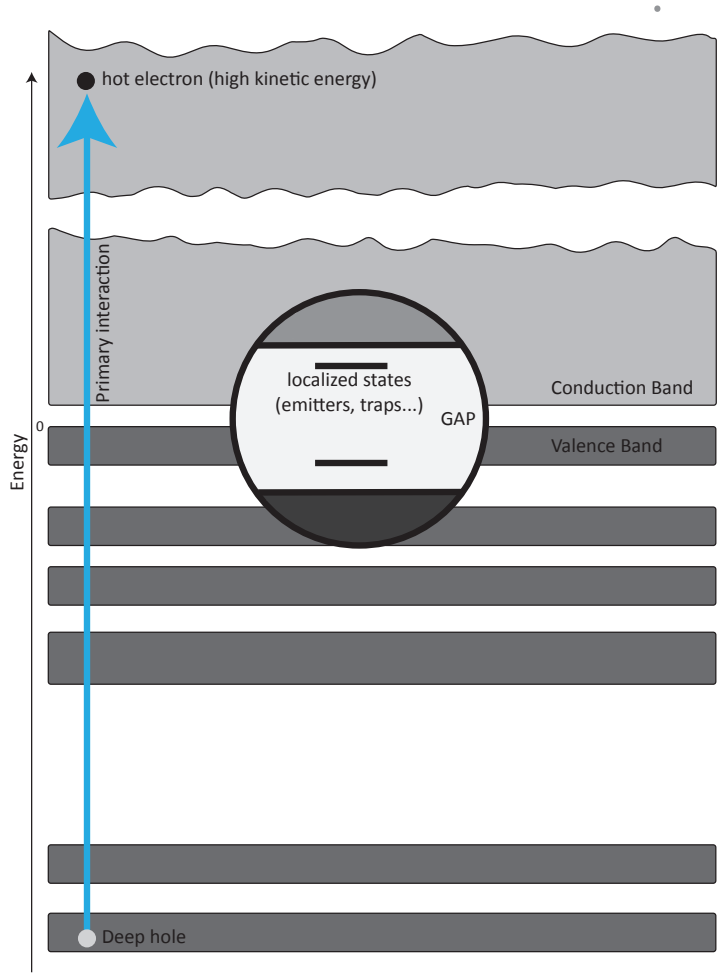
type of non-radiative processes

- electron-phonon interactions
- transfer toward non-radiative centers
- concentration quenching

A hole in the barrel

Overview of the processes

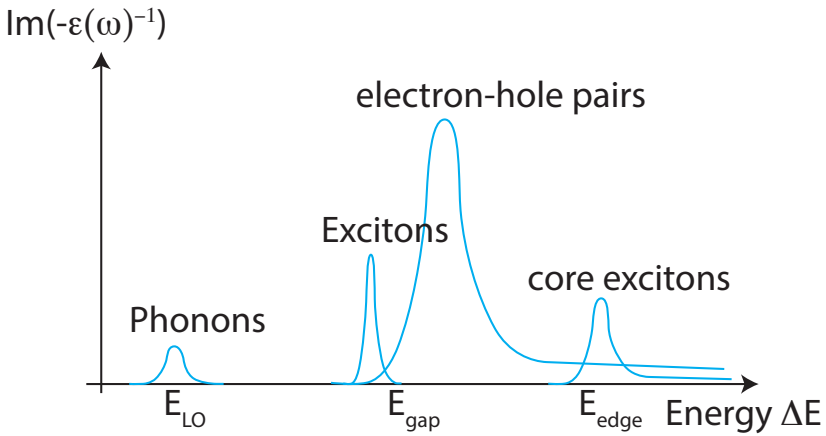
Primary interaction → first excitation: *solid**

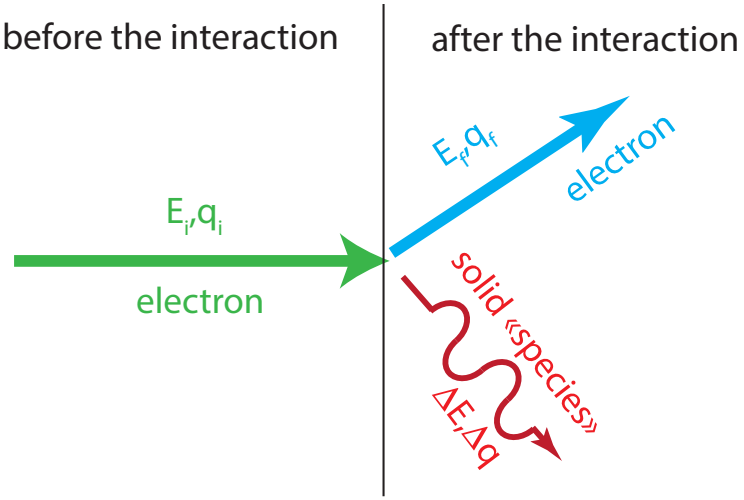


The initial situation: a hot electron and a deep hole

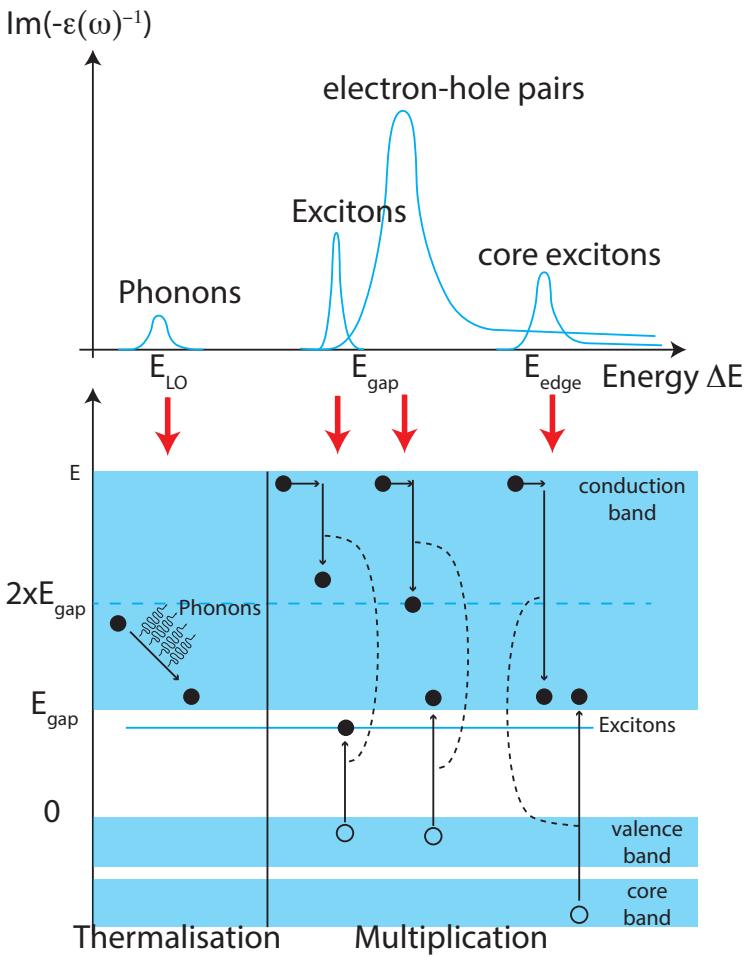
Overview of the processes

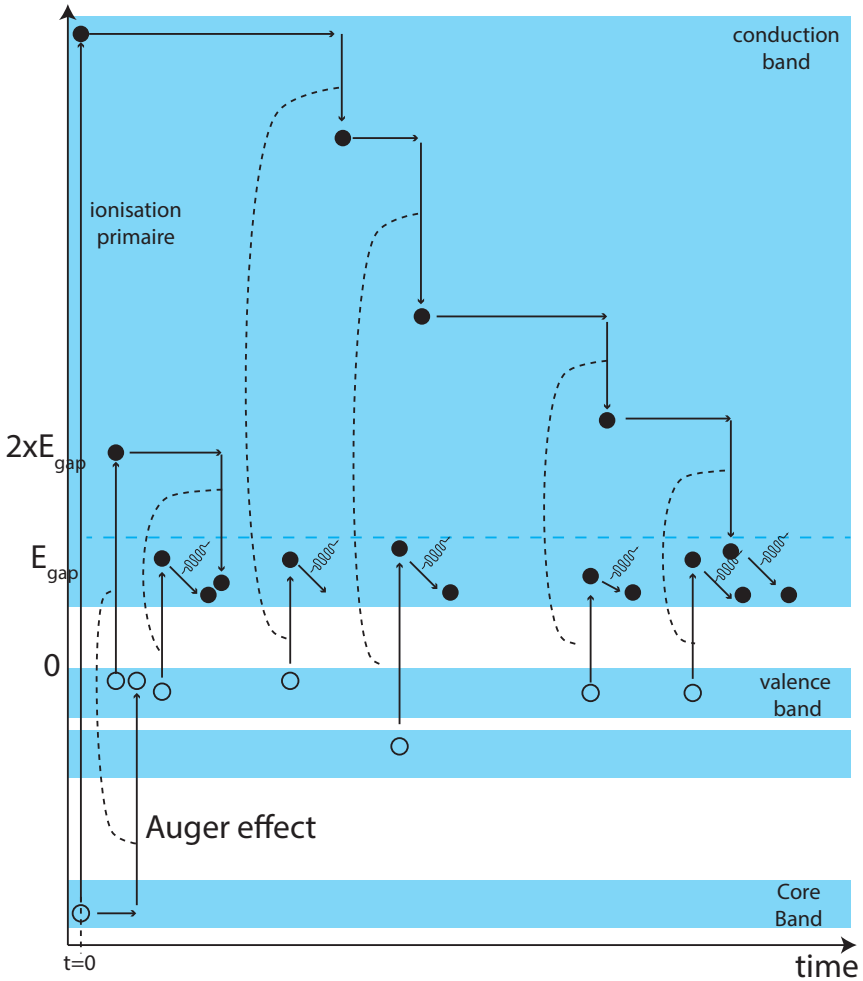
- Electron relaxation: connexion with optical constants ϵ
- Electron displacement = electromagnetic flash
- $\rightarrow$ connected to the optical response of the solid $(n^* = \nu + i\kappa)$ (see D.Smith et.al, NIM B, 2006 for details as example)
- Energy loss function: $Im(-\frac{1}{\epsilon})(\Delta E, \Delta q)$
- ΔE and Δq are the energy and momentum transfer





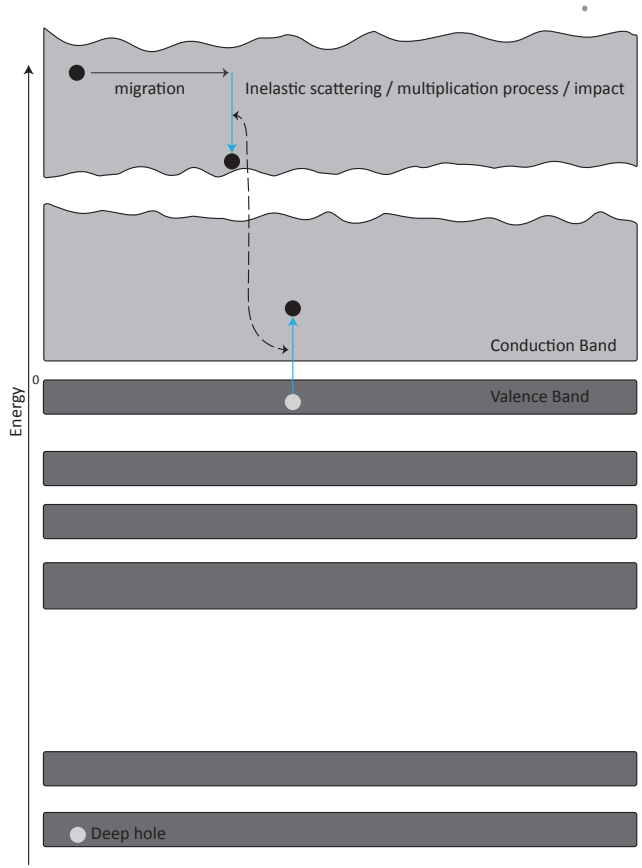
Relation with energy band diagram





Overview of the processes

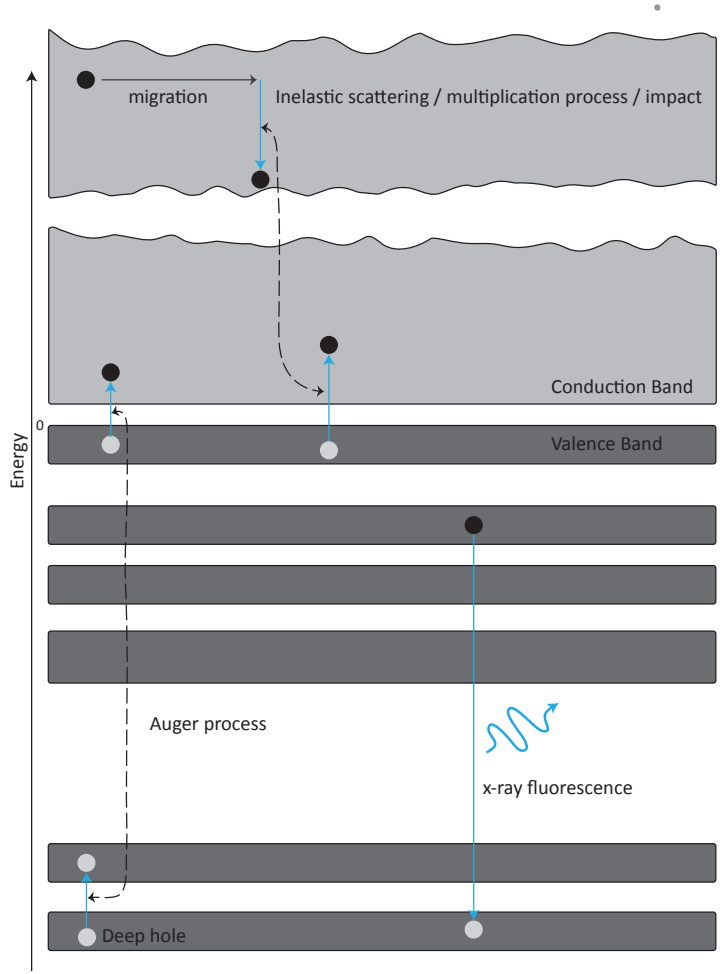
Hot electron relaxation



$\rightarrow$ 1 secondary "excitation" & the primary electron loses the equivalent energy

Overview of the processes

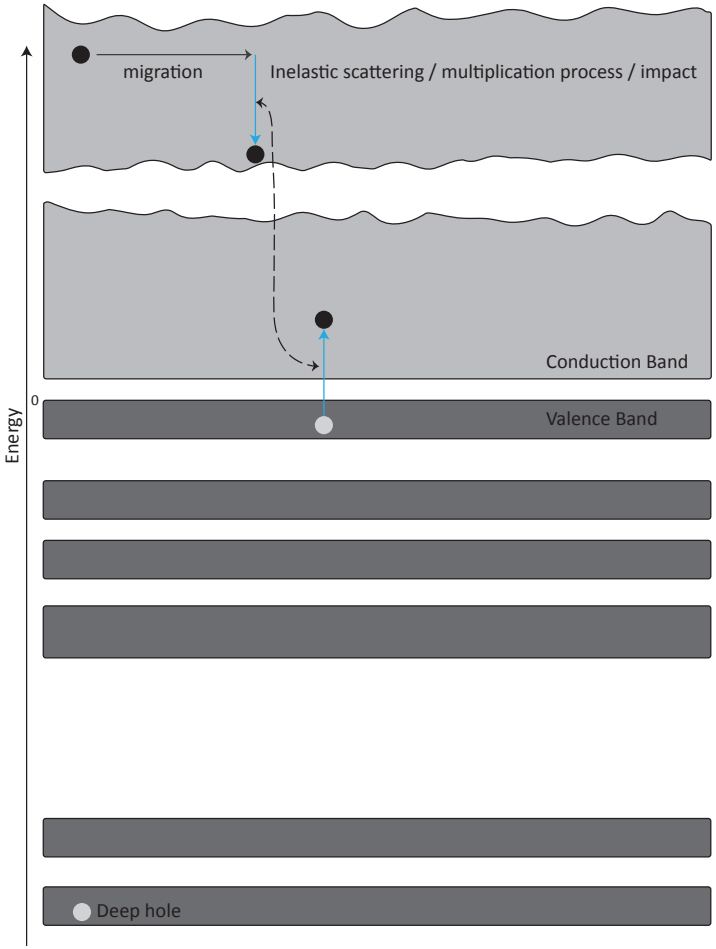
Hole relaxation: Auger process ($\approx$ cross-relaxation) & x-ray fluorescence

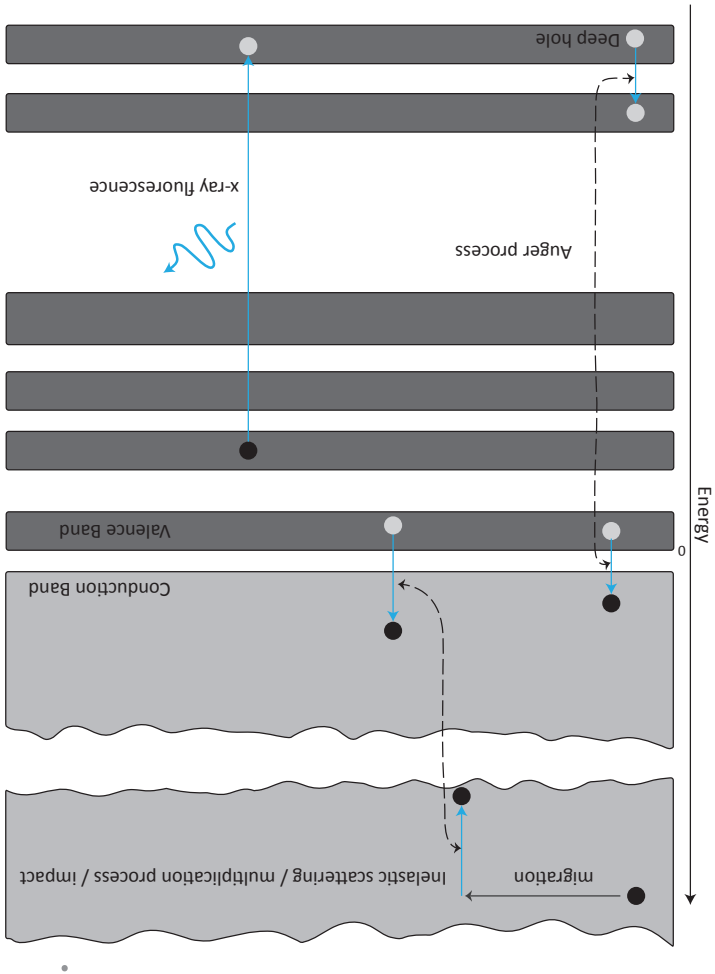


$\rightarrow$ 1 secondary "excitation" & the primary hole lost some energy

Overview of the processes

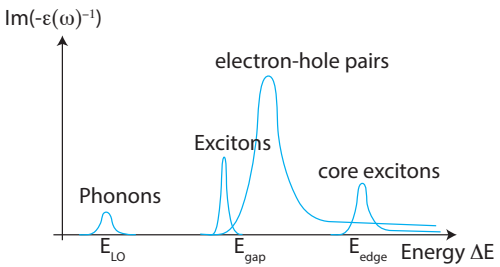
Auger process & multiplication: about the same

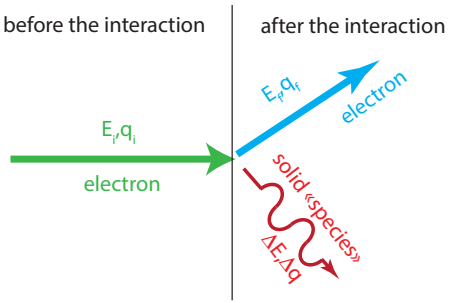


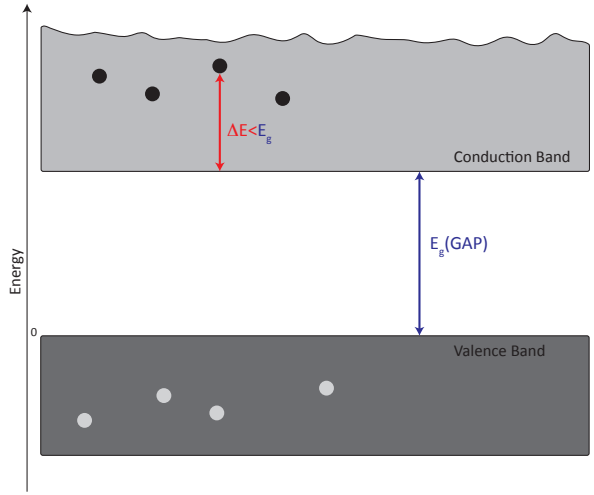


Overview of the processes

At the end of the first relaxation stage $E < E_{gap}$ then interaction with lower energies species (defects, phonon...)



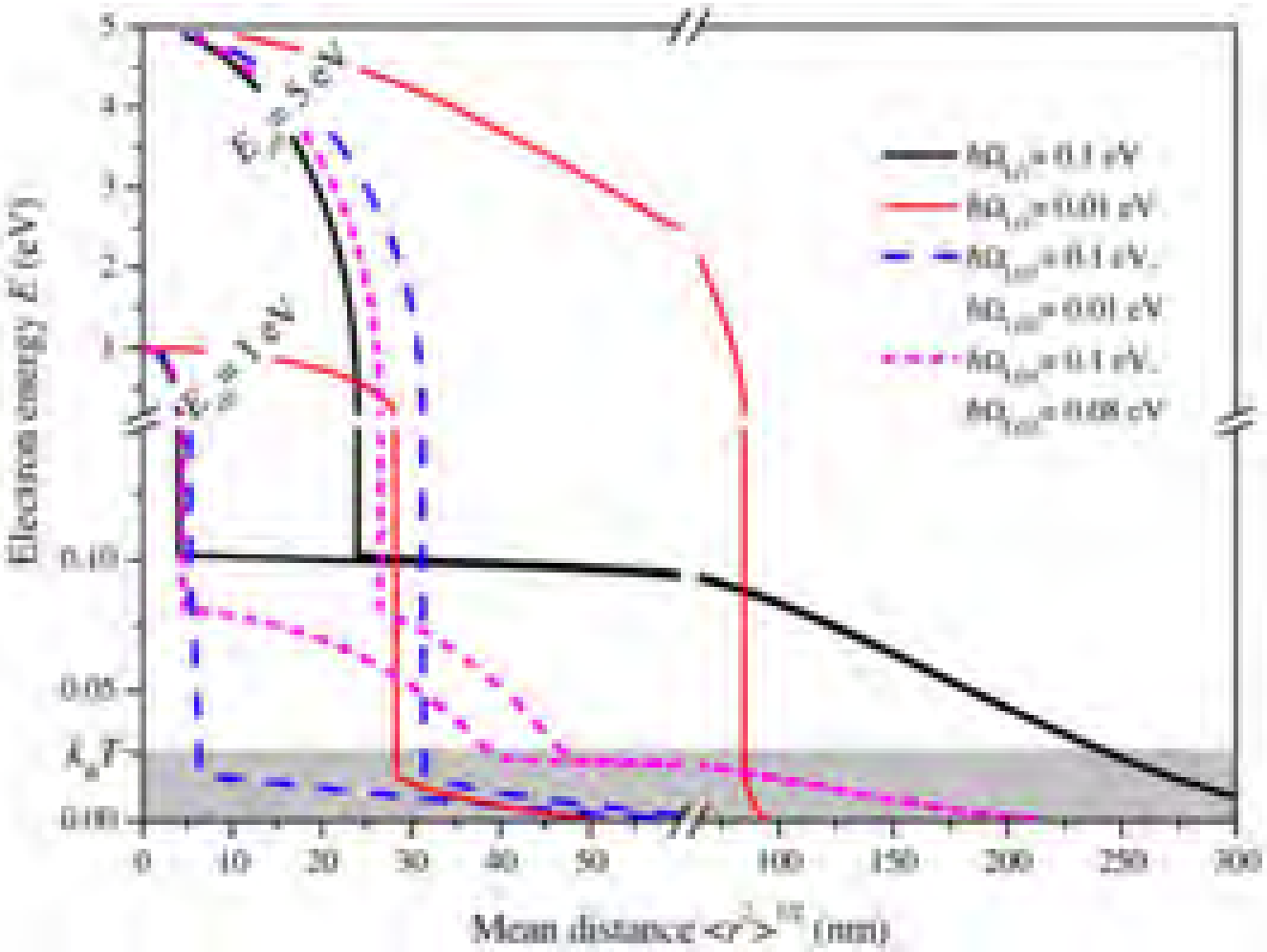




Overview of the processes

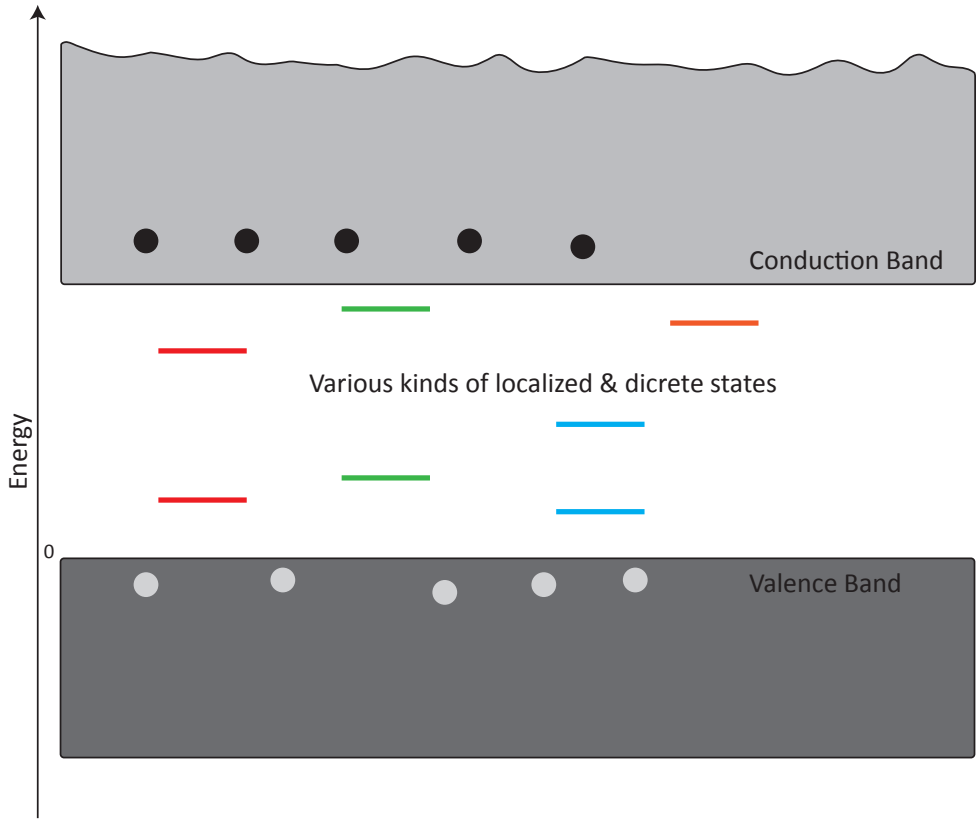
Still some migrations over tens of nanometers

Kirkin et. al. IEEE TNS2012



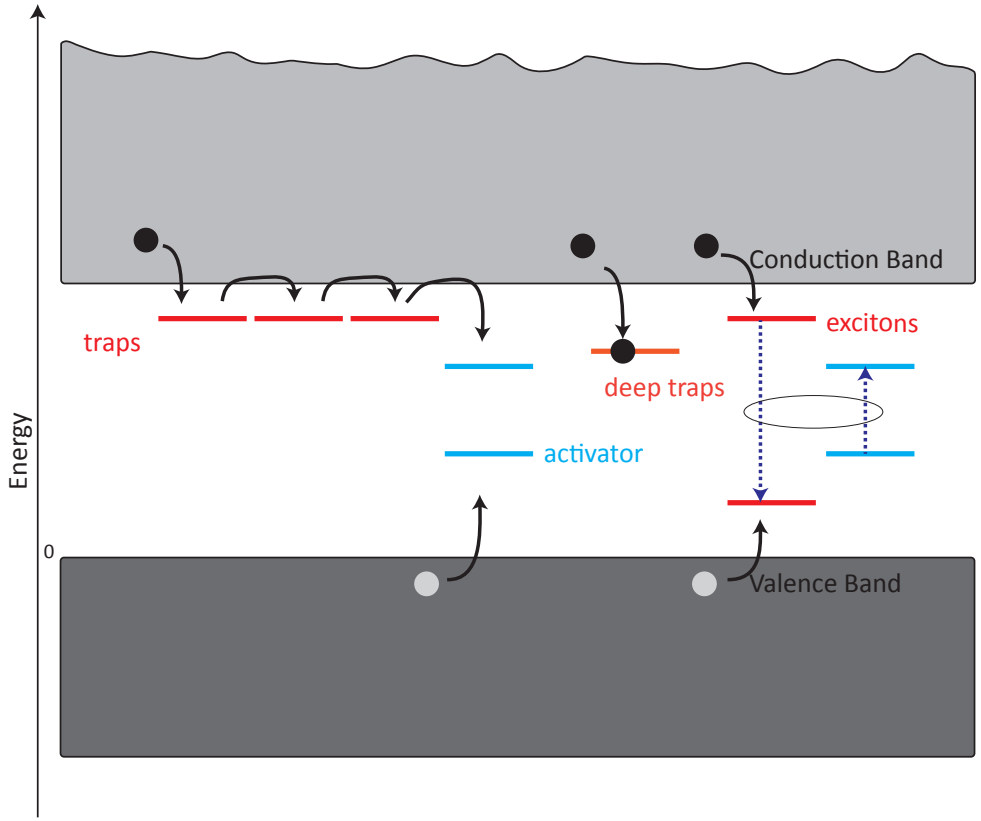
Overview of the processes

When thermalized (relaxed), energy transfer toward lower energy species (activator, traps & excitons)



Overview of the processes

Several transfer processes are possible



$\rightarrow$ may induce delay, quenching, bright-burn: it depends on the temperature

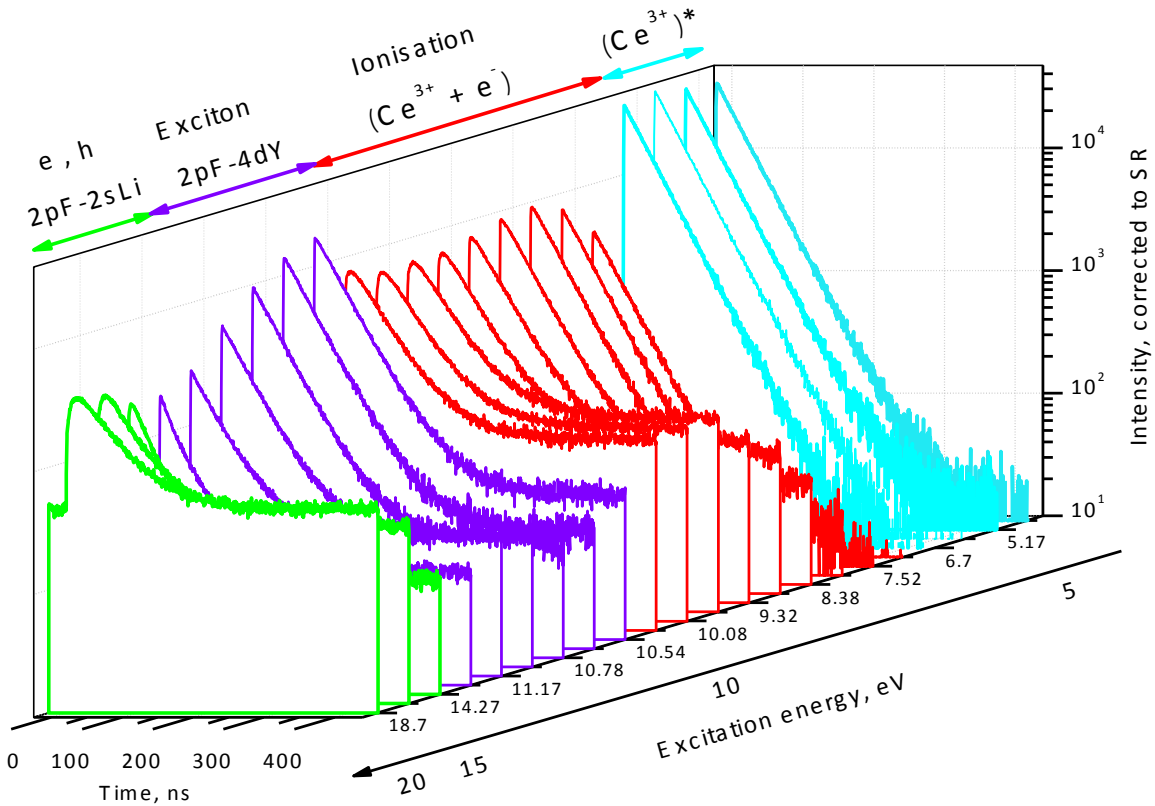
Overview of the processes

Even with a fast emitter, the overall process can be slow

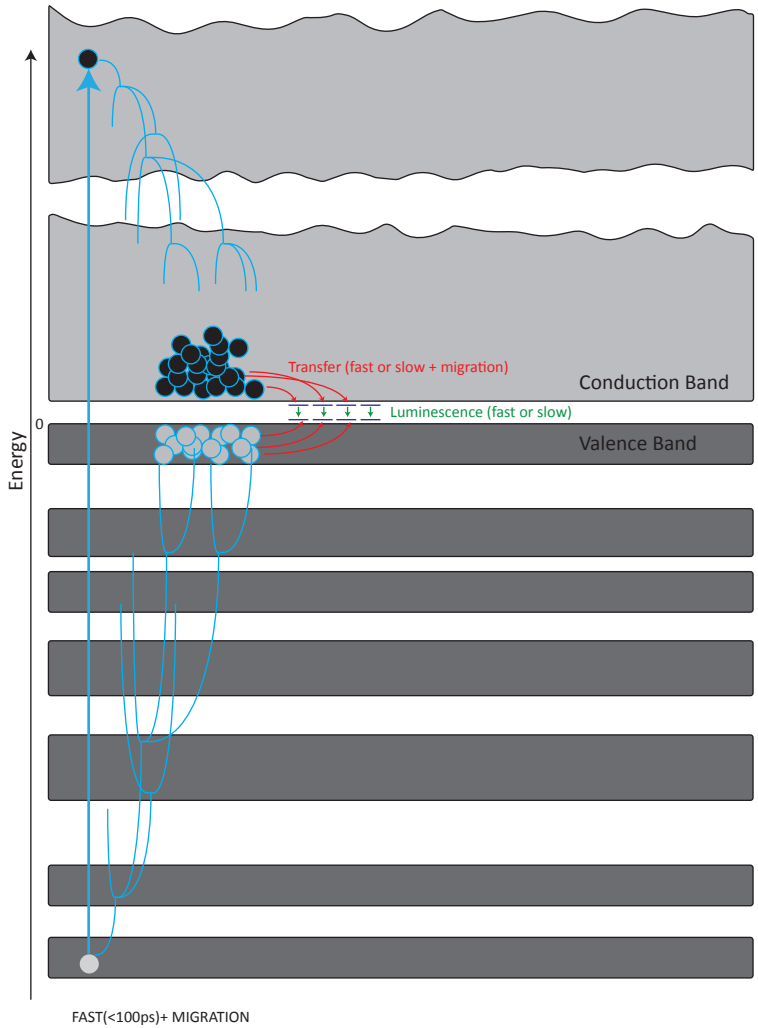
Overview of the processes

An illustration of the evolution of the decay only due to the transfer process (the same emitter: $LiYF_4:Ce^{3+}$)

Belsky et. al. J.Phys. Chem. Lett. 2013



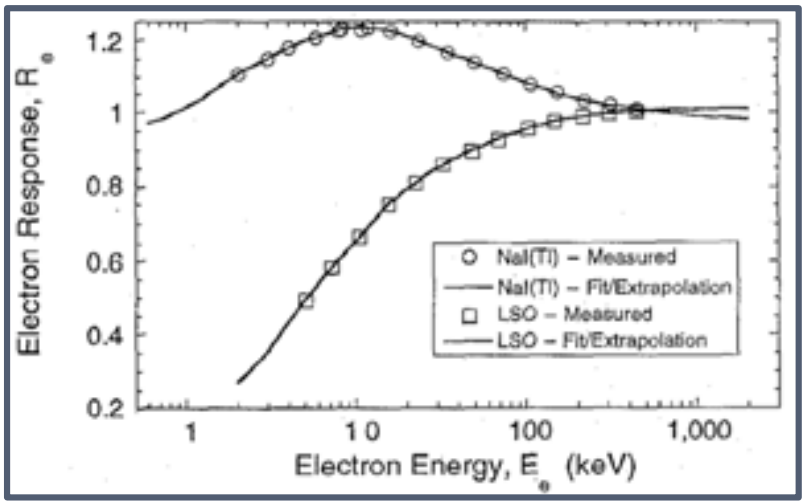
Summary picture



- The timing driven by the slowest process
- Heat, Light generation & trapping
- $\#photons = \frac{E_{gamma}}{(2 \sim 3) E_g} SQ$
- $\rightarrow$ The light yield should be proportional to the energy of the primary particle.

And it is not ....

With electrons



Valentine, IEEE TNS, 1998

With γ-rays

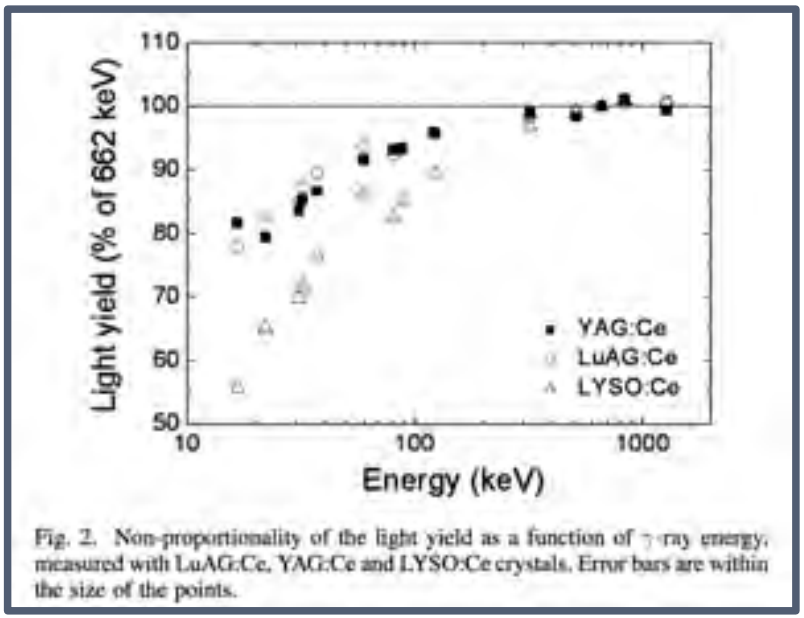
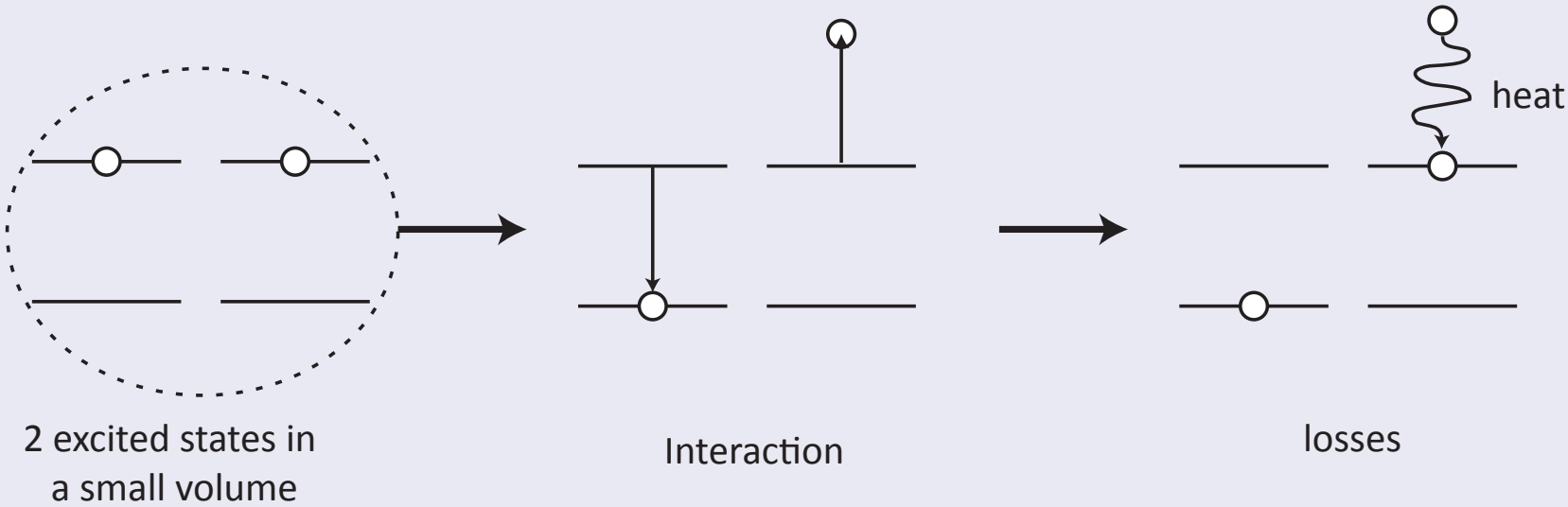


Fig. 2. Non-proportionality of the light yield as a function of γ-ray energy, measured with LuAG:Ce, YAG:Ce and LYSO:Ce crystals. Error bars are within the size of the points.

Chewpraditkul, IEEE TNS, 1998

A few words about non-proportionnality

excitations can interact!



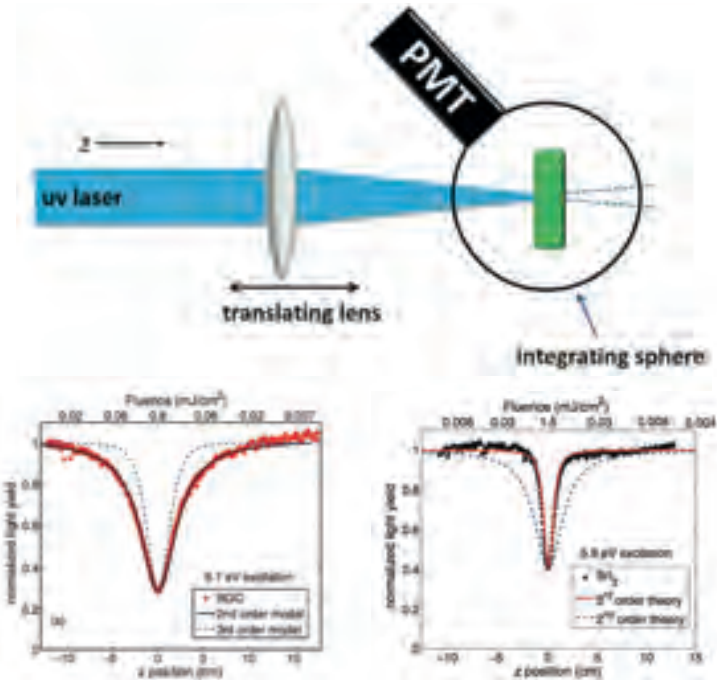
- $\rightarrow$ concentration quenching for excitations
- $\rightarrow$ important effect of the spatial distribution of excitations

A few words about non-proportionnality

Analytical model, Bizarri et. al. JAP 2009

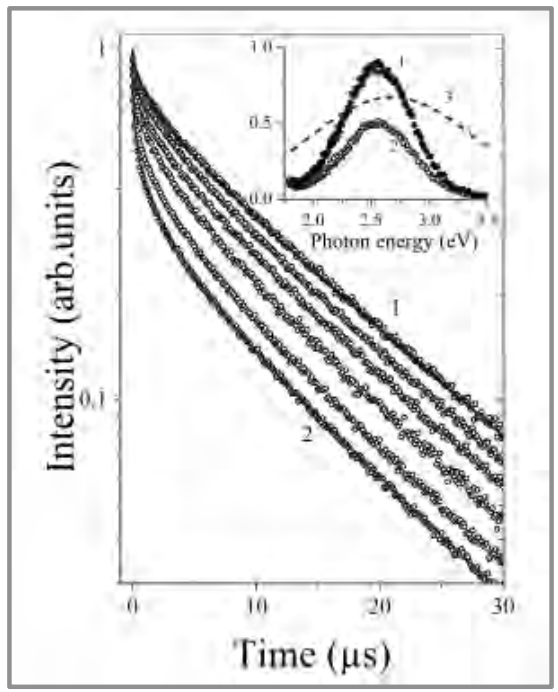
How to analyze it?

Z-scan approach



J.Grim et. al. PRB 2013

effect on the decay $CdWO_4$

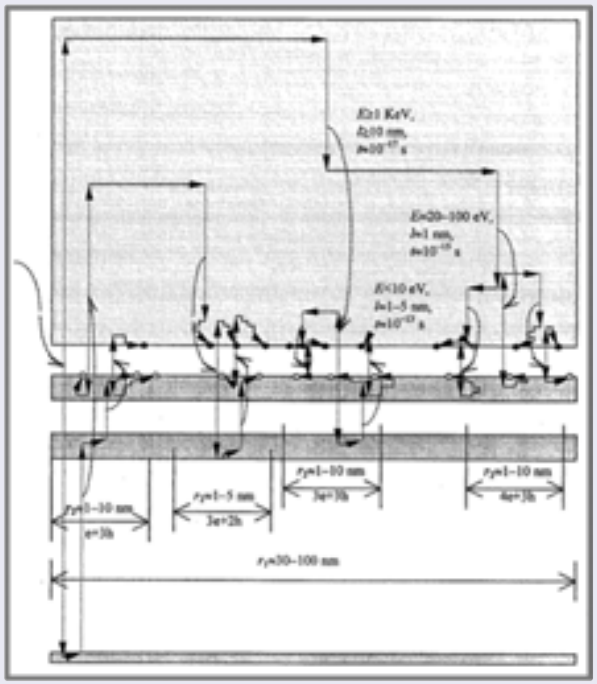


Kirm et al., PRB, 2009

- and also K-dip spectroscopy (Khodyuk et. al., JAP, 2010)

A few words about non-proportionnality

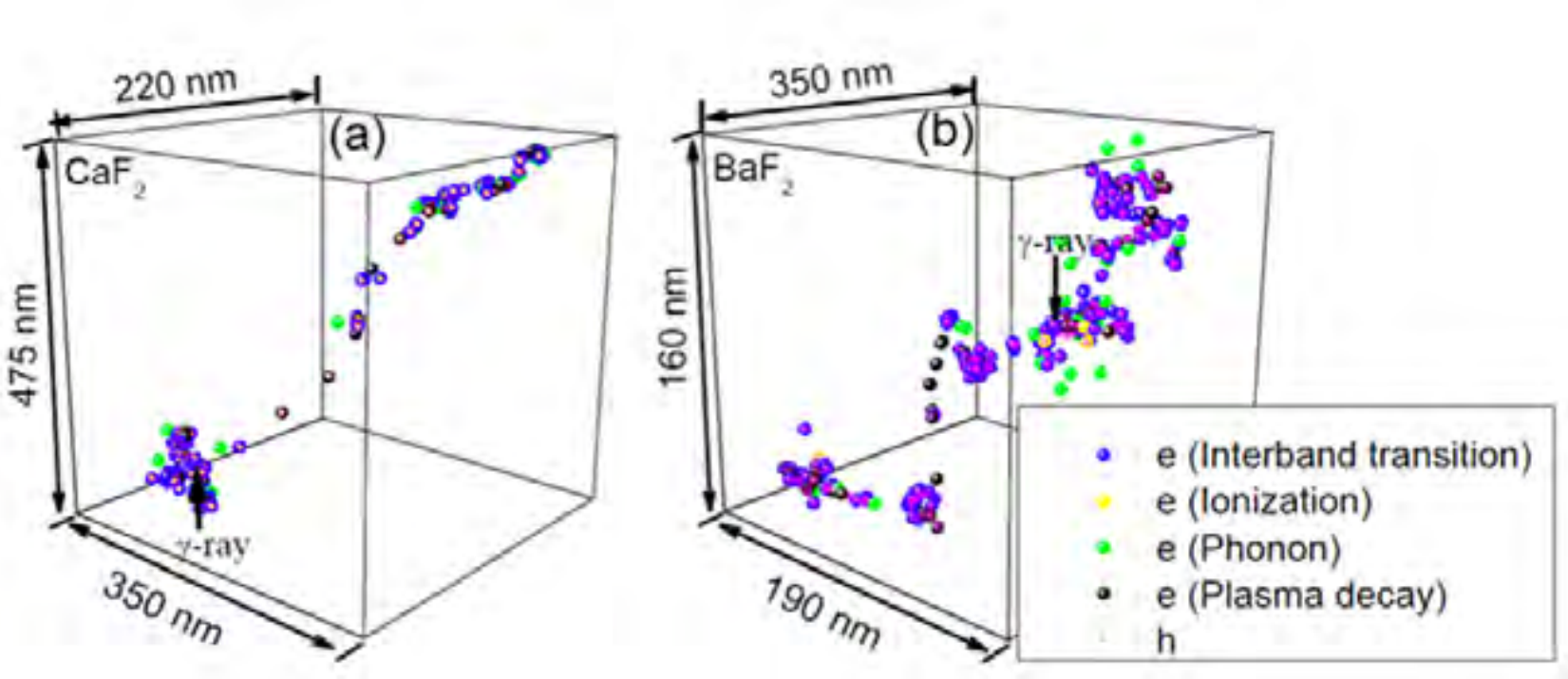
spread of the charges/excitations depends on the initial energy



- $\rightarrow$ from event to event the yield changes
- $\rightarrow$ bad for the energy resolution
- $\rightarrow$ the energy resolution is worse in non-proportional materials
- $\rightarrow$ it requires modeling of the spatial distribution of excitations

A few words about non-proportionnality

An illustration of modeling the energy cascade / spatial distribution

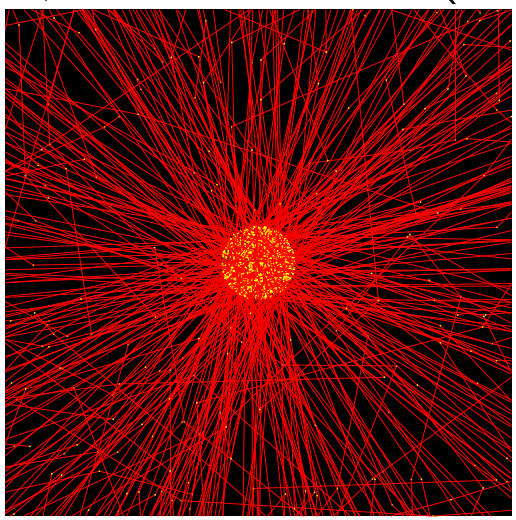


Gao et al., JAP, 2013

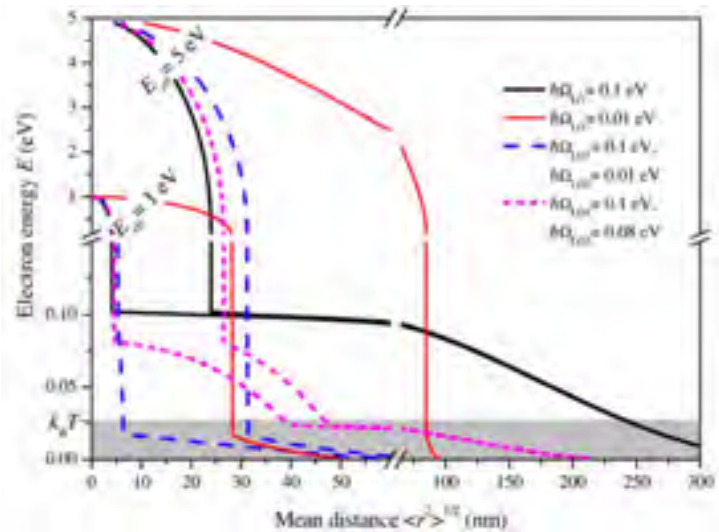
Concluding remark: take care with nanoscintillators

Escape of charges

10keV β in a 50nm NP (Gd_2O_3)



Thermalisation



+ traps, effective index of refraction, confinement effects ...

A bit of litterature

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DE L'INGÉNIEUR

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Inorganic scintillating materials

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par Christophe DUJARDIN

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Needs, Trends, and Advances in Inorganic Scintillators

C. Dujardin, E. Auffray, E. Bourret-Courchesne, P. Dorenbos, P. Lecoq, M. Nikl, A. N. Vasil'ev, A. Yoshikawa, and R.-Y. Zhu