Quantum tunneling in scintillating materials

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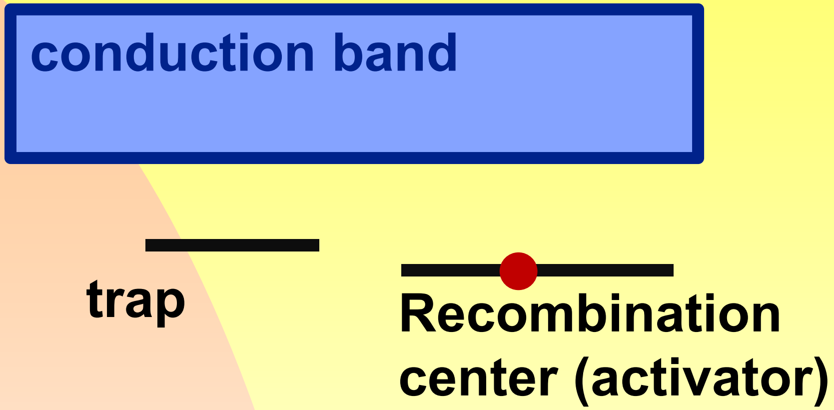
Goal:
Improvement of scintillator performance

understanding the physical processes involved in the scintillation mechanism

losses of fast scintillation light due to the presence of traps in the host materials



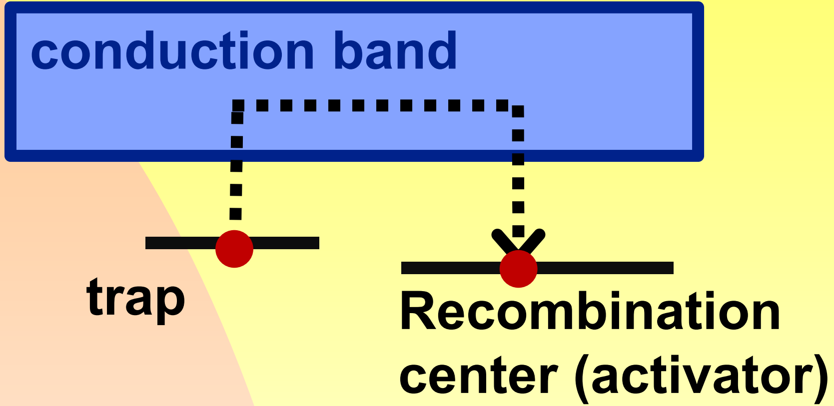
conduction band

trap

Recombination center (activator)

Escape from the trap

1. thermal escape via conduction band



conduction band

trap

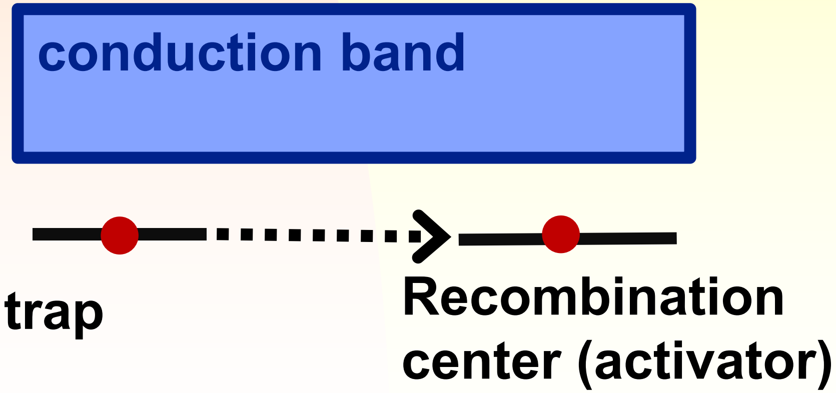
Recombination center (activator)

Shallow electron traps
Conduction band **is** involved

Similar scheme can apply for holes and the valence band

2. tunneling between traps and recombination centers

quantum

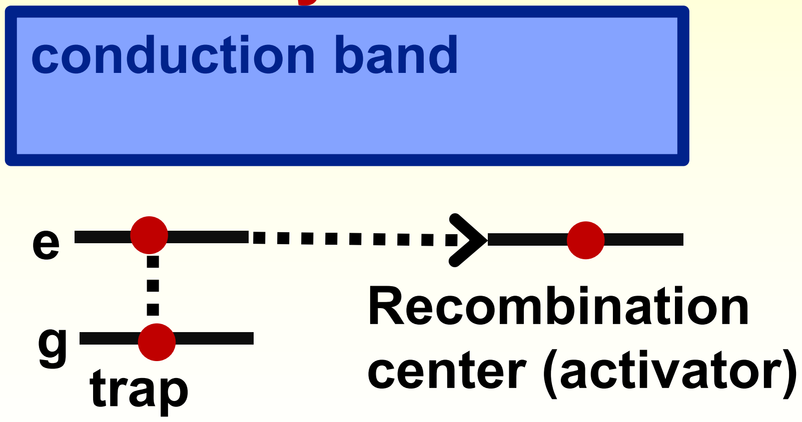


conduction band

trap

Recombination center (activator)

thermally assisted



conduction band

e

g

trap

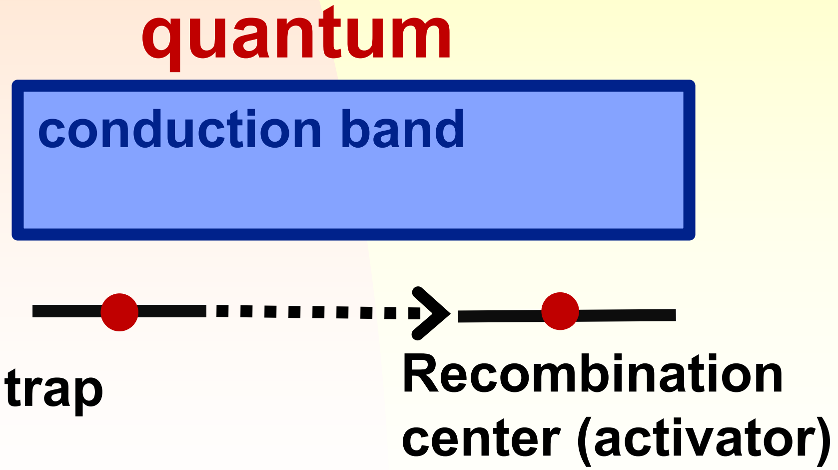
Recombination center (activator)

Shallow or deep electron traps
Conduction band **is not** involved

Delayed delivery to the recombination center → **Slow light**

Escape from the trap

2. tunneling between traps and recombination centers



quantum

conduction band

trap

Recombination center (activator)

Shallow or deep electron traps
Conduction band **is not** involved

How to detect the presence of quantum tunneling

Experimental tools

- **monitoring the tail of the afterglow decay after X-ray irradiation**
- **scintillation decay measured over extended time scale**
- **thermally stimulated luminescence – glow peak analysis by the initial rise technique**
- **delayed recombination decay measurement**

Tail of the afterglow decay

Quantum tunneling considered in the description of luminescence decay from early 1970s

C. J. Delbecq, Y. Toyozawa and P. H. Yuster, Phys. Rev. B **9**, 4497 (1974)

Anomalous fading of luminescence observed in materials used in TSL and OSL dating ⇒ associated with quantum tunneling

From 1990s on

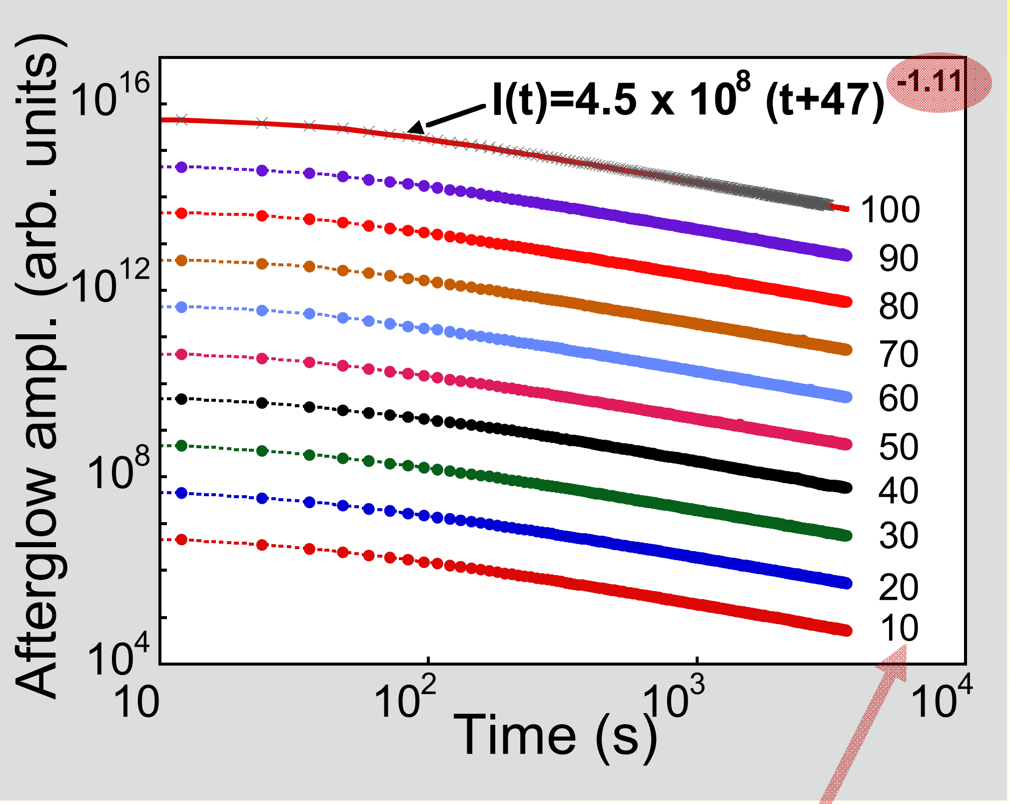
Theoretical models of luminescence decay based on quantum tunneling between traps and **randomly distributed** recombination centers

$\boxed{I(t) \sim 1/t^{p}}$ $p \sim 1$

M. Tachyia and A. Mozumder, Chem. Phys. Lett. **28**, 87 (1974)
M. Tachyia and A. Mozumder, Chem. Phys. Lett. **34**, 77 (1975)
P. Avouris and T. N. Morgan, J. Chem. Phys. **74**, 4347 (1981)
D. J. Huntley, J. Phys.: Condens. Matter **18**, 1359 (2006)

Tail of the afterglow decay

LuAG:Ce^{3+}



M. Nikl et al., Phys. Rev. B **76,** 195121 (2007)

Temperature in K

Decays are vertically shifted

Afterglow decay after X-ray irradiation at constant T

Fit formula:

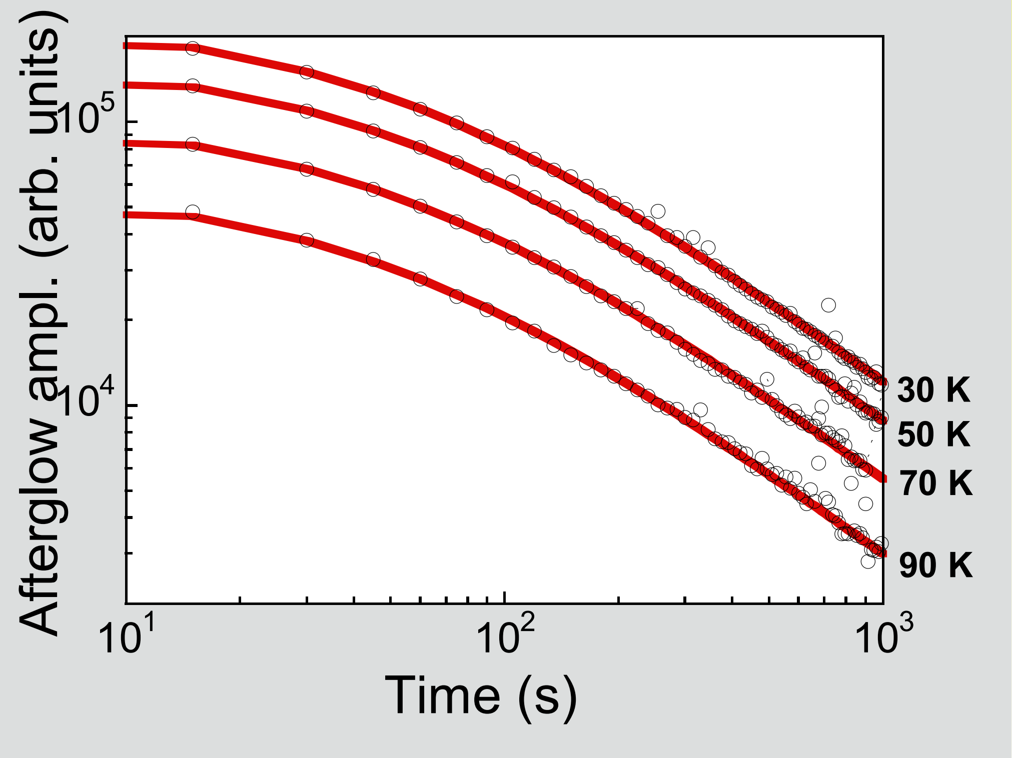
$$I(t) = A \times (t + t_0)^{-p}$$

A, t_0 are constants
Exponent $p \sim$ **1**

Afterglow tail is due to quantum tunneling of **electrons** between the traps and Ce^{3+} recombination centers – confirmed up to 100 K

Tail of the afterglow decay

$Lu_4Hf_3O_{12}$



E. Mihóková et al., Opt. Mater. **34,** 228 (2011)

Afterglow decay after X-ray irradiation at constant T

Decays for different T are vertically shifted

Fit formula:

$$\boxed{I(t) = A/(t + t_0)}$$

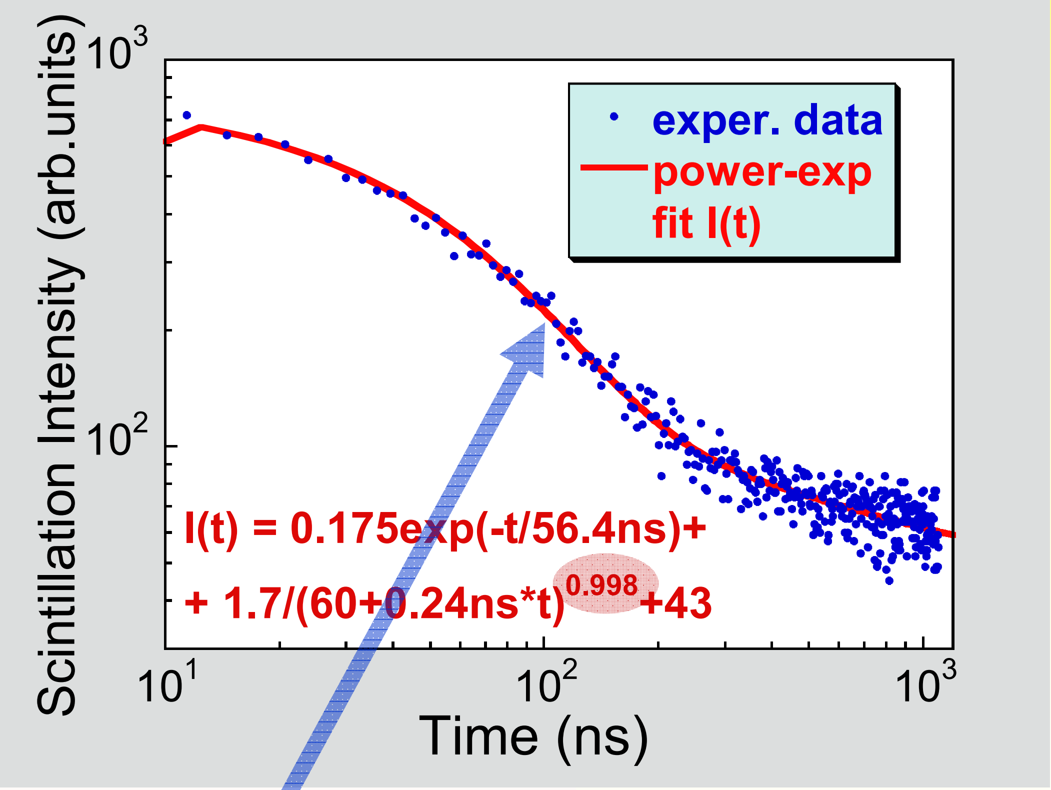
A, t_0 are constants

Afterglow tail is due to quantum tunneling of **holes** between the traps and recombination centers

Scintillation decay

measured over extended time scale

LuAG:Ce^{3+}



M. Nikl et al., Phys. Rev. B **76,** 195121 (2007)

Scintillation decay at RT

Fit formula:

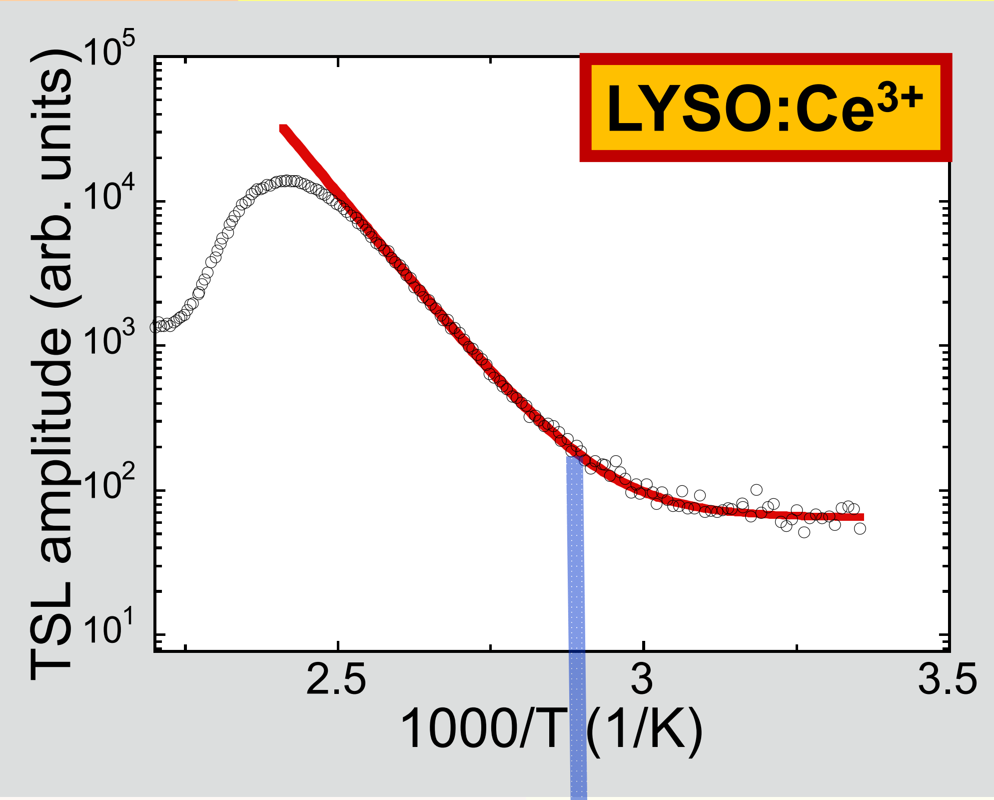
$$\boldsymbol{I(t) = B \times \exp(-t/\tau) + A/(t+t_0)^p + C}$$

A, B, t_0 are constants,
C is a background
Exponent $p \sim 1$

Linear part in log-log plot is due to quantum tunneling between the traps and recombination centers

TSL glow peak analysis

by the initial rise technique



Arrhenius plot after partial cleaning at 140 °C

frequency factor ***s***

$$\beta E/k\,T_{\mathrm{m}}^{2} = s \times \mathrm{e}^{-E/kT_{\mathrm{m}}}\ ,$$

T_{m} - TSL peak maximum

β - heating rate

Detrapping time τ

$$\tau = s \times \mathrm{e}^{E/kT_{\mathrm{m}}}\ ,$$

Fit function:

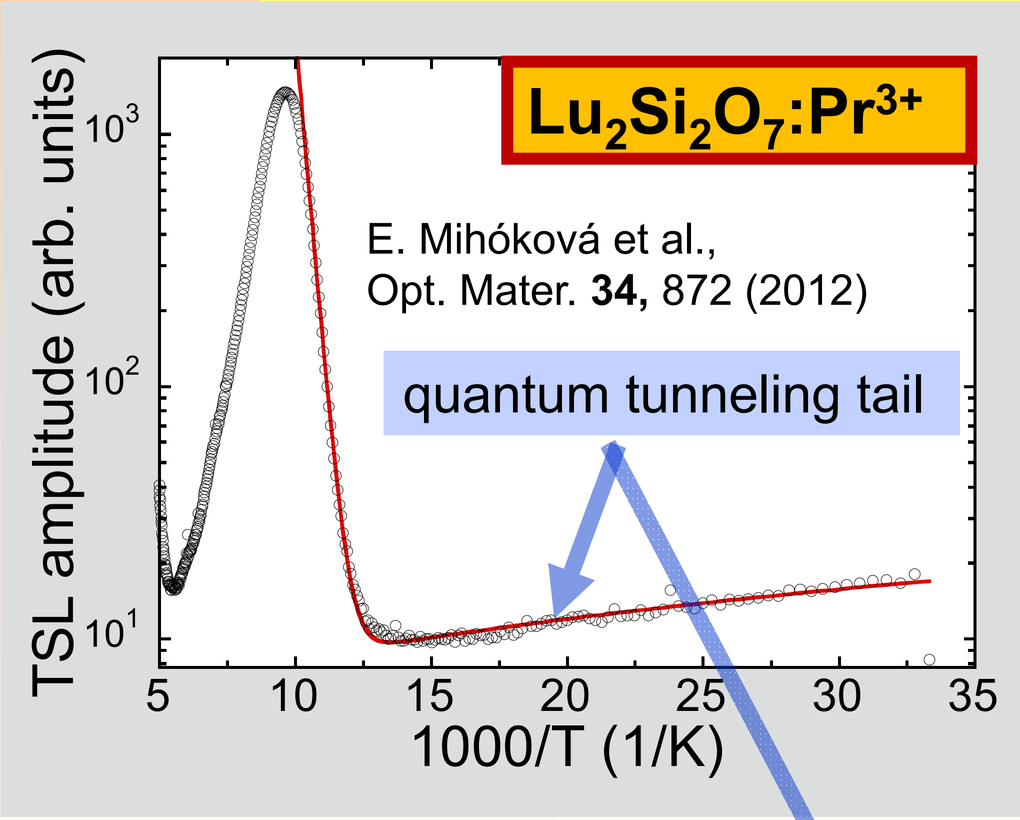
$$Amp\,(T) = b + w \times \mathrm{e}^{-E/kT}$$

trap depth ***E***

b -background, ***w*** -preexp. factor, ***k***- Boltzmann constant, ***A***- constant

TSL glow peak analysis

by the initial rise technique



$Lu_2Si_2O_7:Pr^{3+}$

E. Mihóková et al.,
Opt. Mater. **34,** 872 (2012)

quantum tunneling tail

Arrhenius plot after partial cleaning at 90 K

quantum tunneling tail ~ 1/*t*

linear heating *T* ~ *t*

quantum tunneling tail ~ 1/*T*

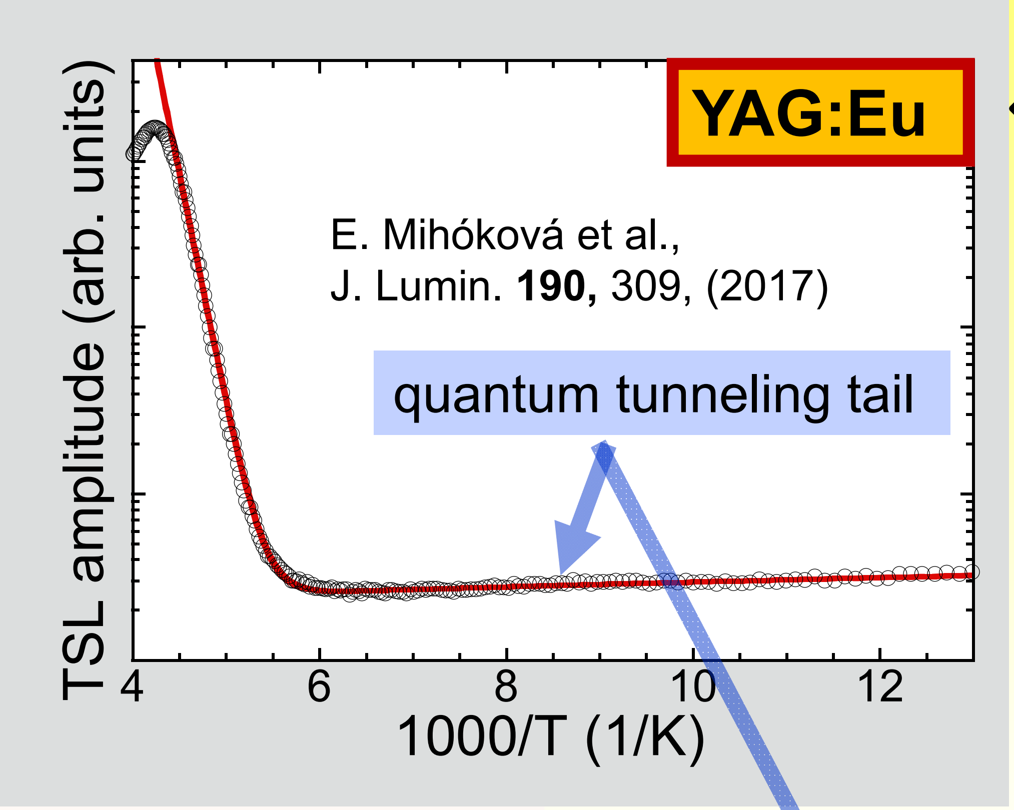
Fit function:

$$\boxed{Amp\,(T) = b + w \times \mathrm{e}^{-E/kT} + \frac{A}{T}}$$

trap depth ***E***

b -background, ***w*** -preexp. factor, ***k***- Boltzmann constant, ***A***- constant

TSL glow peak analysis
by the initial rise technique



YAG:Eu

E. Mihóková et al.,
J. Lumin. **190,** 309, (2017)

quantum tunneling tail

Arrhenius plot after partial cleaning at 219 K

quantum tunneling tail ~ 1/*t*

linear heating *T* ~ *t*

quantum tunneling tail ~ 1/*T*

Fit function:

$$Amp\,(T) = b + w \times \mathrm{e}^{-E/kT} + \frac{A}{T}$$

trap depth ***E***

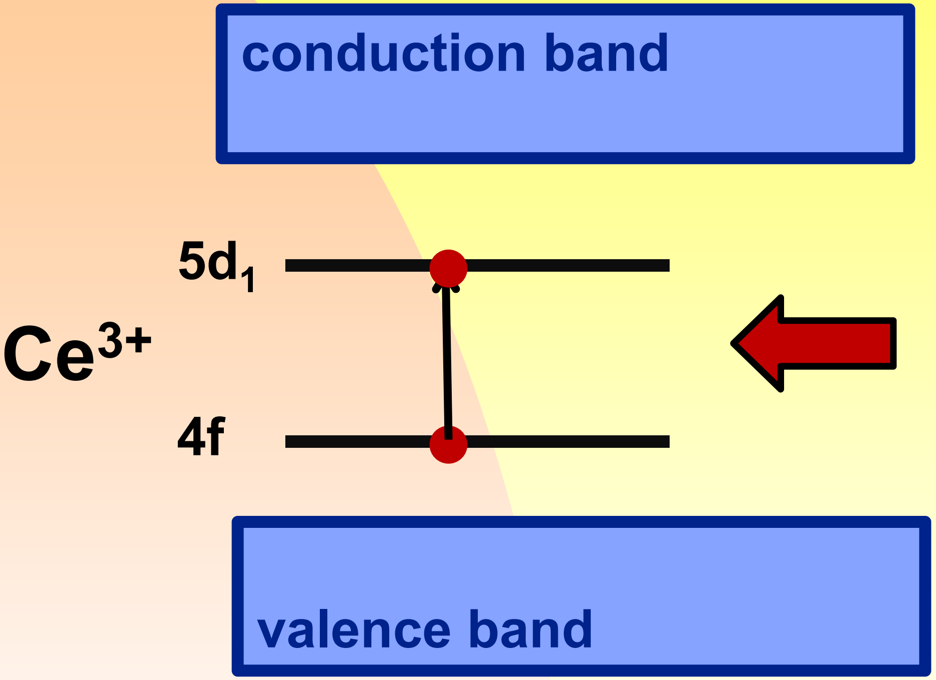
b -background, ***w*** -preexp. factor, ***k***- Boltzmann constant, ***A***- constant

Delayed recombination decay

Originally developed as a **contactless purely optical technique** to study the process of thermal ionization of the activator's excited state

Delayed recombination decay

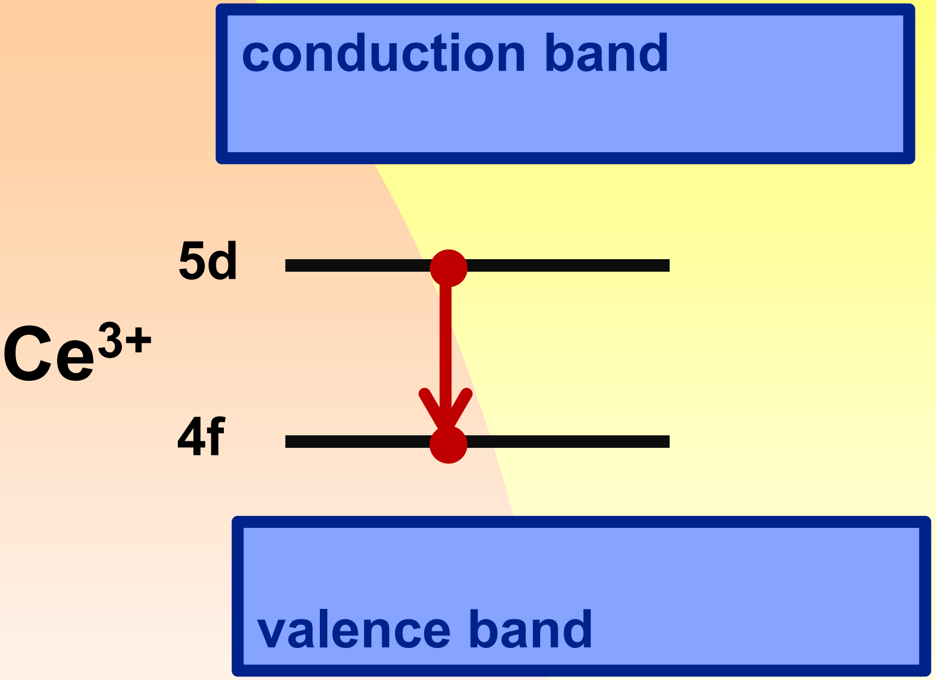
Principle



Selective excitation of the activator by UV light

Delayed recombination decay

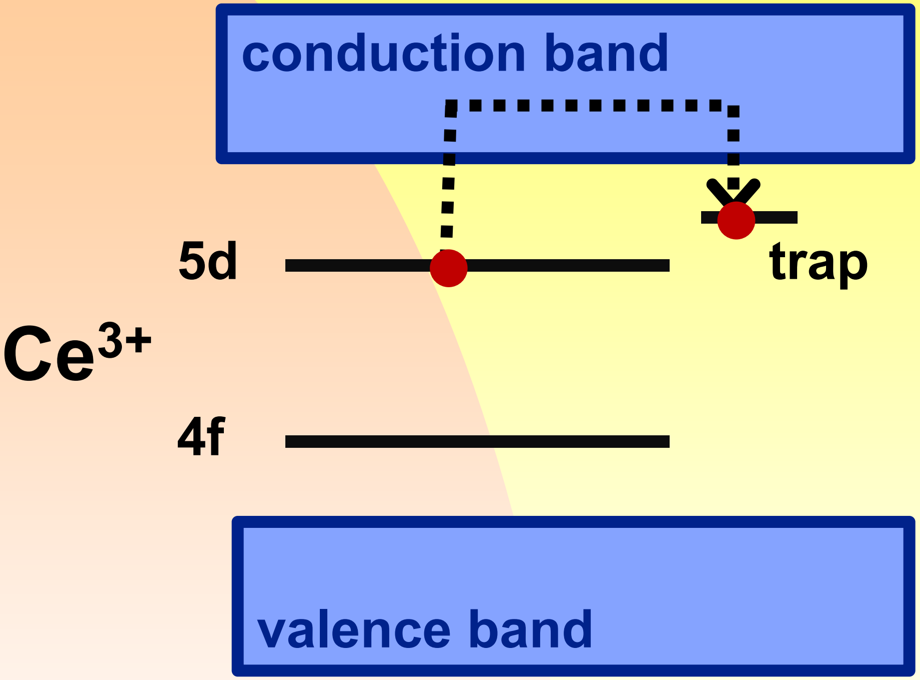
Principle



Some electrons instantly decay–
prompt decay

Delayed recombination decay

Principle

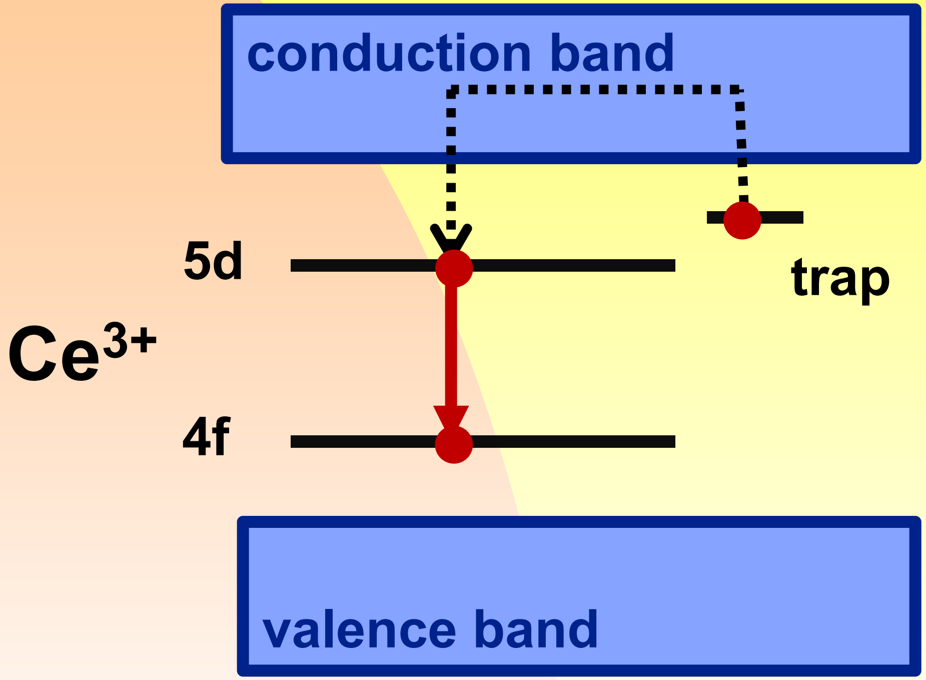


Some electrons **do not** decay promptly

If there is sufficient thermal energy around, electron can escape from the excited state into the conduction band and be trapped

Delayed recombination decay

Principle



Electron **after some time** spent in the trap escapes and can be recaptured at the luminescence center

Electron recombines with the hole in the ground state and produces the **delayed recombination light**

↓

slow tail in the luminescence decay

Delayed recombination decay vs **afterglow**

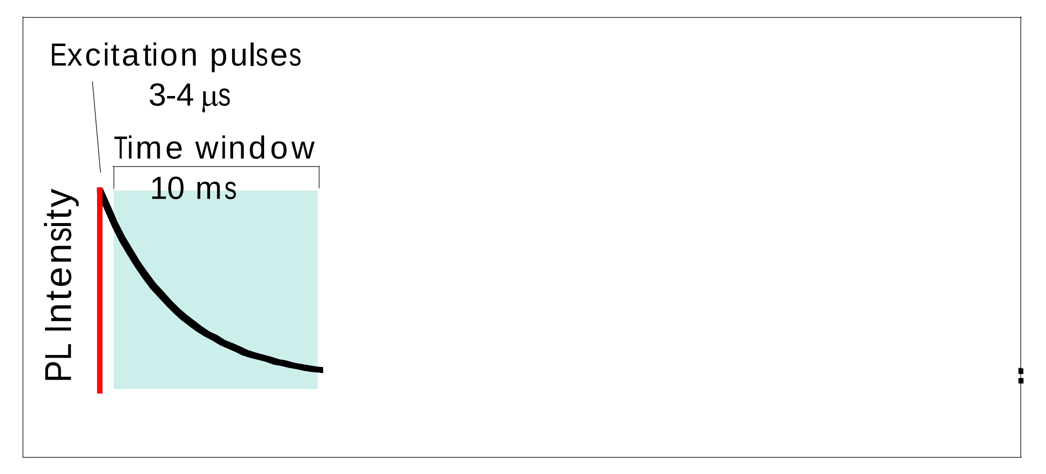
↓ ↓

Selective UV excitation **excitation by ionizing radiation**

Monitoring the T dependence of the decay supplies the information about the excited state thermal ionization

Delayed recombination decay

Measurement



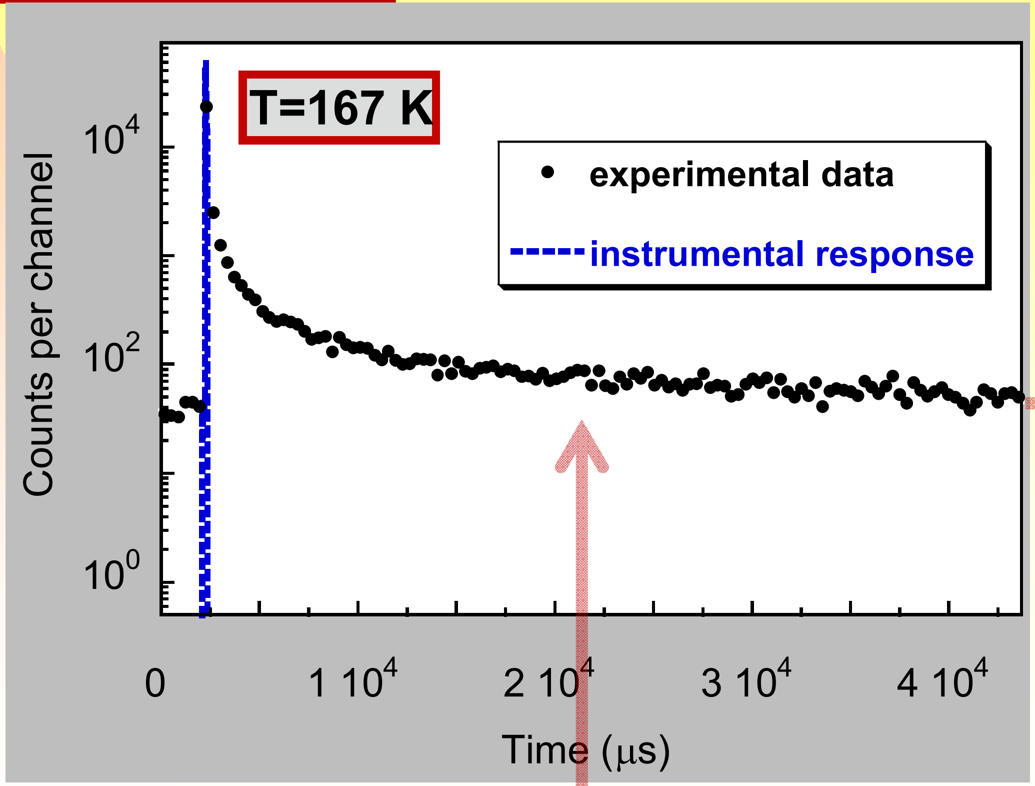
PL decay measurement

the signal is accumulated in the **extended** time window (up to 10 minutes) for a set of different temperatures

Delayed recombination decay

Example

$SrHfO_3:Ce^{3+}$



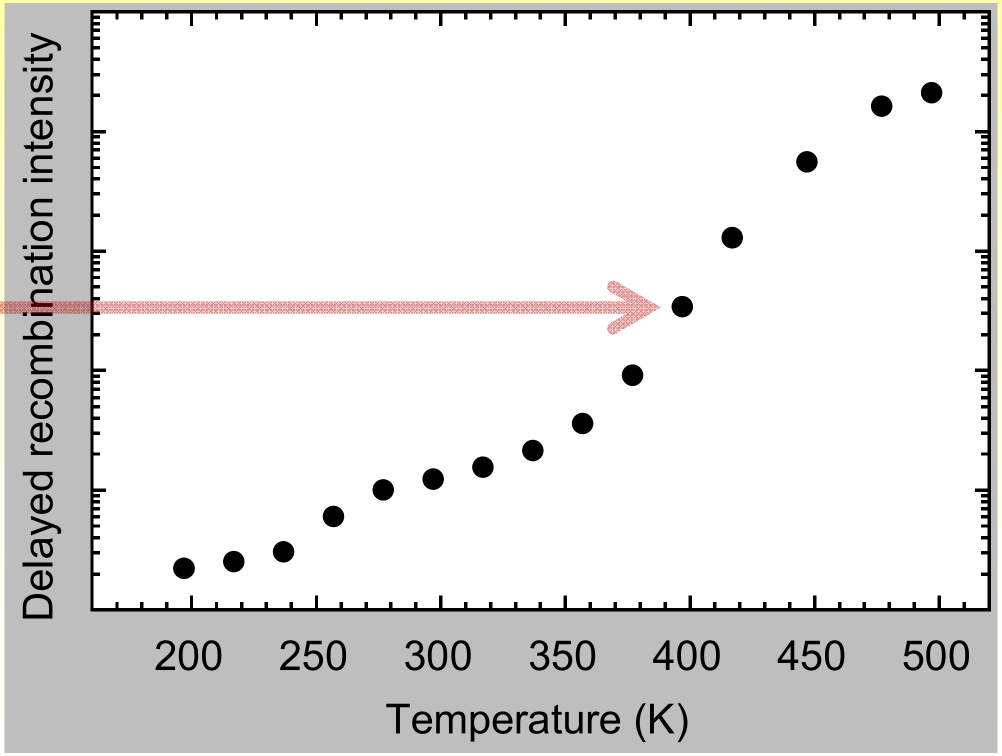
For each temperature we integrate the **decay** in time within the time (interval) of the measurement

Temperature dependence of delayed recombination decay

Experiment

$Lu_2Si_2O_7:Pr^{3+}$

Each data point is time integrated decay at the temperature T



Temperature dependence of delayed recombination decay

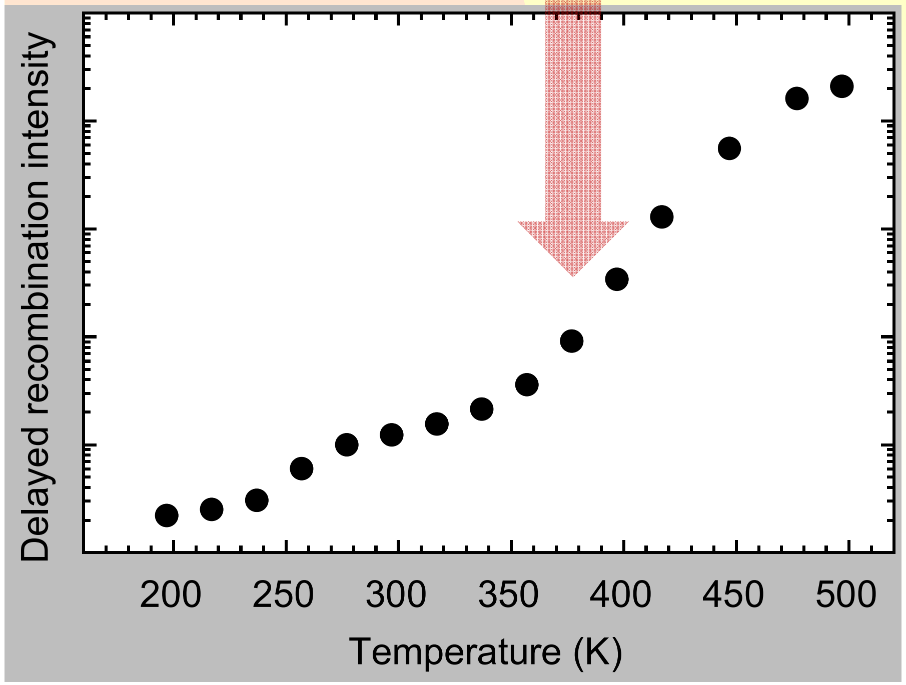
Model

$$I_{DR}(T) = w e^{-\frac{E_{ion}}{kT}} \sum_{k=1}^{n} A_k \left[e^{-\frac{t_b}{\tau(E_k)}} - e^{-\frac{t_e}{\tau(E_k)}} \right]$$

M. Fasoli, A. Vedda, E. Mihóková, M. Nikl, PRB 85, 085127 (2012)

$Lu_2Si_2O_7:Pr^{3+}$

crystal



Temperature dependence of delayed recombination decay

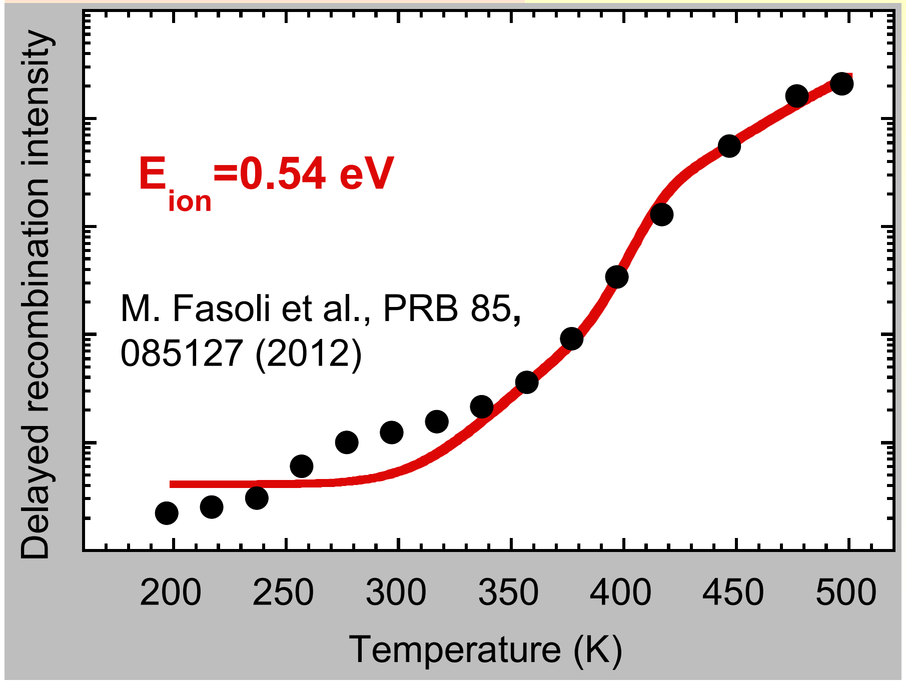
Model

$$I_{DR}(T) = w e^{-\frac{E_{\text{ion}}}{kT}} \sum_{k=1}^{n} A_k \left[e^{-\frac{t_b}{\tau(E_k)}} - e^{-\frac{t_e}{\tau(E_k)}} \right]$$

M. Fasoli, A. Vedda, E. Mihóková, M. Nikl, PRB 85, 085127 (2012)

Ionization energy is determined from the fit

$Lu_2Si_2O_7:Pr^{3+}$ **crystal**



Temperature dependence of delayed recombination decay

Model

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M. Fasoli, A. Vedda, E. Mihóková, M. Nikl, PRB 85, 085127 (2012)

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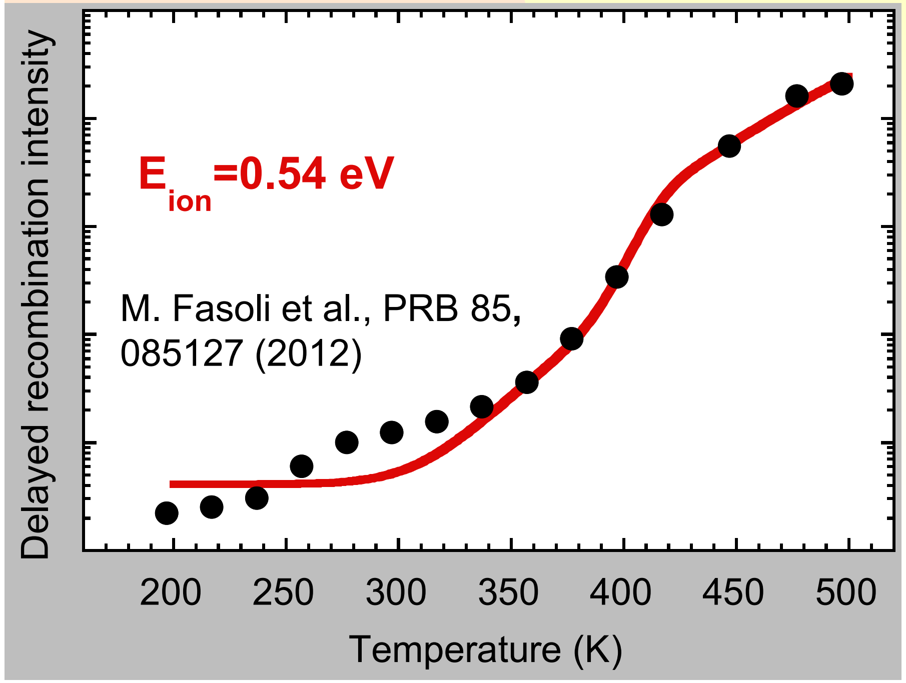
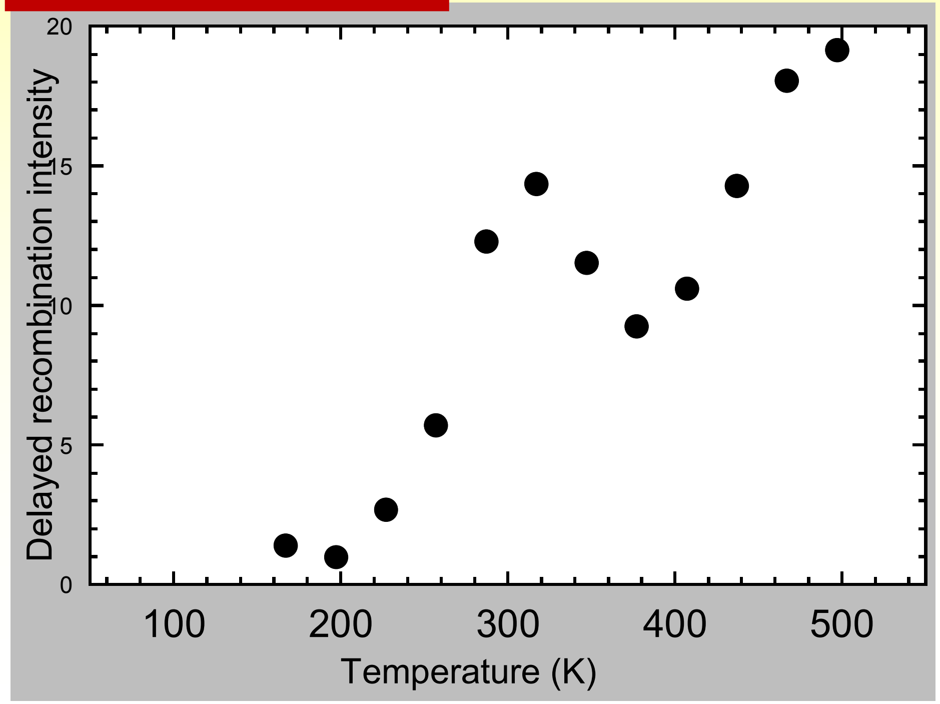


E_{ion}=0.54 eV

M. Fasoli et al., PRB 85, 085127 (2012)

$SrHfO_3:Ce^{3+}$ **powder**



Temperature dependence of delayed recombination decay

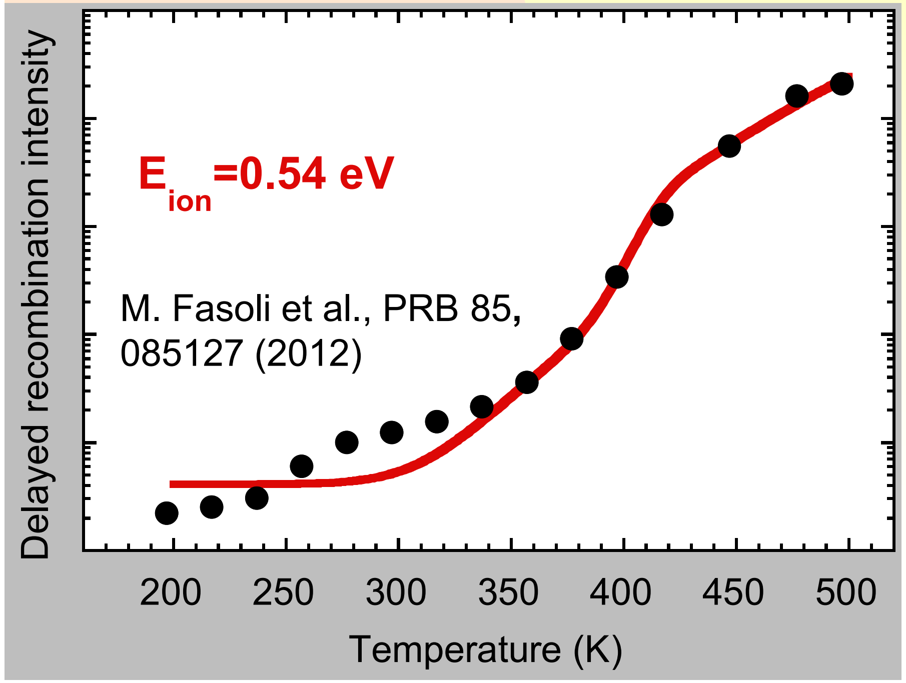
Model

$$I_{DR}(T) = w e^{-\frac{E_{\mathrm{ion}}}{kT}} \sum_{k=1}^{n} A_k \left[e^{-\frac{t_b}{\tau(E_k)}} - e^{-\frac{t_e}{\tau(E_k)}} \right]$$

M. Fasoli, A. Vedda, E. Mihóková, M. Nikl, PRB 85, 085127 (2012)

Ionization energy is determined from the fit

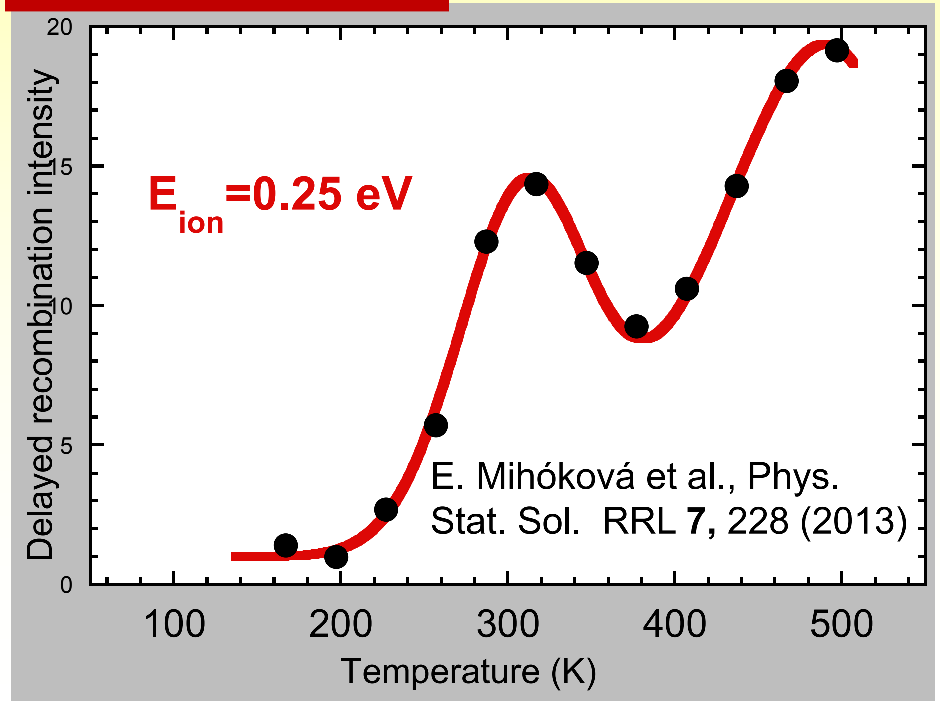
$Lu_2Si_2O_7:Pr^{3+}$ crystal



E_{ion}=0.54 eV

M. Fasoli et al., PRB 85, 085127 (2012)

$SrHfO_3:Ce^{3+}$ powder



E_{ion}=0.25 eV

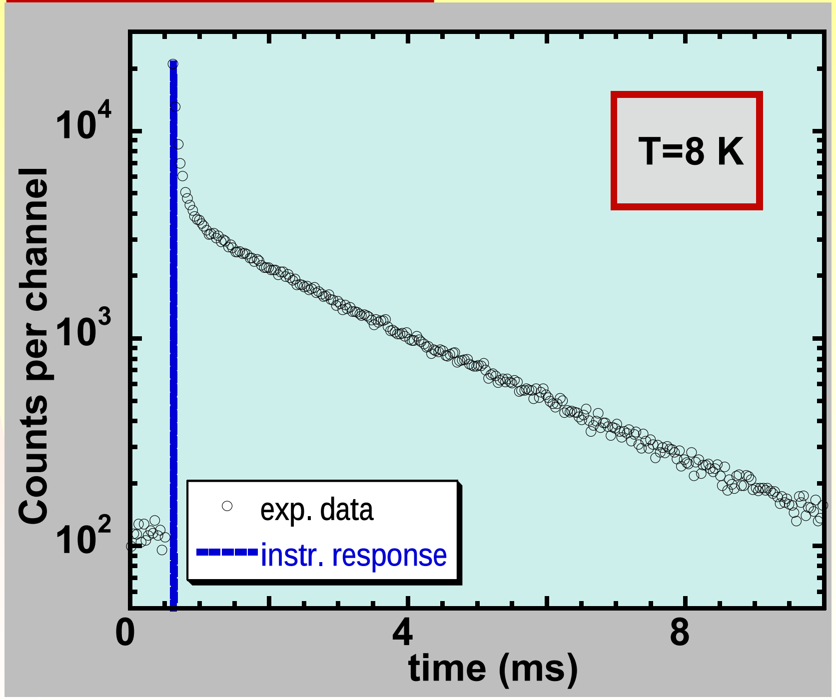
E. Mihóková et al., Phys. Stat. Sol. RRL **7,** 228 (2013)

Delayed recombination decay and quantum tunneling

Low temperature contribution to delayed recombination decay

Experiment

Lu_2SiO_5:Pr^{3+}

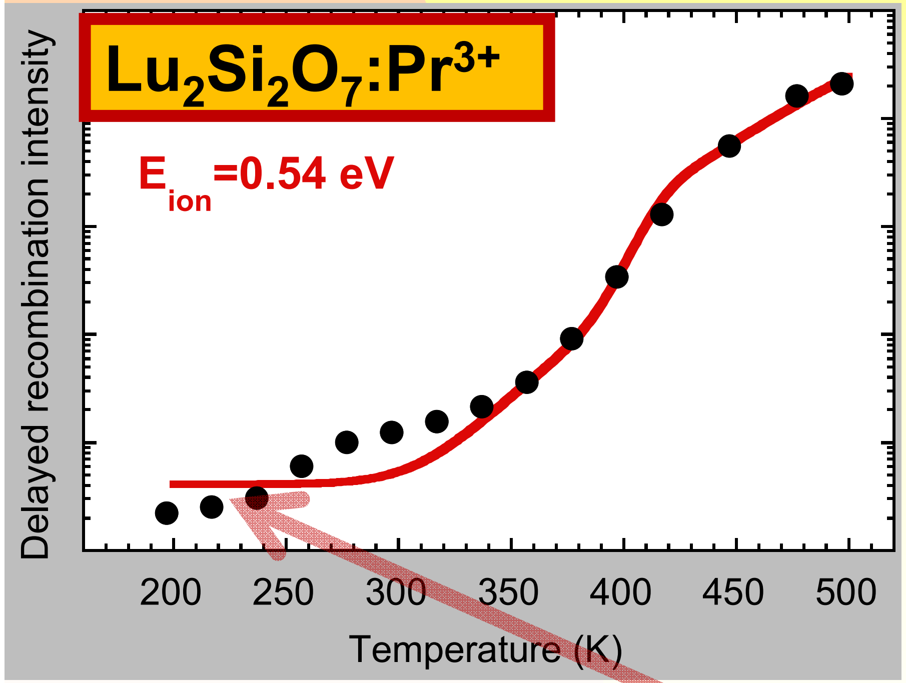


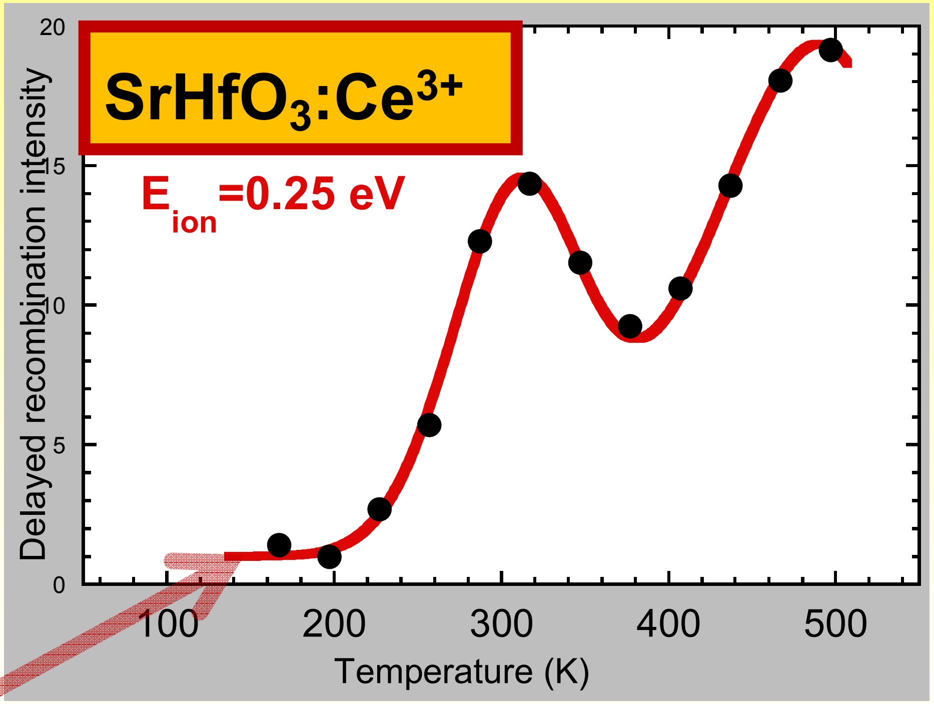
There is **low T contribution** to the delayed recombination that is **NOT** due to thermal ionization

Fit of the model to the data

$$I_{DR}(T) = w e^{-\frac{E_{ion}}{kT}} \sum_{k=1}^{n} A_k \left[e^{-\frac{t_b}{\tau(E_k)}} - e^{-\frac{t_e}{\tau(E_k)}} \right]$$

Low T limit of the modelled $I_{DR}(T)$ is zero





Actual fit requires an additive constant to reproduce the low T data

Origin of the low temperature contribution

quantum tunneling

between the activator and trap(s)

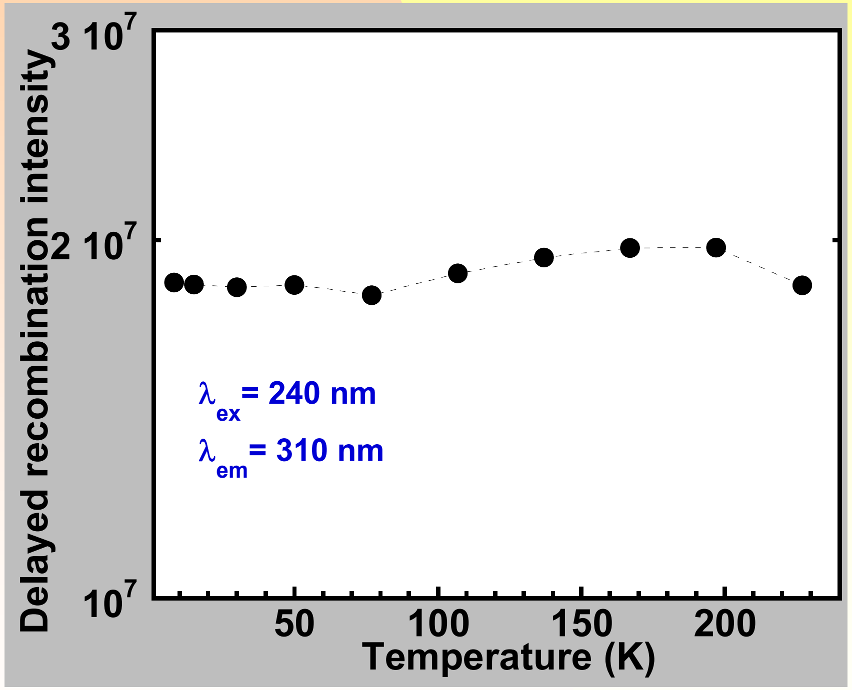
Experimental verification: observation of temperature independent delayed recombination intensity within certain low T interval

Theoretical verification: modelling of quantum tunneling shows it can cause several orders of magnitude delay of the decay

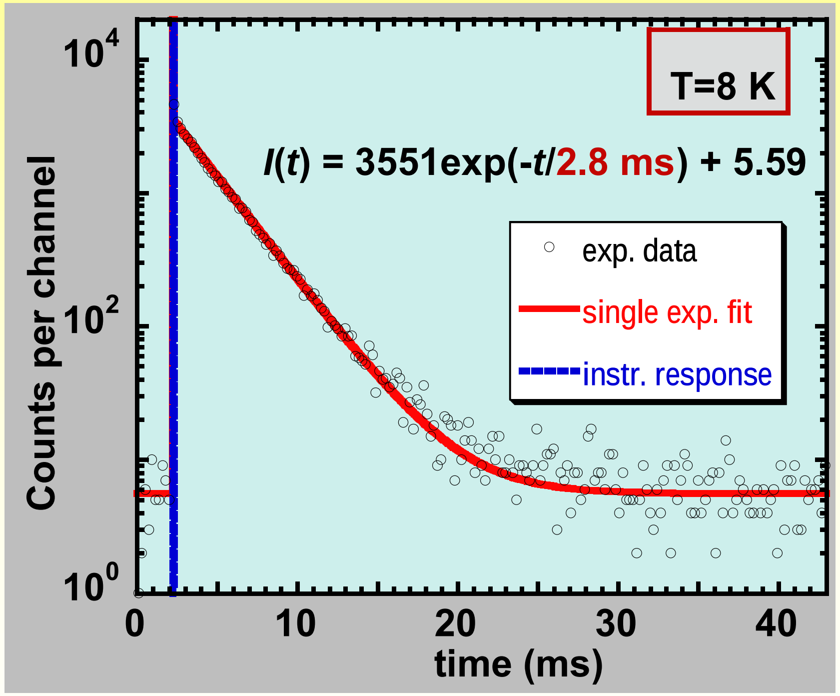
Experimental support

Delayed recombination decay at the low temperature limit

$Y_2SiO_5:Pr^{3+}$



constant signal up to about 200 K



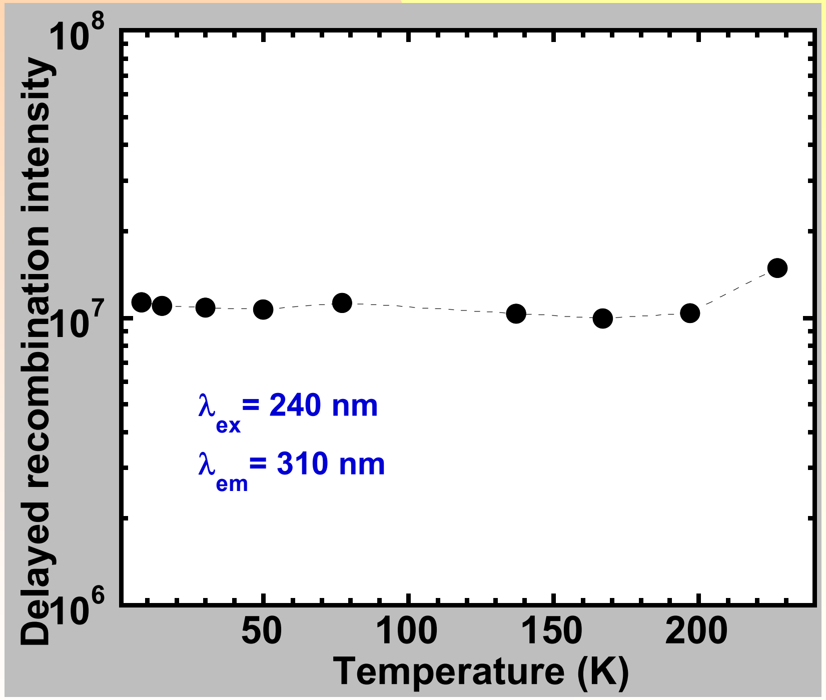
single exponential decay up to 200 K

Quantum tunneling between the activator and a single trap

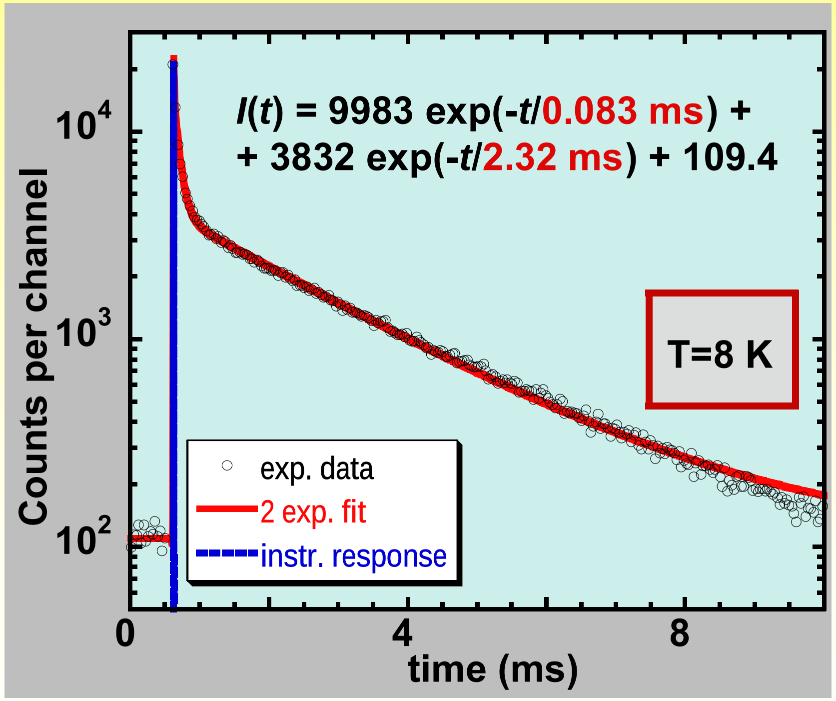
Experimental support

Delayed recombination decay at the low temperature limit

$Lu_2SiO_5:Pr^{3+}$



constant signal up to about 200 K



complex decay

Quantum tunneling between the activator and several traps

Experimental support

Delayed recombination decay at the low temperature limit

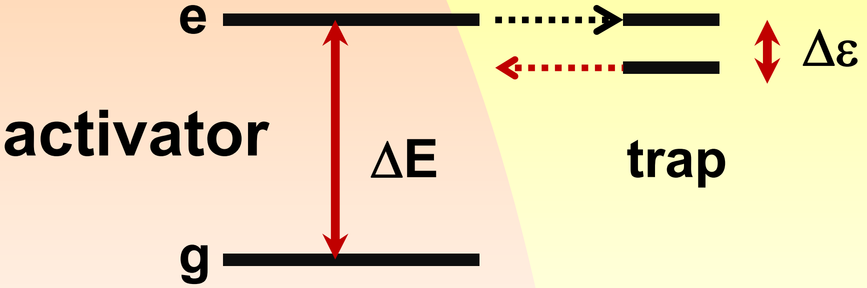
Quantum tunneling experimentally verified in a variety of Ce^{3+} and Pr^{3+} -doped scintillating complex oxides in various forms (single crystals, thin films, nanopowders)

E. Mihóková et al., IEEE Trans. Nucl. Sci. **61,** 257 (2014)
E. Mihóková et al., Opt. Mater. **40,** 127 (2015)

Theoretical support

One dimensional model of quantum tunneling between the trap and activator

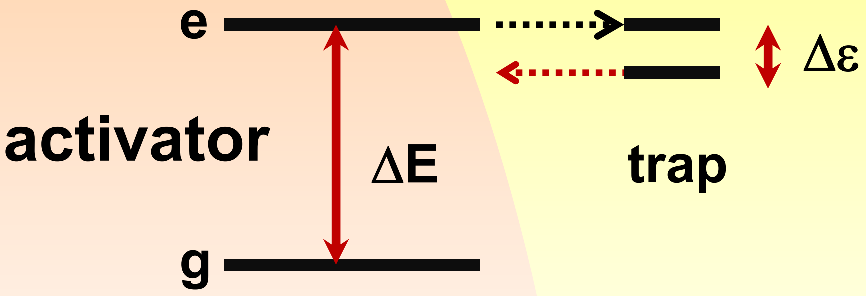
Scenario



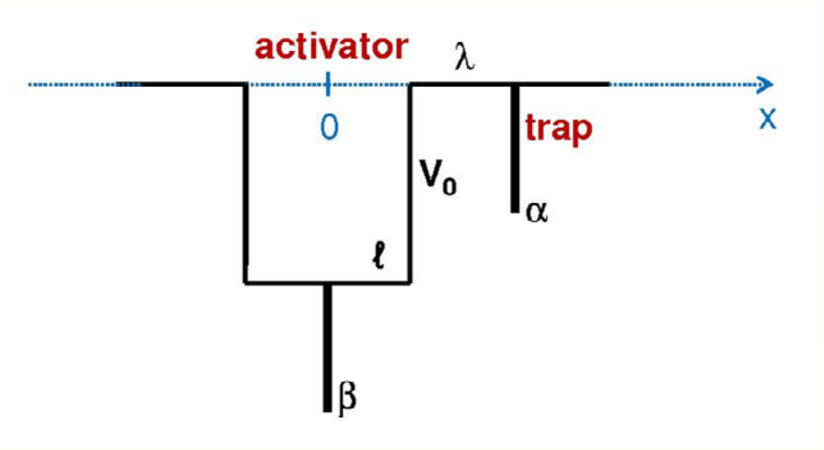
Theoretical support

One dimensional model of quantum tunneling between the trap and activator

Scenario



Model potential



$$V = -\beta\delta(x) - V_0\,\theta(\ell - |x|) - \alpha\delta(x - \ell - \lambda)$$

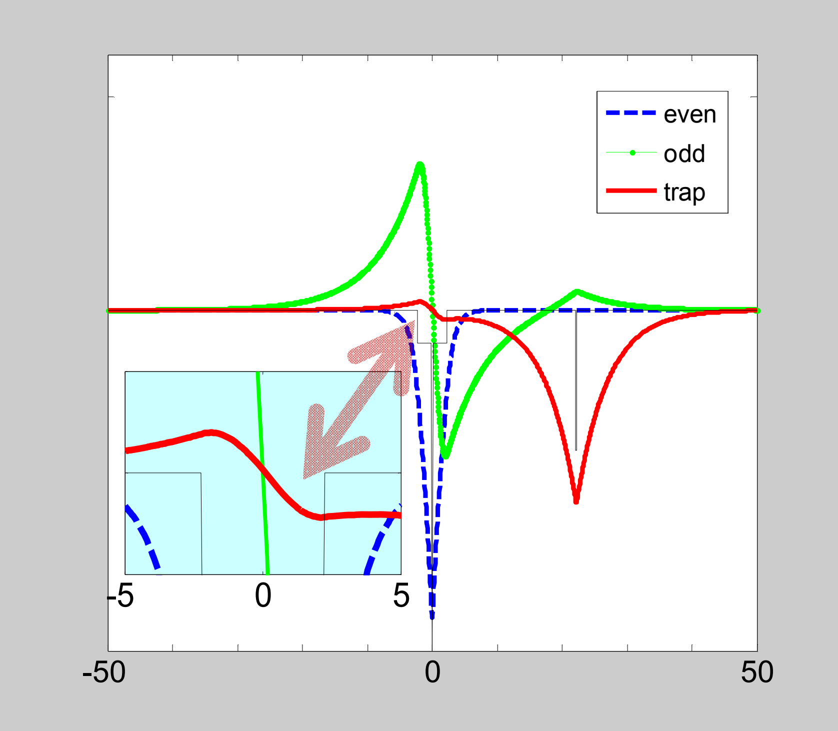
We solved the Schrödinger equation and calculated the **decay rate slowed by quantum tunneling**

$$\Gamma = R \times \Gamma_0$$

slow rate reduction factor prompt rate

Theoretical support

One dimensional model of quantum tunneling between the trap and activator



Wave functions

even= ground state of the activator
odd= excited state of the activator
trap= trap state

trap wave function in the activator region
→ its norm gives the reduction factor **R**

With reasonable parameter values the decay is delayed **by several orders of magnitude** which is what we see in the experiment

E. Mihóková et al., Chem. Phys. Lett. **578,** 66 (2013)

Theoretical support

Two dimensional model of quantum tunneling between the trap and activator

Trap and activator – isotropic Gaussian wells

Model potential

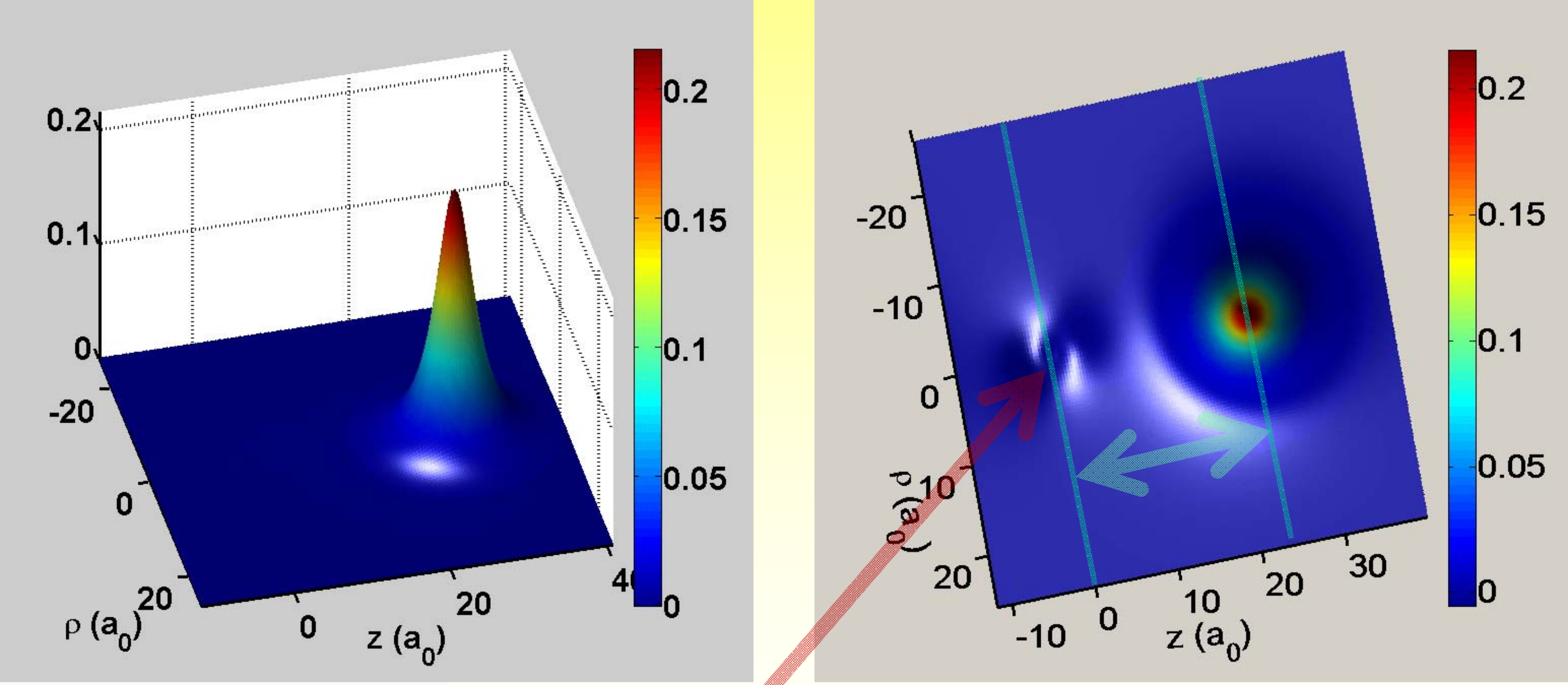
$$\boxed{V(\rho,z) = -\alpha\, e^{-(\rho^2+z^2)/r_A^2} + \frac{\beta}{2(\rho^2+z^2)} - \gamma\, e^{-(\rho^2+(z-\lambda)^2)/r_T^2}}$$

Solution of the Schrödinger equation by the “Wave packet” program

E. Mihóková and L. S. Schulman, J. Phys. Cond. Matter **27,** 075501 (2015)

Theoretical support

Two dimensional model of quantum tunneling between the trap and activator



trap wave function shown from two different perspectives

the portion of the wave function in the activator region

trap – activator distance is 23 a_0 ~ 12 Å

the delay of the decay ~ 5 orders of magnitude

Analytical estimates of R

$$\Gamma = R \times \Gamma_0$$

slow rate

reduction factor

prompt rate

ground state: E_G, ψ_G
excited state: E_E, ψ_E
trap state: E_T, ψ_T

$$\Gamma_0 \sim \left|\langle \psi_E | r | \psi_G \rangle\right|^2$$

trap wave function dropoff in 3D:

$$\sqrt{\kappa/2\pi}\,\exp(-\kappa r)/r$$

r- distance from the trap center

$$\kappa = \sqrt{-2mE_T}/\hbar$$

Because in the region of the activator ψ_T resembles ψ_E, the reduction, R, arises simply from the smaller amplitude of ψ_T

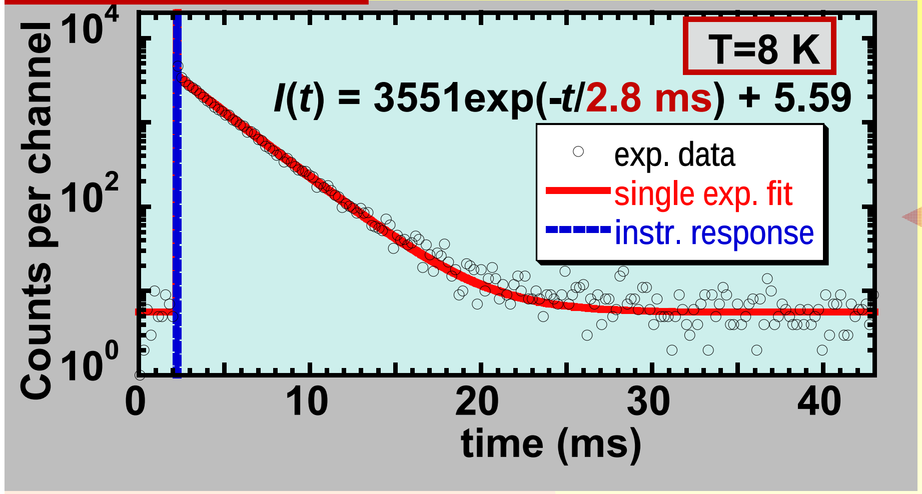
$$R = \frac{\eta \int_{\text{activator}} \left|\sqrt{\frac{\kappa}{2\pi}}\frac{\exp(-\kappa r)}{r}\right|^2 d^3 r_{\text{activator}}}{\langle \psi_T | \psi_T \rangle}$$

$\eta = 2\text{-}3$, correction factor

Application

$Y_2SiO_5:Pr^{3+}$

single exp. decay ⇔ **Quantum tunneling between the activator and a single (kind of) trap**



delayed recombination decay

$1/\Gamma_0$ = 18 ns

$1/\Gamma$ = 2.8 ms

$R = 8.2 \times 10^{-6}$

trap depth $E_T \approx E_E$ ~ 0.4 eV

J. Pejchal et al., J. Phys. D: Appl. Phys. **42** 055117 (2009)

J. Pejchal et al., J. Phys. D: Appl. Phys. **42** 055117 (2009)

Analytical estimates of R + experimental data

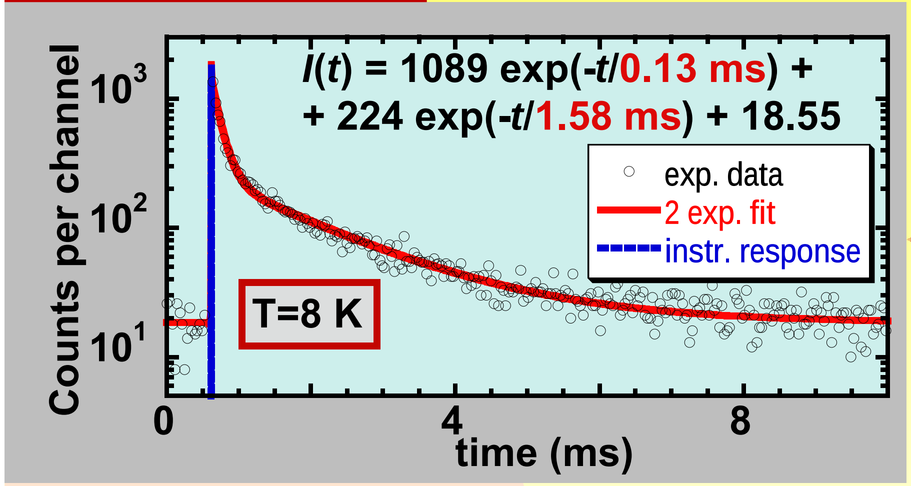
⇓

Trap ↔ Pr $^{3+}$ distance

λ = 12-14 Å

Application

$Lu_2Si_2O_7:Pr^{3+}$ complex decay ⟺ **Quantum tunneling between the activator and traps at various distances from the activator**



delayed recombination decay

M. Nikl et al., Chem. Phys. Lett. **493** 72 (2010)

$1/\Gamma_0 = 19$ ns

$1/\Gamma_1 = 0.13$ ms $1/\Gamma_2 = 1.58$ ms

$R_1 = 1.5 \times 10^{-4}$ $R_2 = 1.3 \times 10^{-5}$

trap depth $E_T \approx$ **$E_E = 0.54 \pm 0.05$ eV**

M. Fasoli et al., Phys. Rev. B **85**, 085127 (2012)

Analytical estimates of R + experimental data ⟹

Trap ↔ Pr^{3+} distance

$\lambda_1 = 6\text{-}8$ Å **$\lambda_2 = 10\text{-}11$ Å**

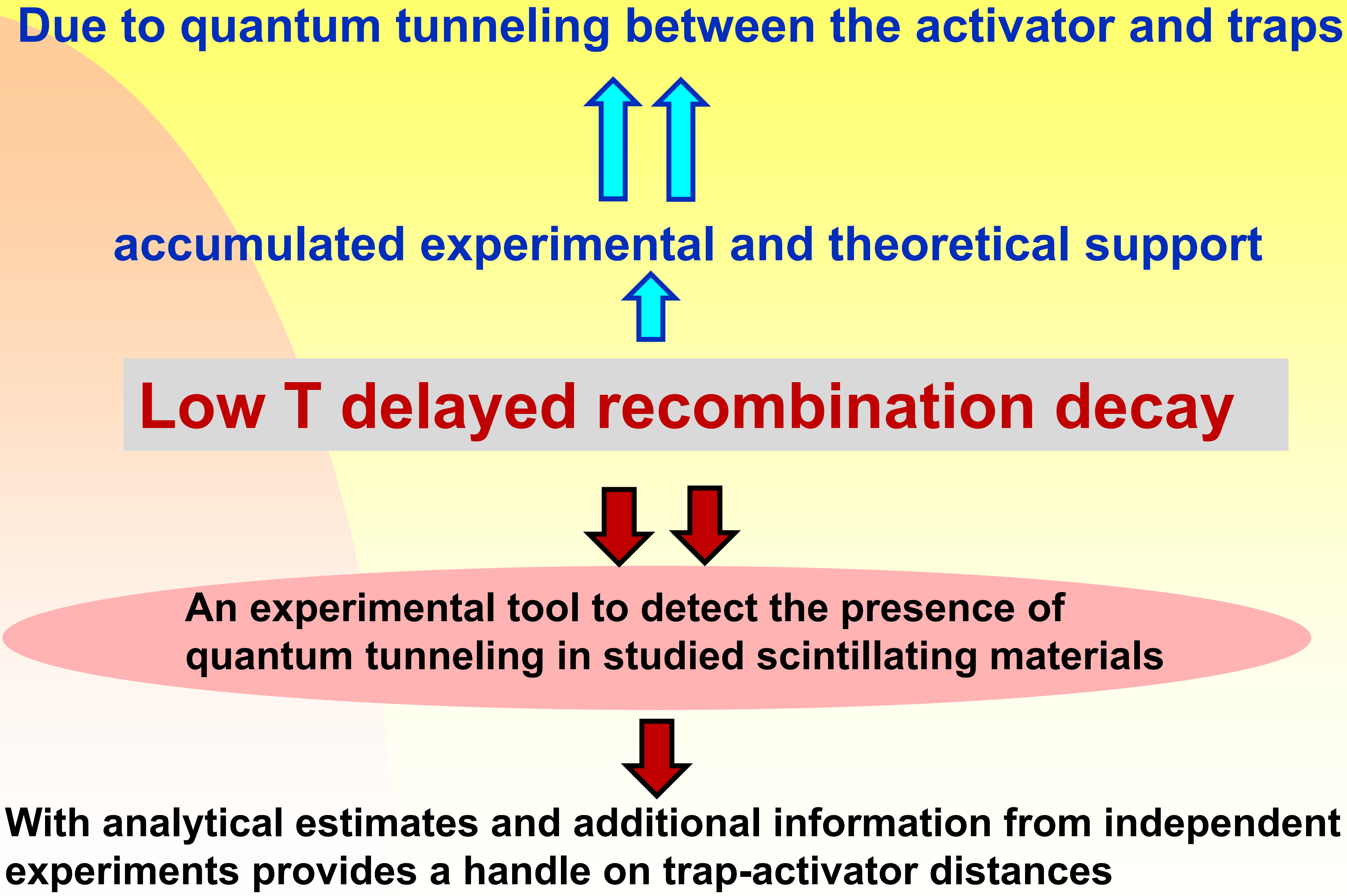
Independent TSL experiment confirms the presence of the trap with **$E_T = 0.51 \pm 0.01$ eV**

E. Mihóková et al., Opt. Mater. **34**, 872 (2012)

Trap is likely to be an oxygen vacancy

Mean distance Lu-O in $Lu_2Si_2O_7:Pr^{3+}$ is 2.23 Å ⟹ 3rd or 4th nearest O site

E. Mihóková and L. S. Schulman, J. Phys. Cond. Matter **27,** 075501 (2015)



Due to quantum tunneling between the activator and traps

accumulated experimental and theoretical support

Low T delayed recombination decay

An experimental tool to detect the presence of quantum tunneling in studied scintillating materials

With analytical estimates and additional information from independent experiments provides a handle on trap-activator distances

Summary

- **Quantum tunnelling between traps and recombination centers belongs to sources of losses of fast scintillation light**
- **Quantum tunneling is quite frequently encountered in scintillating materials**
- **Detection of the presence of quantum tunnelling:**
  - **monitoring the afterglow tail**
  - **scintillation decay**
  - **initial rise in TSL**
  - **delayed recombination decay**

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