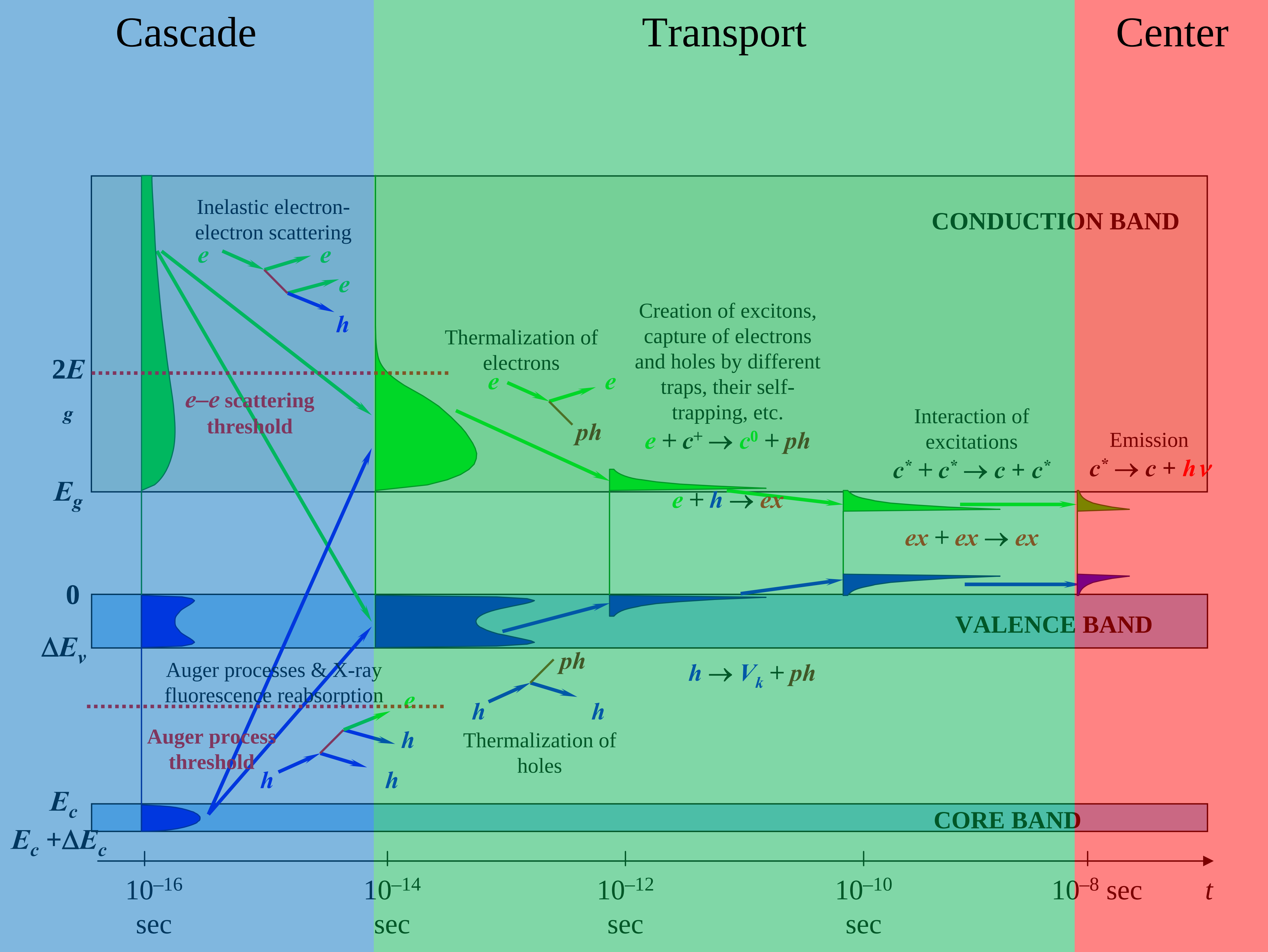
Localized states and electronic excitation mobility in solids with short order fluctuation of crystal structure

Andrei Belsky

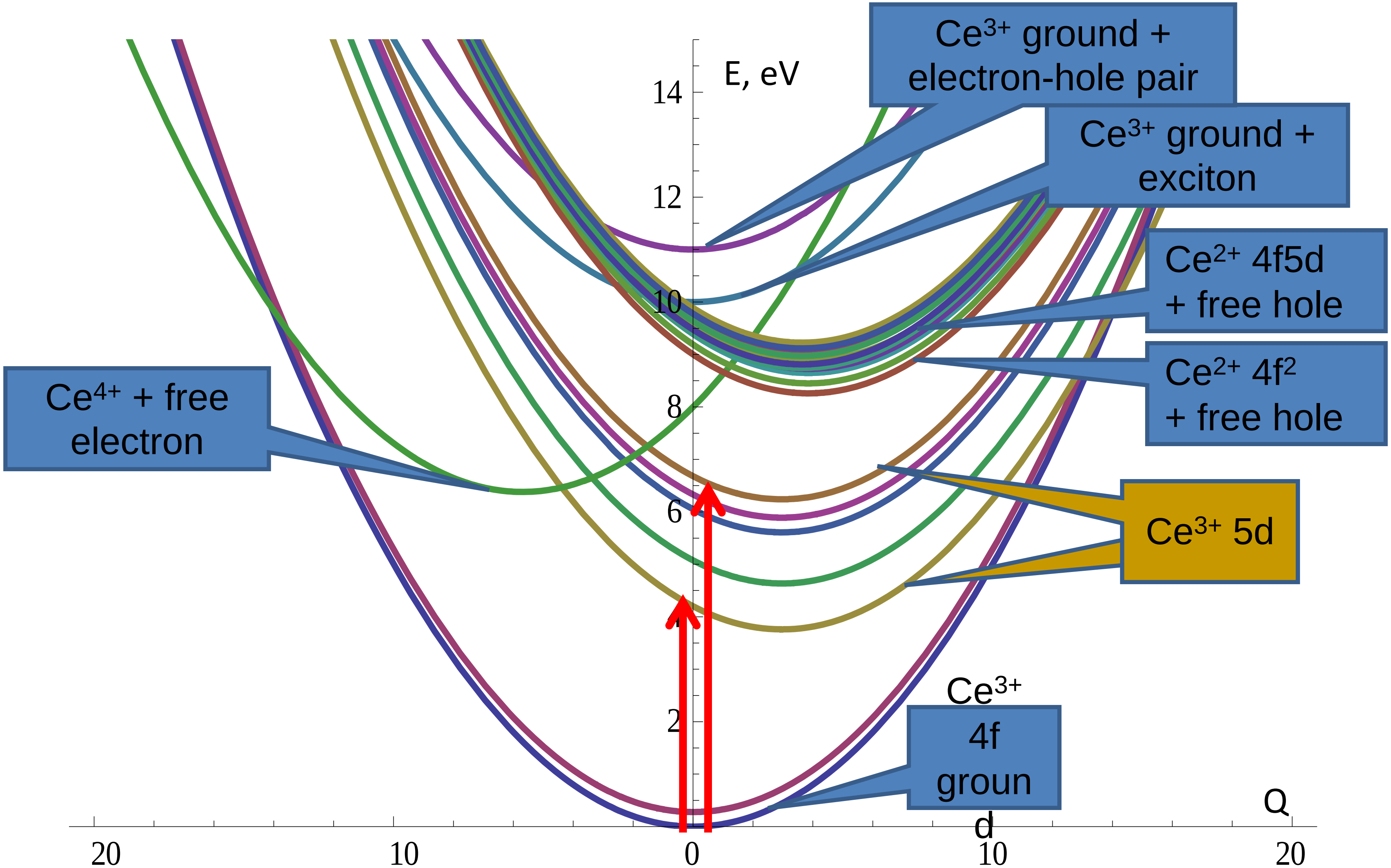
Laboratoire de Physico-Chimie des Matériaux Luminescents,
Université Lyon 1, France

- Experimental study of relaxation dynamics:
  - Decay kinetics under VUV excitation and elementary processes in scintillators
- Spatial scales for processes in scintillators:
  - Solid solutions of scintillators



Cascade
Transport
Center
CONDUCTION BAND
Inelastic electron-electron scattering
e e e h
2E g
e–e scattering threshold
Thermalization of electrons
e e ph
Creation of excitons, capture of electrons and holes by different traps, their self-trapping, etc.
$e + c^{+} \rightarrow c^{0} + ph$
Interaction of excitations
$c^{*} + c^{*} \rightarrow c + c^{*}$
Emission
$c^{*} \rightarrow c + h\nu$
E_g
$e + h \rightarrow ex$
$ex + ex \rightarrow ex$
0
VALENCE BAND
ΔE_v
Auger processes & X-ray fluorescence reabsorption
e
ph
h h
$h \rightarrow V_k + ph$
Auger process threshold
h h h
Thermalization of holes
E_c
CORE BAND
$E_c + \Delta E_c$
10^{-16} sec
10^{-14} sec
10^{-12} sec
10^{-10} sec
10^{-8} sec
t

Excitation & ionization of Ce^{3+}



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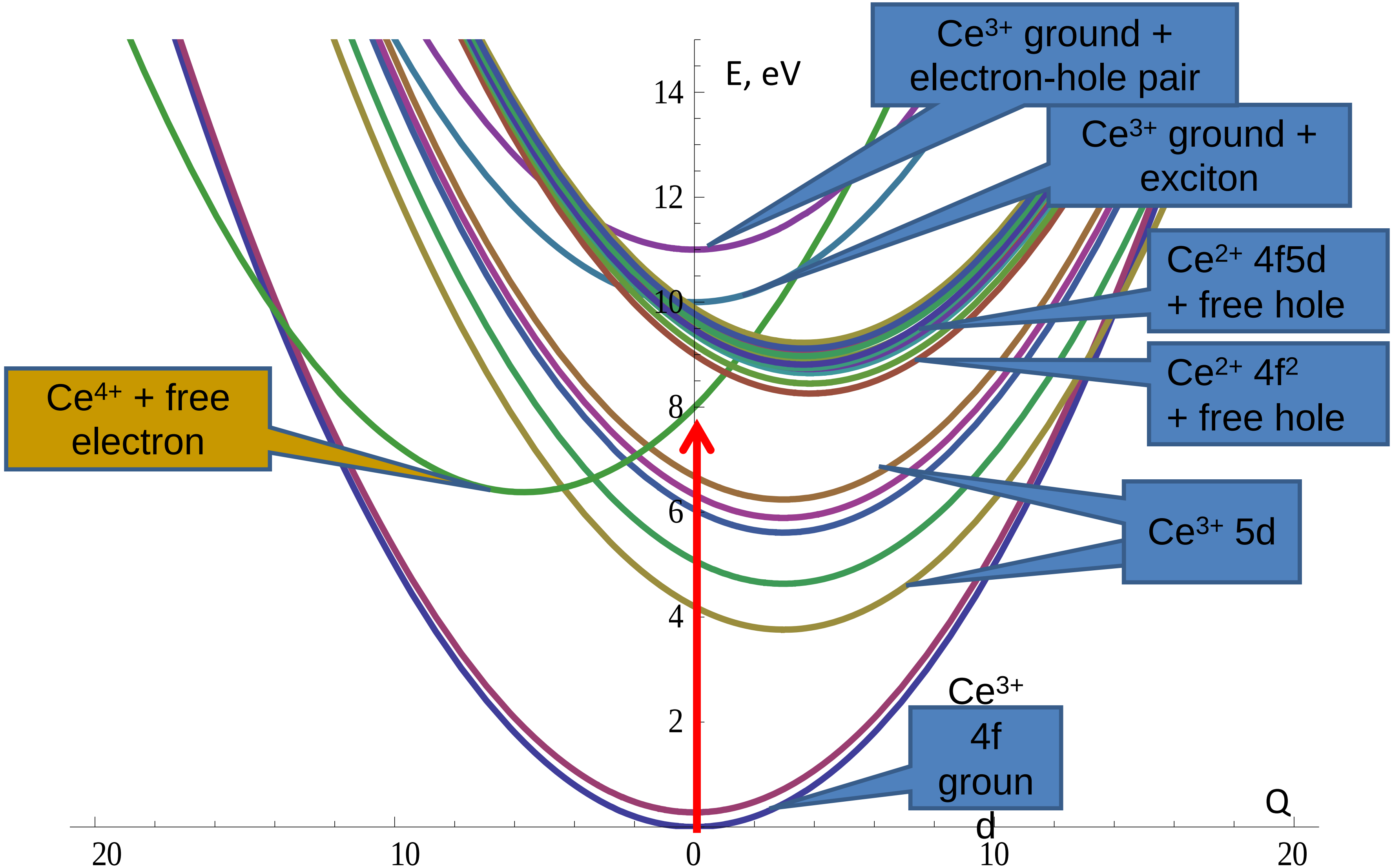
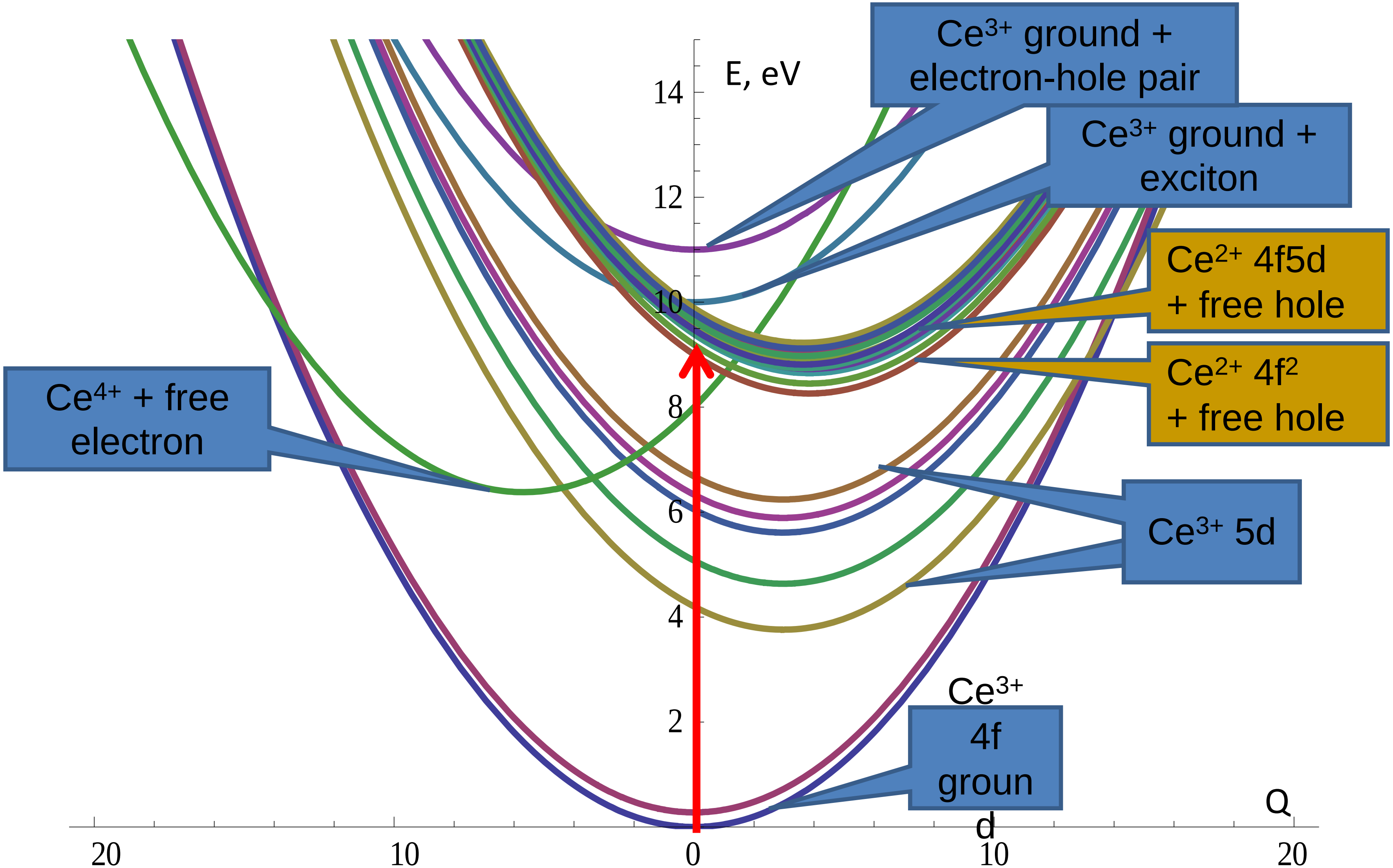


Excitation & ionization of Ce^{3+}



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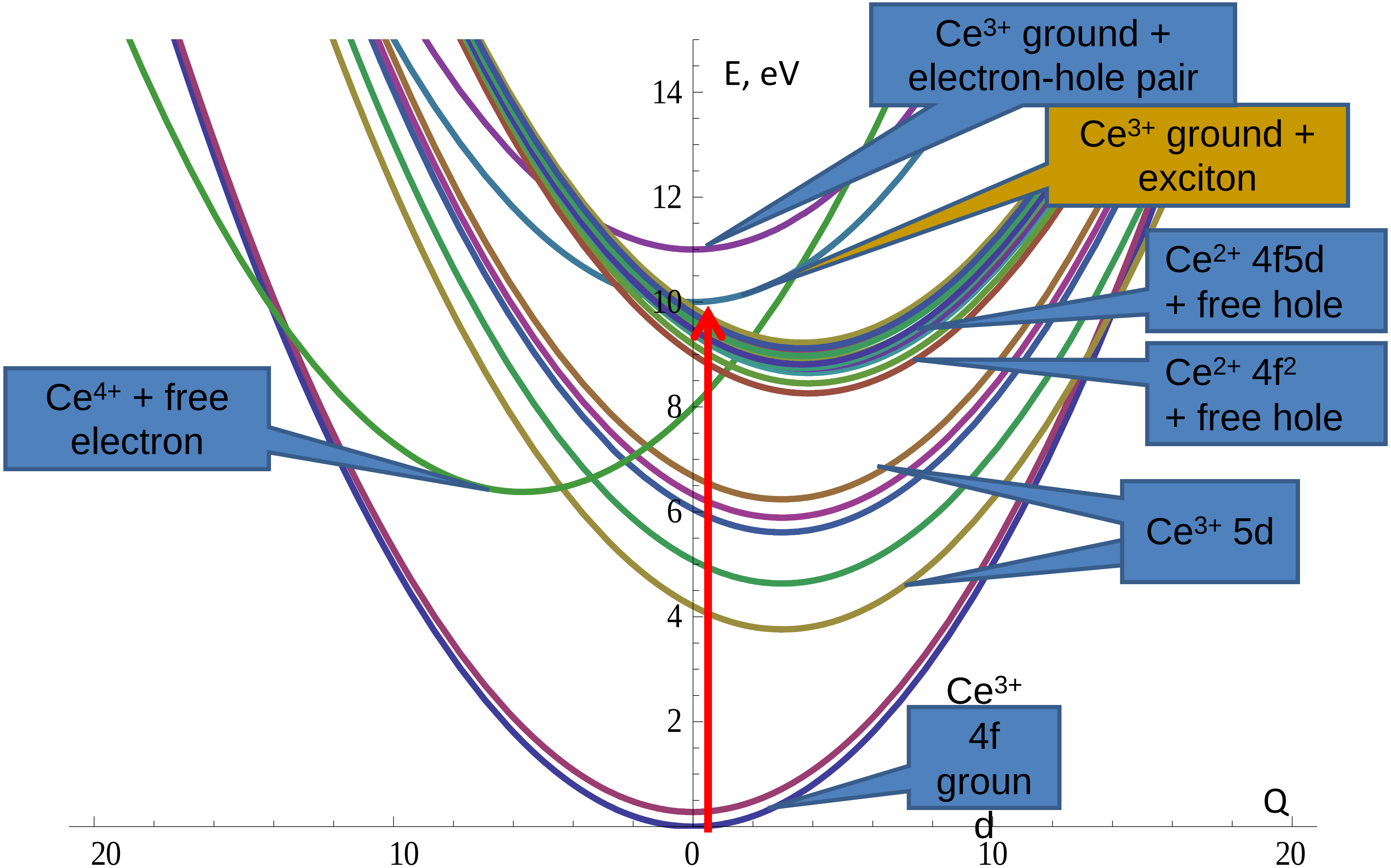

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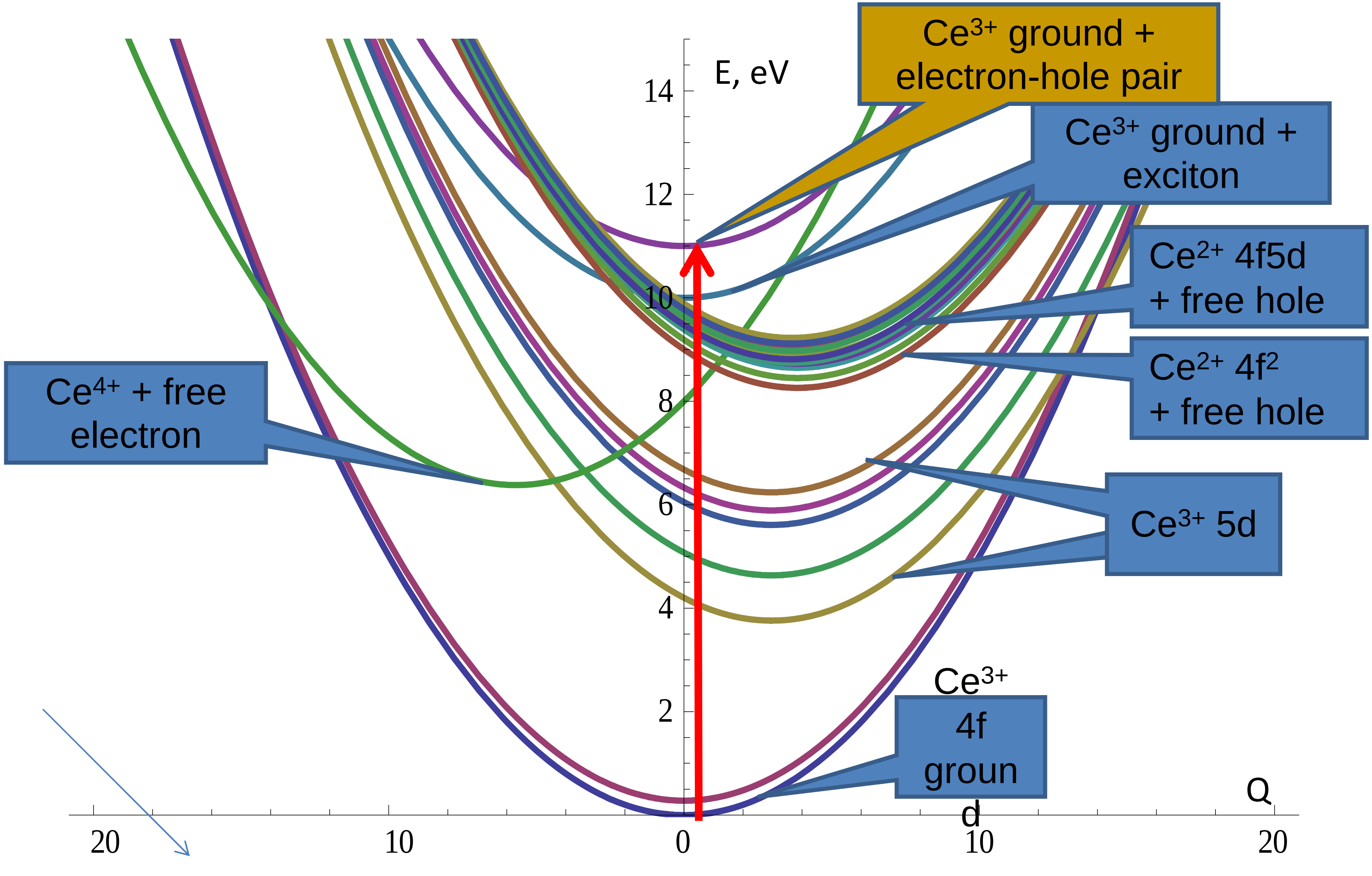
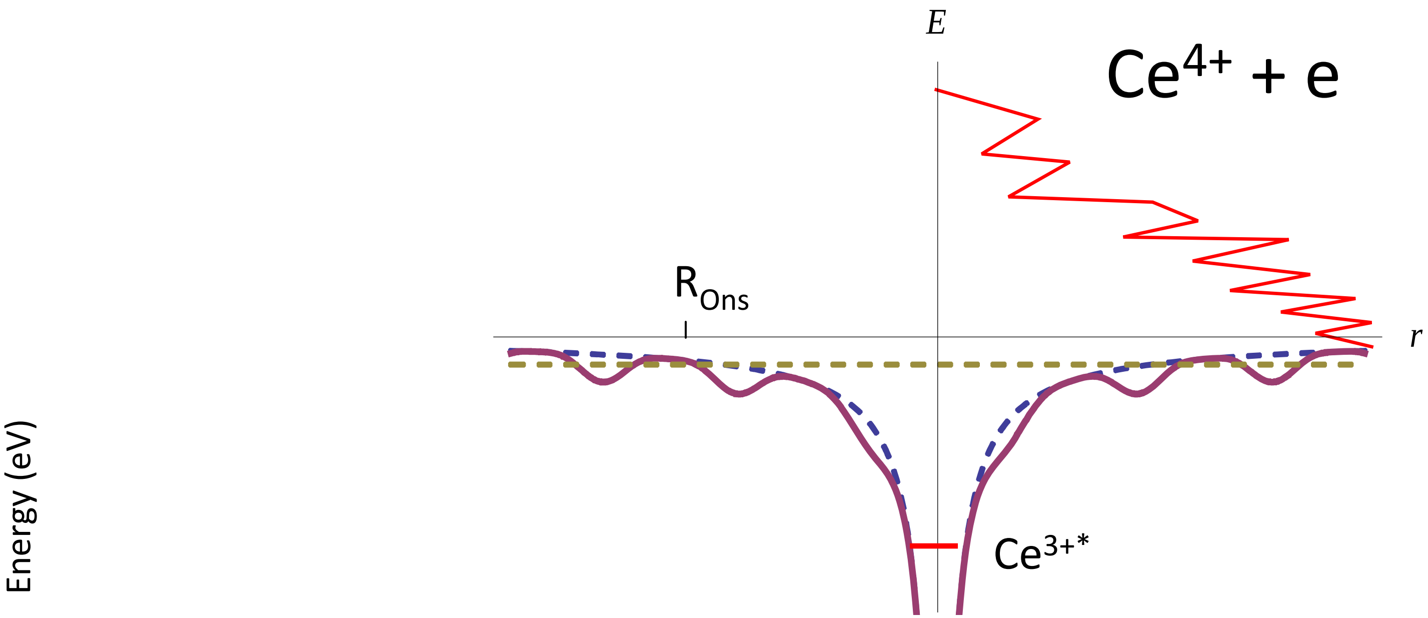
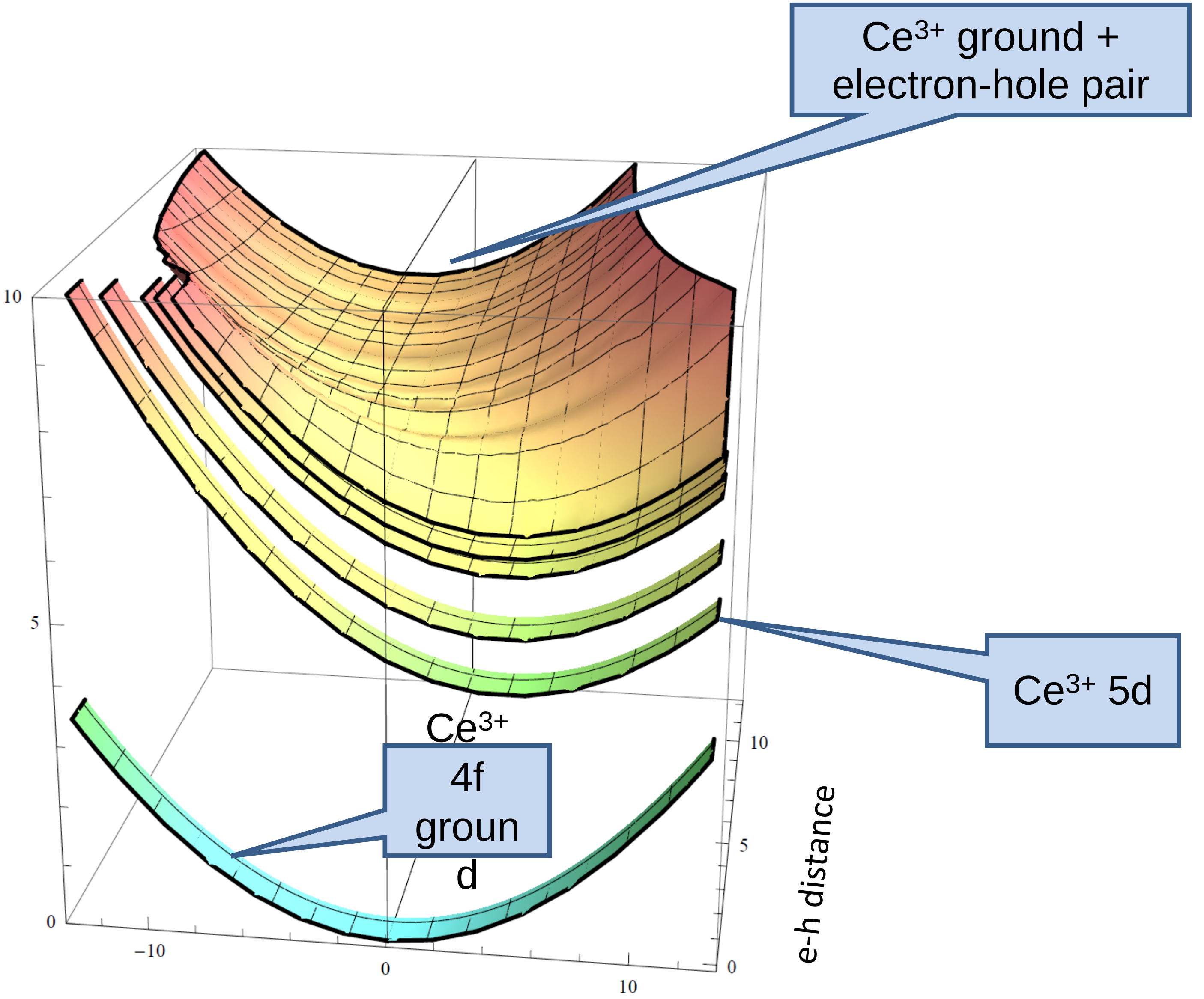


Ionization of Ce^{3+}

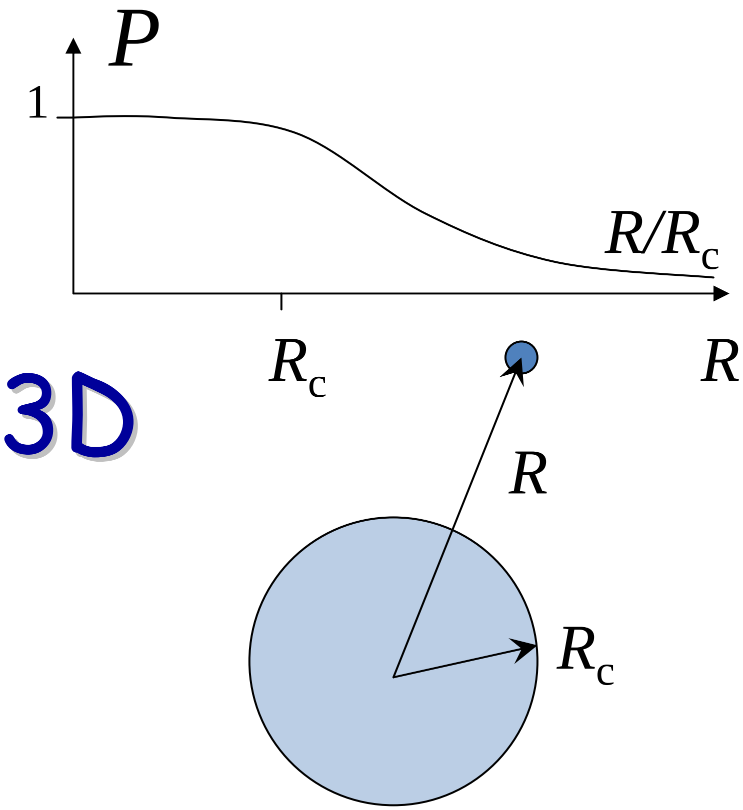


Excitation & ionization of Ce^{3+}



3D diffusion-controlled recombination

Recombination probability



Black sphere

$$P = \begin{cases} 1, & r_{eh} < R_c \\ R_c / r_{eh}, & r_{eh} > R_c \end{cases}$$

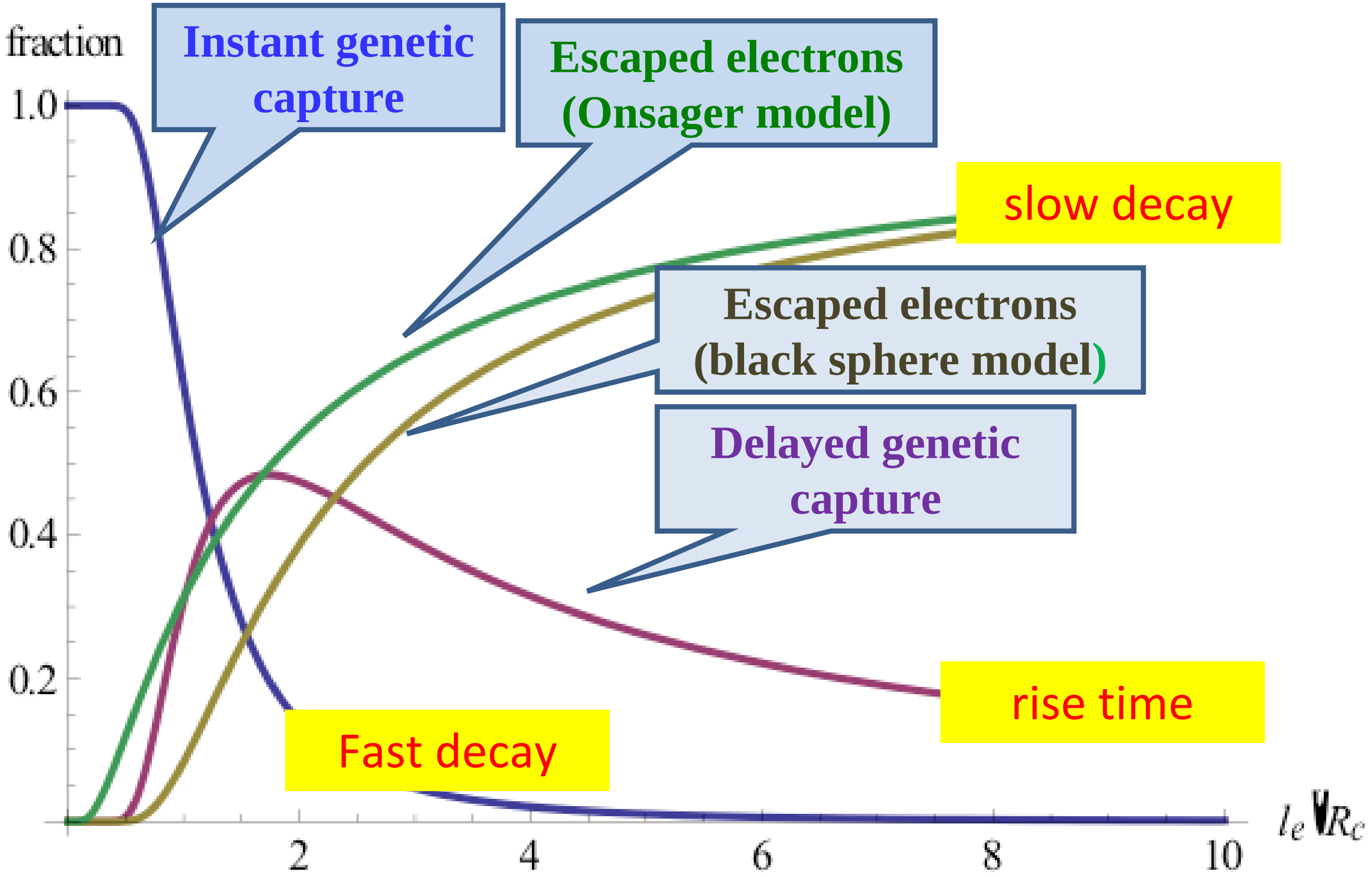
Coulomb

$$P = 1 - \exp\left(-R_{Ons}/r_{eh}\right)$$

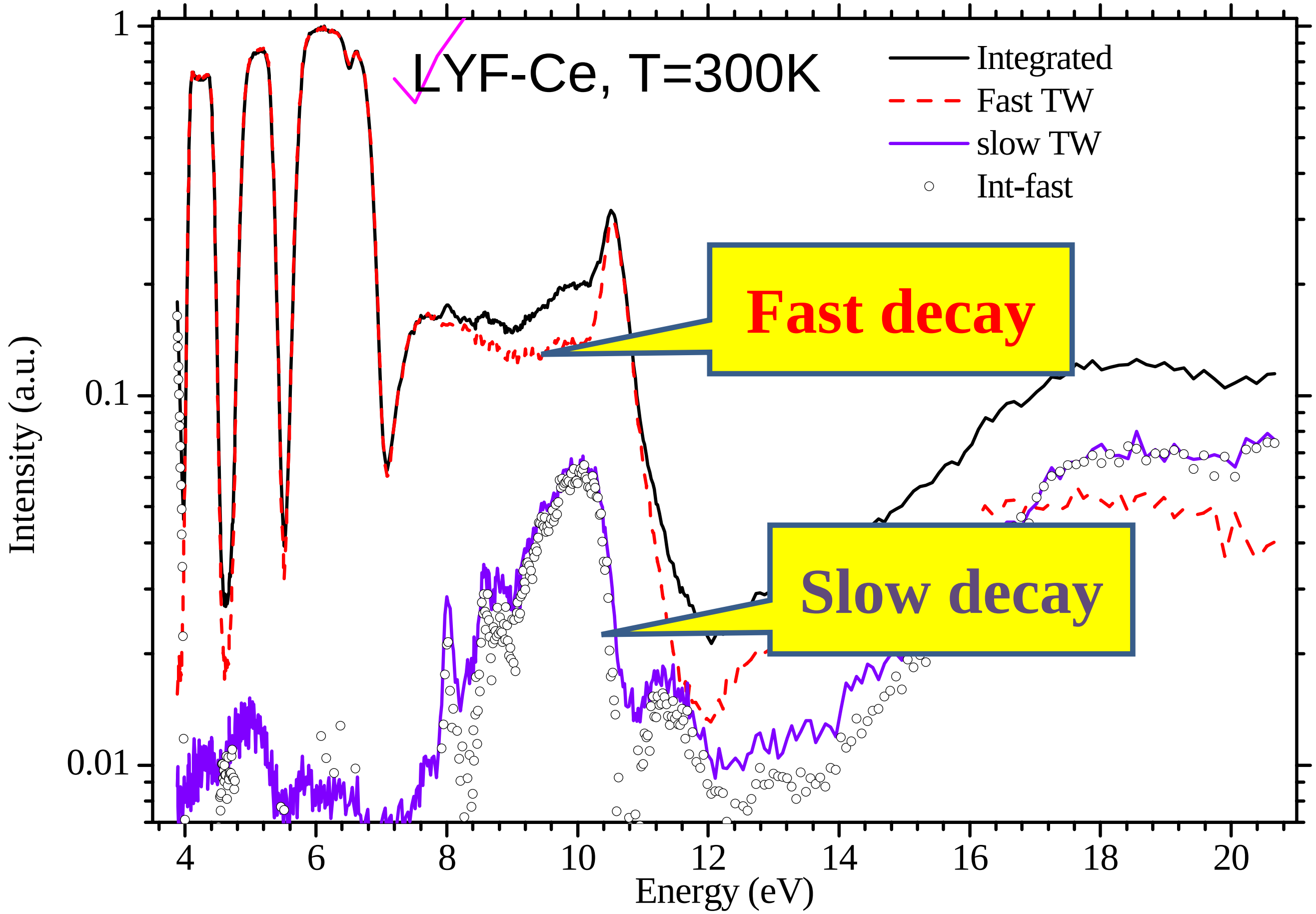
$$\frac{e^2}{\varepsilon R_{Ons}} = k_B T$$

ε=5.7	T=300K	R_{Ons}=10 nm
	T=77K	R_{Ons}=38 nm
	T=10K	R_{Ons}=300 nm ???

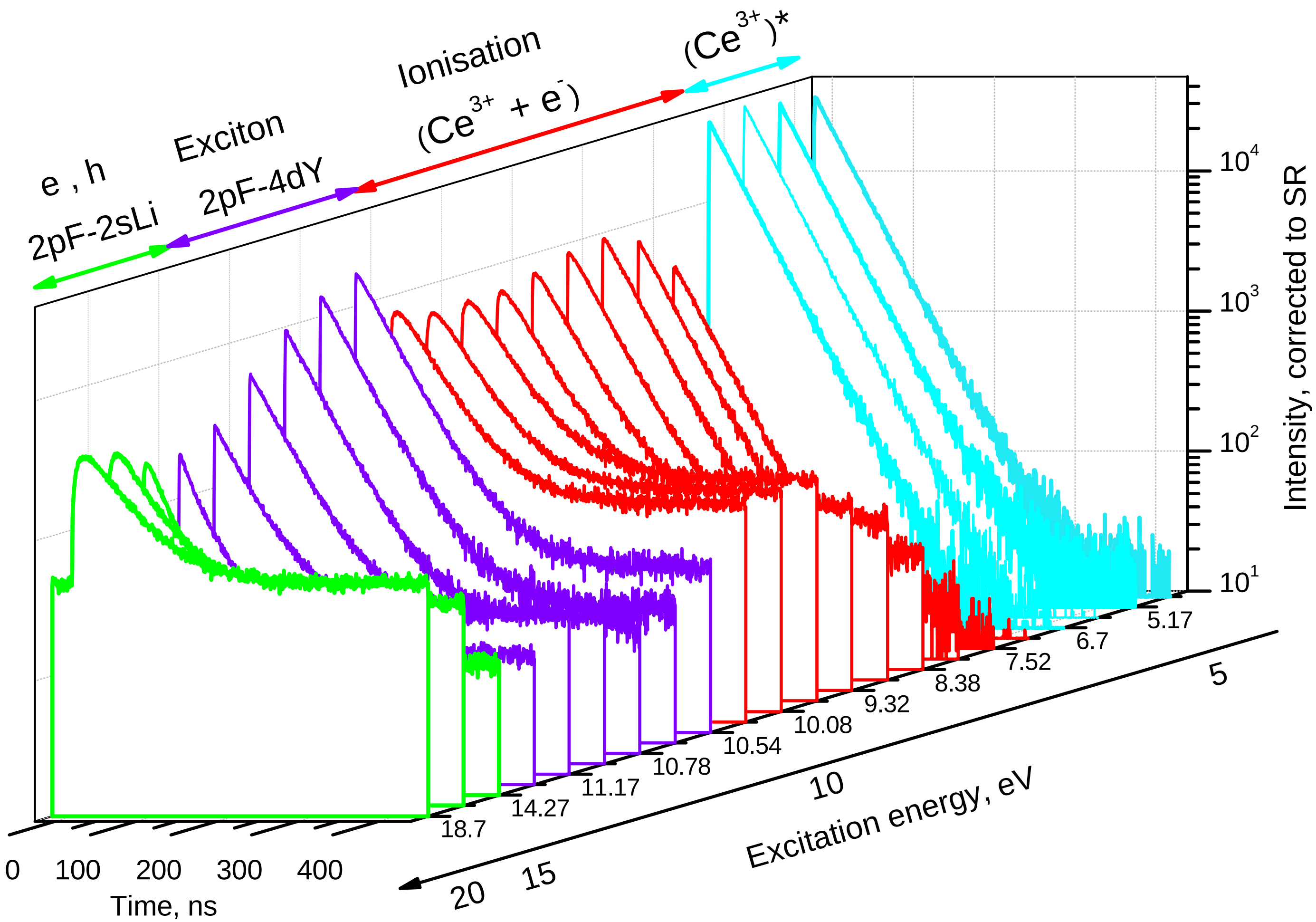
Recovery of Ce^{3+} centers after ionization



$LiYF_4:Ce^{3+}$ time resolved excitation spectra



$LiYF_4:Ce^{3+}$ decays, RT



Recovery of Ce^{3+} centers after ionization

$$-\left(\frac{d\,n_{Ce^{4+}}(t)}{dt}\right)_{diff} = \frac{N}{V}\left[\Phi\left(\frac{R_c}{R_0}\right) - \frac{2}{\sqrt{\pi}}\frac{R_c}{R_0}\exp\left(-\frac{R_c^2}{R_0^2}\right) + \frac{4}{3}\pi R_c^3 n_{nc}\right]\delta(t+0)$$

$$+\frac{N}{V}\frac{4R_c^2 R_0\sqrt{D}\exp\left(-\frac{R_c^2}{R_0^2}\right)}{\pi\sqrt{t}\left(R_0^2+4Dt\right)^2} + \frac{N}{V}\frac{4R_c D\left(R_0^2+4Dt-2R_c^2\right)}{\sqrt{\pi}\left(R_0^2+4Dt\right)^{5/2}}\exp\left(-\frac{R_c^2}{R_0^2+4Dt}\right)\left[1-\Phi\left(2\frac{R_c}{R_0}\sqrt{\frac{Dt}{R_0^2+4Dt}}\right)\right]$$

$$+4\pi D R_c n_{nc}\left(1+\frac{R_c}{\sqrt{\pi D t}}\right)n_{Ce^{4+}}(t)$$

3 main parameters:

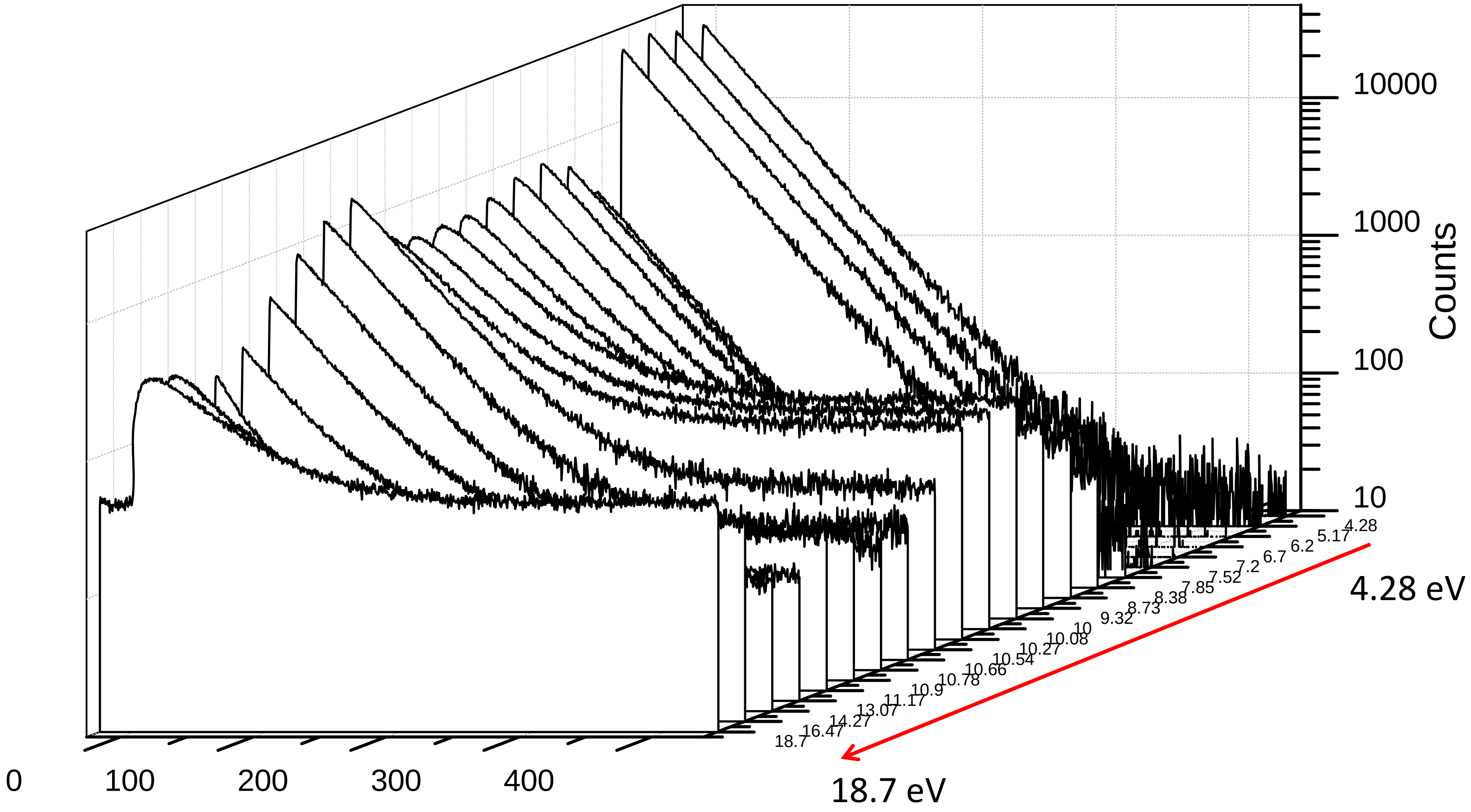
R_0/R_c (thermalization radius to capture radius)

n_{nc} (concentration of non-correlated carriers)

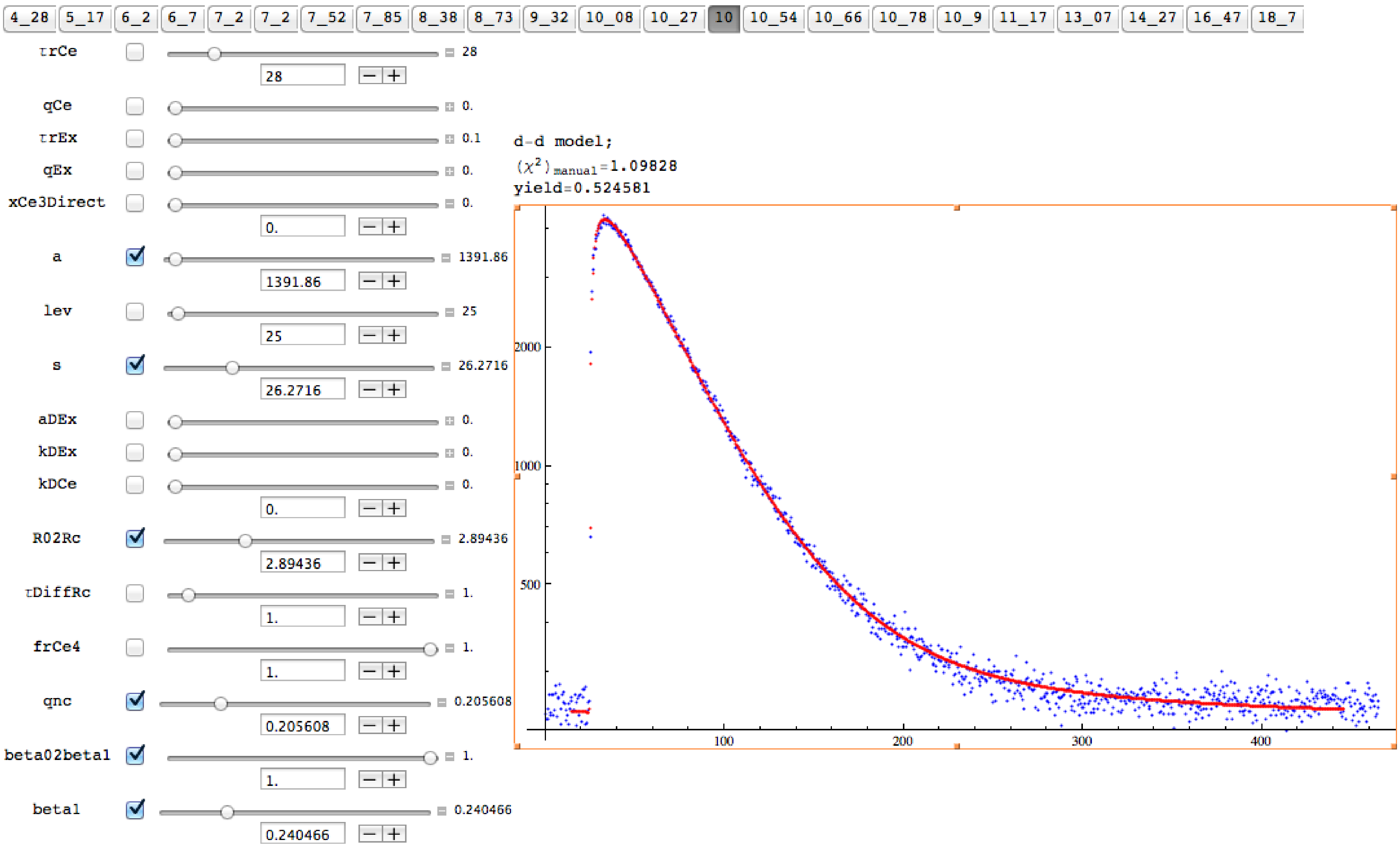
R_c^2/D (time of diffusion across capture sphere)

$LiYF_4:Ce^{3+}$ decays

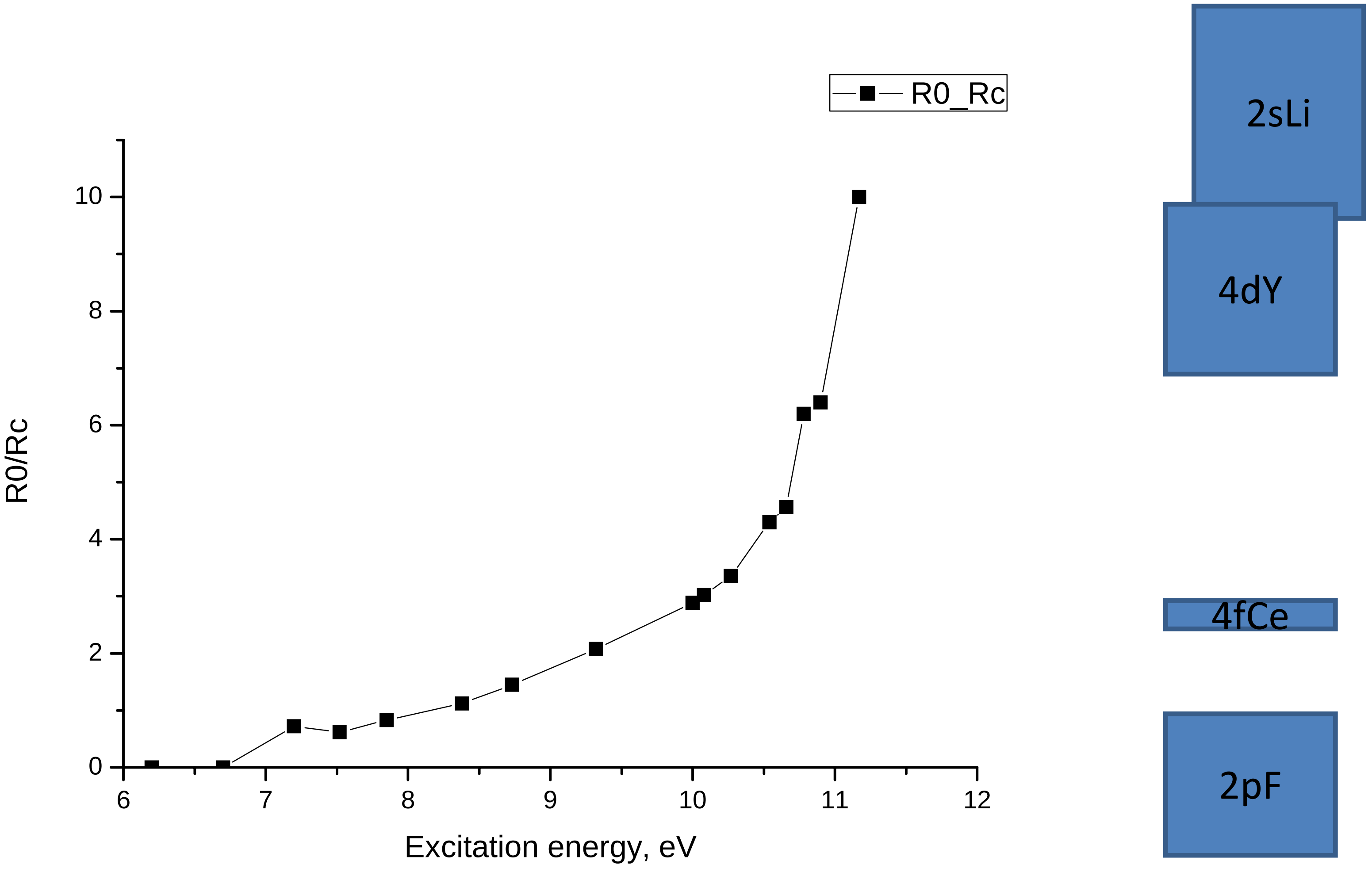
K. Ivanovskikh, A. Belsky, M. Reid, Y. Guyot, L. Nurtdinova, V. Semashko, M.-F. Joubert,
to be published



$LiYF_4:Ce^{3+}$ 10 eV



$LiYF_4:Ce^{3+}$ R_0/R_c vs energy



Coupled processes of thermalization and spatial diffusion

Mean square of the thermalization distance

$$< r^2 >_{E_{e0} \to E_e^{kin}} = 6 \int_{E_e^{kin}}^{E_{e0}} \frac{D^R(E')}{S(E')} dE'$$

Spatial distribution function

$$f(r, l_e(E_{e0})) = \frac{3\sqrt{6}\, r^2}{\sqrt{\pi}\, l_e^3(E_{e0})} \exp\left(-\frac{3r^2}{2 l_e^2(E_{e0})} \right)$$

where thermalization length is

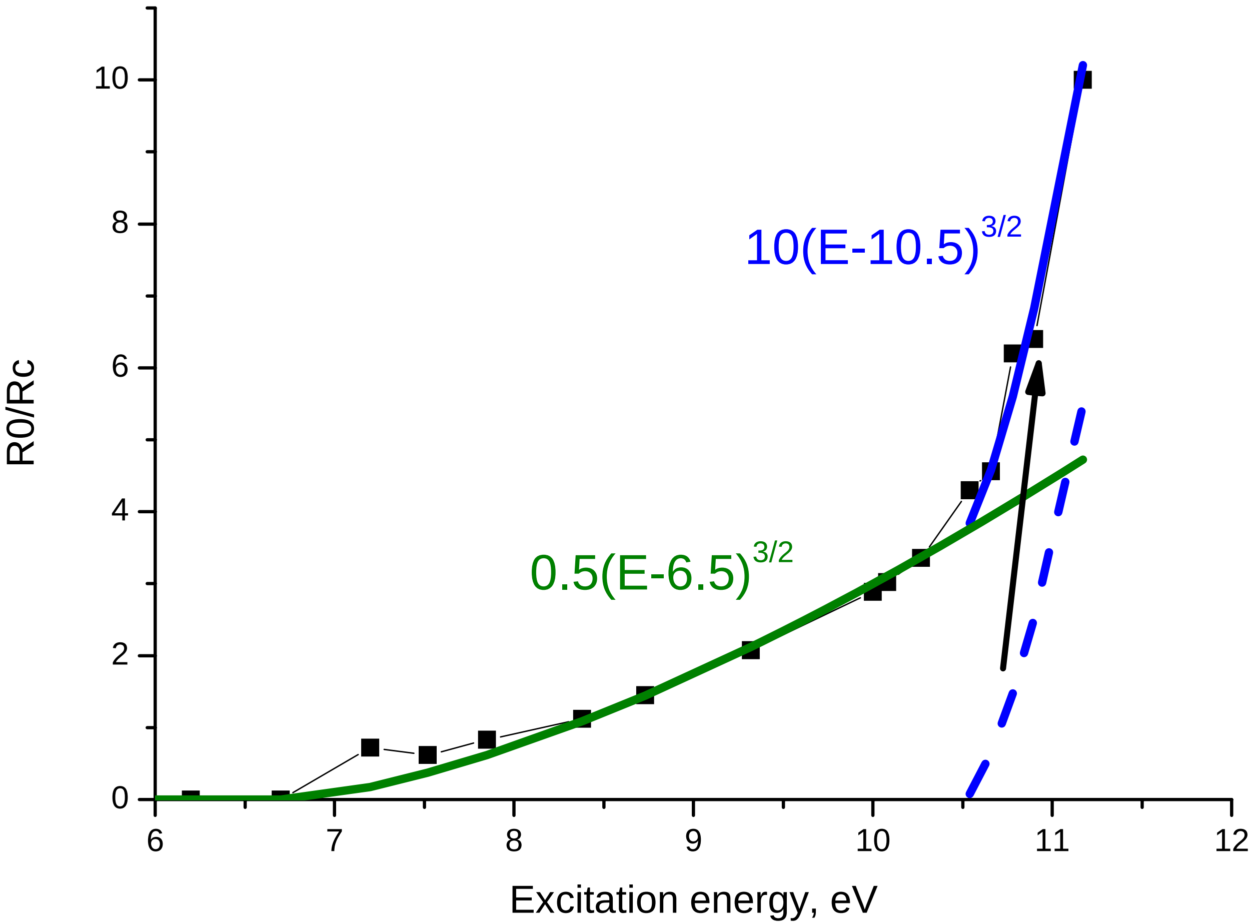
$$l_e(E_{e0}) = \sqrt{< r^2 >_{E_{e0} \to k_B T}}$$

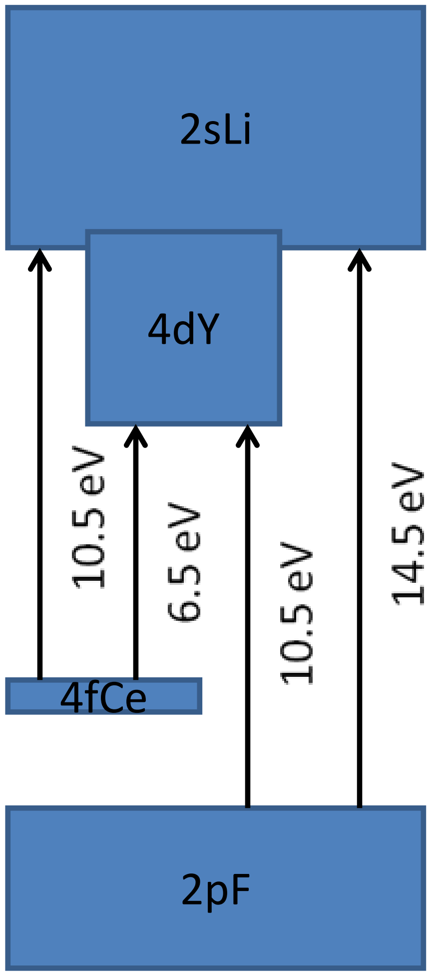
Thermalization length for one LO phonon branch

$$l_{e,LO}^2(E_{e0}) = \frac{8}{3} a_B^2 \left(\frac{\tilde{\varepsilon}}{m_e^* / m_0} \right)^2 \tanh\left(\frac{\hbar\Omega_{LO}}{2k_B T} \right) \int_{\hbar\Omega_{LO}}^{E_{e0}} \left(\frac{E'}{\hbar\Omega_{LO}} \right)^2 \frac{1}{\ln(4E'/\hbar\Omega_{LO})} \frac{dE'}{\hbar\Omega_{LO}}$$

$$= \frac{1}{24} a_B^2 \left(\frac{\tilde{\varepsilon}}{m_e^* / m_0} \right)^2 \tanh\left(\frac{\hbar\Omega_{LO}}{2k_B T} \right) \mathrm{Ei}\left(3\ln\left(\frac{4E_{e0}}{\hbar\Omega_{LO}} \right) \right),$$

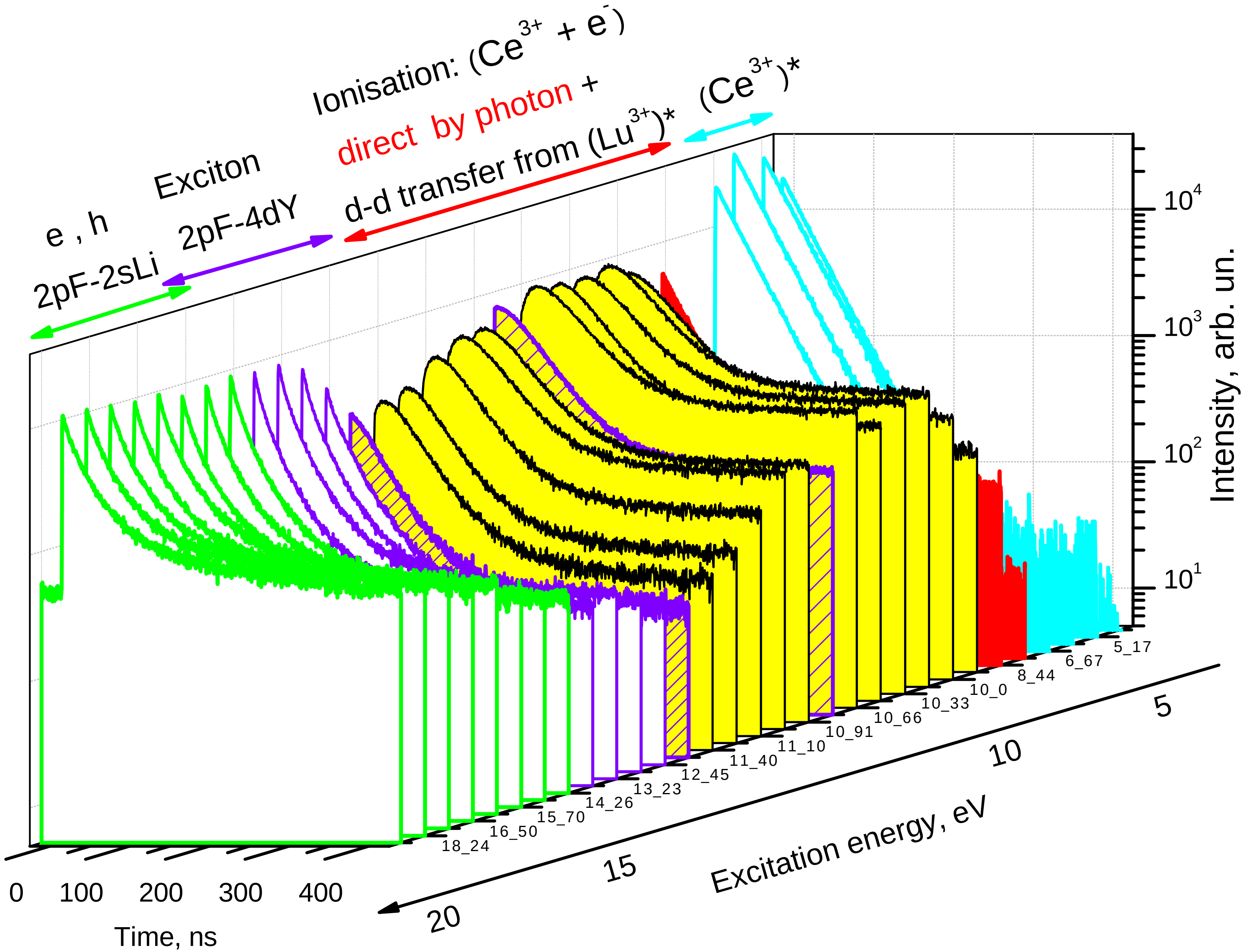
$LiYF_4:Ce^{3+}$ R_0/R_c vs energy



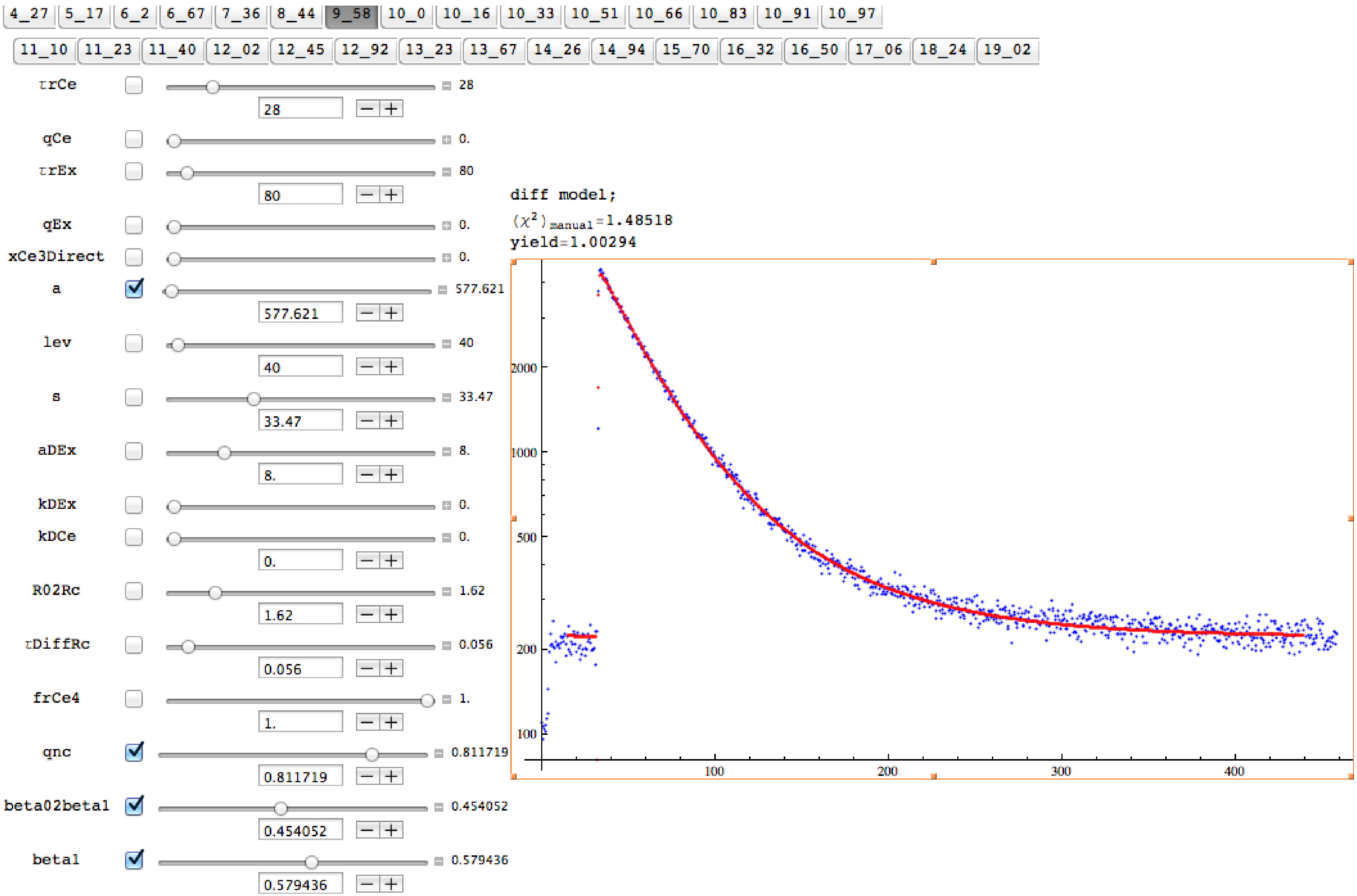


$m_{eff,4dY}/m_{eff,2sLi}=20$

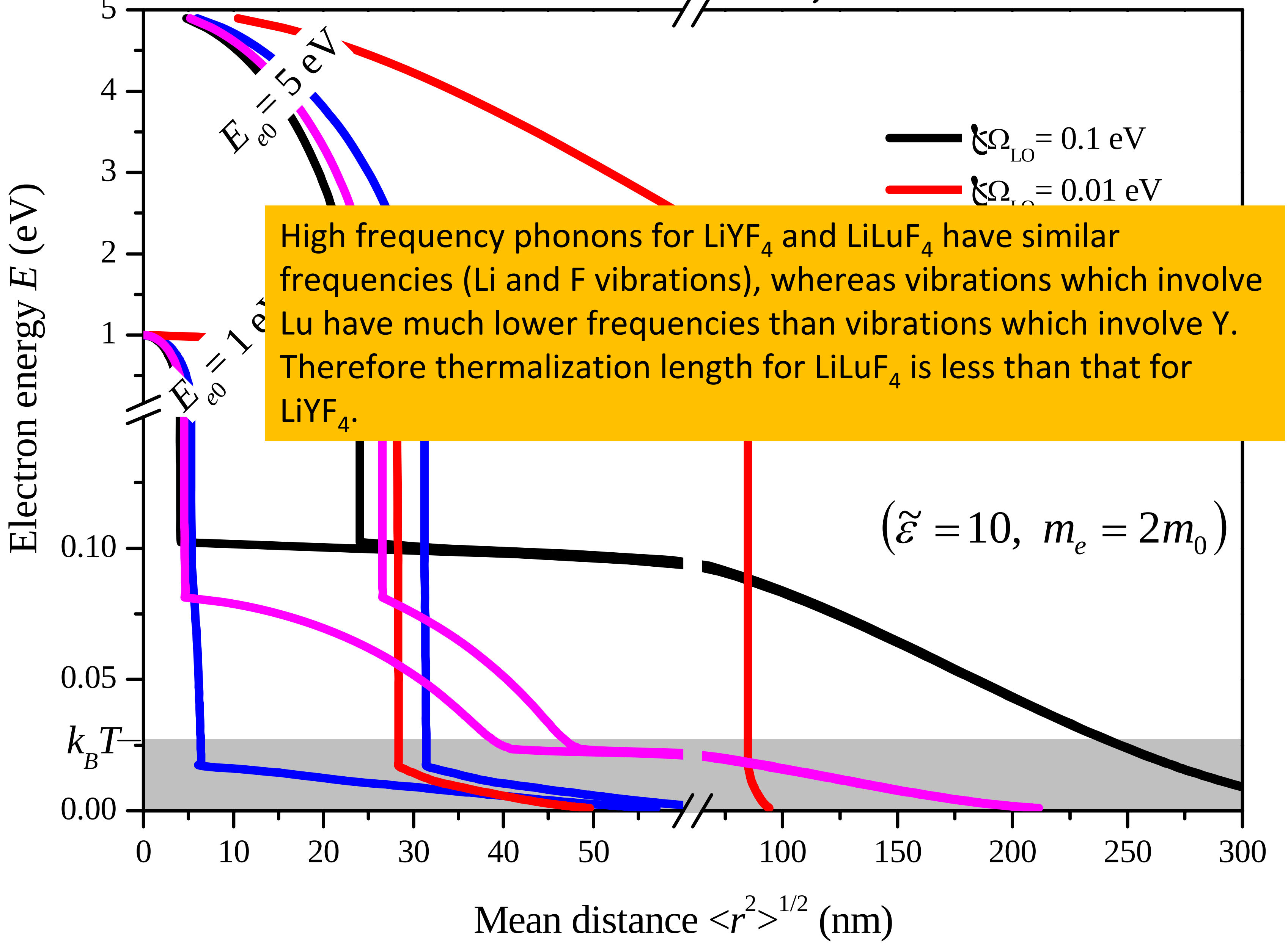
LiLuF$_4$:Ce^{3+} decays, RT



$LiLuF_4$:Ce^{3+} 9.58 eV

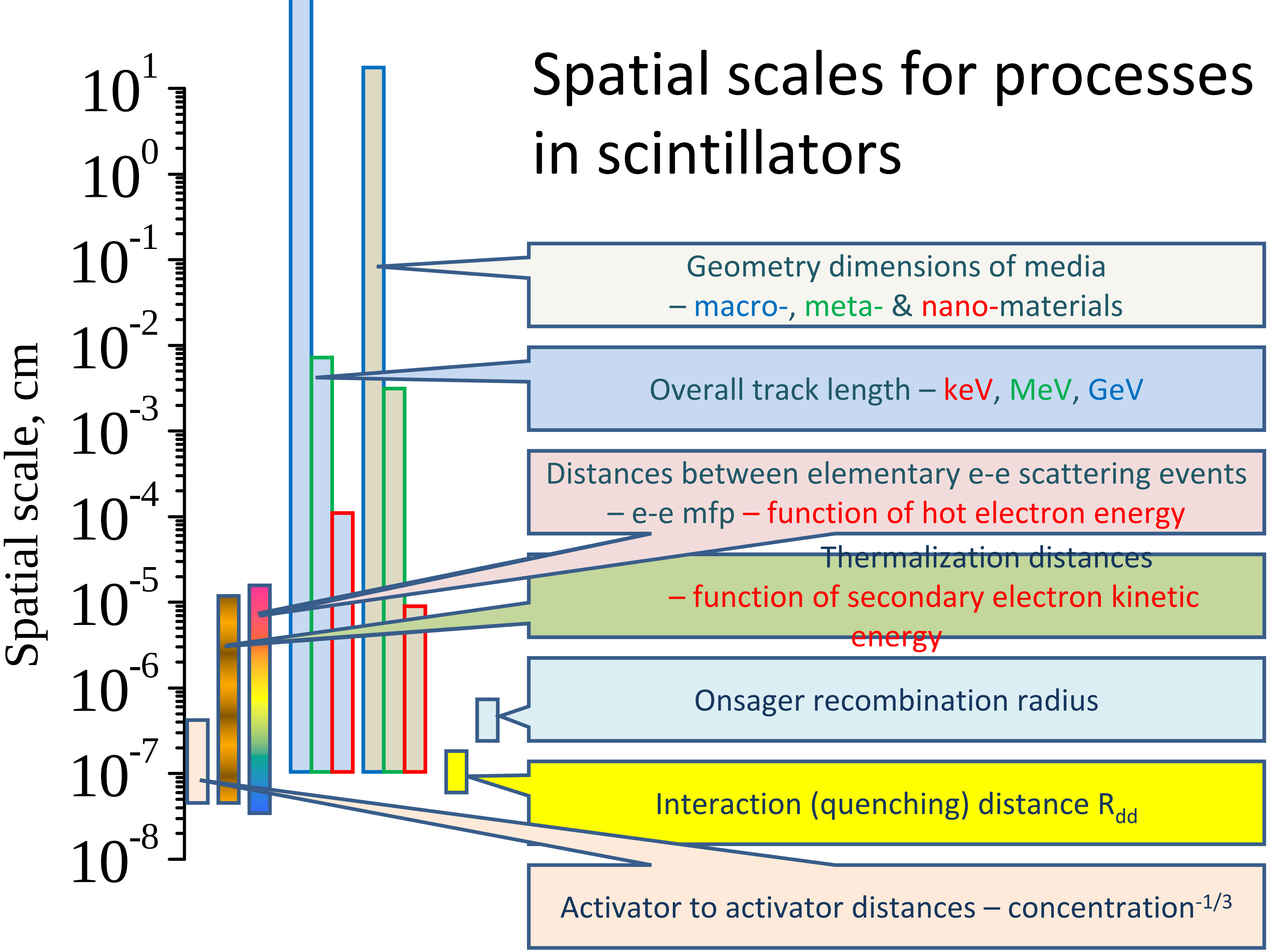


Estimation of mean thermalization distance R_0 for different initial kinetic energy energy (R.Kirkin, V.Mikhailin, A.N.Vasil'ev, IEEE TNS, DOI 10.1109/TNS.2012.2194306)



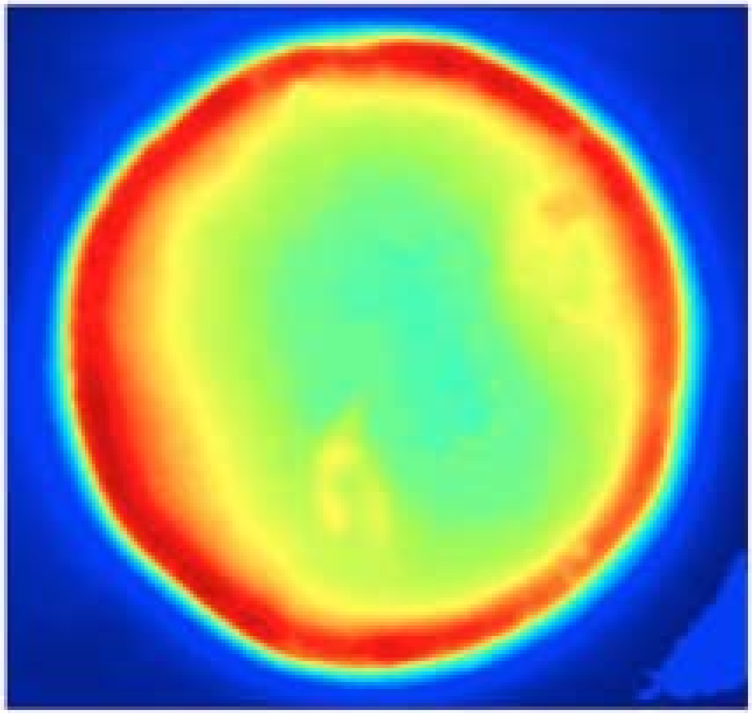
High frequency phonons for $LiYF_4$ and $LiLuF_4$ have similar frequencies (Li and F vibrations), whereas vibrations which involve Lu have much lower frequencies than vibrations which involve Y. Therefore thermalization length for $LiLuF_4$ is less than that for $LiYF_4$.

Spatial scales for processes in scintillators



Meta-scale

10 KeV electron excitation of LuAG:Ce fiber d=1 mm

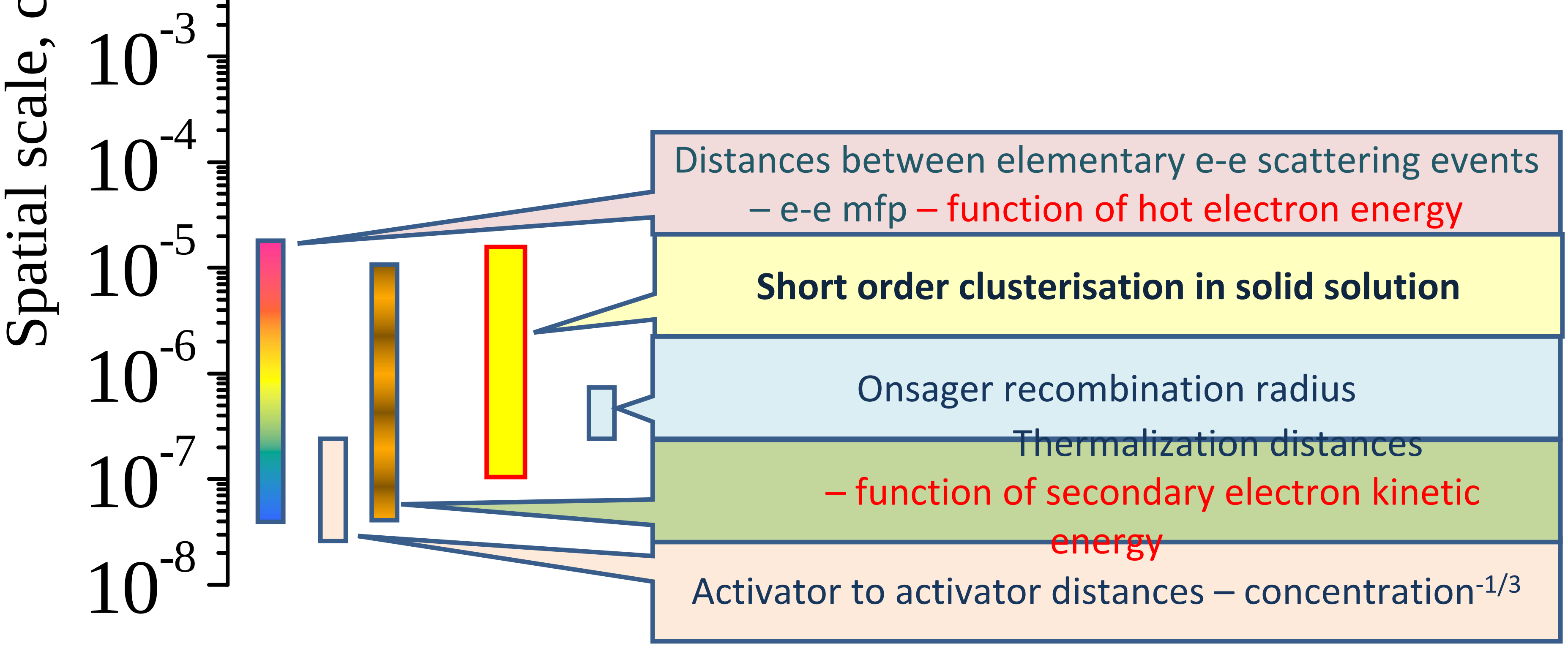


Non-uniform distribution of properties

understanding the relaxation in real materials

Spatial scales for processes
Solid solutions of scintillators

Micro-nano-scale:
Characteristic dimension of relaxation process



Spatial scales for processes
Solid solutions of scintillators

Micro-nano-scale:
Modulation of crystal electronic structure

More evident reason is the modulation of band gap by variation of cations or anions ratio in solid solutions. It the case of very now (Zn,Cd)S solutions, and many others.

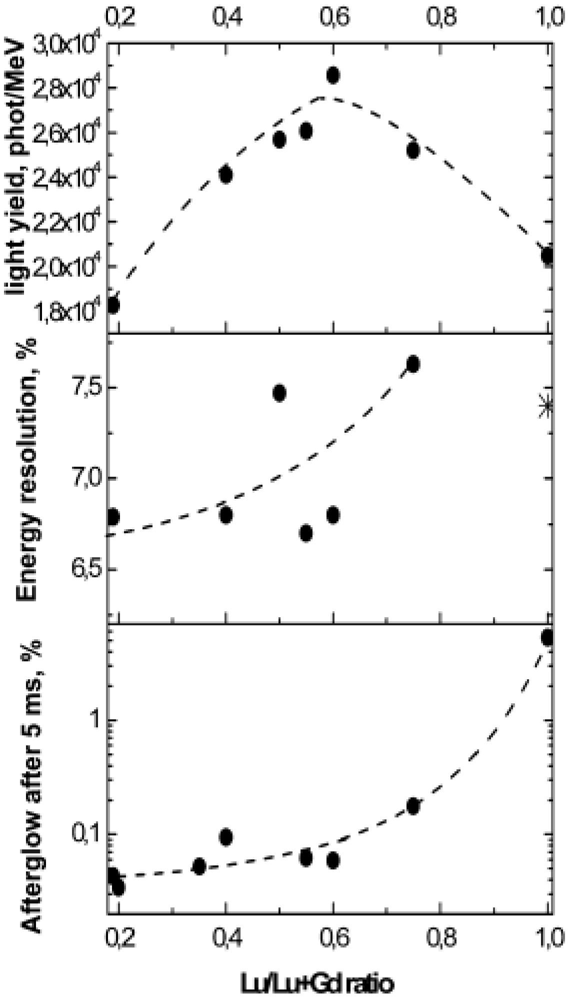
In this type of solid solution the suppression / creation of local states in forbidden energy gap is possible.

Spatial scales for processes
Solid solutions of scintillators

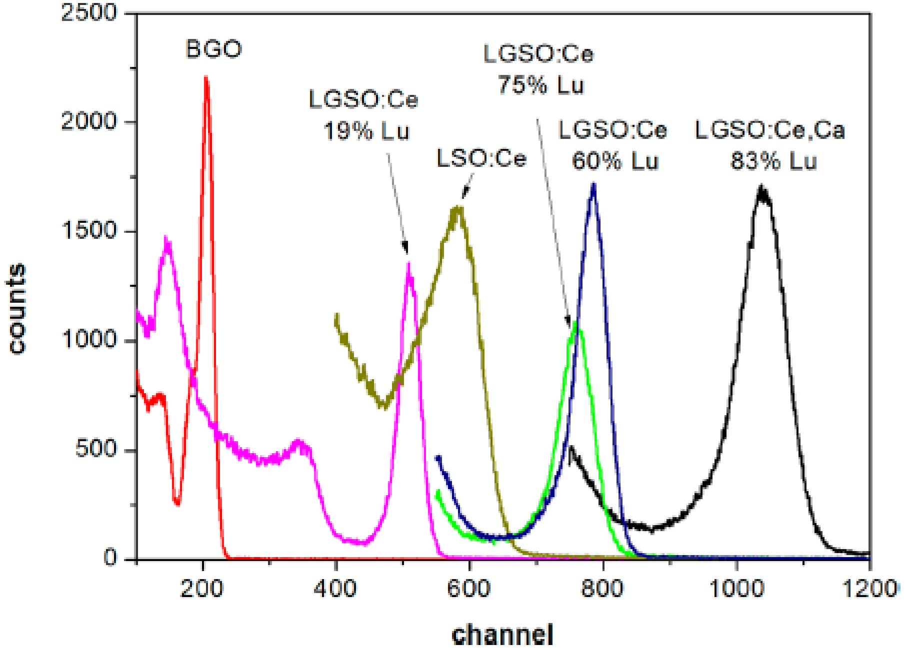
Micro-nano-scale:
Short range separation of components of solid solutions

short-range separation in solid solution may lead to formation of potential barriers limiting the e &h diffusion length. Clusterization should modify not only the edges of conductance and valence bands. Phonon spectrum of the crystal and distribution of density of electronic states inside the bands may slow down hot carriers and

Ce-Doped (Lu,Gd)2SiO5:Ce



Light yield (a), energy resolution (b) at 662 KeV, and afterglow (c) after 5 ms in LGSO:Ce crystals vs Lu concentration in host.



Pulse height spectra of some LGSO:Ce and LGSO:Ce,Ca crystals in comparison with BGO and LSO:Ce

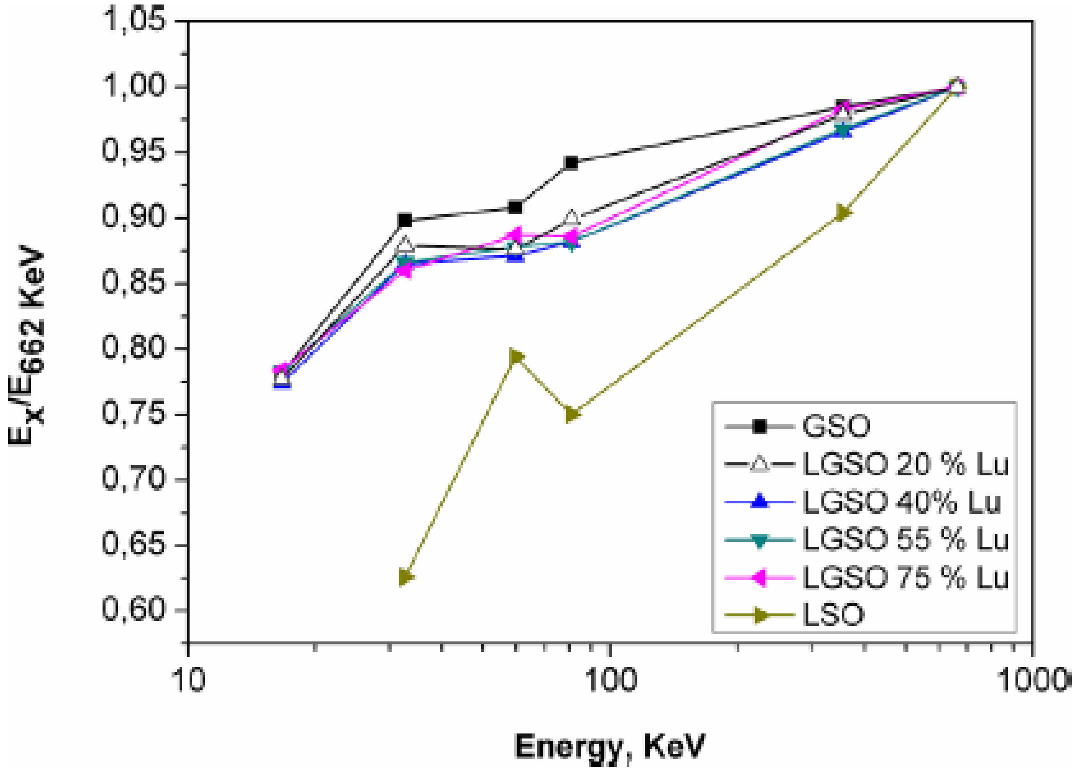


Figure 7. Nonproportionality characteristics of LGSO crystals with the different Lu contents.

Thank you for attention