Radioluminescence and scintillation mechanisms

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What is luminescence?

Luminescence is the cold emission of light ($\neq$ black body radiation)

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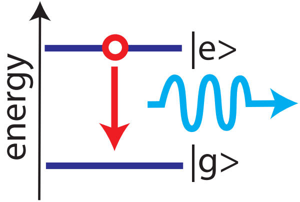
The "system" for the physicist:
→ quantum states = authorized energy levels
→ fundamental and excited states



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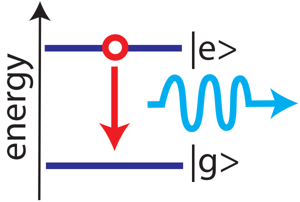
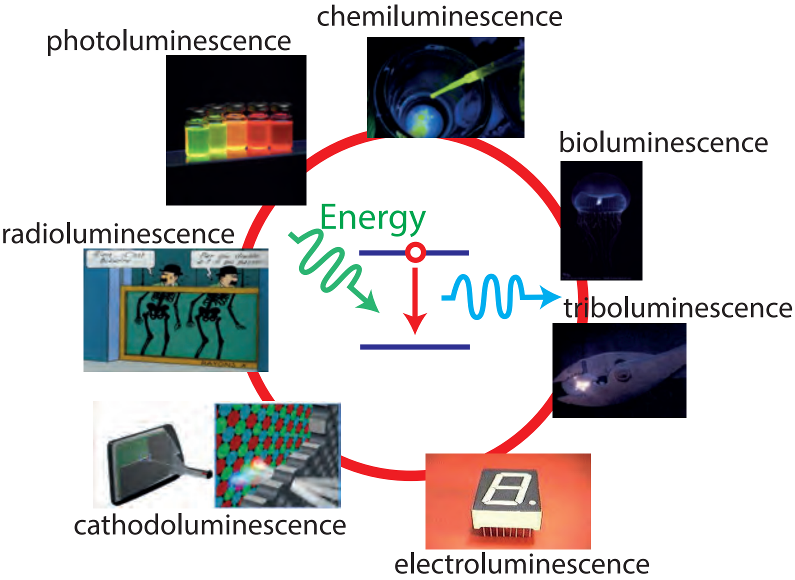


The physics of the energy level might originate from:

- Atoms (quantum numbers)
- Molecules (HOMO-LUMO)
- Nanoparticles (HOMO-LUMO or Energy bands)
- Solids (Energy bands)

prior to emit photon, it requires energy input



Scintillator: detecting ionizing radiations

Basics

- Ionizing radiations: x-ray; γ-ray, α, neutrons, ions, electrons...
- Detection requires electric pulse
- Interaction radiation-matter: ionizing $\rightarrow$ electron extraction

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Direct charge detection

Geiger systems, semiconductors

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Indirect detection

Charges to light conversion

$\downarrow$

Light detection

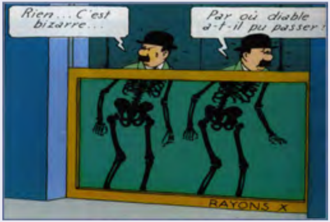
(PMT,CCD, SiPM...)

$\Downarrow$

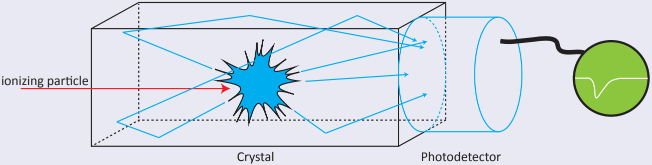
Scintillation

Scintillators in general

Detection of ionizing radiation: Old style

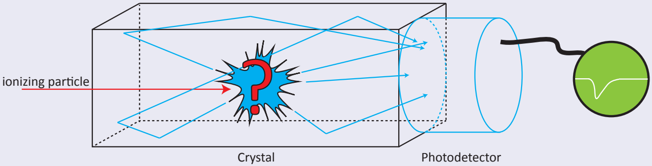


Detection of ionizing radiation: Modern one



About processes

Huge relaxation of Energy



1 high energy photon (keV-MeV) → thousands of IR-Vis photons (eV)

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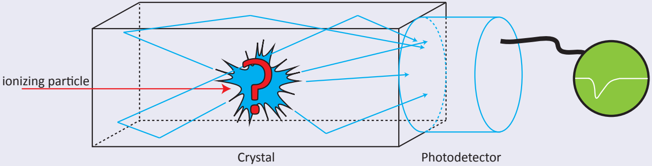

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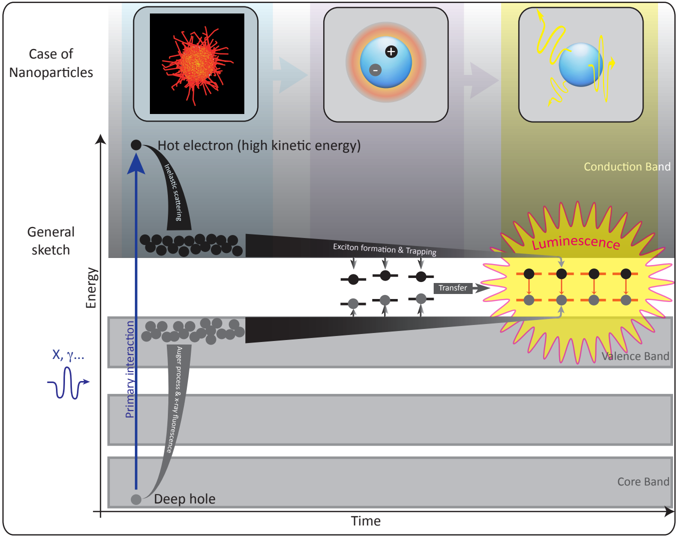
Multiscale Physics

- As cutting a 10km string in pieces of a few cm!
- First steps in the ps range, last ones can be in the s time range
- Energy deposition is structured at the nm and mm scale

Scintillation mechanisms

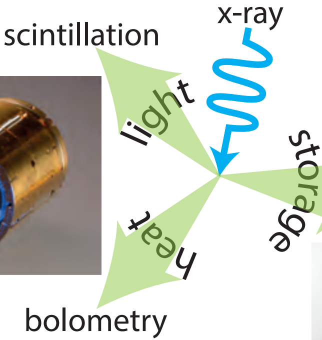
A brief description



Scintillation mechanisms

As a result

Energy sharing during the relaxation process → light, heat & storage



x-ray

scintillation

light

storage

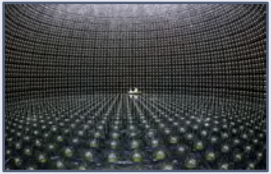
storage phosphors

heat

bolometry

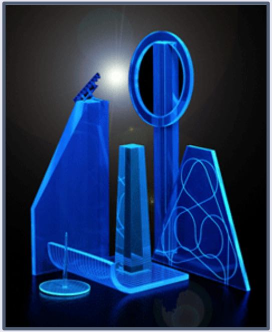
Several scintillator classes

Liquid



Kamiokande (neutrino)

Organic solids



Plastics @ Saint Gobain

Inorganic solids

$PbWO_4$ @ CERN

Why so many materials and researches?

It does not exist universal scintillators!

- Requirements in terms of performances and shapes depend on the application

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First rank parameters

- Density & Z_{eff} (host selection): Stopping power, photoelectric effect
- Scintillation yield: Easier to detect, energy resolution, timing
- Scintillation decay (luminescent center): Counting rate, coïncidence gate, Time Of Flight...
- → cerium doped Lutetium based compounds were very popular (LSO)

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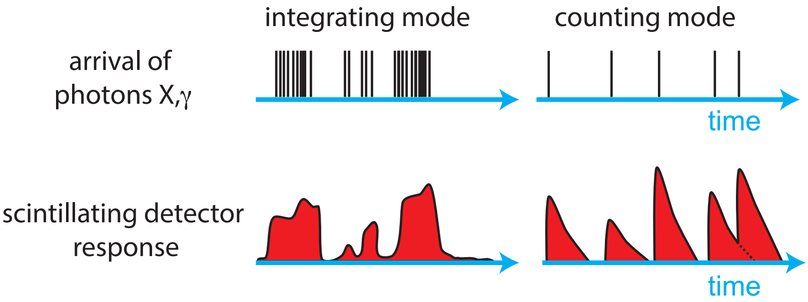
Second rank parameters

Mechanical and chemical stability, emission wavelength, cost, mass production capability, radio-isotopes purity, thermal stability, shaping possibilities . . . . . .

Why so many materials and researches?

2 main uses: counting and integration



Integrating

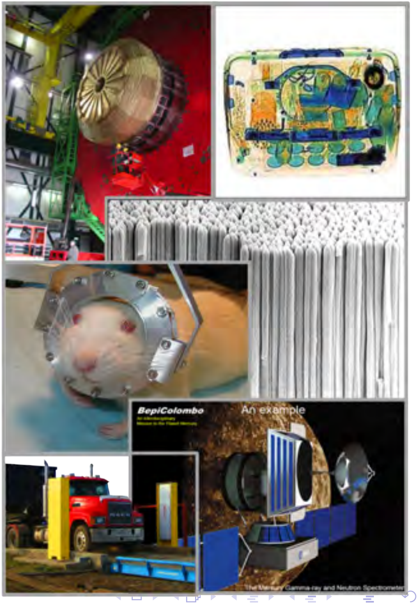
Scintillator can be "slow" (ms)
(except afterglow)
→ X-ray imaging, Dosimetry

Counting

Scintillator has to be "fast" ($< \mu s$)
→ PET, Homeland security, Calorimetry...

Various applications using scintillators

- High energy calorimetry
- Medical imaging (PET-Dosimetry-X-ray CT...)
- Homeland security
- Oil drilling
- Space exploration
- Dark Matter search
- Industrial control
- Nuclear industry
- Nuclear waste survey
- ...



Research on new compositions → Light production

It doesn't exist universal scintillator and each application has its own requirements

- host
- doping
- codoping
- defects
- synthesis protocols
- in connection with the theory of processes

see SCINT conference series
http://Scint.univ-lyon1.fr

Next one: Chamonix 2017

First announcement:
14th International Conference on
Scintillating materials and their applications

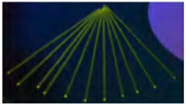
September 18-22, 2017
Le Majestic, Chamonix, France
https://scint2017.web.cern.ch
Scint2017@cern.ch

or / and shapes → Light collection

Single Crystal

Many applications

Inorganic Fibers

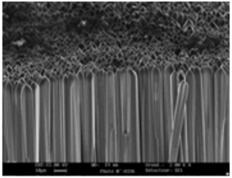


Calorimetry?

ZnS:Mn NP in PMMA

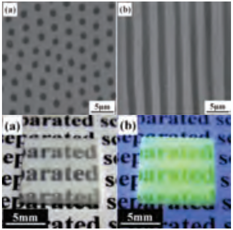
http://chm.tu-dresden.de

CsI:Tl Needles



Medical x-ray imaging

CsI-NaCl eutectic



@Canon, Adv. Mat. 2012

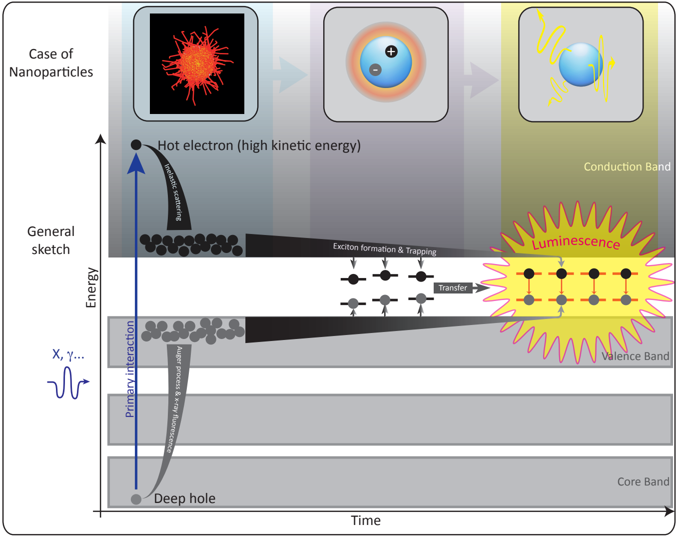
Thin films

High resolution x-ray imaging

Phosphor powder

x-ray imaging

The scintillation mechanisms in mode details: Absorption-relaxtation-tranfer-emission



Step one: the primary interaction

The interaction depends on the particle type and photon $\neq$ massive particles.

- If photon → absorption or transmission
- If massive particle → energy loss ($-\frac{dE}{dx}$)

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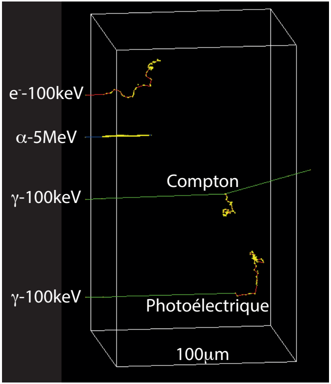
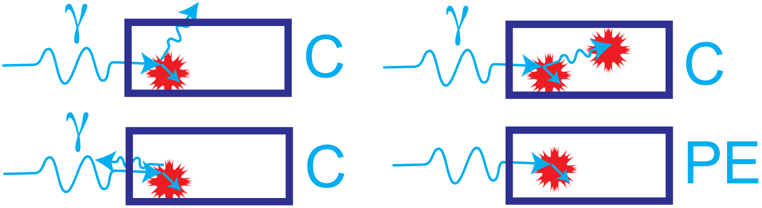
- Photons (x or γ):
  Photoelectric-Compton
  pair creation (if E>2x511keV)
- α: $M_\alpha \gg M_{e^-}$, Bethe-Bloch formula
- electrons (β^-): inelastic scattering or Bremsstrahlung (X-ray emission)
- neutrons: if fast, scattering on nucleus with recoil, if thermal (slow) capture by nucleus having a high neutron capture cross-section (^{6}Li, ^{10}B, ^{105}Gd, ^{107}Gd)

Simulation with GEANT4



example with NaI:Tl

interaction with photons (E<2x511keV)

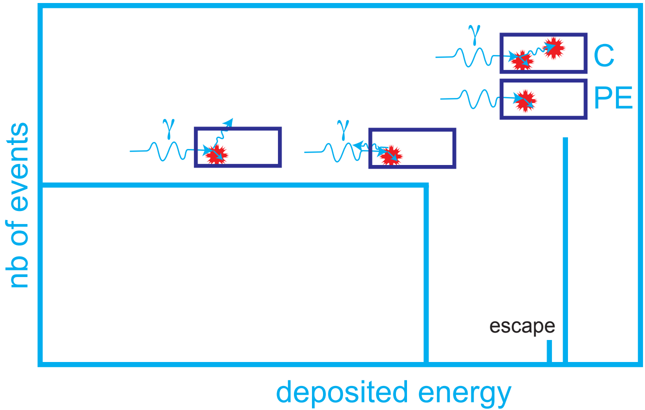


Compton and Photoelectric effects occur

- It generates a fast electron (which will generate the light at the end)
- In the case of Compton scattering, a γ photon generally escapes from the crystal and the full energy of the incoming γ is not deposited in the crystal. The energy deposition depends on the scattering angle.
- In some cases (top - right), the secondary γ is absorbed by the crystal, it appears like a photoelectric event from the energy deposition point of view

interaction with photons (E<2x511keV)

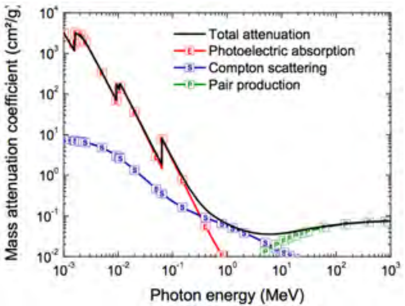
As a result, the energy deposition following the interaction with a photon leads to this schematic histogram



Crucial to understand the spectroscopy, the energy resolution and the light yield measurement

about absorption

- Linear probability of interaction: $\mu = \frac{n_e . \sigma_e}{Z_{eff}}$
- with n_e the density of electrons
- $Z_{eff} = W_A Z_A + W_B Z_B + W_C Z_C$ the effective atonic number of compound $A_X B_Y C_Z$ and W_i the mass fraction
- $\sigma_e = \sigma_{pe} + \sigma_c + \sigma_{pp}$ (various interaction cross sections)
- $\sigma_{pe} \alpha \frac{Z_{eff}^5}{E_\gamma}$ (+ effect of K, L, M. . . edges)
- $\sigma_c \alpha \frac{Z_{eff}}{E_\gamma}$

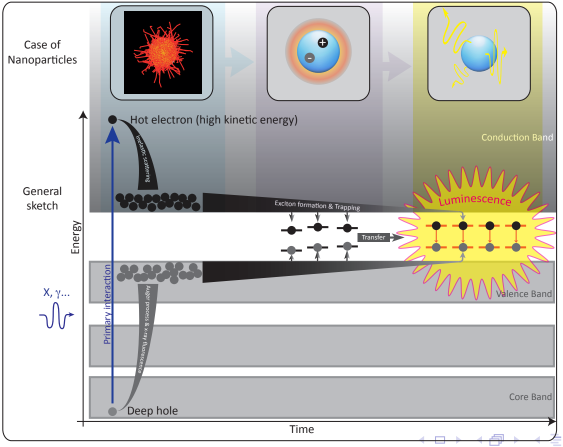


Mass attenuation of LuAG (curve from PhD thesis of K.Pauwels)

step2: from fast electron to light emission

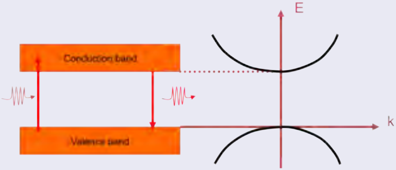
A crude description: $n_{photon} = \beta . E_{\gamma} \times S \times Q$

- 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: energy bands & dispersion curves

energy band: too rough description



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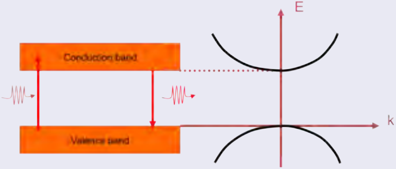
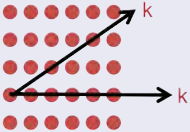


The shape depends on k directions



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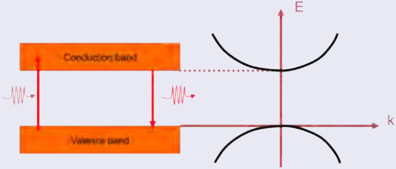

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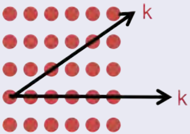
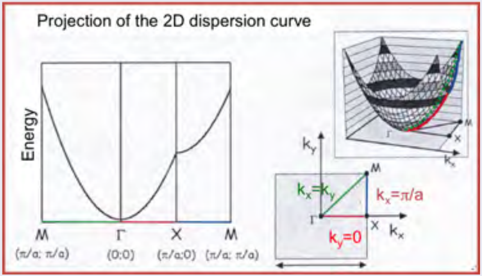


How to plot dispersion curves in 2D & 3D cases

$$1D \rightarrow E = \frac{\hbar^2 k^2}{2m}$$

and

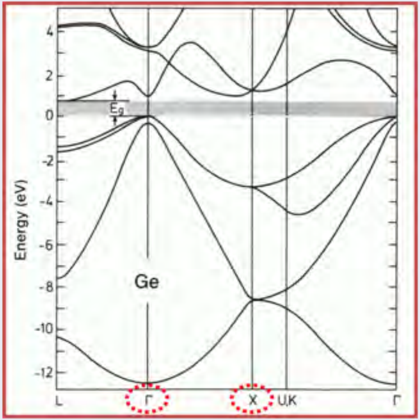
$$2D \rightarrow E = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m}$$



Solid description: energy bands & dispersion curves

in real life: example with Ge (simple material)

Dispersion curve



(k=0)

Specific direction

Simplified diagramme

Solid description: discrete states & localized states

We need to complete the Energy diagram: Excitons

- We saw the energy bands: 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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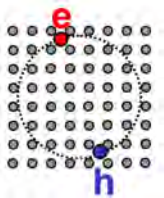
We need to complete the Energy diagram: Defects

- The crystal can contain defects: unwanted and wanted
- A defect brings its own set of energy level to the schem: spatially localized, but a large number of defects
- unwanted defects → traps, parasitic luminescence, quenching centers
- wanted defects → 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
- Hydrogenoïde model: effective mass of e & h; ϵ_r...
- Common in inorganic semi conductor (AsGa, CdS...)
- Can migrate → wavevector → dispersion curve

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

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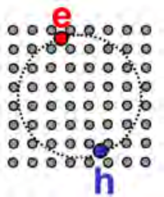

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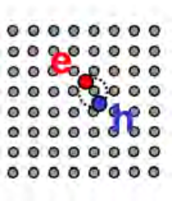
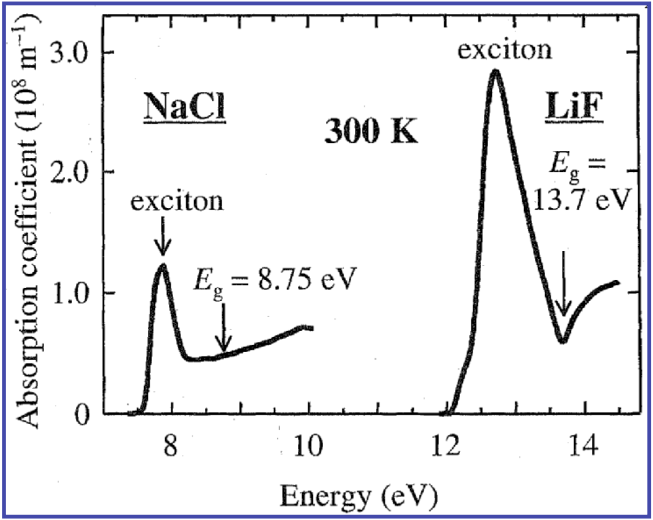
Frenkel excitons



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

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

Typical spectroscopic absorption



Palik, E.D. (1985) HandBook of the Optical constants, San Diego

Brief description of Excitons: relaxation

Various luminescence behaviors

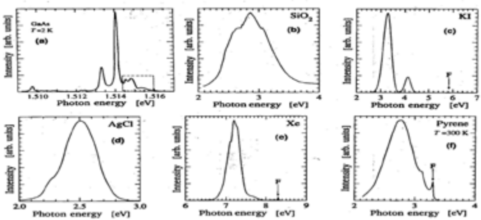


Fig. 1.4. Luminescence spectra of excitons in (a) GaAs, (b) SiO_2, (c) KI, (d) AgCl, (e) Xe, (f) pyrene ($C_{16}H_{10}$) [1.35–39, 1.7]

self-trapping

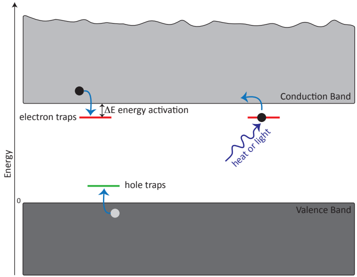
- A charge induces ions displacement → potential well in the CB
- It travels with the displacement
- → trapped in the potential it created: Self trapped Exciton (STE)
- → self-trapped means localization
- → light or heat or transfer

Text book: Song & Williams, Self-Trapped excitons, Springer

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 → photostimulation (x-ray imaging)
- With heat → 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
- → 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

Solid description: discrete states & localized states

Activators

- Various kind of active ions: rare earth in 2+ or 3+ states, transition metal ...
- Weak interaction with the crystal field: quite insensitive from host to host

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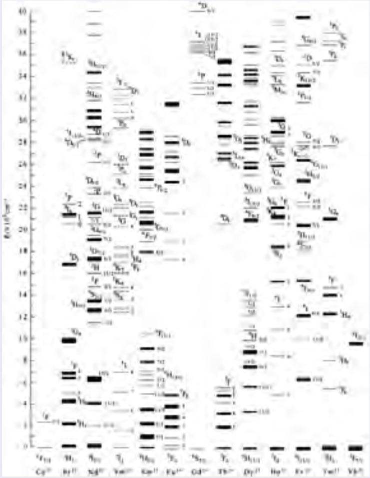
Example with the 3+ rare earth (shielded f orbitals=insensitive case)



Dieke diagram

Solid description: discrete states & localized states

Activators

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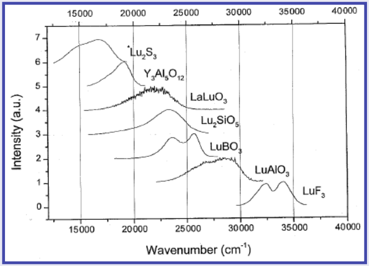
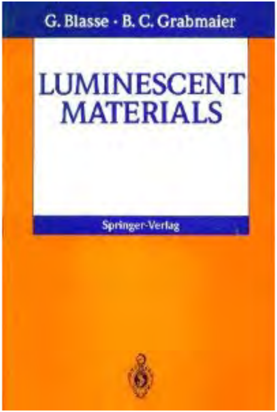
Example with the cerium 3+ (d → f transitions sensitive case)



C.Dujardin et. al., Encyclopedia of Materials , 2001

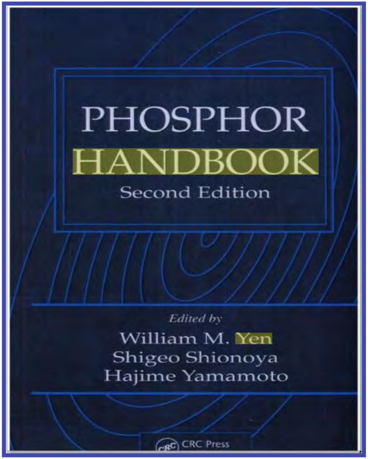
Some essential Books on Luminescent centers



G. Blasse · B. C. Grabmaier

LUMINESCENT
MATERIALS

Springer-Verlag

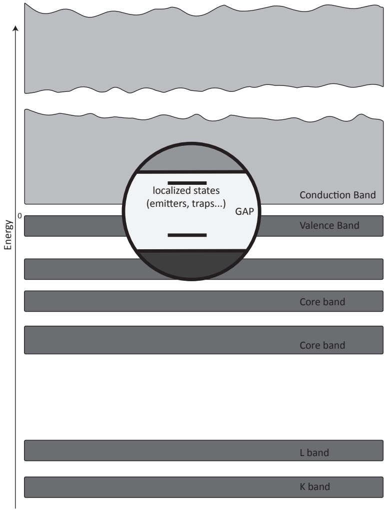


PHOSPHOR
HANDBOOK
Second Edition

Edited by
William M. Yen
Shigeo Shionoya
Hajime Yamamoto

CRC Press

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



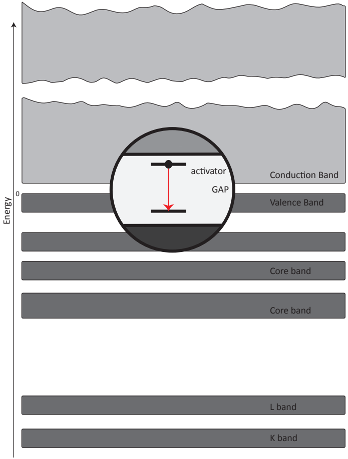
Luminescence: Last stage of the scintillation process

Timing

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

Light yield

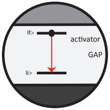
- Electron phonon interactions
- Concentration quenching



Luminescence: timing & light yield

decay time

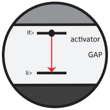
- about the timing properties
- Population: $n(t)$ in the excited state.
- $dn = -n(t) W_{rad} dt$ (W_{rad}: spontaneous emission rate)
- $\rightarrow n(t) = n_0 e^{-W_{rad} t} = n_0 e^{-\frac{t}{\tau}}$
- $\rightarrow$ weak probability = slow decay



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



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 $W_{rad} \rightarrow$ fast

Middle W_{rad}

Low $W_{rad} \rightarrow$ 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 $\searrow$

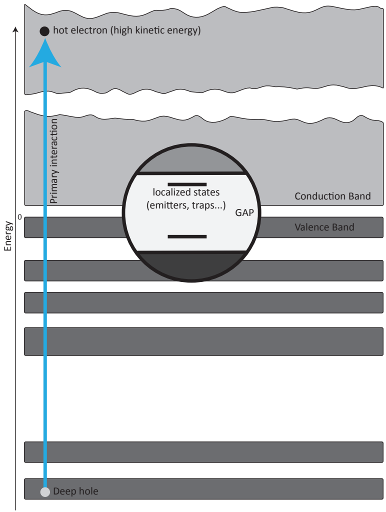
type of non-radiative processes

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

A hole in the barrel

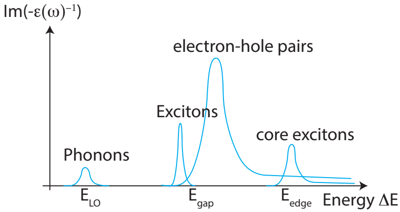
Overview of the processes - first approach

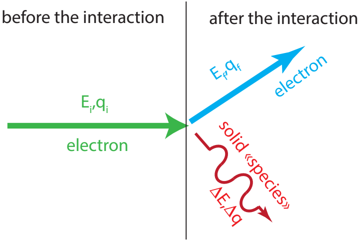
Primary interaction → first excitation: *solid**



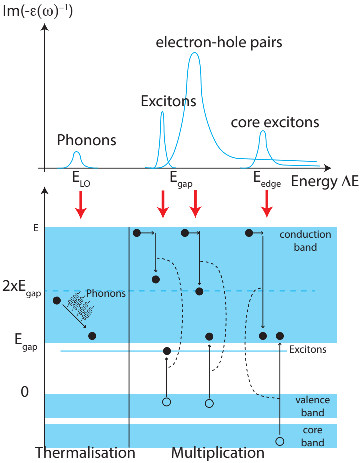
Overview of the processes - first approach

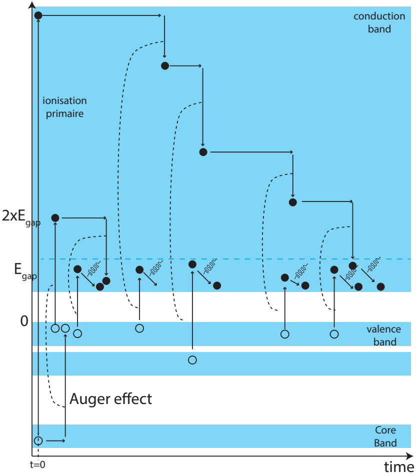
- Electron relaxation: connexion with optical constants ϵ
- Electron displacement = electromagnetic flash
- $\rightarrow$ connected to the optical response of the solid $(n^* = \nu + i\kappa)$ (see D.Smith et.al, NIM B, 2006 for details as example)
- Energy loss function: $Im(-\frac{1}{\epsilon})(\Delta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





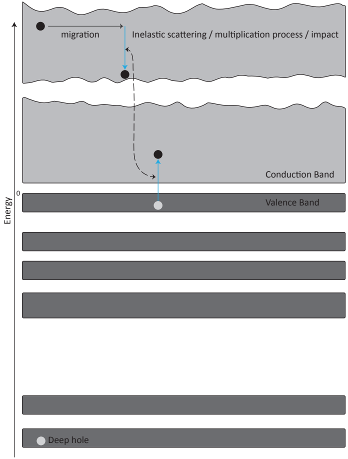
Relation with energy band diagram





Overview of the processes - first approach

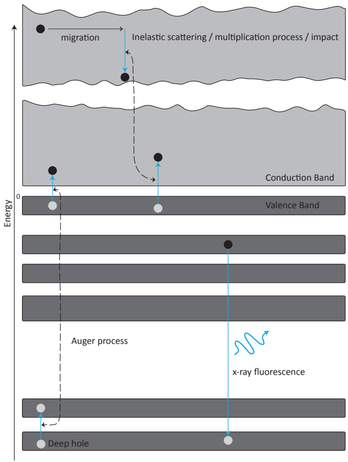
Hot electron relaxation



→1 secondary "excitation" & the primary electron loses the equivalent energy

Overview of the processes - first approach

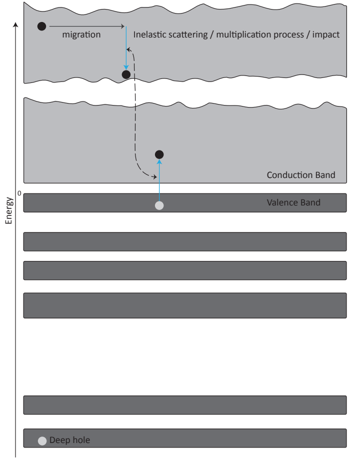
Hole relaxation: Auger process (≈ cross-relaxation) & x-ray fluorescence

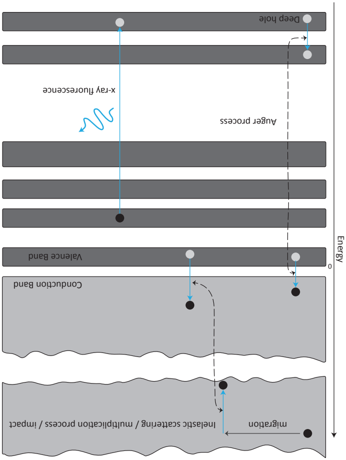


1 secondary "excitation" & the primary hole lost some energy

Overview of the processes - first approach

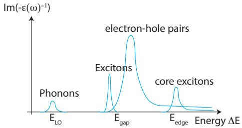
Auger process & multiplication: about the same

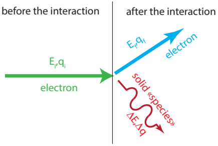


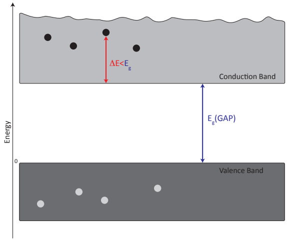


Overview of the processes - first approach

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



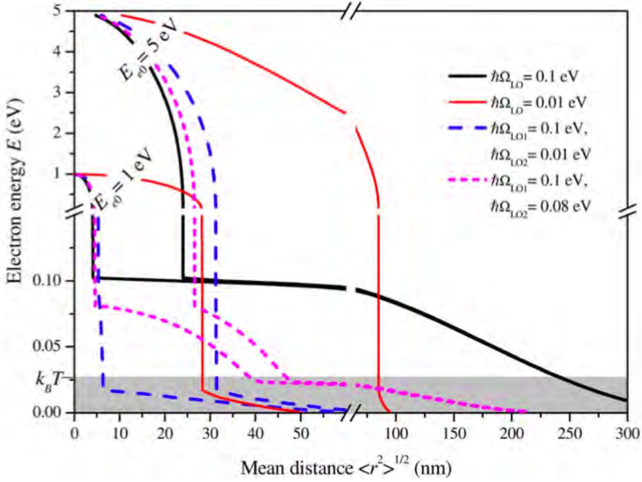




Overview of the processes - first approach

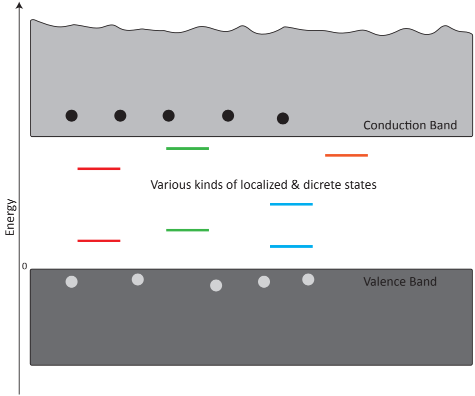
Still some migrations over tens of nanometers

Kirkin et. al. IEEE TNS2012



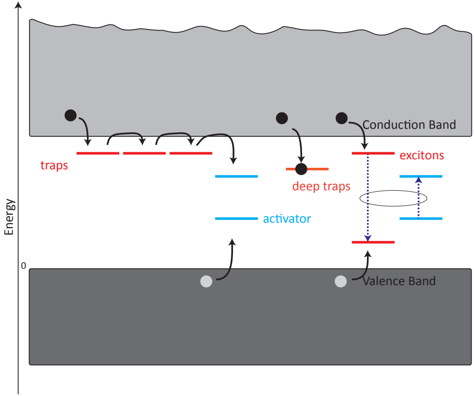
Overview of the processes - first approach

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



Overview of the processes - first approach

Several transfer processes are possible



→ may induce delay, quenching depending on the temperature

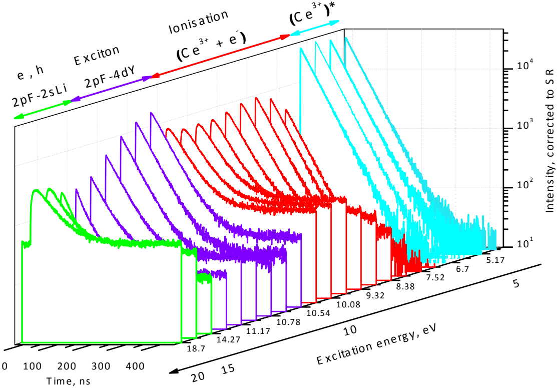
Overview of the processes - first approach

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

Overview of the processes - first approach

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



Overview of the processes - first approach

Illustration of trapping effect with YAG:Yb

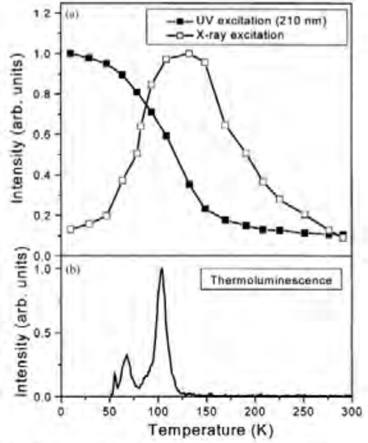
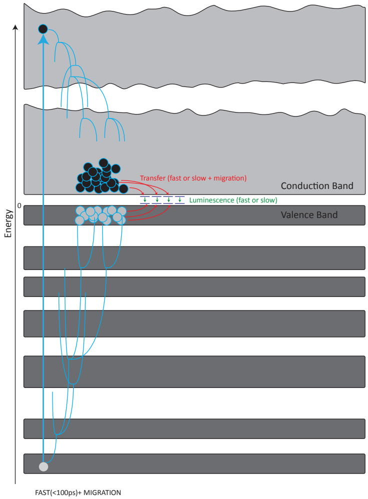


Fig. 3. Temperature dependence of the 333 nm integrated emission band intensity (a), and thermoluminescence (b) of YAG : Yb (50%).

Guerassimova et al., J. of Lum (2001)

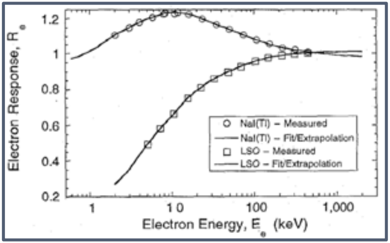
Summary picture



- The timing driven by the slowest process
- Heat, Light generation & trapping
- $LY = \frac{E_{gamma}}{2 \sim 3 E_g} SQ$
- → 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

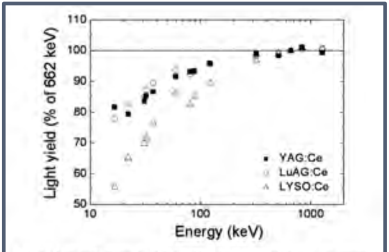
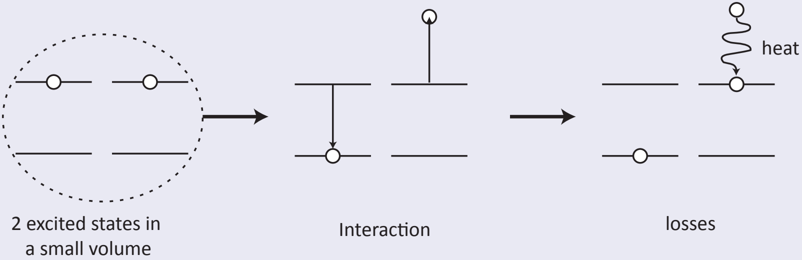


Fig. 2. Non-proportionality of the light yield as a function of γ-ray energy, measured with LuAG:Ce, YAG:Ce and LYSO:Ce crystals. Error bars are within the size of the points.

Chewpraditkul, IEEE TNS, 1998

A few words about non-proportionnality

excitations can interact!



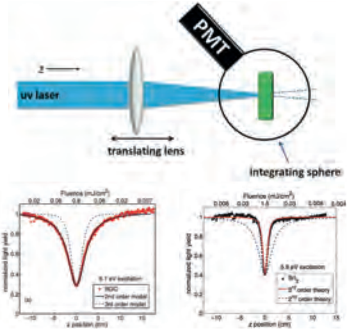
- → concentration quenching for excitations
- → important effect of the spatial distribution of excitations

A few words about non-proportionnality

Analytical model, Bizarri et. al. JAP 2009

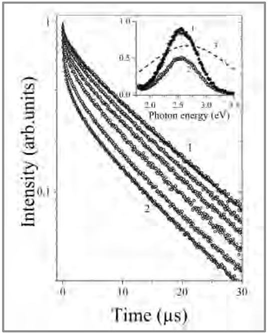
How to analyze it?

Z-scan approach



J.Grim et. al. PRB 2013

effect on the decay $CdWO_4$

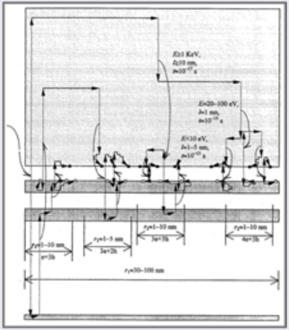


Kirm et al., PRB, 2009

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

A few words about non-proportionnality

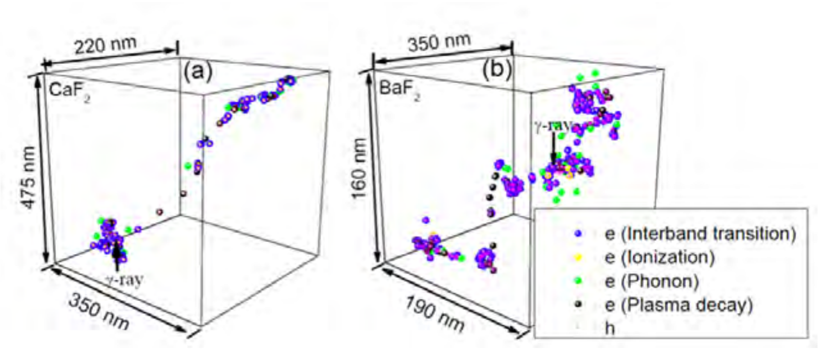
spread of the charges/excitations depends on the initial energy



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

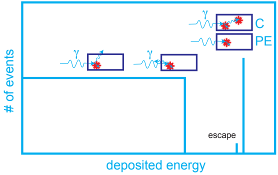
A few words about non-proportionnality

An illustration of modeling the energy cascade / spatial distribution



Gao et al., JAP, 2013

How to measure light yield? what is the resolution?

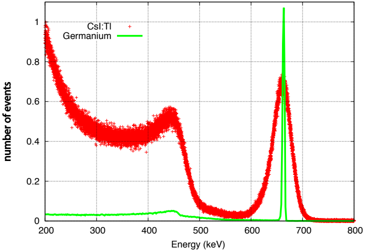


A monochromatic radioactive source is deposited on the top of the crystal itself coupled to a PMT

- 1 event → deposited energy → light flash production
- → light detection → electrical pulse
- → shaping the signal (as a gaussian)→ histogram
- → the photo peak represents the full energy deposition, its position represents the amplitude of the signal
- → knowing the the single photoelectron position and the detector efficiency → # photon for xx keV deposited
- but: it depends on the wrapping, the crystal shape, the detector efficiency. . . .
- CAUTION: it is a time resolved measurement → it depends on the shaping time and it is different from radio luminescence efficiency

How to measure light yield? what is the resolution?

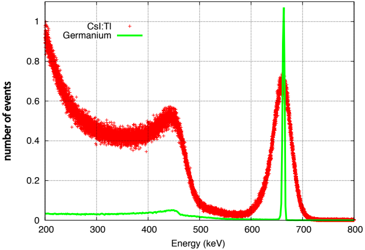
real spectra (Ge: direct conversion)



- It is used for spectroscopy, once calibrated, the shape of the spectra gives the nature of the radioactive source
- The "width" of the photopeak divided by the position is the energy resolution ($\frac{\Delta E}{E}$)

How to measure light yield? what is the resolution?

real spectra (Ge: direct conversion)



- $(\frac{\Delta E}{E})^2 = (2.3\sqrt{\frac{1+\epsilon}{N}})^2 + (\delta_p)^2 + (\delta_c)^2$
- the first term is the statistic resolution
- δ_p is the transfer resolution
- δ_c is the crystal resolution → connected to the proportionality response
- because each event leads to a different energy cascade, a crystal having a bad proportionality curve shows a bad energy resolution

About imaging

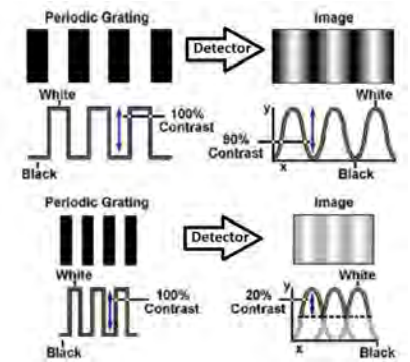
For imaging, quality criteria are very different

- image quality? how to define it?
- time acquisition per image

About imaging

The modulation transfer function (MTF)

- The contrast: $M = \frac{I_{max} - I_{min}}{I_{max} + I_{min}}$
- it depends on the frequency of the image (ν)
- $MTF = \frac{M^{image}(\nu)}{M^{object}(\nu)}$



About imaging

The Detective Quantum Efficiency (DQE)

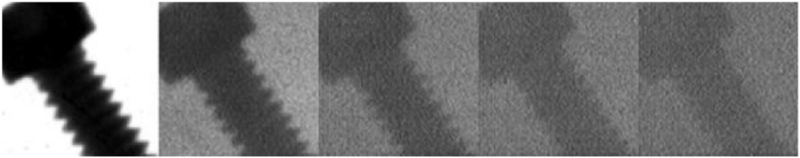
- DQE$=\frac{(Signal-to-noise)_{Output}}{(Signal-to-noise)_{Intput}}=\frac{\frac{S_o}{\sigma_o}}{\frac{S_i}{\sigma_i}}$
- S and σ are the average values and standard deviation of the signal
- Assuming a poison distribution of the incoming number of incident x-ray photons DQE$=\eta_{abs}\left[1+\frac{1+\frac{1}{\eta_{QE}}}{\eta_{col}\eta_{LY}}\right]^{-1}$
- η_{abs} is the scintillator absorption
- η_{abs} is the scintillator Light Yield
- η_{col} is the light collection efficiency
- η_{QE} is the detector quantum efficiency

→ it gives the main quality criteria for the scintillator

About imaging

And take care to the memory effects (traps)

- afterglow
- bright burn



Nagarkar et al., 2007