Chapter IX:
Thermoluminescent dosimeters

Thermoluminescent dosimeters (TLD)

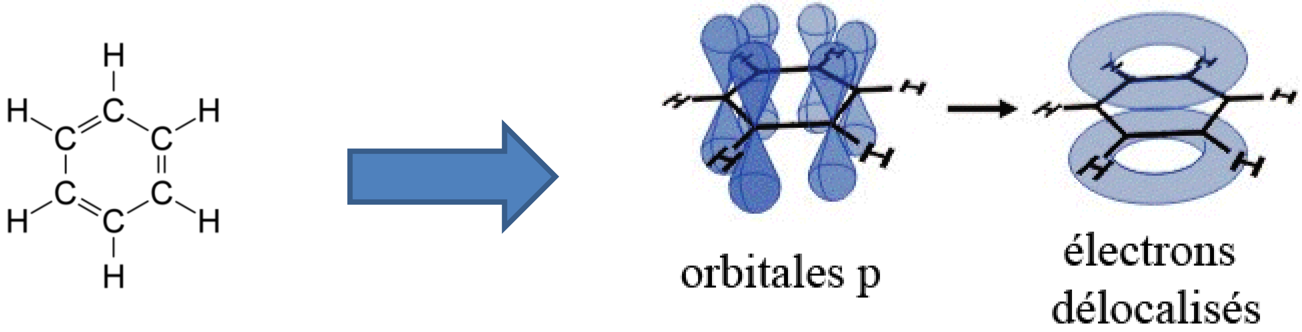
- Following the radiation absorption → some materials (semiconductors or insulators, not metals) retain a part of the absorbed energy in metastable states
- When this *E* is liberated as UV radiation, visible or IR → phenomenon called luminescence
- The luminescence process can be accelerated due to an external stimulus (heat, light)
- When external stimulus = heat → thermoluminescence
- When thermoluminescence is used for dosimetry → thermoluminescent dosimeter (TLD)
- References:
  - A.J.J. Bos, *High sensitivity thermoluminescence dosimetry,* Nuclear Instruments and Methods in Physics Research Section B 184 (2001) 3-28
  - A.J.J. Bos, *Theory of thermoluminescence*, Radiation Measurements 41 (2007) S45–S56

Luminescence

- When ionizing radiation interacts with matter → a large number of molecules are excited or ionized
- When these molecules return to the ground state → possible creation of luminescence centers → possible emission of photons in the visible or near to the visible energy range → luminescence
- 3 types of luminescence
  1. Fluorescence: light emission occurs “immediately” after absorption (more precisely: $< 10^{-8}$ s, i.e. time for atomic transition)
  2. Phosphorescence: light emission is delayed because excited state is metastable (time between absorption and emission can be from μs to days, months)
  3. Delayed fluorescence: a center of phosphorescence can be transformed into a fluorescence center following an external excitation → « normal » fluorescence but after a much longer time

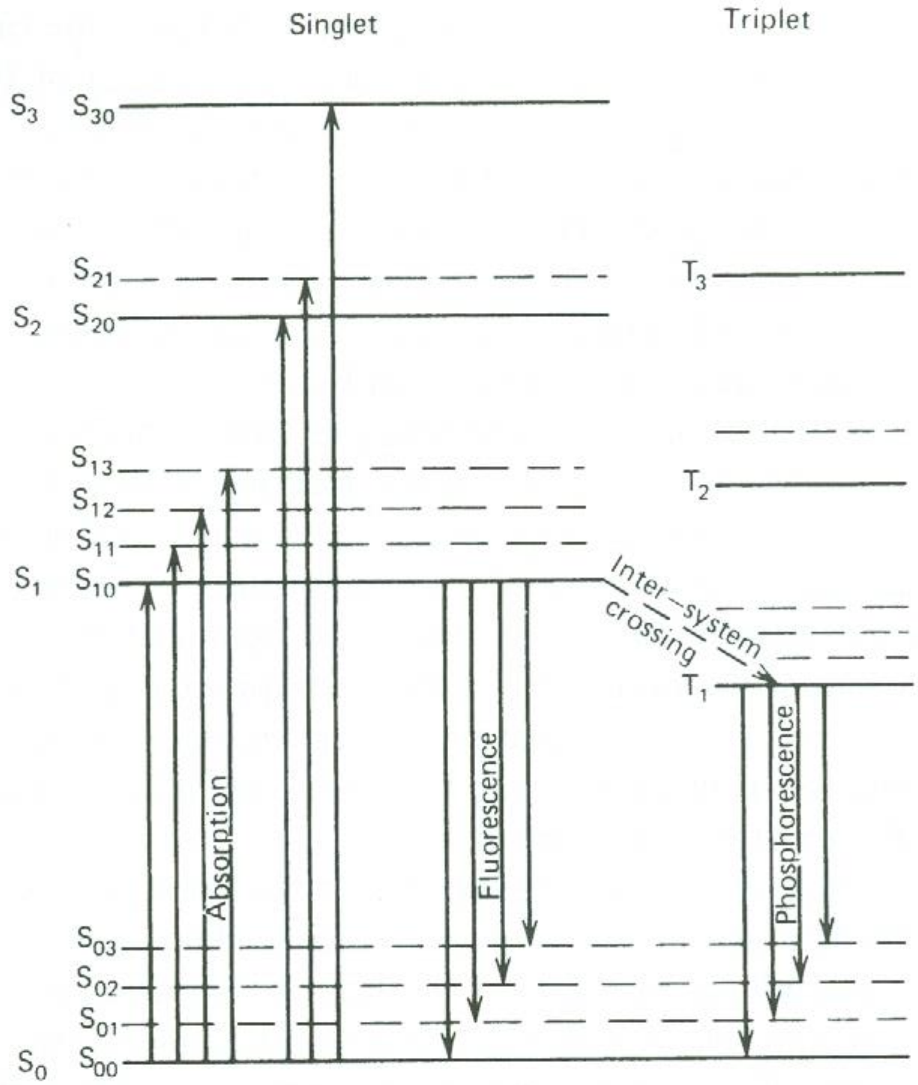
Example fluorescence ↔ phosphorescence: Benzene

- Benzene (C_6H_6) → π-electrons → spin = 0 (singlet: S_i) or spin = 1 (triplet: T_i)



- Energy absorption → radiationless decay from high energy levels to S_{10} state
- Transitions between S_{10} and S_{0i} with light emission (fluorescence)
- Transition between S_{10} and T_{10} → slow transition to S_0 (phosphorescence) or excitation to S_{10} due to ouside

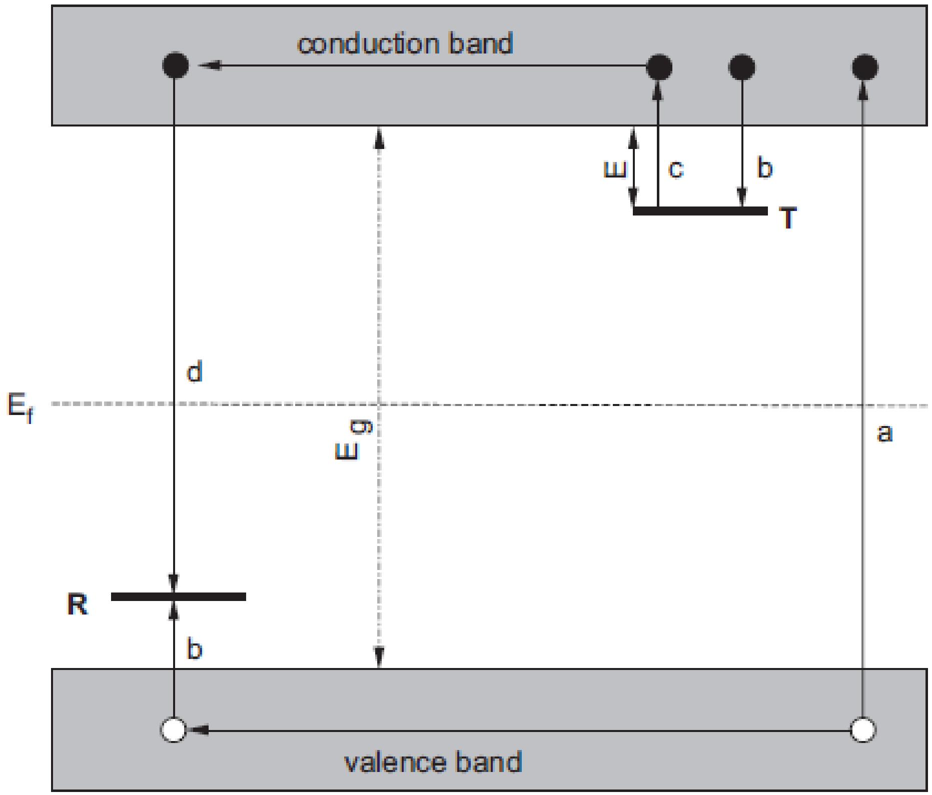
Energy levels of benzene



Model: 1 trap – 1 recombination centre

- Energy band model
- Intensity of light
- First-order kinetics
- Second-order kinetics
- General-order kinetics
- Luminescence efficiency

Energy band model (1)



- E_g : energy band gap
- E_f : Fermi level
- *T*: electron trap (with *E*, *E* of the trap or activation *E*)
- *R*: recombination centre

Energy band model (2)

- Semiconductors or insulators → band structure
- Structural defaults or impurities (→ complete characterization is impossible → never 2 identical TLD) → levels inside the forbidden band gap → <u>simple model</u> → 2 levels: 1 below the conduction band (T) and another above the valence band (R)
- $E_T > E_f$ → empty at equilibrium and before irradiation
- When $h\nu > E_g$ is absorbed → ionization of valence band e^- → after thermalization → free e^- in the conduction band and h^+ in the valence band (a transition)

Energy band model (3)

- 2 possibilities
  1. Direct recombination → excitation of a luminescence centre (corresponding to a recombination centre)
  2. Trapping of an e^- at T and of a h^+ at R (b transition)

- The probability *p* of liberation per time unit (c transition) of the trapping e^- is given by the equation of d’Arrhenius:

$$p = s \exp\left(-\frac{E}{kT}\right)$$

with *s*, the frequency factor or attempt-to-escape factor (constant in the simple models simples and ≈ 10^{12} - 10^{14} s^{-1}, i.e. the lattice vibration frequency), *k* = 8.617 10^{-5} eVK^{-1}, Boltzmann’s constant and *T*, the temperature (in K^{-1})

Energy band model (4)

- If $E \gg kT_0$, with T_0 the T during irradiation ($T \approx 300$ K) → the e^- are indefinitely trapped (or at least during a long time compared to the analysis time)
- $N(e^-) = N(h^+)$ because they are created by pairs
- $E(R) < E_f < E(T)$ → non-equilibrium situation → transition to equilibrium is always open but the relaxation rate is slow → metastable state
- The return to equilibrium is speeded if T ↗→ the e^- migrates to the conduction band up to a recombination centre R (corresponding to a luminescence centre) → emission of light (d transition) → thermoluminescence
- Attention: practically some radiationless process occurs

Intensity of light (1)

- The intensity of light *I(t)* in photons per second at any time *t* during heating is $\propto$ to the rate of recombination of e^- and h^+ at R (each recombination produces a photon which is detected) → with *m* (m^{-3}), the concentration of h^+ at R →

$$I(t) = -\frac{dm}{dt}$$

- The recombination rate is also $\propto$ to the concentration of free e^- in the conduction band, n_c, and of h^+ →

$$I(t) = -\frac{dm}{dt} = n_c m A_m$$

with A_m, the probability of recombination ($m^3 s^{-1}$) independent on *T*

Intensity of light (2)

- The rate of change of the concentration of trapped e$^-$, *n*, is equal to the rate of thermal release minus the rate of retrapping →

$$-\frac{dn}{dt} = np - n_c(N-n)A_n$$

  with *N*, the concentration of e$^-$ traps and A_n, the probability of retrapping

- Moreover → the rate concentration of free e$^-$ in the conduction band is equal to the rate of thermal release minus (the rate of retrapping + the rate of recombination) →

$$\frac{dn_c}{dt} = np - n_c(N-n)A_n - n_c m A_m$$

Intensity of light (3)

- No analytical solution to these equations → hypothesis of Chen and Mc Keever → quasi-equilibrium (QE):

$$\left|\frac{dn_c}{dt}\right| \ll \left|\frac{dn}{dt}\right| \quad \text{et} \quad \left|\frac{dn_c}{dt}\right| \ll \left|\frac{dm}{dt}\right|$$

  → the concentration of free e^- in the conduction band is quasi stationnary

- As $dn_c/dt \approx 0$ →

$$n_c = \frac{np}{(N-n)A_n + mA_m}$$

➡

$$I(t) = \frac{mA_m ns \exp\left(-E/kT\right)}{(N-n)A_n + mA_m}$$

First-order kinetics (1)

This eq. cannot be analytically resolved → additional assumption of Randall et Wilkins → negligible retrapping →

$$mA_m \gg (N-n)A_n$$

➡ $$I(t) = -\frac{dn}{dt} = ns\exp\left(-\frac{E}{kT}\right) = np$$

If T = cste → p = cste ➡

$$I(t) = I_0\exp\left(-tp\right)$$

with I_0: initial intensity

➡ Simple exponential function

First-order kinetics (2)

If $T \nearrow \rightarrow p \neq$ cste ⇒

$$I(t) = -\frac{dn}{dt} = n_0 s \exp\left(\frac{-E}{kT(t)}\right) \times \exp\left[-s\int_0^t \exp\left(\frac{-E}{kT(t')}\right) dt'\right]$$

with n_0: number of e^- trapped at $t = 0$

- $T \nearrow \rightarrow$ detrapping of e^- and recombination $\rightarrow I(t) \nearrow$
- $T \nearrow \rightarrow$ maximum
- $T \nearrow \rightarrow$ decrease of the number of charge carriers $\rightarrow I(t) \searrow$

⇒ Peak → first-order « glow peak » (GP)

First-order GP

- If *T* is raised as a linear function of time →

$$T(t) = T_0 + \beta t$$

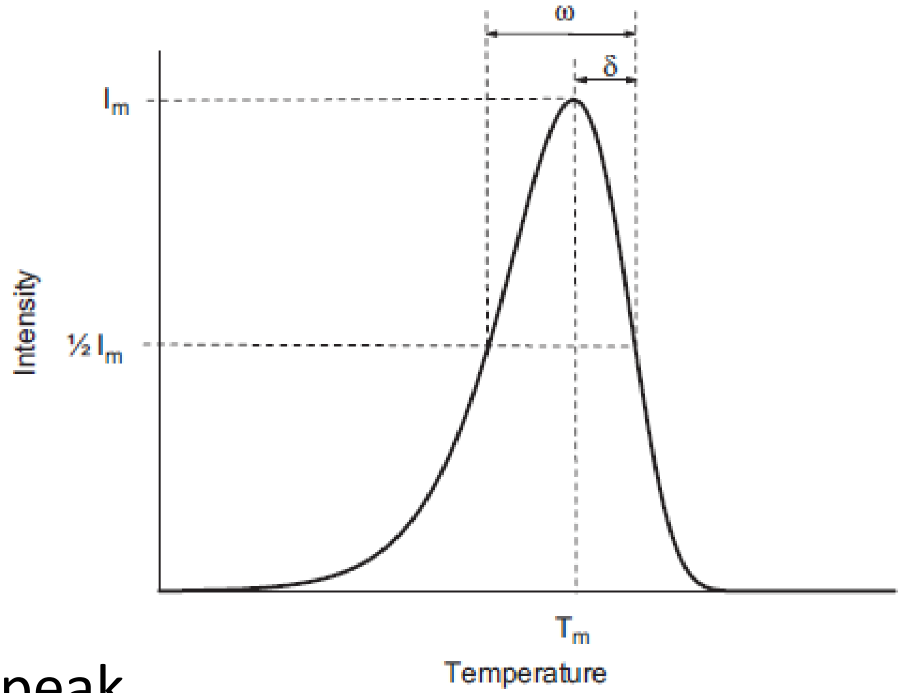
with T_0: *T* for *t = 0* and β, the constant heating rate

- The GP becomes (as a function of *T*) →

$$I(T) = -\frac{1}{\beta}\frac{dn}{dT} \quad = \quad n_0 \frac{s}{\beta} \exp\left(\frac{-E}{kT}\right) \times \exp\left[-\frac{s}{\beta}\int_{T_0}^{T} \exp\left(\frac{-E}{kT'}\right) dT'\right]$$

⇨ First-order expression of Randall-Wilkins for the GP

Form of the first-order GP



- Asymmetric peak
- Geometry factor $\mu_g = \delta/\omega$ with ω, the full width at half maximum and δ, the half width at half maximum (for high *T*) → typically $\mu_g = 0.42$
- T_m: the *T* at maximum I_m
- For small *T* → exponential decrease (*exp[-E/kT]*) is dominating

Maximum of GP

- The condition to have the maximum →

$$\frac{dI}{dt} = 0 \quad \text{ou} \quad \frac{d[\ln I(T)]}{dT} = 0$$

- This gives the Randall-Wilkins relation →

$$\frac{\beta E}{kT_m^2} = s \exp\left(-\frac{E}{kT_m}\right)$$

that can be iteratively resolved

- In the Randall-Wilkins relation → there is no n_0 → T_m is independent on n_0

Importance of n_0

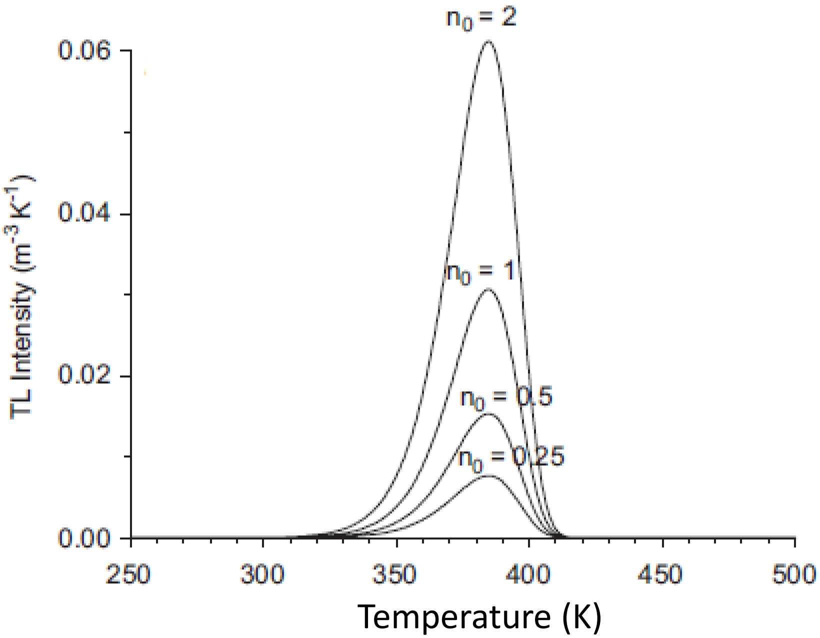
- n_0: important parameter in radiation dosimetry → $n_0 \propto D$

- n_0 is equal to the area of the GP →

$$\int_0^\infty I(t)dt = -\int_0^\infty \frac{dn}{dt}dt = -\int_{n_0}^{n_\infty} dn = n_0 - n_\infty$$

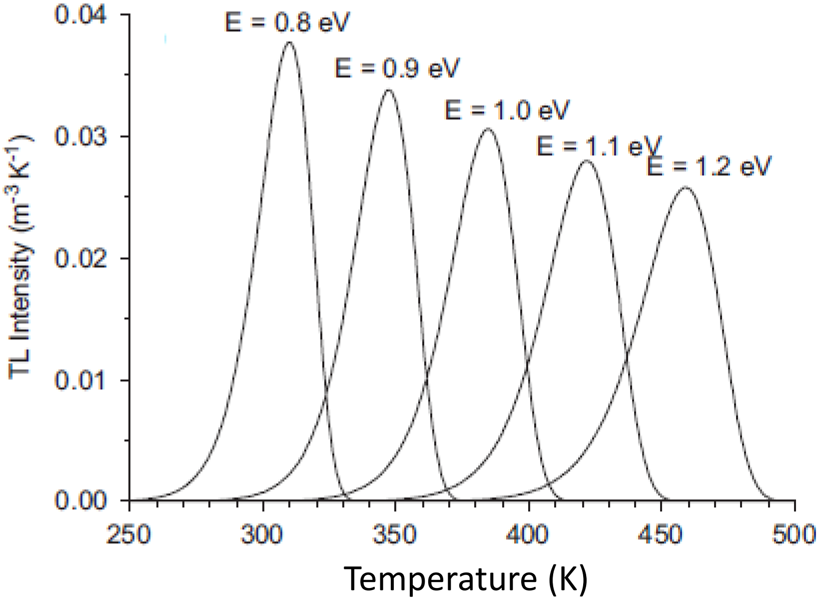
with $n_\infty \rightarrow 0$ for $t \rightarrow \infty$

Variation of the GP with *n_0*



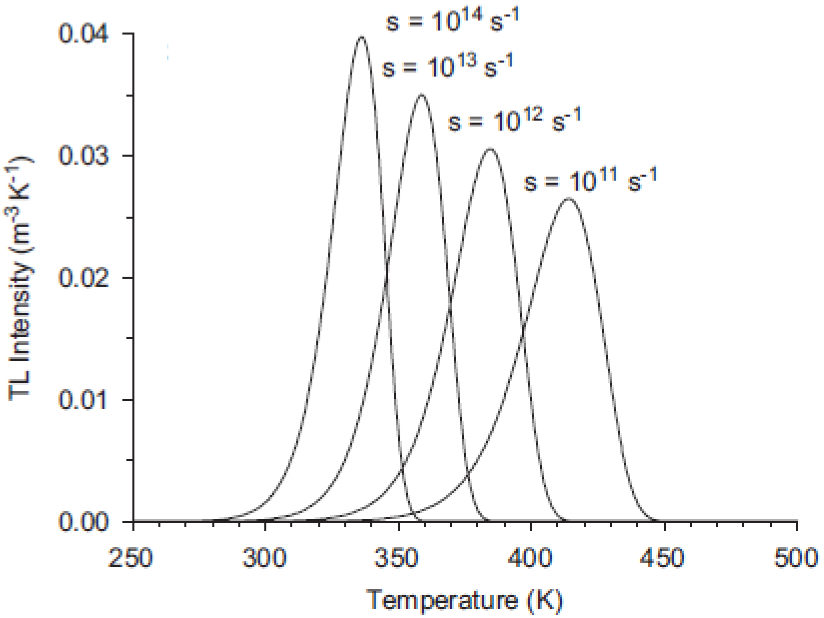
- GP(T,n_0) for E = 1 eV, s = 10^{12} s^{-1} and β = 1 Ks^{-1} ([n_0] = m^{-3})
- T_m is constant for varying n_0

Variation of the GP with *E*



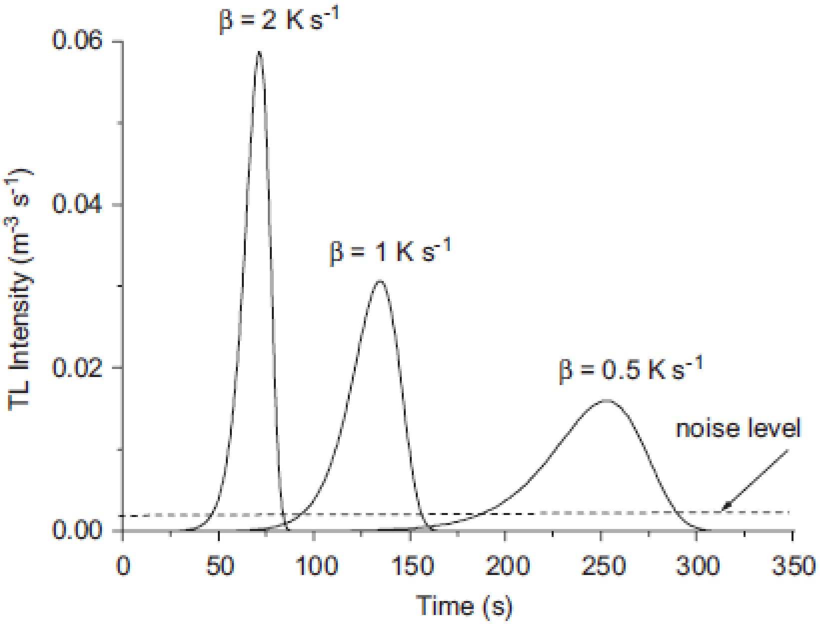
- GP(T,E) for $n_0 = 1$ m^{-3}, $s = 10^{12}$ s^{-1} and $\beta = 1$ Ks^{-1} ([E] = eV)
- E ↗ → shift of the GP to high T, ↘ of the height and ↗ of ω with a constant area
- Shift of the GP to high T for E ↗ because deeper trap → more energy is needed (→ higher T) for e$^-$ detrapping

Variation of the GP with *s*



- GP(T,s) for $n_0 = 1\ m^{-3}$, $E = 1$ eV and $\beta = 1\ Ks^{-1}$ ($[s] = s^{-1}$)
- s ↗ → shift of the GP to small T, ↗ of the height and ↘ of ω with a constant area
- s ↗ → probability to free the e^- is larger → less E necessary (→ smaller T)

Variation of the GP(t) with β



- GP(t,β) for $n_0 = 1$ m^{-3}, $E = 1$ eV and $s = 10^{12}$ s^{-1} ([β] = Ks^{-1})
- Height of the GP $\propto$ to n_0 but also to β → it is confirmed by the I_m expression due to Hoogenboom →

$$I_m = n_0 \frac{\beta E}{k T_m^2} e^{-g_m}$$

I_m expression of Hoogenboom (1)

$$I(t) = n_0 s \exp\left(\frac{-E}{kT(t)}\right) \exp\left[-s\int_0^t \exp\left(\frac{-E}{kT(t')}\right)dt'\right]$$

$$I_m = I(t_m) = n_0 s \exp\left(\frac{-E}{kT_m}\right) \exp\left[-s\int_0^{t_m} \exp\left(\frac{-E}{kT(t')}\right)dt'\right]$$

With $T(t) = T_0 + \beta t$, we consider:

$$\begin{aligned}
\int_0^t e^{-E/kT'}\,dt' &= \frac{E}{\beta k}\int_{E/kT}^{E/kT_0} e^{-z}\frac{dz}{z^2} \\
&\approx \frac{E}{\beta k}\int_{E/kT}^{\infty} e^{-z}\frac{dz}{z^2} \\
&= \frac{kT^2}{\beta E} e^{-E/kT} g\left(\frac{E}{kT}\right)
\end{aligned}$$

Correct for $T_0 \ll T_m$

I_m expression of Hoogenboom (2)

with $$g(x) = x^2 e^x \int_x^\infty e^{-z}\frac{dz}{z^2} = x e^x \int_1^\infty e^{-xu}\frac{du}{u^2} = x e^x E_2(x)$$

and $E_2(x)$, the exponential integral of second-order

By taking again:

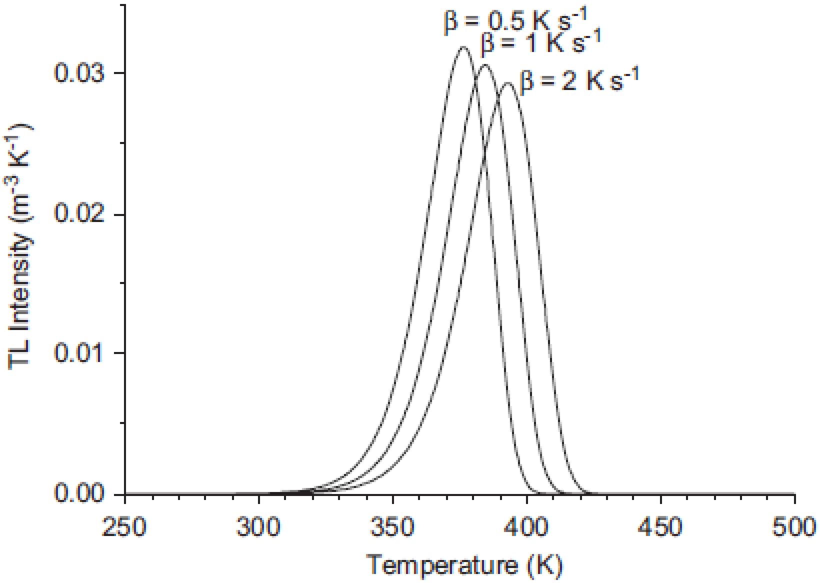
$$\frac{\beta E}{kT_m^2} = s \exp\left(-\frac{E}{kT_m}\right)$$

→

$$I_m = n_0 \frac{\beta E}{kT_m^2} e^{-g_m}$$

Considering $g_m = 1$ → I_m underestimation of 10%

Variation of the GP(T) with β



- GP(T,β) for $n_0 = 1$ m^{-3}, $E = 1$ eV and $s = 10^{12}$ s^{-1} ([β] = Ks^{-1})
- β ↗ → shift of the GP to high T, ↘ of the height and ↗ of ω with a constant area → opposite behaviour compared to s → normal because of the ratio s/β in the expression of $I(T)$

Approximated expression of *I(T)*

- Approximation of Kitis → the integral is approximated by asymptotic series →

$$
\begin{aligned}
I(T) \quad = \quad & I_m \exp\left[1 + \frac{E}{kT}\frac{T - T_m}{T_m} - \frac{T^2}{T_m^2}\right.\\
& \left. \times \exp\left(\frac{E}{kT}\frac{T - T_m}{T_m}\right)(1 - \Delta) - \Delta_m\right]
\end{aligned}
$$

  with Δ =2kT/E and Δ_m=2kT$_m$/E

- Useful expression utile for fitting

Second-order kinetics (1)

- Unlike Randall and Wilkins, Garlick and Gibson consider that retrapping is dominating →

$$mA_m \ll (N-n)A_n$$

- 2 more assumptions → $N \gg n$ (trap is far from saturation) and $n = m$ →

$$I(t) = -\frac{dn}{dt} = s\frac{A_m}{NA_n}n^2 \exp\left(-\frac{E}{kT}\right)$$

- Thus → $dn/dt \propto n^2$ → second-order reaction

Second-order kinetics (2)

- By assuming equal probabilities for recombination and trapping → $A_m = A_n$ and T = constant →

  $$I(t) = \frac{I_0}{(1 + n_0 \alpha t)^2}$$

  with $\alpha = s/N \exp(-E/kT)$ → second-order equation

- We observe now a decrease hyperbolic and no more exponential

Second-order GP

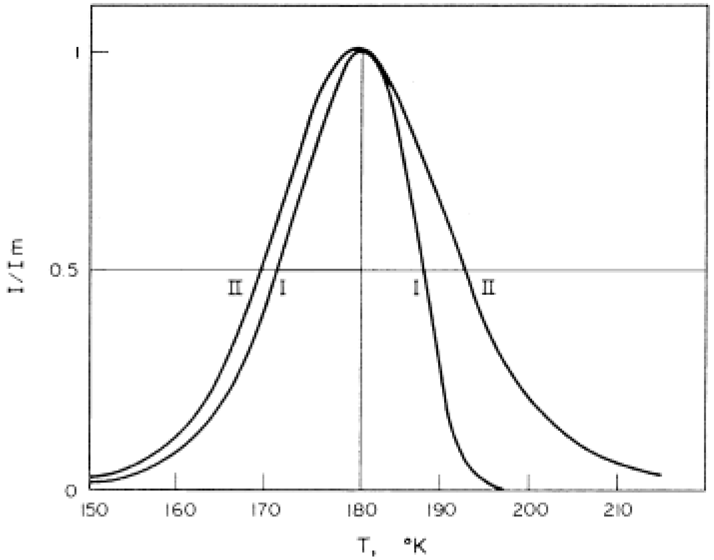
- Assuming again that → $T(t) = T_0 + \beta t$ →

$$\begin{aligned} I(T) = \quad = \quad & \frac{n_0^2}{N}\frac{s}{\beta}\exp\left(\frac{-E}{kT}\right) \\ & \times\left[1 + \frac{n_0 s}{N\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{kT'}\right)dT'\right]^{-2} \end{aligned}$$

⇨ Garlick-Gibson’s expression for the second-order GP

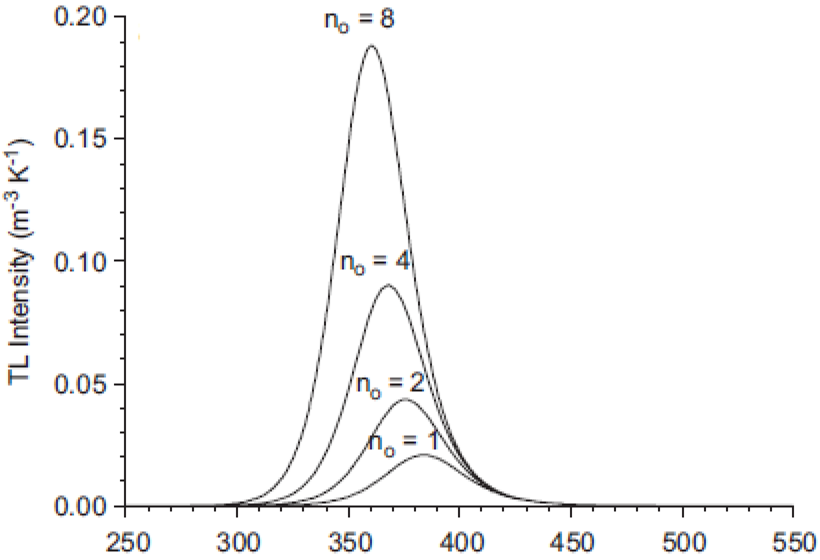
Form of the second-order GP

Comparison between GP of first and second order



- The half width at half maximum for high *T* > the half width at half maximum for small T
- Typically μ_g = 0.52 (larger than for first-order) → significant concentration of released e$^-$ are retrapped before they recombine → delay in the luminescence emission and spreading out of the emission over a wider temperature range

Variation of the second-order GP with n_0



- GP$^{(2)}(T,n_0)$ for $E = 1$ eV, $s = 10^{12}$ s^{-1} and $\beta = 1$ Ks^{-1} ($[n_0]$ = m^{-3})
- T_m ↘ when n_0 ↗ → main difference compared to first order
- Area of the peak $\propto n_0$ as for first-order but the intensity of the peak is no more directly proportional to n_0 (even if the deviation is small)

Approximated expression of *I(T)*$^{(2)}$ (second-order)

Approximation of Kitis (with again Δ =2kT/E and Δ_m=2kT$_m$/E) →

$$\begin{aligned} I(T) \quad &= \quad 4I_m \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right) \times \left[\frac{T^2}{T_m^2}(1-\Delta)\right. \\ &\left. \times \exp\left(\frac{E}{kT}\frac{T-T_m}{T_m}\right) + 1 + \Delta_m\right]^{-2} \end{aligned}$$

General-order kinetics

- In most of the practical cases → we are faced with models of first- (largely dominating) or second-order ↔ the displayed conditions have to be respected
- If conditions are not respected → empirical expression for general-order kinetics of May and Partridge →

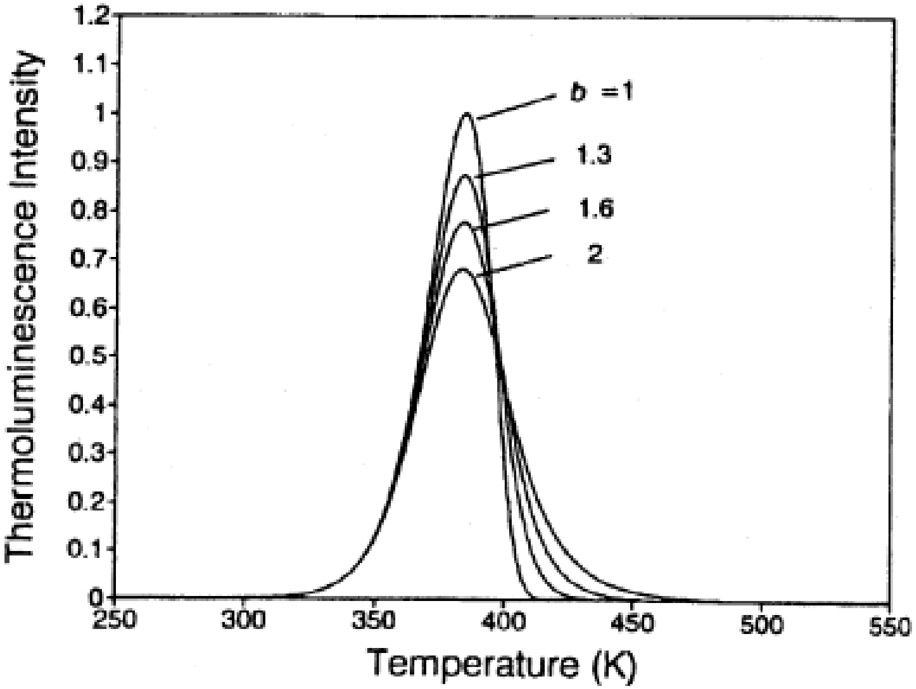
$$I(t) = -\frac{dn}{dt} = s' n^b \exp\left(-\frac{E}{kT}\right)$$

with *b*, the general-order parameter and $[s'] = m^{3(b-1)}s^{-1}$

- For $b \neq 1$ (with $s'' = s' n_0^{(b-1)}$)→

$$\begin{aligned} I(T) \quad &= \quad \frac{s''}{\beta} n_0 \exp\left(\frac{-E}{kT}\right) \\ &\times \left[1 + (b-1)\frac{s''}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-b/b-1} \end{aligned}$$

Comparison of ≠ orders GP

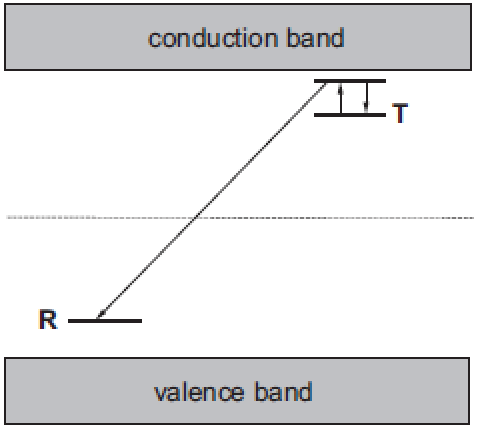


GP(T,b) for $n_0 = 1$ m^{-3}, $E = 1$ eV, $s = 10^{12}$ s^{-1} and $\beta = 1$ Ks^{-1} for b = 1, 1.3, 1.6, 2

Discussion about various assumptions (1)

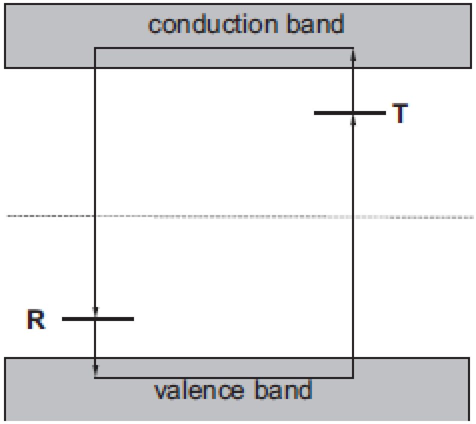
- QE assumption → more complex models (without QE) give results very close to those obtained for a first-order GP
- Assumption of the simple model: recombination via a transition from an e^- into the conduction band → other possibilities exist:

(a)



Recombination with a thermally stimulated e^- in the trap

(b)



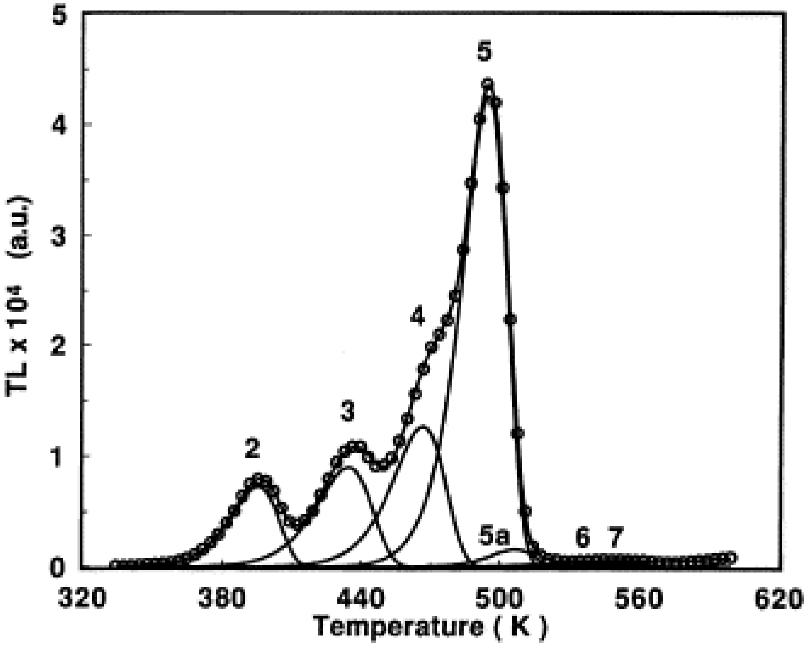
e^- and h^+ are simultaneously released

Discussion about various assumptions (2)

- (a) → the trap has to be in the proximity of a centre → however, traps and recombination centres « really » isolated are rare → frequent phenomenon → the frequency factor *s* is replaced by the « suitable quantity »
- (a) → probability of retrapping is zero → first-order equation → that explains, among other things, why first-order kinetics is in reality dominating
- (b) → eqs. of first- or second order valid by replacing *E* and *s* by adapted quantities → more complicated

Discussion about various assumptions (3)

- The presence of more than 1 trap (→ several possible E values) implies a « glow curve » (GC) composed of several GP →



GC of LiF: Mg,Ti

- A GC can (generally) be deconvoluted into several GP → attention: the parameters of each GP (*E* and *s*) have not the same meaning as for a simple GP

Luminescence efficiency

- Simple model → description of kinetics → no indication about absolute intensity of luminescence

- The intrinsic efficiency η_{i} is defined as the ratio of the energy emitted as visible light during heating to the energy absorbed during the exposure to ionizing radiation

- For the calculation of η_{i}, distinct steps are considered

Different physical steps for the calculation of η_i

1. The absorption of ionizing radiation → creation of N e$^-$-h$^+$ pairs → $N \propto 1/W$ et $W = \beta' E_g$ (avec $1 < \beta' < 4$)
2. Thermalization and trapping of the charge carriers → the fraction that is captured in traps, which can be thermally stimulated → trapping efficiency: η_tr
3. Release of the charge carriers (probability p), transport to a luminescent centre (efficiency S), exciting the luminescent centre that de-excite under emission of a photon (quantum efficiency Q)
4. Escape of the produced thermoluminescent photons from the sample (escape fraction: η_{esc})

Intrinsic efficiency

- With $h\nu$, the mean *E* of the emitted TL photons →

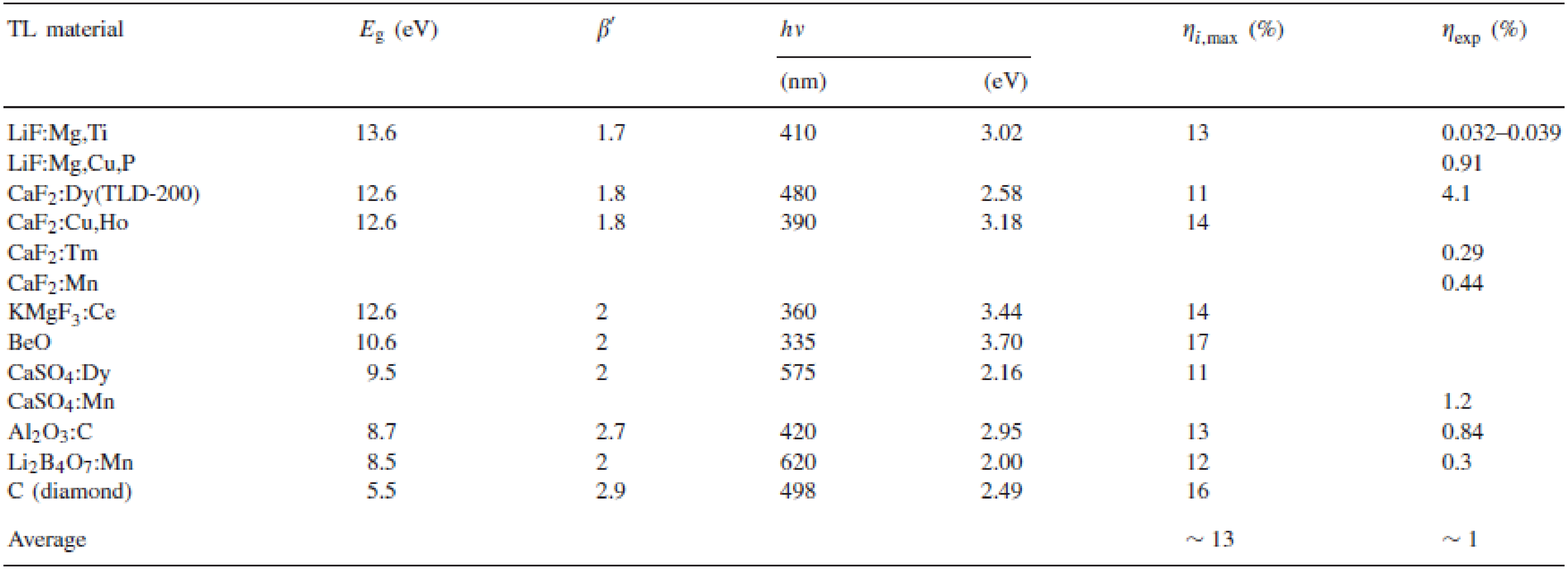
$$\eta_i = \frac{h\nu}{\beta' E_g} \eta_{tr} p S Q \eta_{esc}$$

- With all steps efficiency at maximum →

$$\eta_i^{max} = \frac{h\nu}{\beta' E_g}$$

- For all media used as TL → η_i^{max} ≈ 13% → only a small part of the absorbed *E* is converted into e^--h^+

Intrinsic and maximum efficiencies



TL material	E_g (eV)	β'	$h\nu$		$\eta_{i,\max}$ (%)	$\eta_{\exp}$ (%)
			(nm)	(eV)		
LiF:Mg,Ti	13.6	1.7	410	3.02	13	0.032–0.039
LiF:Mg,Cu,P						0.91
CaF_2:Dy(TLD-200)	12.6	1.8	480	2.58	11	4.1
CaF_2:Cu,Ho	12.6	1.8	390	3.18	14	
CaF_2:Tm						0.29
CaF_2:Mn						0.44
$KMgF_3$:Ce	12.6	2	360	3.44	14	
BeO	10.6	2	335	3.70	17	
$CaSO_4$:Dy	9.5	2	575	2.16	11	
$CaSO_4$:Mn						1.2
Al_2O_3:C	8.7	2.7	420	2.95	13	0.84
$Li_2B_4O_7$:Mn	8.5	2	620	2.00	12	0.3
C (diamond)	5.5	2.9	498	2.49	16	
Average					~ 13	~ 1

Parameters influencing the efficiency (1)

- Trapping efficiency : η_{tr} → crystal imperfections serve as trapping centres and by adding dopants → ↗ of the number of traps → increase of η_{tr} only for low traps concentration ↔ when the traps concentration is too large → average distance among the dopants become so small that interaction becomes possible → the energy levels are no more localized → decrease of η_{tr} (« concentration quenching »)

- For *S* → for a direct recombination of a thermally excited e^- into a trap → $S \approx 1$

Parameters influencing the efficiency (2)

- *Q* strongly depends on temperature → when T ↗ → *Q* ↘ (« thermal quenching ») (→ when β ↗ → *Q* ↘) → with C and W: quenching parameters:

$$Q(T) = \frac{1}{1 + C\exp\left(-W/kT\right)}$$

- Escape fraction: η_{esc} → for monocrystals which can be transparent to their own radiation: η_{esc} ↗ and for powders and sintered materials: η_{esc} ↘ (ex: η_{esc}($Al_2 0_3$:C) = 94% and η_{esc}(BeO) = 35%)

Thermoluminescent dosimeters (TLD)

- The most used TLD in radiation dosimetry are:
  - LiF:Mg,Ti
  - LiF:Mg,Cu,P
  - $Li_2B_4O_7$:Mn

  because they are tissue-equivalent
- Are also used due to their large sensitivity:
  - $CaSO_4$:Dy
  - Al_2O_3:C
  - CaF_2:Mn
- They are available as variable forms (powders, pastilles, ribbons,…)

General characteristics of TLD

- Fading
- Sensitivity
- Detection limits
- Response to the dose
- Response to the energy
- Annealing

Fading (1)

- A « perfect » TLD has the capacity to store information (trapped charge carriers) during an infinite time without losses
- However → there is always a probability of escape for the e^- before reading → fading → underestimation of the absorbed dose
- Various causes for fading
  - Thermal fading: following Arrhenius' law →

$$p = s \exp\left(-\frac{E}{kT}\right)$$

it is possible to obtain the half-live of thermal fading →

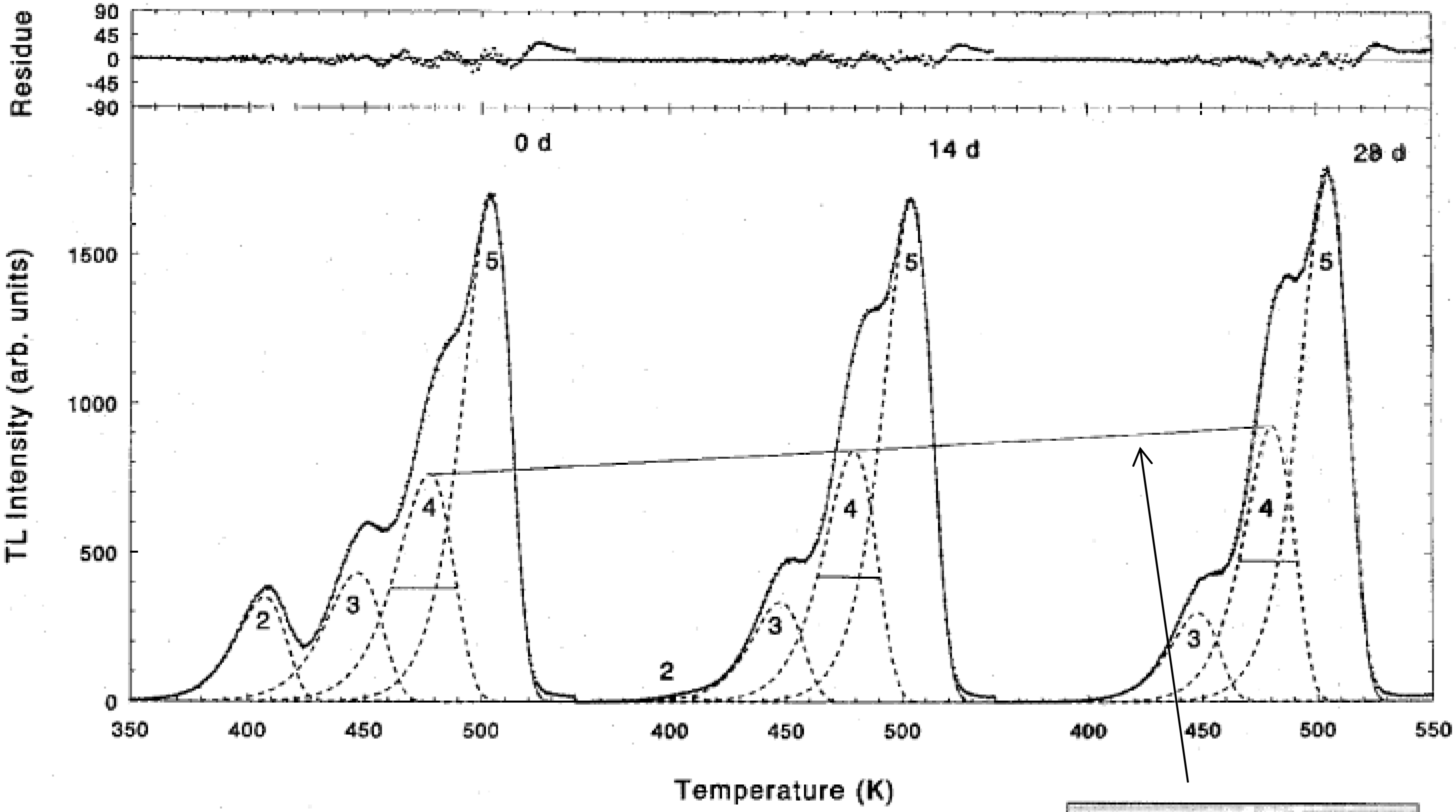
$$t_{1/2} = \frac{\ln 2}{p} = \frac{\ln 2}{s \exp\left(-\frac{E}{kT}\right)}$$

Fading (2)

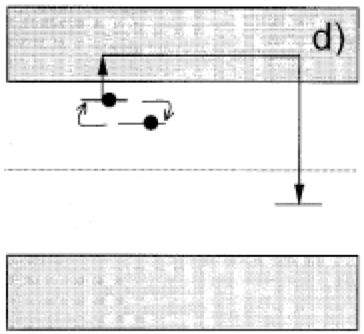
- Optical fading: some materials ($CaSO_4$, CaF_2) are very sensitive to light (materials with best sensitivity obviously) → must be store in opaque containers
- Quantum fading: quantum tunnelling between the trap and the recombination site

- Recommendation of the European Communauty: fading < 5 % during monitoring time at 25°C

Fading (3)



GC for a LiF:Mg,Ti after a 60 mGy irradiation from ^{60}Co measured after 0, 14 and 28 days



Interactions between defaults

Sensitivity

- TLD sensitivity: Intensity of the signal integrated over a time given per unit of absorbed dose and per unit of mass → depends on the TLD but also on the type of radiation, on the energy of radiation as well as on the reading system (heating, light detection,…)
- Generally → we define sensitivity relatively to the LiF:Mg,Ti TLD in same conditions of radiation and analyze
- Generally → radiations with high linear energy transfer (α, neutron,…) give signal < radiations with low linear energy transfer (γ, β,…)

Detection limits

- Means both: lower and upper levels of detection
- Lower level: smallest absorbed dose that can be detected with a specified confidence level → same order of magnitude a the background
- Upper level: largest dose that can be detected → theoretical maximum limit: all traps are filled → practically: the dose response has to be considered

Response to the dose (1)

- The signal of the TLD depends on the dose → *F(D)*: response to the dose
- Ideally a TLD has to shown a response to the dose linear over a large range of doses, at least over the range of interesting doses
- Practically → many non-linear effects exist for all materials
- The linearity index *f(D)* (or normalized dose response) is defined as:

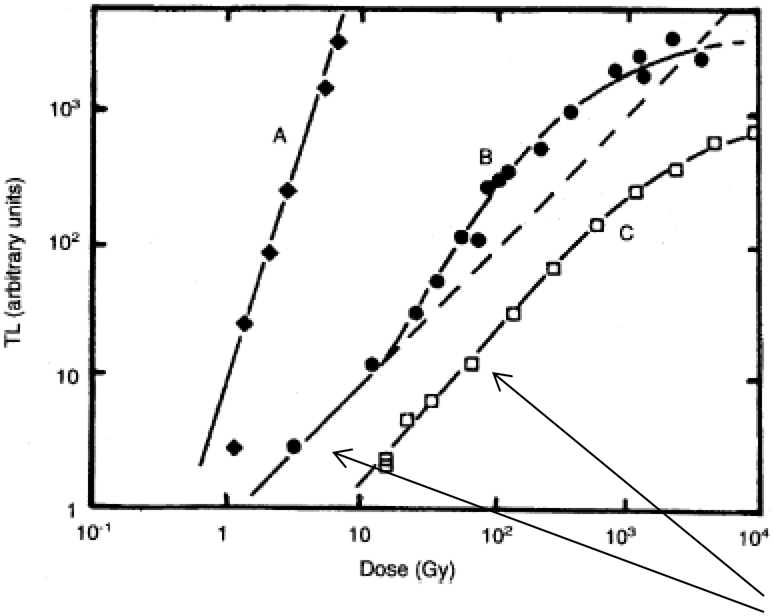
$$f(D) = \frac{F(D)/D}{F(D_1)/D_1}$$

with D_1, a weak dose for which the response is linear

Response to the dose (2)

We have:

- *f(D)* = 1: linear response (ideal TLD)
- *f(D)* > 1: supralinear response
- *f(D)* < 1: sublinear response (traps saturation)



slope = 1 or ≈ 1

A. SiO_2: supralinearity for the whole range of doses
B. LiF:Mg,Ti: behaviour linear - supralinear
C. CaF_2: Mn: very weak supralinearity

Dash-curve: linear response

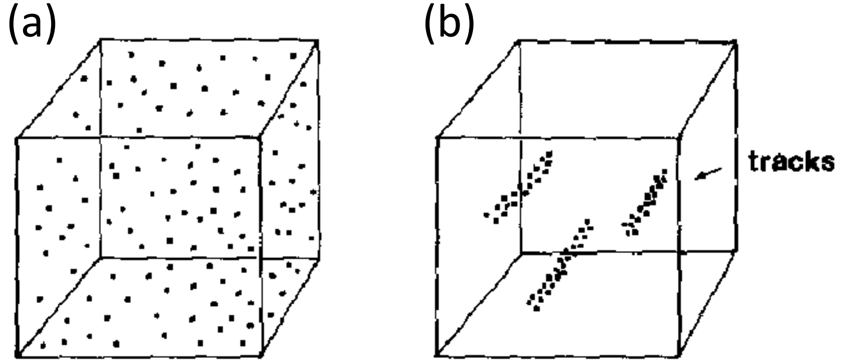
Explanation of supralinearity (1)

- Many parameters influence supralinearity: type of radiation, *E* of the radiation, speed of heating, defaults quantities,…
- To explain supralinearity → many models (up to now) → for some of them: critical process during the *E* absorption, for other ones: critical process during heating
- During heating → e^- are released from traps → recombination with h^+ to create light **or** trapping in deep traps (DT) without creation of light → concurrent centre (CC)

Explanation of supralinearity (2)

1. At small dose → large distance between the trap (T) and the recombination center (RC) → high probability for a e^- released by a trap to reach a DT before a RC → reduced dose response
2. When the dose ↗ → the distance between T and RC ↘ but also the number of DT ↘ (they have a larger probability to be filled → but a DT must be empty) → the dose response ↗ (up to saturation of the T)
3. Combining 1 and 2 → $f(D) > 1$ (SiO_2)
4. If there is no DT in the medium → dose response has to be higher and a linear response is observed up to saturation (CaF_2: Mn)
5. **The supralinearity is an underestimation at small dose rather than an overestimation at large dose**

Supralinearity ↔ linear energy transfer (1)



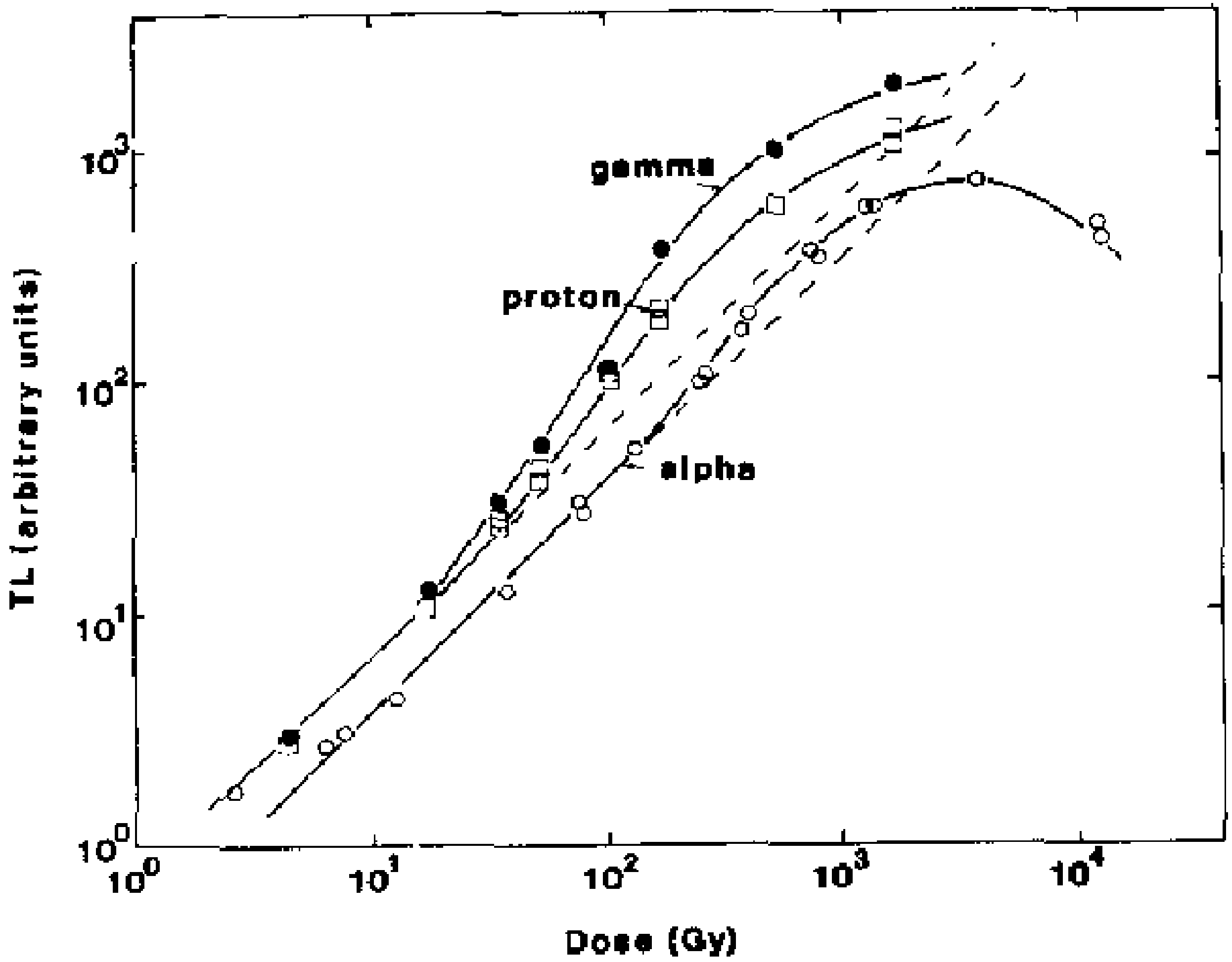
Spatial distributions of T-RC pairs for (a) γ of high energy (weak linear energy transfer) and for (b) heavy charged particles (large linear energy transfer)

- Heavy ions: dose deposited in a cylindrical area of a few tens of nm along the ion trajectory → large concentration of filled traps and few DT in the tracks cylinders / small concentration of filled traps and many DT outside the tracks cylinders
- MFP of the released e^- < cylinder radius → no interaction with a DT → reaching a RC → light → linear response
- Attention → quicker saturation

Supralinearity ↔ linear energy transfer (2)

- For particles with weak linear energy transfer → the released e^- can leave the tracks area and enter the area with large concentration of DT → loss of luminescence
- When the dose ↗ → the inter-tracks distance ↘ → the e^- reaches a RC with a larger probability → the dose response ↗ → supralinearity
- When the linear energy transfer ↘ → supralinearity ↗

Supralinearity ↔ linear energy transfer (3)

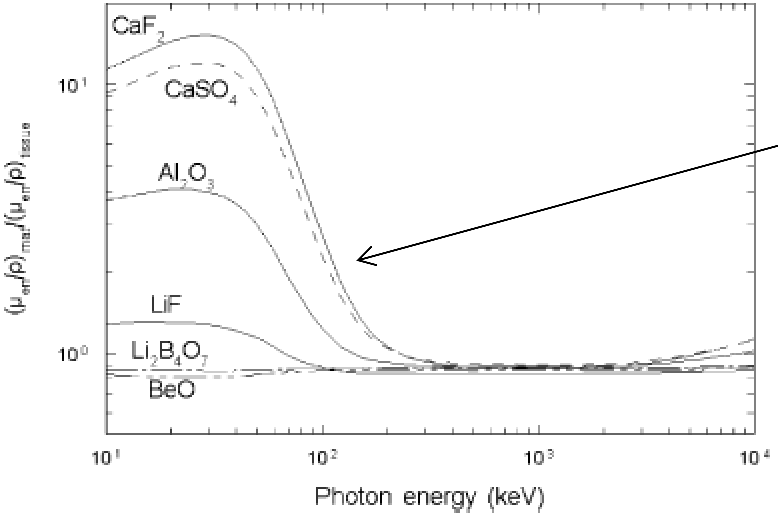


Energy response (1)

- Ideal case → energy response equal (or at least proportional) to human tissue

$$\frac{D_{\mathrm{TLD}}}{D_{\mathrm{tissu}}} \overset{\mathrm{CPE}}{=} \frac{\overline{(\mu_{en}/\rho)}_{\mathrm{TLD}}}{\overline{(\mu_{en}/\rho)}_{\mathrm{tissu}}}$$

- It is desirable for the ratio between the energy absorption coefficients to be constant



Photoelectric effect varying in Z^3 - Z^4

Energy response (2): Effective atomic number

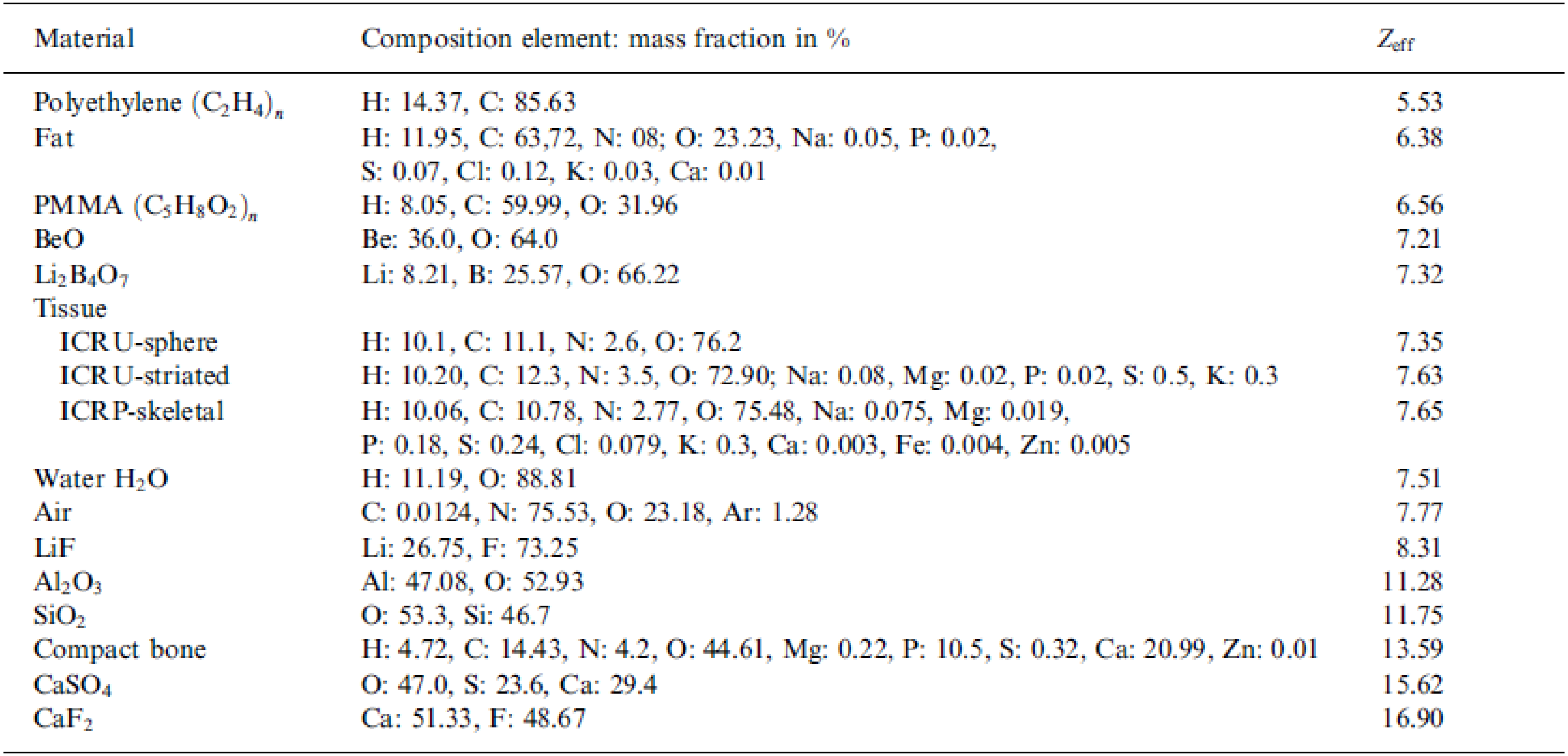
- Instead of comparing the response with curves → useful to define a « number » conveniently allowing this comparison → effective atomic number, Z_{eff}:

$$Z_{eff} = \sqrt[m]{\sum_i a_i Z_i^m}$$

  with a_i, the fraction of the total number of e^- associated to each element with atomic number *i*

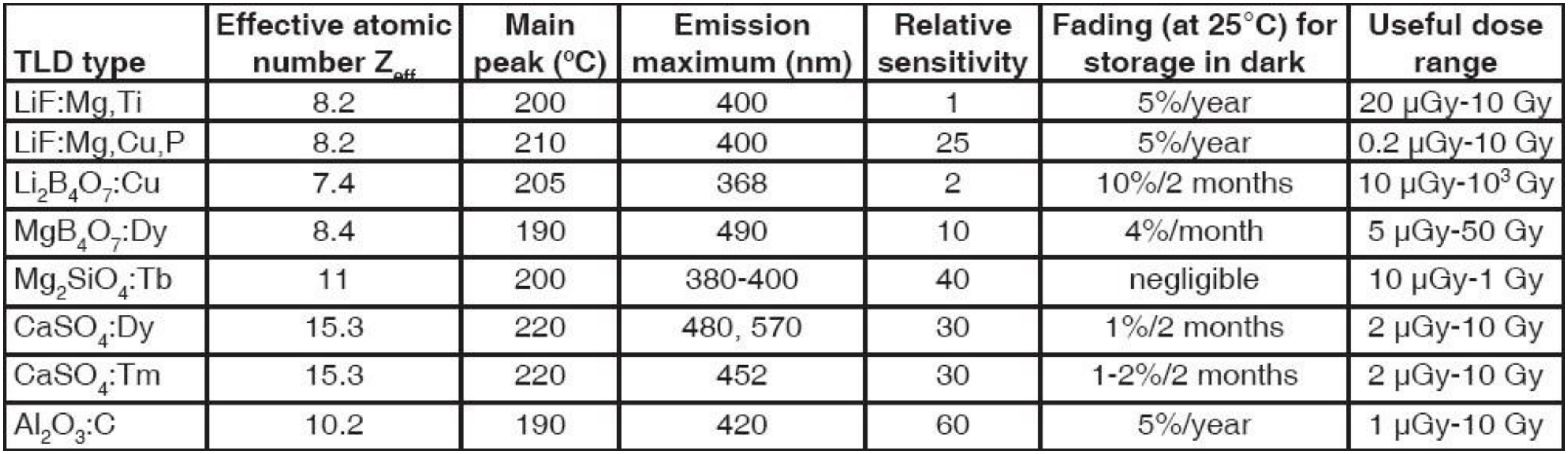
- *m* include between 3 and 4 gives a reasonable agreement with experiment → $m = 3.5$ is generally chosen (empirical choice!)
- $Z_{eff} = 7.35$ for tissues (in this model) → TLD with $Z_{eff} \approx 7.35$ → tissue-equivalent TLD

Examples of Z_{eff}



Material	Composition element: mass fraction in %	Z_{eff}
Polyethylene $(C_2H_4)_n$	H: 14.37, C: 85.63	5.53
Fat	H: 11.95, C: 63,72, N: 08; O: 23.23, Na: 0.05, P: 0.02, S: 0.07, Cl: 0.12, K: 0.03, Ca: 0.01	6.38
PMMA $(C_5H_8O_2)_n$	H: 8.05, C: 59.99, O: 31.96	6.56
BeO	Be: 36.0, O: 64.0	7.21
$Li_2B_4O_7$	Li: 8.21, B: 25.57, O: 66.22	7.32
Tissue		
ICRU-sphere	H: 10.1, C: 11.1, N: 2.6, O: 76.2	7.35
ICRU-striated	H: 10.20, C: 12.3, N: 3.5, O: 72.90; Na: 0.08, Mg: 0.02, P: 0.02, S: 0.5, K: 0.3	7.63
ICRP-skeletal	H: 10.06, C: 10.78, N: 2.77, O: 75.48, Na: 0.075, Mg: 0.019, P: 0.18, S: 0.24, Cl: 0.079, K: 0.3, Ca: 0.003, Fe: 0.004, Zn: 0.005	7.65
Water H_2O	H: 11.19, O: 88.81	7.51
Air	C: 0.0124, N: 75.53, O: 23.18, Ar: 1.28	7.77
LiF	Li: 26.75, F: 73.25	8.31
Al_2O_3	Al: 47.08, O: 52.93	11.28
SiO_2	O: 53.3, Si: 46.7	11.75
Compact bone	H: 4.72, C: 14.43, N: 4.2, O: 44.61, Mg: 0.22, P: 10.5, S: 0.32, Ca: 20.99, Zn: 0.01	13.59
$CaSO_4$	O: 47.0, S: 23.6, Ca: 29.4	15.62
CaF_2	Ca: 51.33, F: 48.67	16.90

Z_{eff} – fading – sensitivity – limits for ≠ TLD

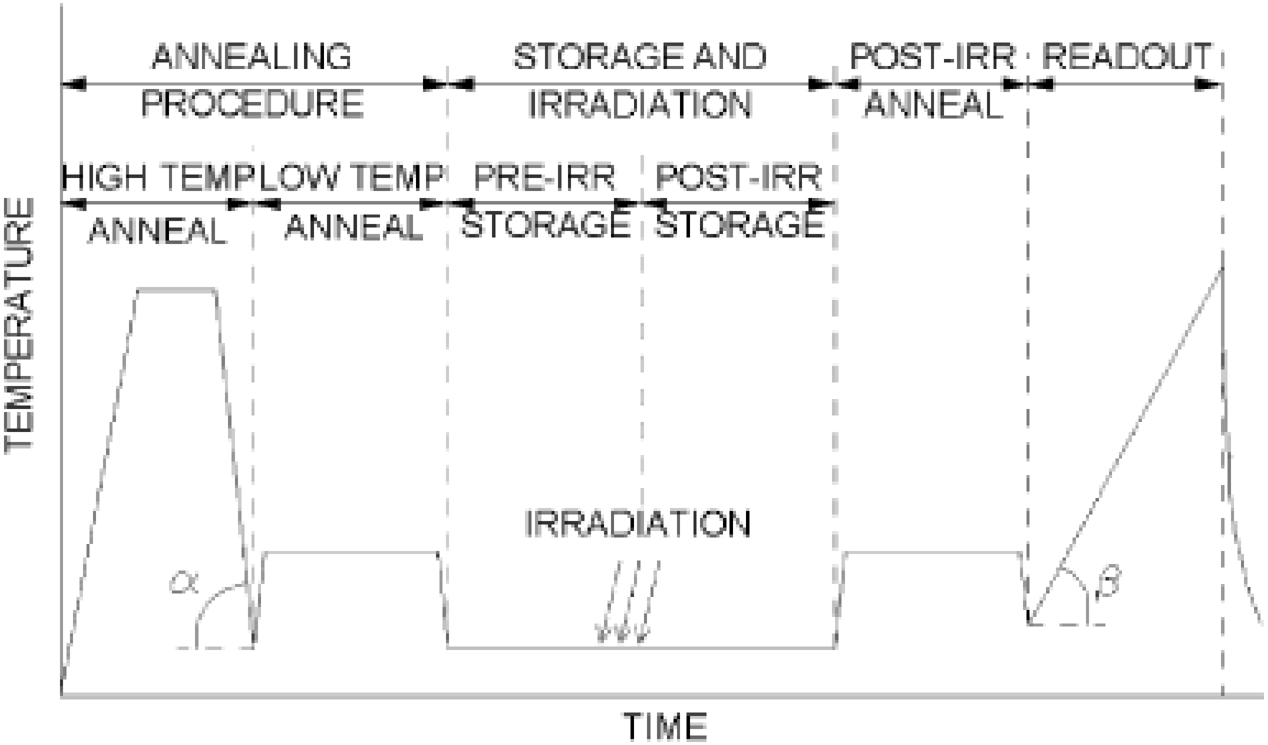


TLD type	Effective atomic number Z_{eff}	Main peak (°C)	Emission maximum (nm)	Relative sensitivity	Fading (at 25°C) for storage in dark	Useful dose range
LiF:Mg,Ti	8.2	200	400	1	5%/year	20 µGy-10 Gy
LiF:Mg,Cu,P	8.2	210	400	25	5%/year	0.2 µGy-10 Gy
$Li_2B_4O_7$:Cu	7.4	205	368	2	10%/2 months	10 µGy-10^3 Gy
MgB_4O_7:Dy	8.4	190	490	10	4%/month	5 µGy-50 Gy
Mg_2SiO_4:Tb	11	200	380-400	40	negligible	10 µGy-1 Gy
$CaSO_4$:Dy	15.3	220	480, 570	30	1%/2 months	2 µGy-10 Gy
$CaSO_4$:Tm	15.3	220	452	30	1-2%/2 months	2 µGy-10 Gy
Al_2O_3:C	10.2	190	420	60	5%/year	1 µGy-10 Gy

Annealing

- One of the interests of the TLD → reuse
- To have always the same properties → procedure of annealing → to maintain the TLD at a high T → to cool it to ambient T at a given velocity, α → following by annealing at low T
- Usefulness:
  1. To empty the traps non-completely emptied during reading
  2. To restore the thermodynamic equilibrium of the defects
  3. To empty deep traps (not used during reading) that can influence the sensitivity of the TLD
- Sometimes → annealing at low T after irradiation → elimination of low T GP with high fading

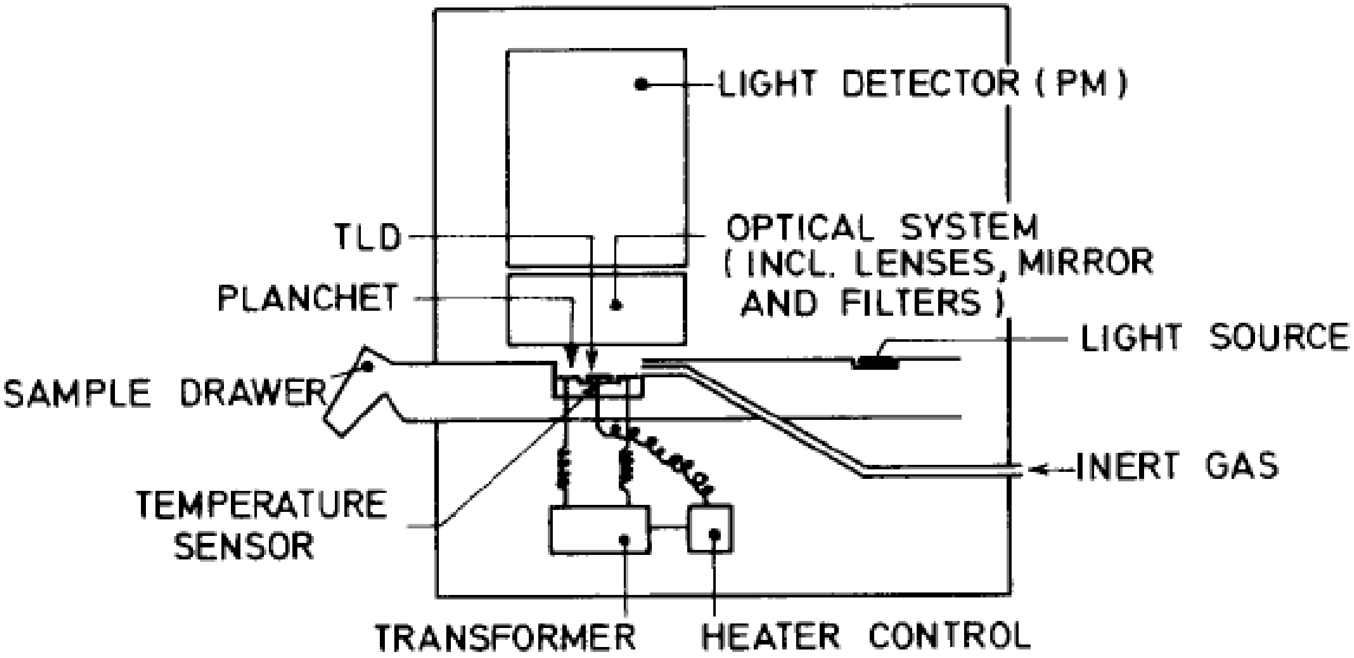
Procedure of annealing



TLD in practice

- TLD has to be placed into a support whish is carried by people that must be controlled
- After some predetermined time → analyze of the signal
- The TLD is heated → luminescence measured with a photomultiplier → classical amplification chain → voltmeter
- The chain is calibrated with a light intensity measurement from a luminescent source submitted to a known dose
- Afterward → annealing at high T° (to empty deep traps) → reusing (depends on the type of TLD)

Reading of the TLD



Examples of TLD

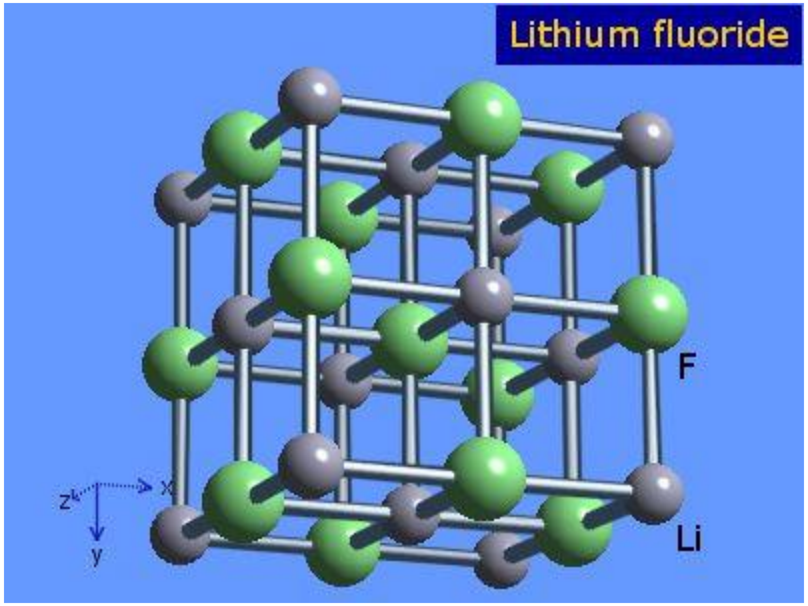
The 2 TLD used actually or having been used at ULB

- LiF: Mg,Ti (TLD-100)
- $CaSO_4$: Dy (TLD-900)

Reference:

S.W.S. McKeever, M. Moscovitch, P.D Townsend, *Thermoluminescence dosimetry materials: Properties and use* (Nuclear technology Publishing) 1995.

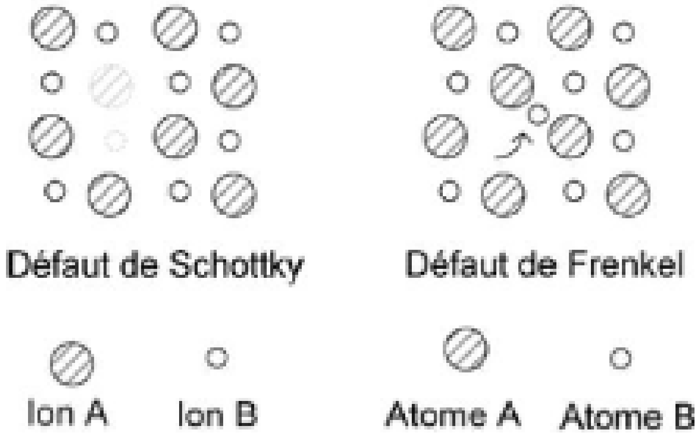
LiF: Mg,Ti: Structure of LiF



- LiF consists of 2 interpenetrating FCC lattices (one for Li^+ and another one for F^-)
- The thermodynamic defaults consist of Shottky and Frenkel defaults

LiF: thermodynamic defaults

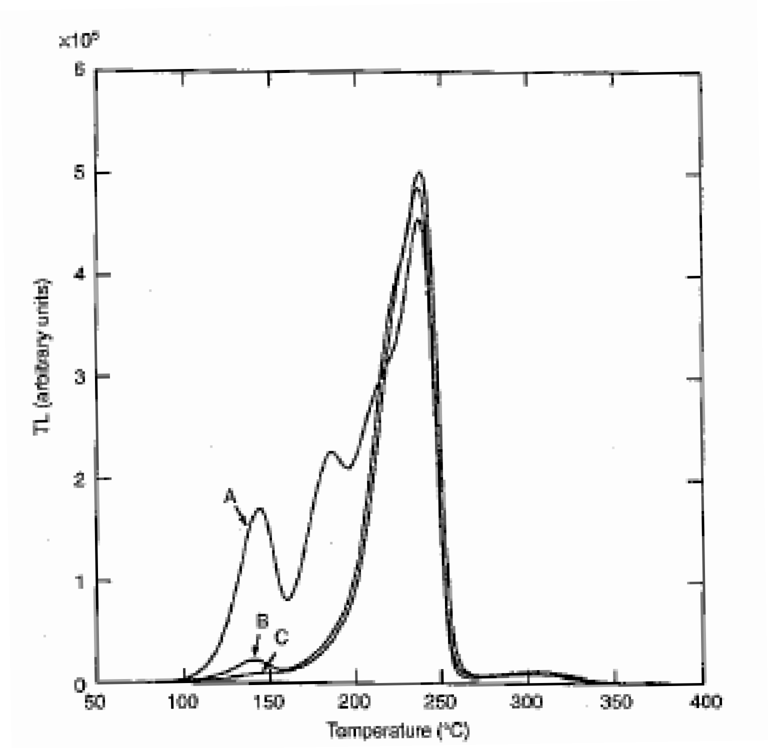
- Shottky default: pair of Li^+ and F^- vacancies
- Frenkel default: pair vacancy-interstice of Li^+ or F^-



Additional impurities: Mg

- Mg^{2+} replaces Li^{+} → charge neutrality is kept due to the presence of an excess of Li^{+} vacancies
- Coulomb interaction between the impurity and a vacancy → impurity-vacancy pair ($Mg\text{-}Li_{vac}$): dipole
- At ambient T → free energy of the crystal is minimum for the association of the dipoles into « cluster » → the most important: trimer (cluster of 3 dipoles) because it can be shown that the sensitivity of the TLD is maximum for Mg as trimer → the trimers are the traps
- Process: annealing at 400 °C during 1h → formation of dipoles → annealing at 80 °C during 24h → formation of trimers
- Attention: for $T < 250$ °C → precipitation as MgF_2 → decrease of the sensitivity at ambient T

GC as a function of annealing



A. Annealing at 400 °C (1h) following by fast return at ambient T

B. Annealing at 400 °C (1h) following by annealing at 80°C (24h)

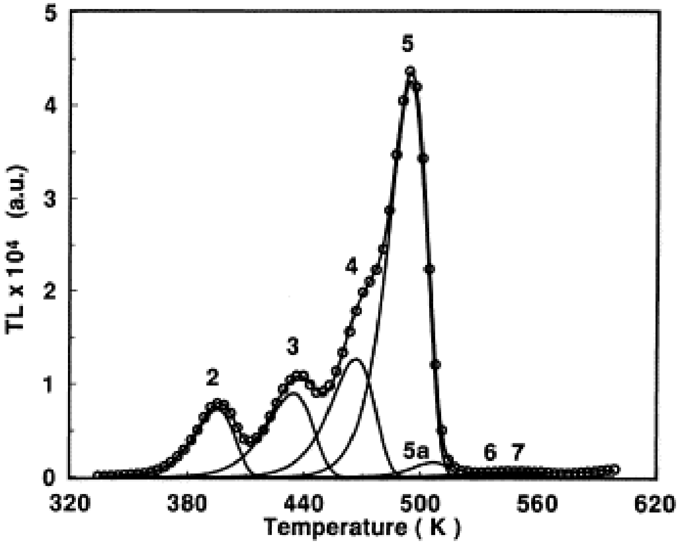
C. Annealing at 400 °C (1h) following by annealing at 100°C (2h)

Additional impurities: Ti

- Substitution of titanium for du Li^+ as Ti^{3+} or Ti^{4+}
- Different mechanisms to keep the charge neutrality → formation of $Ti^{4+}(O^{2-})_3$ and especially $Ti(OH)_n$ → responsible for the light emission at 3.01 eV (412 nm) → essential for the luminescence
- The $Ti(OH)_n$ are the luminescence centres
- Other mechanism → bonding with Mg and formation of $Mg(OH)_n$ → decrease of the TL emission → conflictual role between $Ti(OH)_n$ and $Mg(OH)_n$ → concentration of Mg and Ti is preponderant and must be scrupulously controled

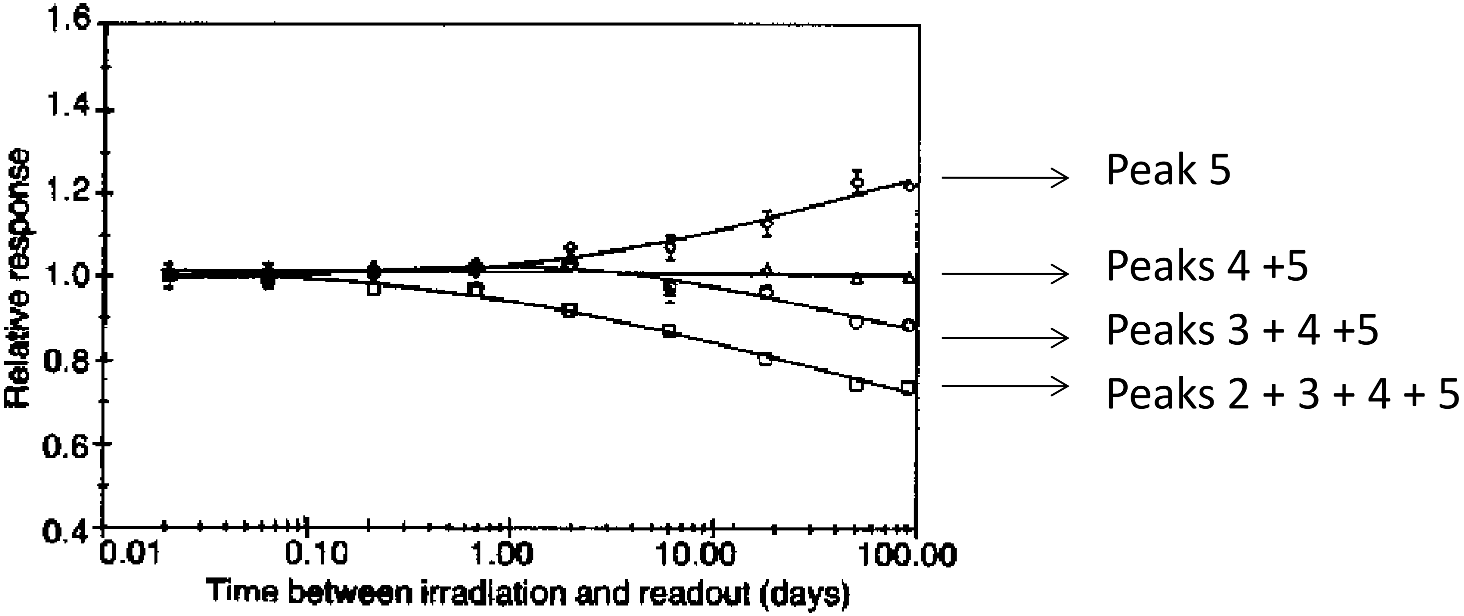
Global effect of the impurities: emission mechanisms

- The traps responsible of the main peak in dosimetry are the Mg-Li$_{vac}$ trimers
- The Mg of the default is spatially correlated with a Ti(OH)$_n$
- The Ti(OH)$_n$ is a luminescence centre → Peak 5
- The other combinations of defaults create supplementary peaks in the GC



Fading for LiF: Mg,Ti (1)

- The fading depends on a large number of parameters: storage T, process of annealing, type of radiation, integration range of the GC
- Peaks at « small » T (peaks 2, 3, 4) → more important fading → fading depends on the peaks considered in the GC integration



Fading for LiF: Mg,Ti (2)

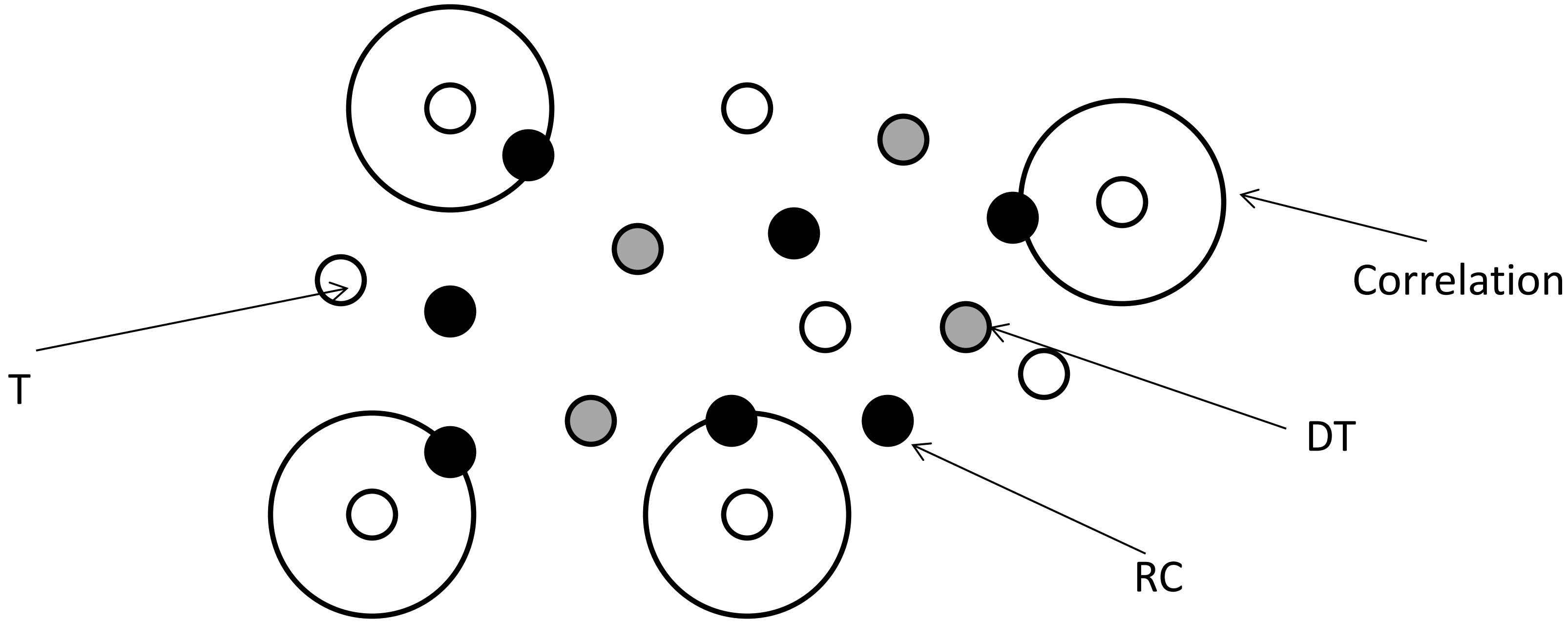
- Light sensitivity → 11% of luminescence loss is observed after 3h exposure to sun (9000 lux)
- It remains a small light sensitivity

Sensitivity of LiF: Mg,Ti

- LiF: Mg,Ti is considered as the standard of sensitivity
- Sensitivity depends on a large number of parameters → ≠ LiF: Mg,Ti will have ≠ sensitivities
- Some companies keep TLD in conditions perfectly controlled → considered as standards
- Deviations of ± 15% between various LiF: Mg,Ti commercially available

Response to the dose for LiF: Mg,Ti (1)

- D < 1 Gy → linear response for LiF: Mg,Ti
- 1 Gy < D < 1000 Gy → supralinear response
- D > 1000 Gy → sublinear response (saturation region)
- Spatial correlation between a Mg-Li$_{vac}$ trimer and a Ti(OH)$_n$ →



Response to the dose for LiF: Mg,Ti (2)

- When RC and T are correlated → no interaction with a DP → linear response
- When the dose is weak → important proportion of correlated RC and T → linear response
- When the dose ↗ → contribution of non-correlated RC and T ↗ (because non-linear ↗)
- For a given dose → non-linear contribution is dominating → supralinearity

Response to the dose for LiF: Mg,Ti (3)

- Useful to determine a correction factor for supralinearity (phenomenological expression)
- Experimentally it can be shown that in the supralinear region →

$$f(D) = aD + bD^2 \Rightarrow f(d) = A + BD$$

- With $K = F(D_1)/D_1$ (weak dose for which the response is linear) →

$$\frac{F(D)/D}{K} = A + BD$$

- Assuming $A = 1$ (in agreement with experimental results)→

$$D = \frac{F(D)}{K(1 + BD)}$$

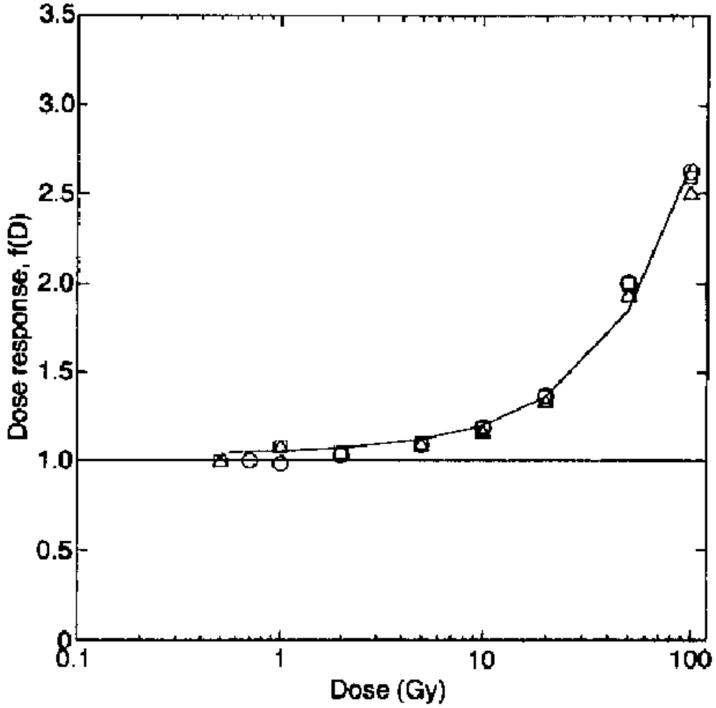
Response to the dose for LiF: Mg,Ti (4)

- Assuming $BD < 1$ (with $B \approx 0.015 \rightarrow D < 65$ Gy) →

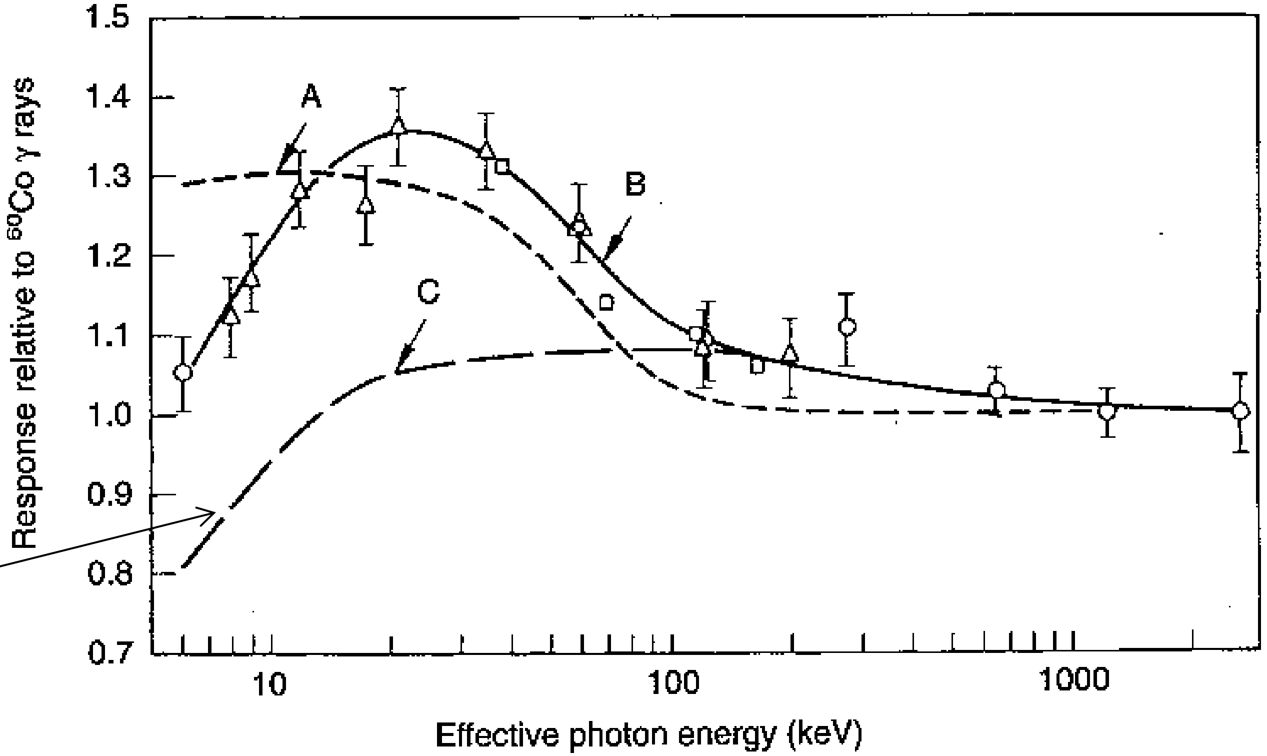
$$D = \frac{F(D)(1 - BD)}{K}$$

- Resolving for D with $D_0 = F(D)/K \rightarrow D = D_0(1+D_0B)^{-1}$

Response curve of LiF: Mg,Ti irradiated by ^{60}Co γ at ≠ depths in plastic equivalent water



Energy response of LiF: Mg,Ti

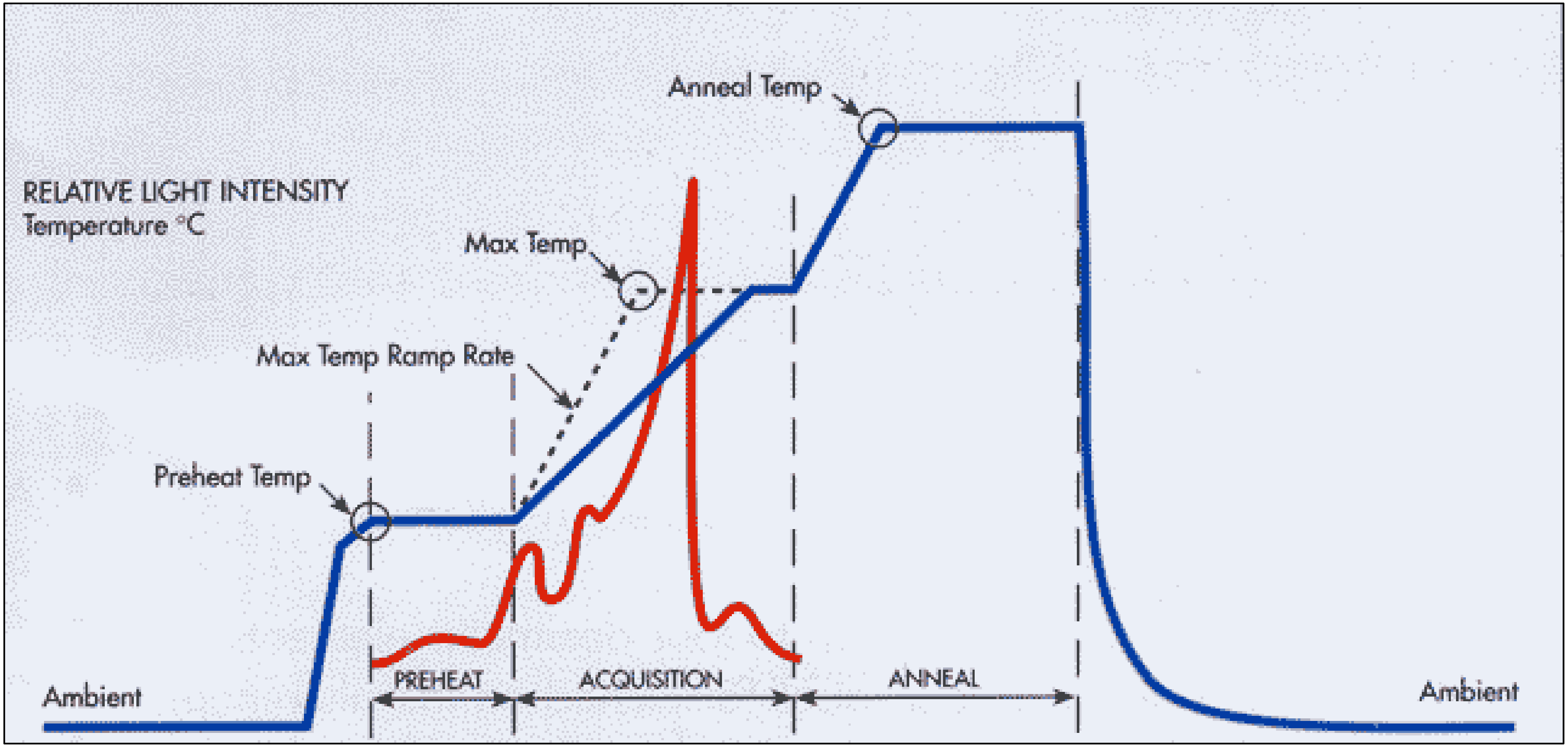


↘ of the efficiency of the TLD for a ↗ E linear transfer

A. Absorbed dose in the LiF by X unit calculated via the ratio of the E mass absorption coefficients of LiF and air
B. Response of LiF: Mg,Ti by X unit (experimental result)
C. Response of LiF: Mg,Ti by dose unit → B/A

Considering Z_{eff}(LiF) = 8.2 → tissue-equivalent

Reading procedure



Sensitivity to neutrons

- The LiF has besides the advantage to be made in natural condition of 92.6 % of Li^7 and of 6.4 % of Li^6 → Li^6 has a very large cross section for thermal neutrons (945 barns) → shows the presence of neutrons according to:

$$ {}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{3}_{1}H + {}^{4}_{2}He $$

- Li^7 has a negligible cross section for these neutrons →measure of everything that is not neutrons (electrons, photons)
- By simple difference → highlight the presence of neutrons

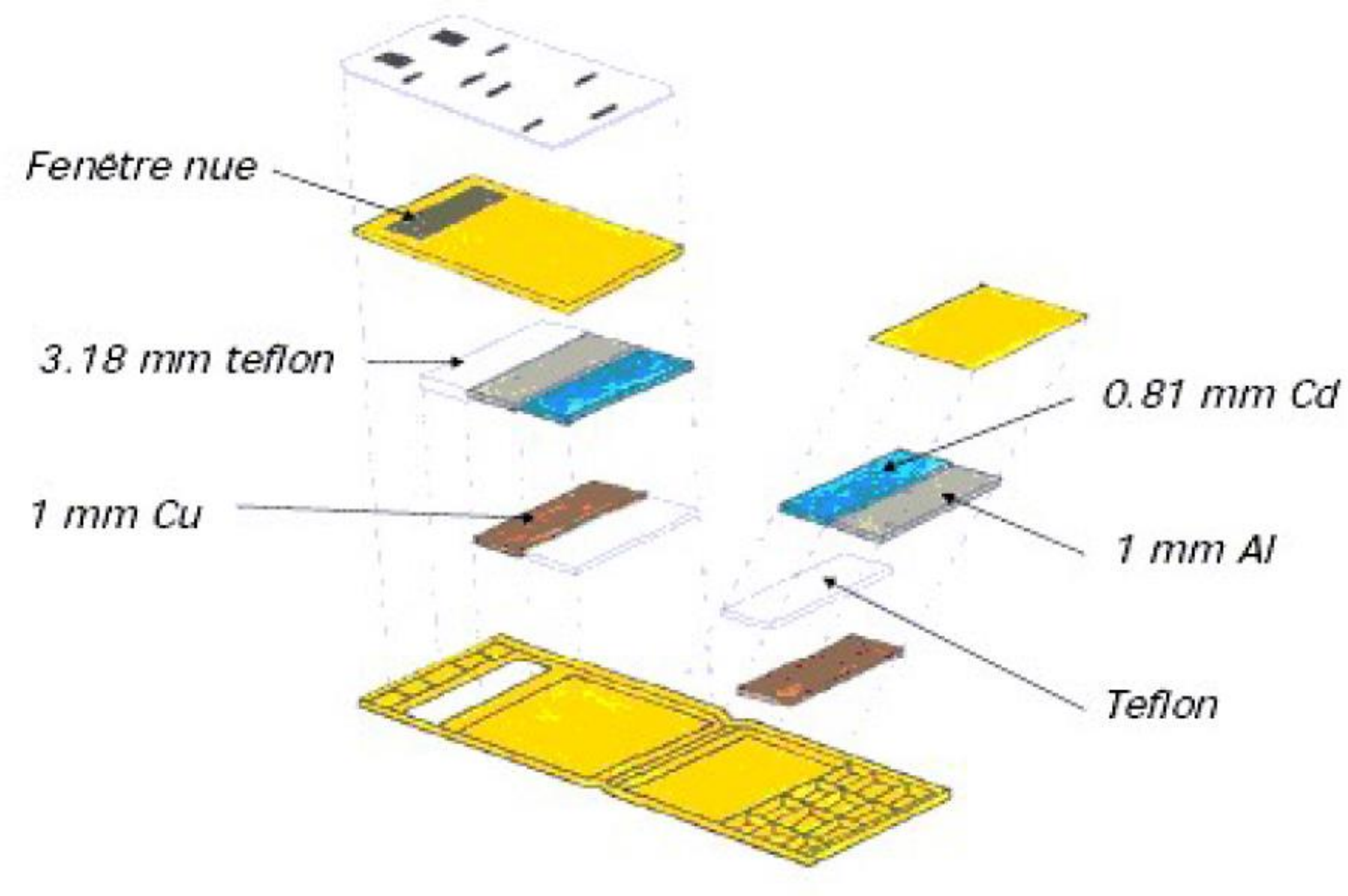
Summary for LiF: Mg,Ti

- Tissue-equivalent (Z_{eff}(LiF) = 8.2)
- Energy independent between $\sim$ 100 keV and 1.3 MeV for γ radiation
- The main luminescence is at ≈ 500 K for a maximum of the emission spectrum at 412 nm
- The response of the LiF as a function of the absorbed dose is linear up to a γ dose of at least 5 Gy
- Minimum boundary of dose ≈ 20 μGy
- Good stability at long term of information
- Optimum reusing

LiF: Mg,Ti dosimeter in practice (ULB - old) (1)

- The dosimeter is made as a sheet composed of a mixing Teflon-lithium fluoride
- The sensitive material is LiF: Mg,Ti with a concentration of 15% → the Teflon is the mechanical support for the LiF and a heat insulator between the different reading slots
- In addition to the reading slot, the dosimeter has a back-up slot (use in case of reading incident or for confirmation of a large dose)
- The body of the dosimeter is composed of four distinct slots having different filters allowing an analyze of the type of incident radiation as well as its intensity →
  - slot I : 2.4 mm Teflon (plastic) + 0.8 mm Cd
  - slot II : 1 mm Cu + 1 mm Al
  - slot III : 3.2 mm Teflon
  - slot IV : bare window

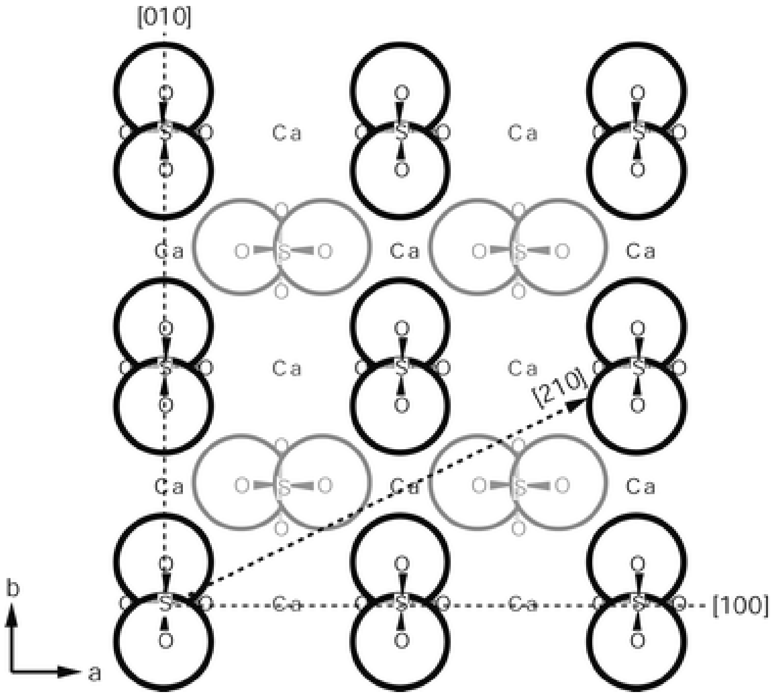
LiF: Mg,Ti dosimeter in practice (ULB - old) (2)



LiF: Mg,Ti dosimeter in practice: Interpretation of results

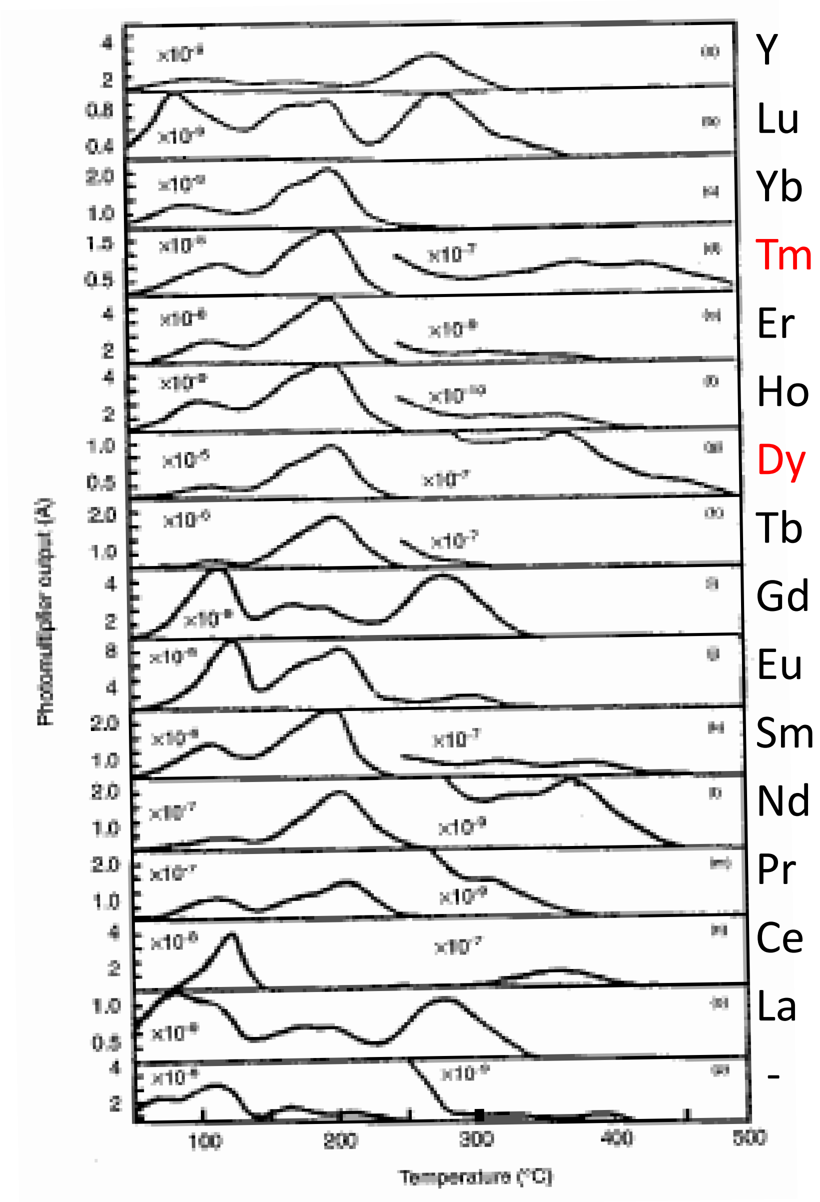
- Slot under Teflon/Cd filter→ neutrons dosimetry
- The Cu/Al filter allows a discrimination between γ rays and X rays generally used in medicine (20 keV < E < 60 keV) → the absorbed dose under this filter is due to large E γ (as a first approximation)
- Teflon filter → this window is used to discriminate the β rays and to settle an electronic equilibrium sufficient for γ with larger E
- The deep dose is the combining result of these 2 slots: Cu/Al and Teflon
- The bare window has practically a response curve identical to the one of the plastic window for γ with E > 20 keV → this window allows the detection of γ with E < 10 keV and of β rays (fragile window)

$CaSO_4$:Dy: Structure of $CaSO_4$



- Orthorhombic structure largely more complicated than LiF
- *(…) efforts have been focused on making an efficient material, and this has been achieved. Understanding the mechanisms has been of secondary importance. Indeed for a material of such great complexity (…), it is well beyond the scope of current condensed matter scientists.*

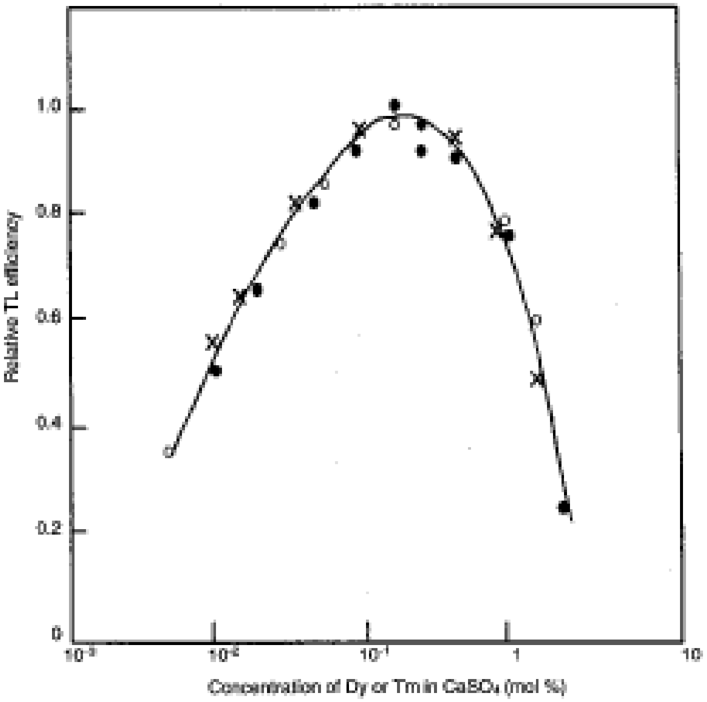
Additional impurities: primary impurities



- Rare earths are chosen as primary impurities, give a good sensitivity, limit the peaks at small T° and induce a good stability at about 200 °C
- Dysprosium (Dy) and Thulium (Tm) give the best sensitivity

Sensitivity as a function of the amount of Dy

- Each Dy (or Tm) site requires an independent volume of the crystal → if these volumes are superimposed (large concentration of impurities) → sensitivity ↘
- There is an optimum concentration of impurities



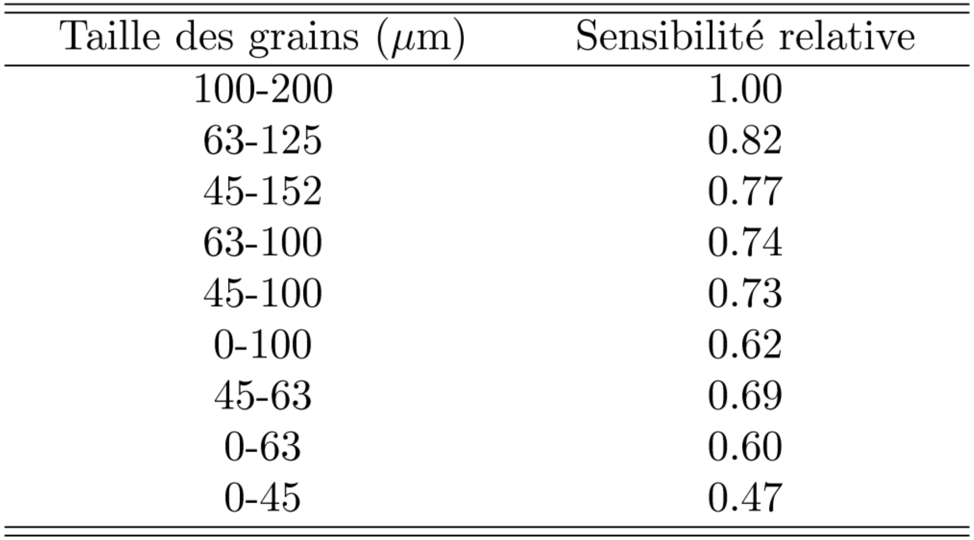
Additional impurities: secondary impurities

- Dy^{3+} replaces a Ca^{2+}ion → compensation is required to conserve the charge → ≠ mechanisms have been considered:
  1. Dy^{3+} is compensated by a secondary impurity deliberately added to the TLD (hydrogen or alkaline) → good results have been obtained with Na^{+}
  2. A Dy^{3+} pair is associated to a Ca^{2+} vacancy
  3. Replacement of oxygen by nitrogen as secondary impurity

- Practically → it « seems » that there is a combination of the 3 mechanisms

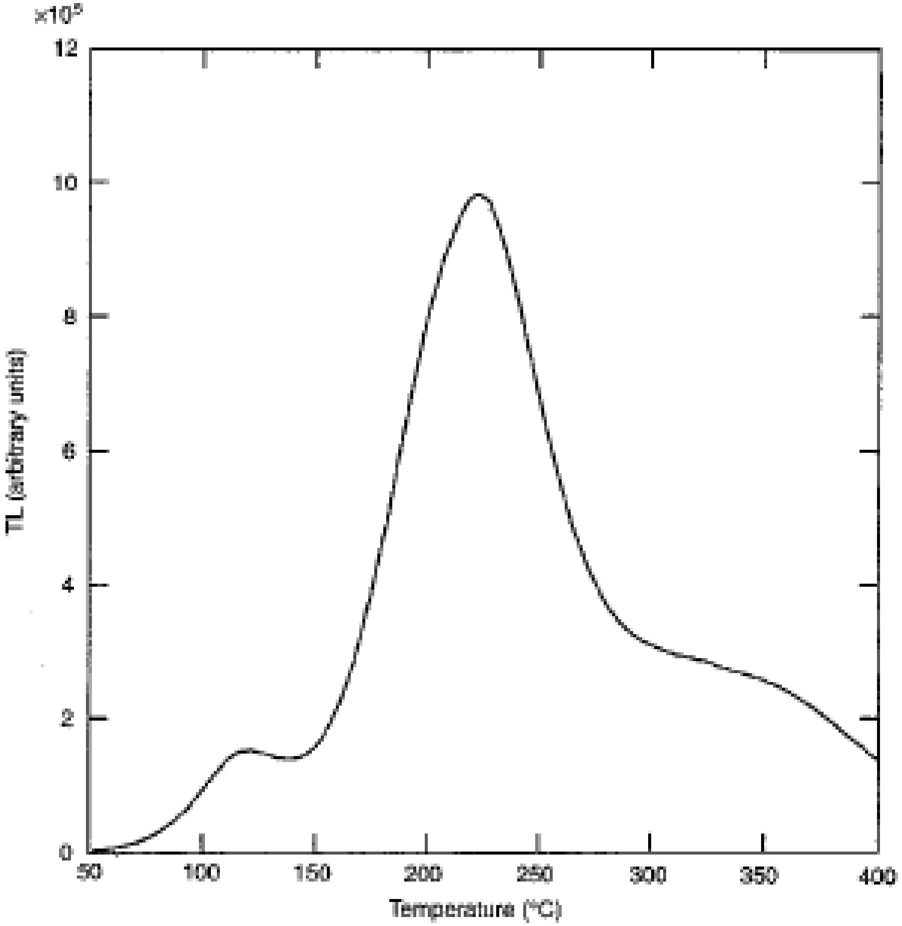
Size of the $CaSO_4$ grains

- $CaSO_4$ is generally obtained as polycrystal with grain size depending of the manufacturing process
- If the grain size ↗ → the sensitivity ↗ ↔ the larger grains have a larger impurities %
- Attention → if the grain size ↗ too much → becomes fragile



Taille des grains (μm)	Sensibilité relative
100-200	1.00
63-125	0.82
45-152	0.77
63-100	0.74
45-100	0.73
0-100	0.62
45-63	0.69
0-63	0.60
0-45	0.47

Example of GC for $CaSO_4$: Dy



- Main Peak at 220 °C
- Large dependence on the annealing conditions and of the secondary impurities (here a small amount of Na)

Emission mechanisms (1)

1. A possibility is that, under irradiation →

$$Dy^{3+} \rightarrow Dy^{2+} + h^{+}$$

   then the recombination of Dy^{2+} with h^{+} produces light

2. Another possibility: considering a « larger » site →

$$(Dy^{3+} + SO_4^{2-}) \rightarrow (Dy^{3+} + SO_4^{-}) + e^{-}$$

   Recombination → light

3. Or also →

$$(Dy^{3+} + O_2^{2-}) \rightarrow (Dy^{3+} + O_2^{3-}) + h^{+}$$

Emission mechanisms (2)

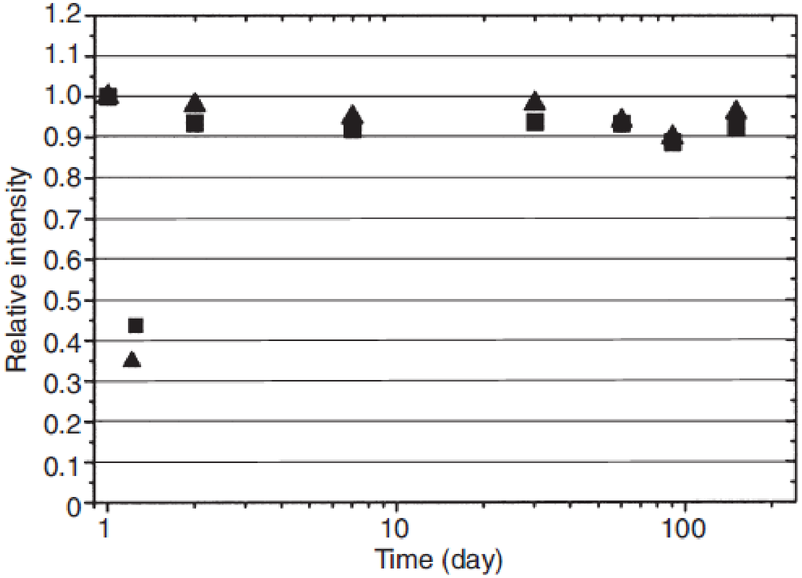
4. We cannot ignore the possibility of a combination of the 2 previous mechanisms

- Anyway the recombination mechanisms are not known

- Roles of the secondary impurities?

Fading for $CaSO_4$: Dy

- The fading of $CaSO_4$: Dy is of about 5% for a 6 months period at ambient T° → 2 × larger than for LiF: Mg,Ti (but it is always very good)
- If small T° peaks are taken into account (80 and 120 C°) → fading of 15% during the 5 first days at ambient T° and then of 5% during 6 months



- Attention: very sensitive to light → luminescence loss of 50% after 3h of sun exposition (9000 lux)

Sensitivity of $CaSO_4$: Dy

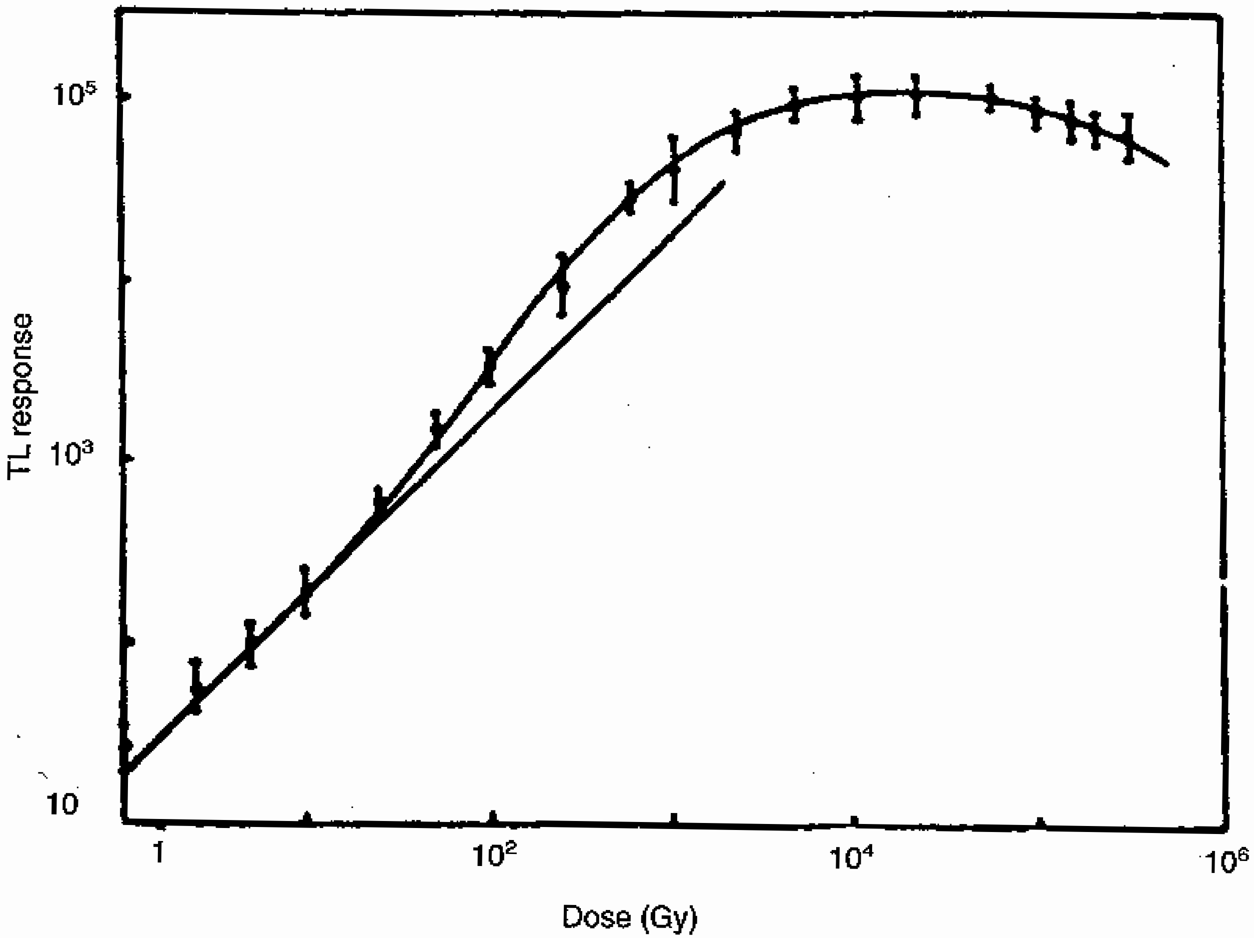
- Sensitivity of $CaSO_4$: Dy → 30 to 50 × larger than the sensitivity of LiF: Mg,Ti
- The property associated to a weak fading → particularly adapted for the measurement of weak doses (environmental applications)
- Attention: large variation of the sensitivity as a function of the manufacturing process

Dose response of $CaSO_4$: Dy (1)

- D < 10 Gy → linear response
- 10 Gy < D < 5 10^3 Gy → supralinear response
- 5 10^3 Gy < D < 10^5 Gy → sublinear response (saturation)
- D > 10^5 Gy → decrease of the luminescence (damages due to irradiation)

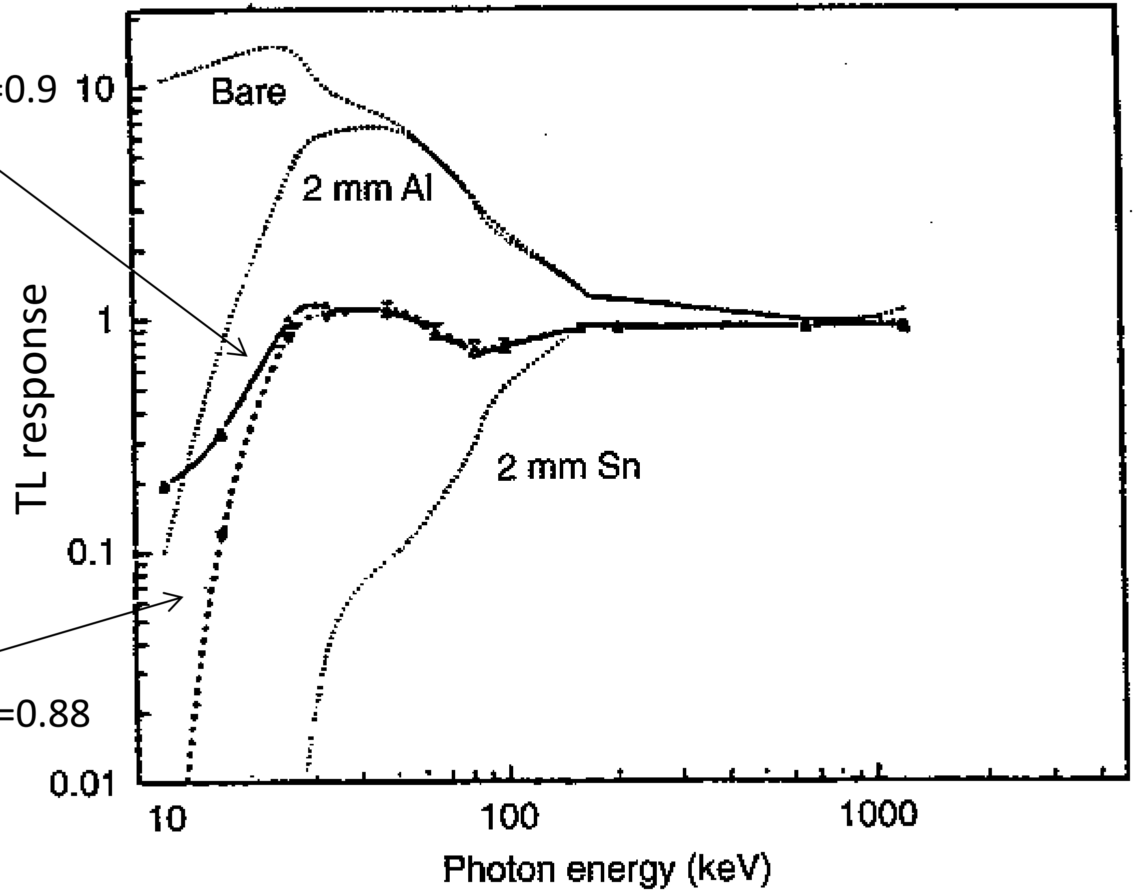
- Addition of secondary dopant → $CaSO_4$: Dy,Cu → linearity extended up to 100 Gy
- The degree of supralinearity strongly depends on the size of the $CaSO_4$ grains
- Unrealistic to theoretically demonstrate these properties

Dose response of $CaSO_4$: Dy (2)



Energy response of $CaSO_4$: Dy (1)

- $CaSO_4$: Dy is characterized by a significant overestimation for energies < 200 keV



k_1=0.1, k_2=0.0, k_3=0.9

k_1=0.00, k_2=0.12, k_3=0.88

Energy response of $CaSO_4$: Dy (2)

- $Z_{eff}(CaSO_4) = 15.3$ → **not tissue-equivalent at all** → major disadvantage of $CaSO_4$: Dy
- Solution → put filters (Al and Sn in previous example)
  - Sn improves the response between 100 keV and 200 keV but implies a loss of sensitivity for $E < 100$ keV
  - Al gives a good result for $E \approx 20$ keV
- The best result is obtained by considering a linear combination R of the 3 responses (bare, Sn, Al) →

$$R = k_1 R_{\text{sans}} + k_2 R_{Sn} + k_3 R_{Al}$$

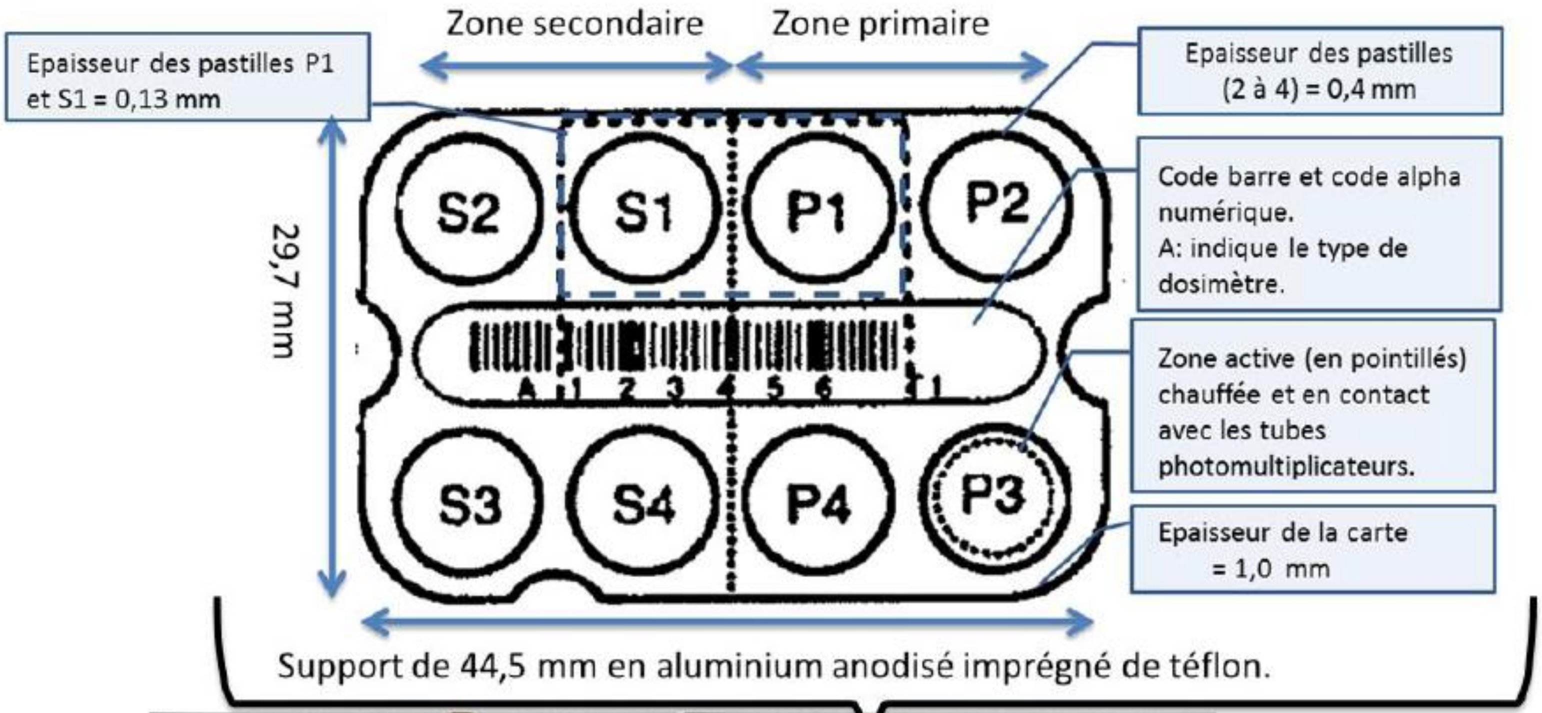
Summary for $CaSO_4$: Dy

- **Not tissue-equivalent**
- Very dependent on the energy for $E < 200$ keV (γ rays) → necessary to use filters
- The main luminescence is at ≈ 220 °C for 2 emission peaks at 478 nm and 571 nm
- The response of $CaSO_4$: Dy as a function of the absorbed dose is linear to a γ dose of 10 Gy (100 Gy if addition of Cu)
- Minimum dose boundary ≈ 2 μGy
- Good long term stability of the information
- Optimum reusing

$CaSO_4$: Dy dosimeter in practice (ULB) (1)

- The dosimeters are made as $CaSO_4$:Dy/PTFE
- PTFE (i.e. polytetrafluoroethylene or Teflon) is added to $CaSO_4$ in order to make the chips more flexible and less brittle
- The dosimeters are symmetric and are composed of 8 reading slots (4 « useful » slots and 4 back-up slots)
- The box in polyethylene is composed of 2 areas → in these 2 areas there are ≠ filters →
  - Polyethylene filter (7 mg/cm^2)
  - Al filter (2.5 mm)
  - PTFE filter (3.18 mm)
  - Filter of Al (0.13 mm) – Cu (0.50 mm) – Pb/Sn (0.75 mm) with holes

CaSO$_4$: Dy dosimeter in practice (ULB) (2)



Zone secondaire

Zone primaire

Epaisseur des pastilles P1 et S1 = 0,13 mm

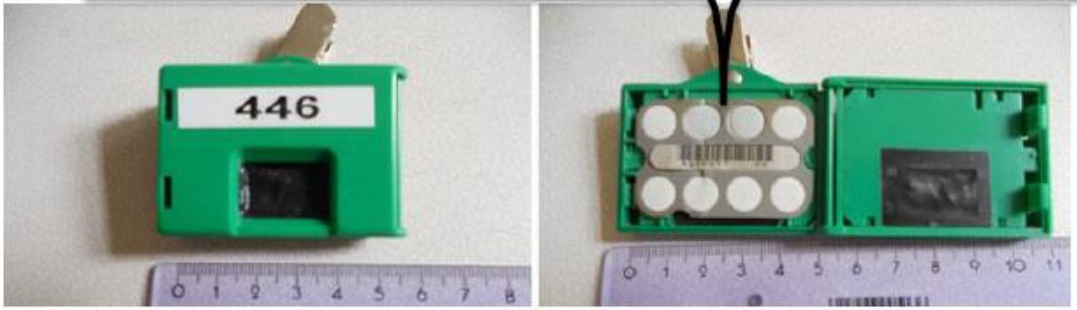
Epaisseur des pastilles (2 à 4) = 0,4 mm

Code barre et code alpha numérique.
A: indique le type de dosimètre.

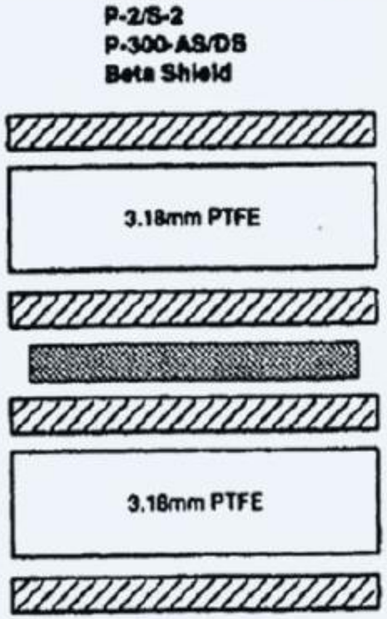
Zone active (en pointillés) chauffée et en contact avec les tubes photomultiplicateurs.

Epaisseur de la carte = 1,0 mm

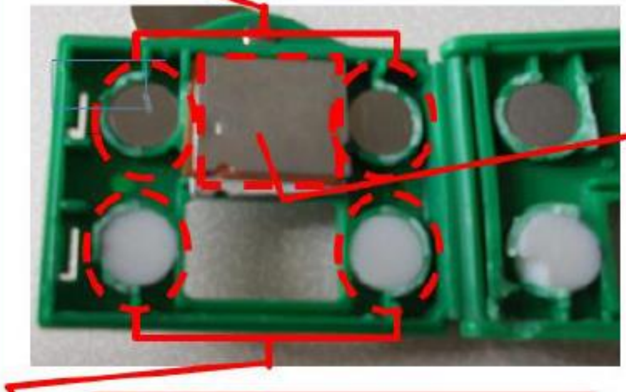
Support de 44,5 mm en aluminium anodisé imprégné de téflon.

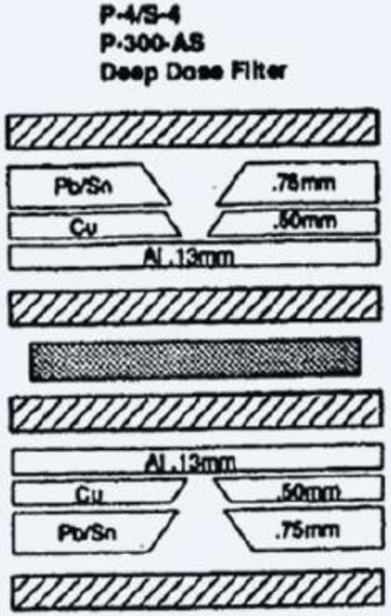


$CaSO_4$: Dy dosimeter in practice (ULB) (3)

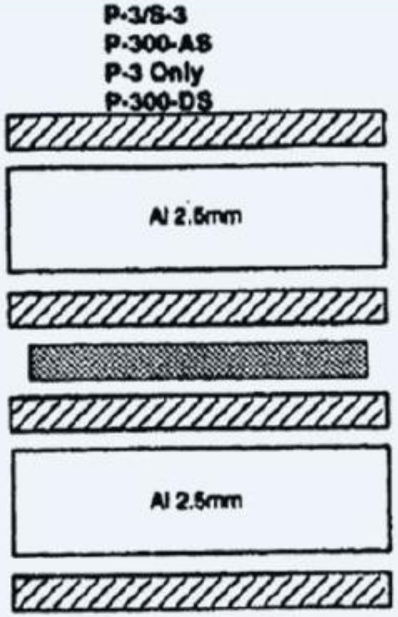


Filtre n°2





Filtre n°4



Filtre n°3

$CaSO_4$: Dy dosimeter in practice: Interpretation of the results

- Slot under polyethylene → this window allows the detection of small *E* γ and of β rays → the *E* response for this slot implies an overestimation of a factor 20 for small *E* (X-ray) → overestimation compensated by the other slots with a calculation algorithm
- Slot under Teflon → allows to approximately determine the energy to which the dosimeter was exposed and to correct the measurement of the previous slot via a algorithm
- Slot under Al → stopping of β with $E < 2.2$ MeV → γ measurement
- Slot with mixing filter → allows to measure the γ dose in depth (the holes hallows the crossing of a part of the γ)