Synchrotron radiation in spectroscopy

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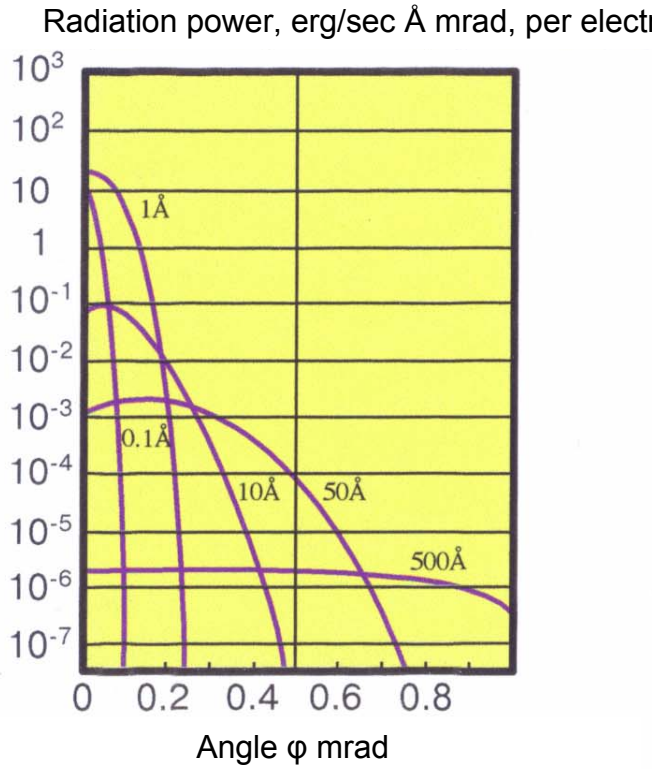
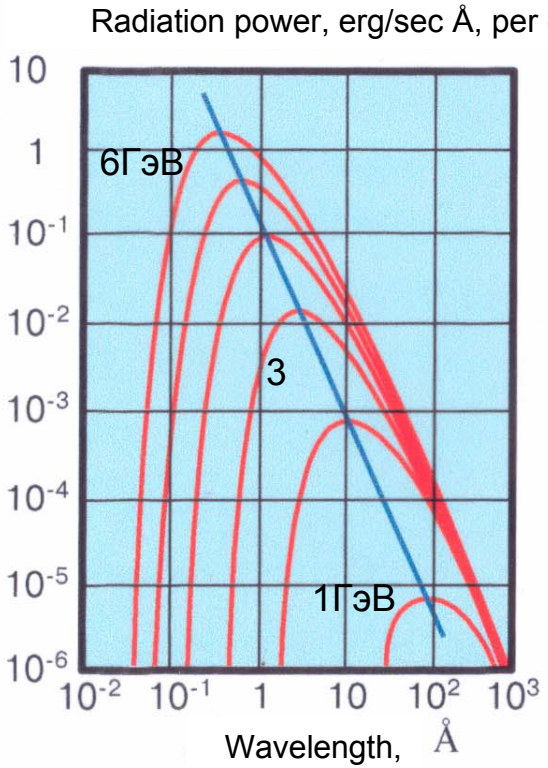
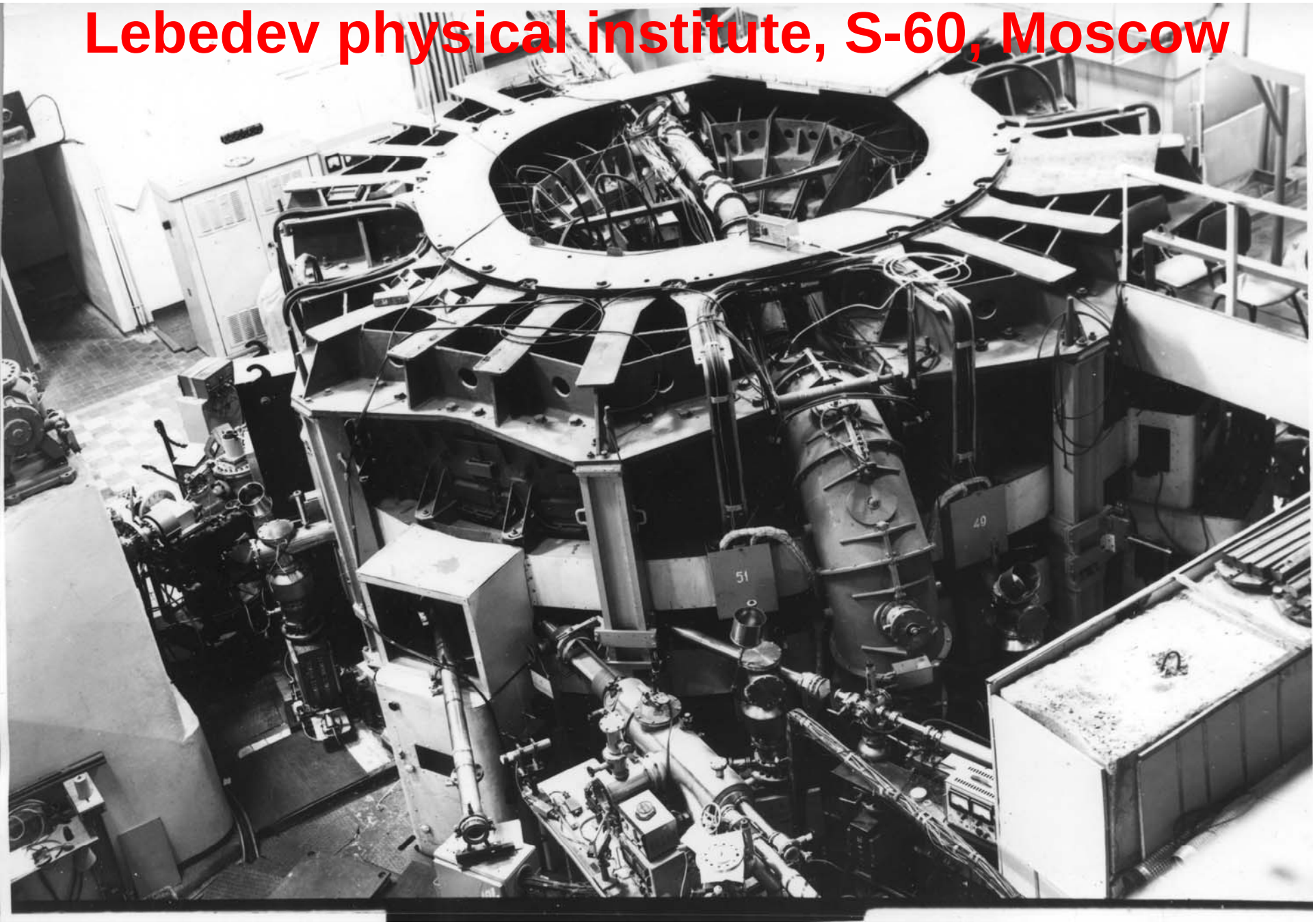
Synchrotron radiation properties: spectral and angular distribution





Lebedev physical institute, S-60, Moscow



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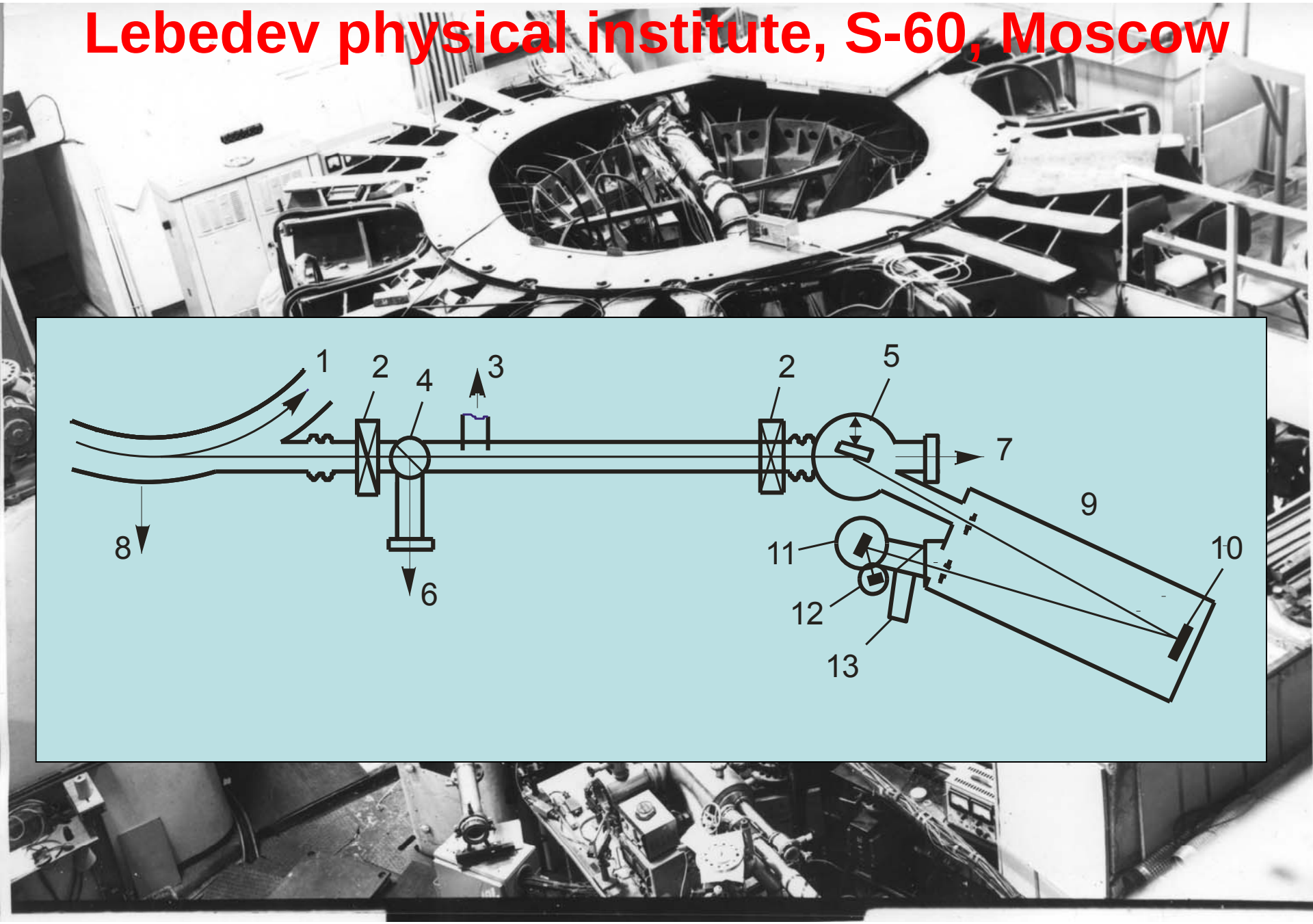
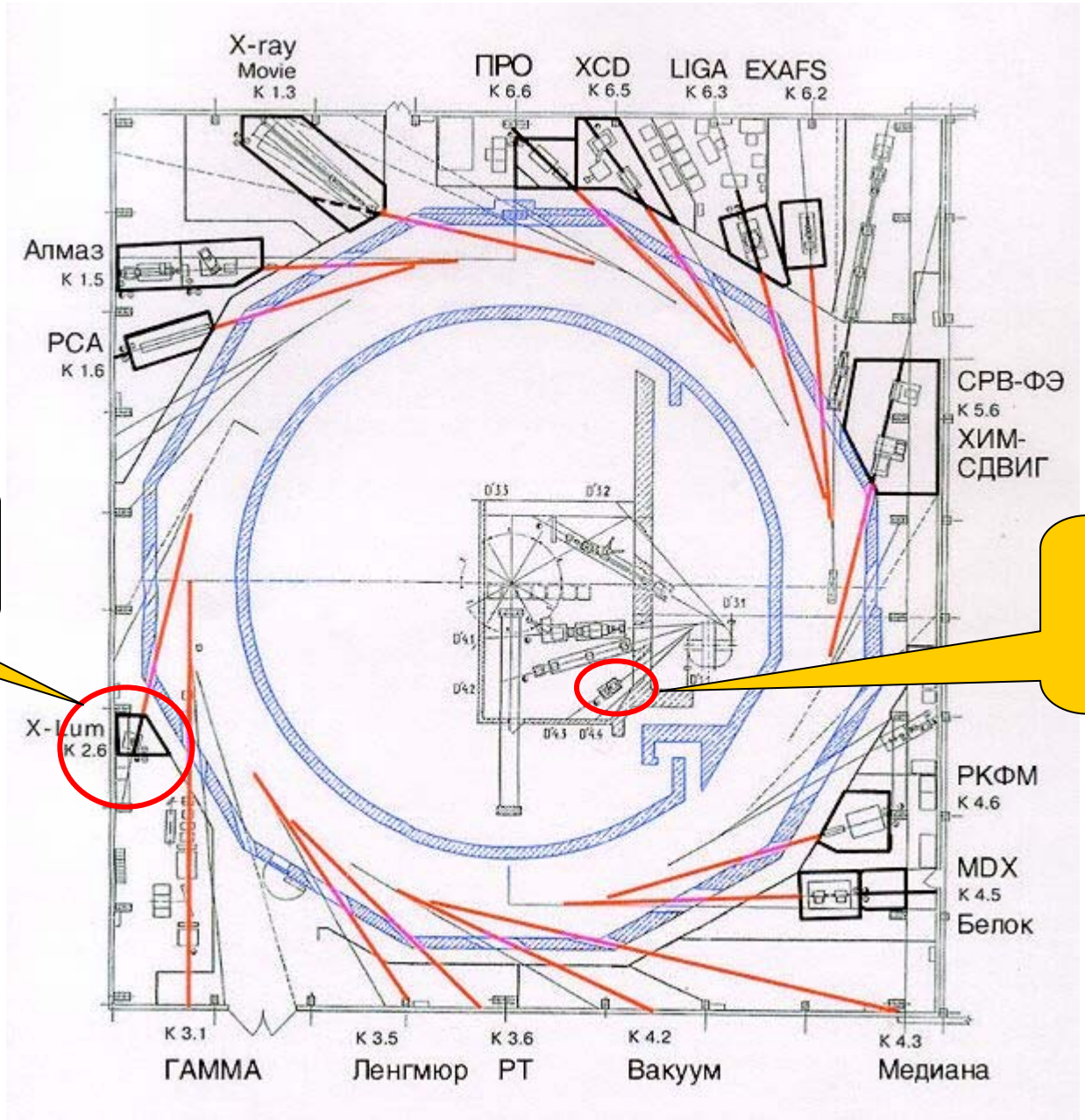


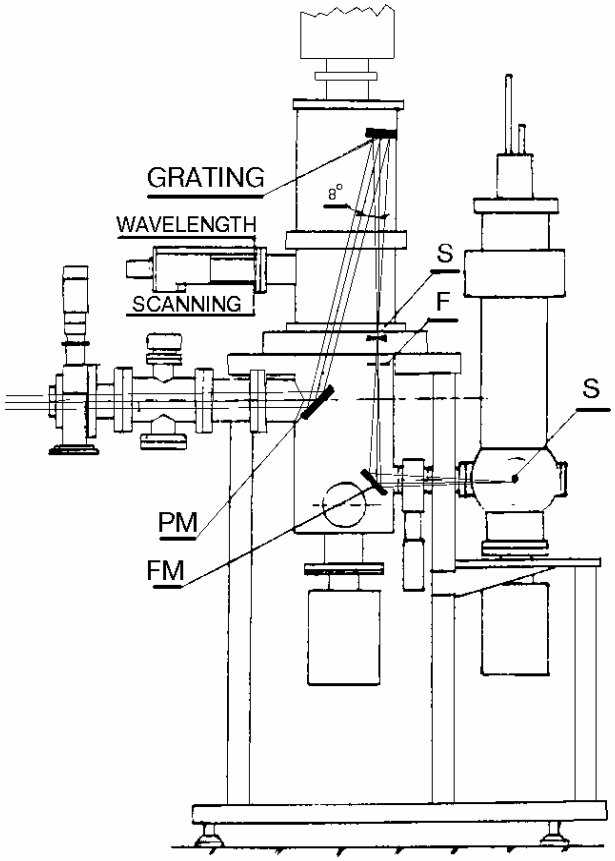
Siberia-2 and Siberia-1 (RNC “Kurchatov Institute”)

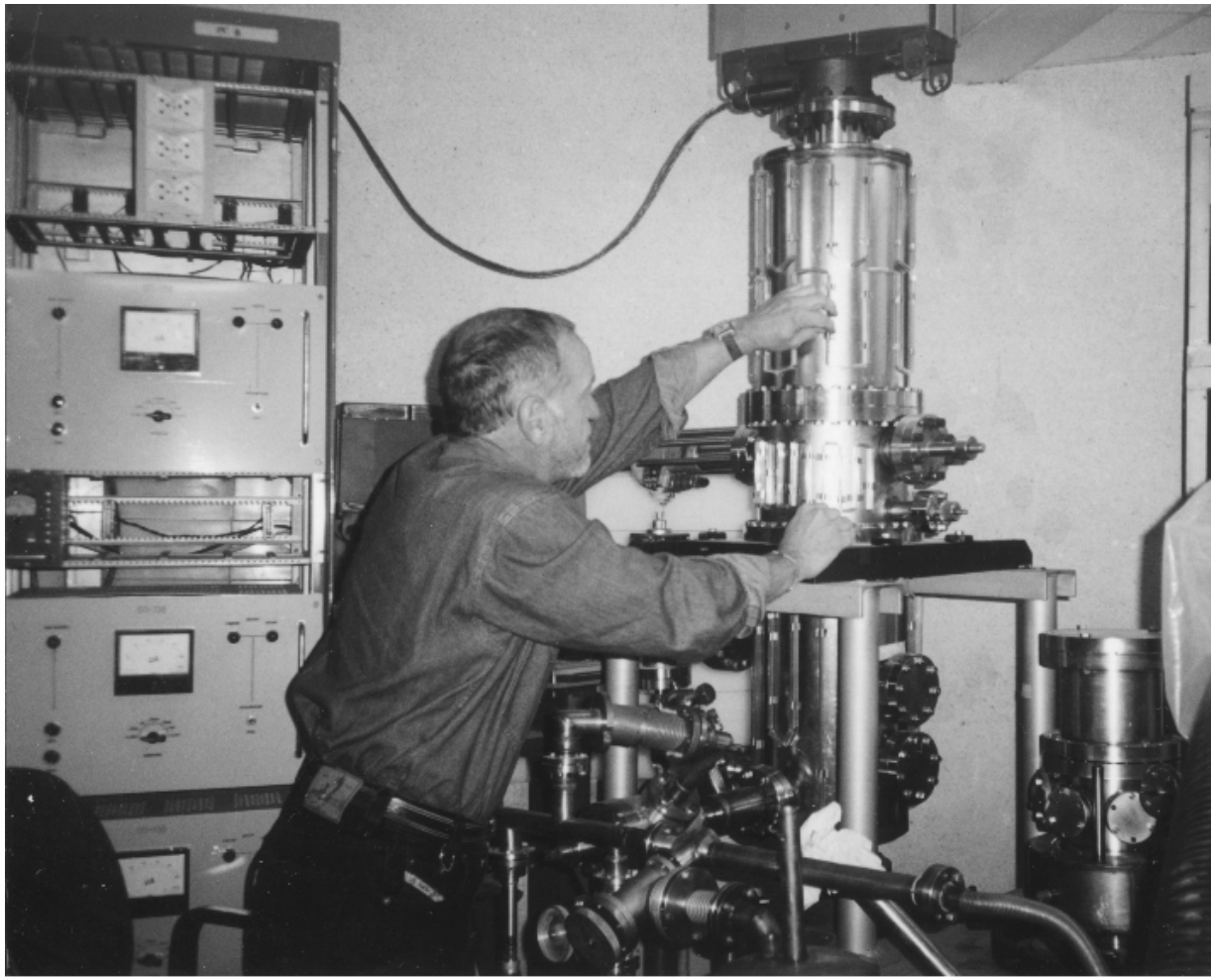


X-ray luminescence station (MSU)

VUV station (MSU)

VUV station at Siberia-1 storage ring (1998)





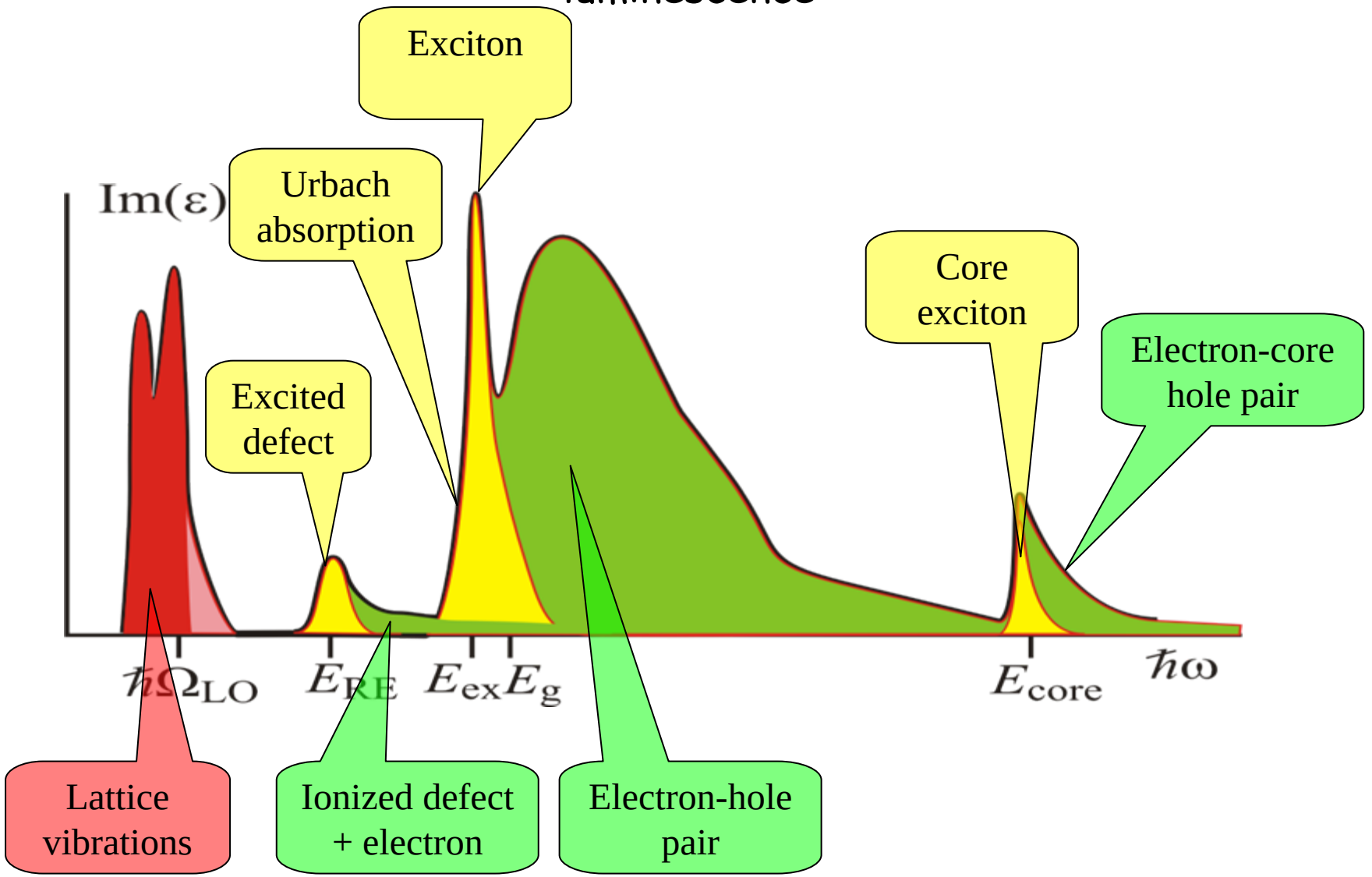
Unique spectral features and time structure of synchrotron radiation allows one to use this kind of excitation in investigation of electronic relaxation processes in insulators with wide band gap. The knowledge of these processes is important for understanding of scintillation efficiency in crystals. Luminescence excitation technique is convenient for study of energy transfer in these systems and for investigation of crystal energy structure.

In general, luminescence excitation spectra can be subdivided into several spectral regions:

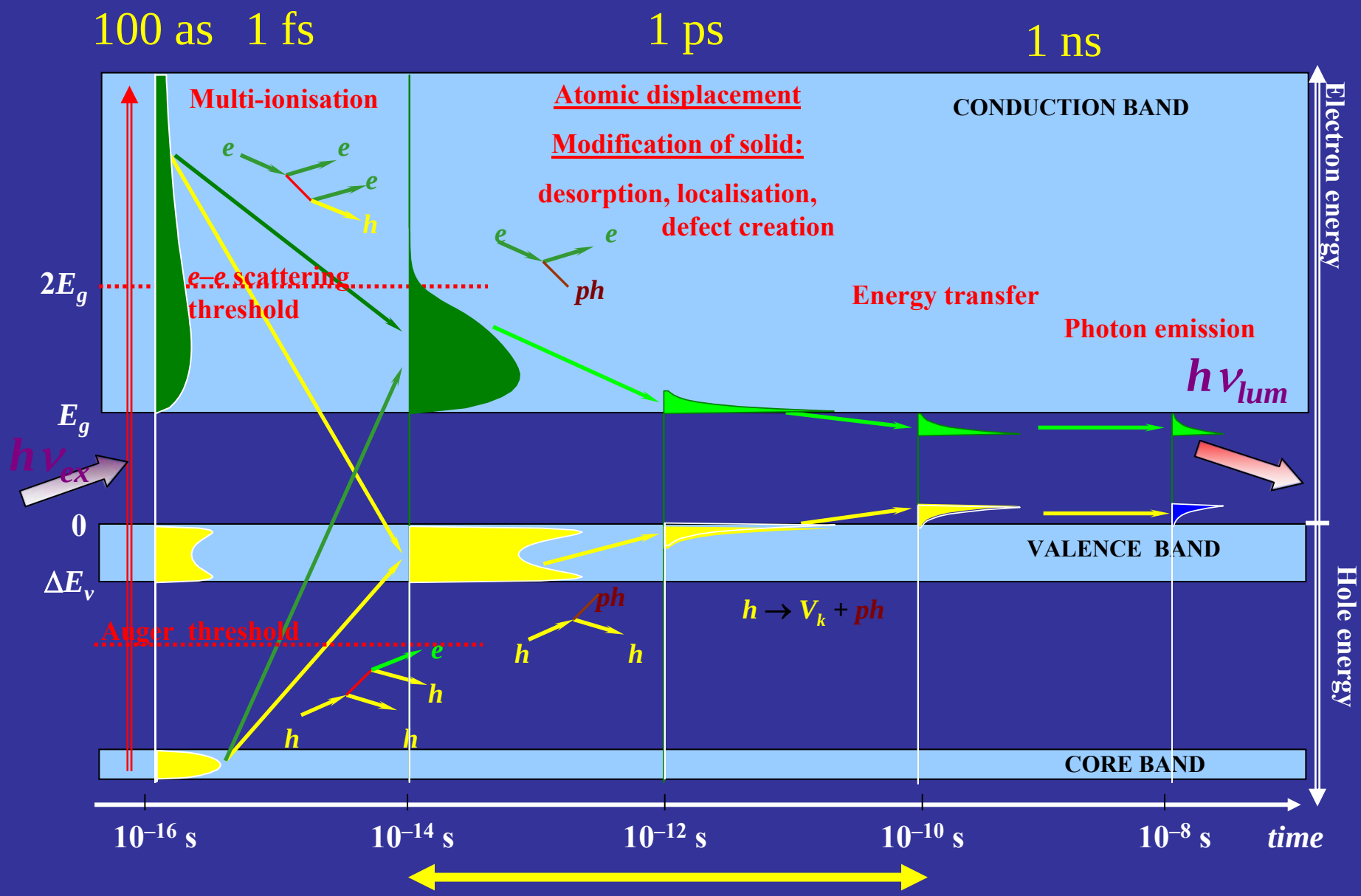
- Direct excitation of lowest defect excited state
- Ionization of defects by photons with energy below the matrix forbidden gap
- Excitation of matrix Urbach tail
- Excitation of excitons
- Production of separated low-energy electron-hole pairs
- Production of high-energy electron-hole pairs followed by impact excitation/ionization of defects

Each of these regions is characterized by different role of relaxation channels. Possible channels of energy transfer and relaxation are discussed in the presentation.

Absorption coefficient in wide photon energy range and different processes studied using synchrotron radiation excitation of luminescence



Dynamics of electronic relaxation in wide bandgap solids

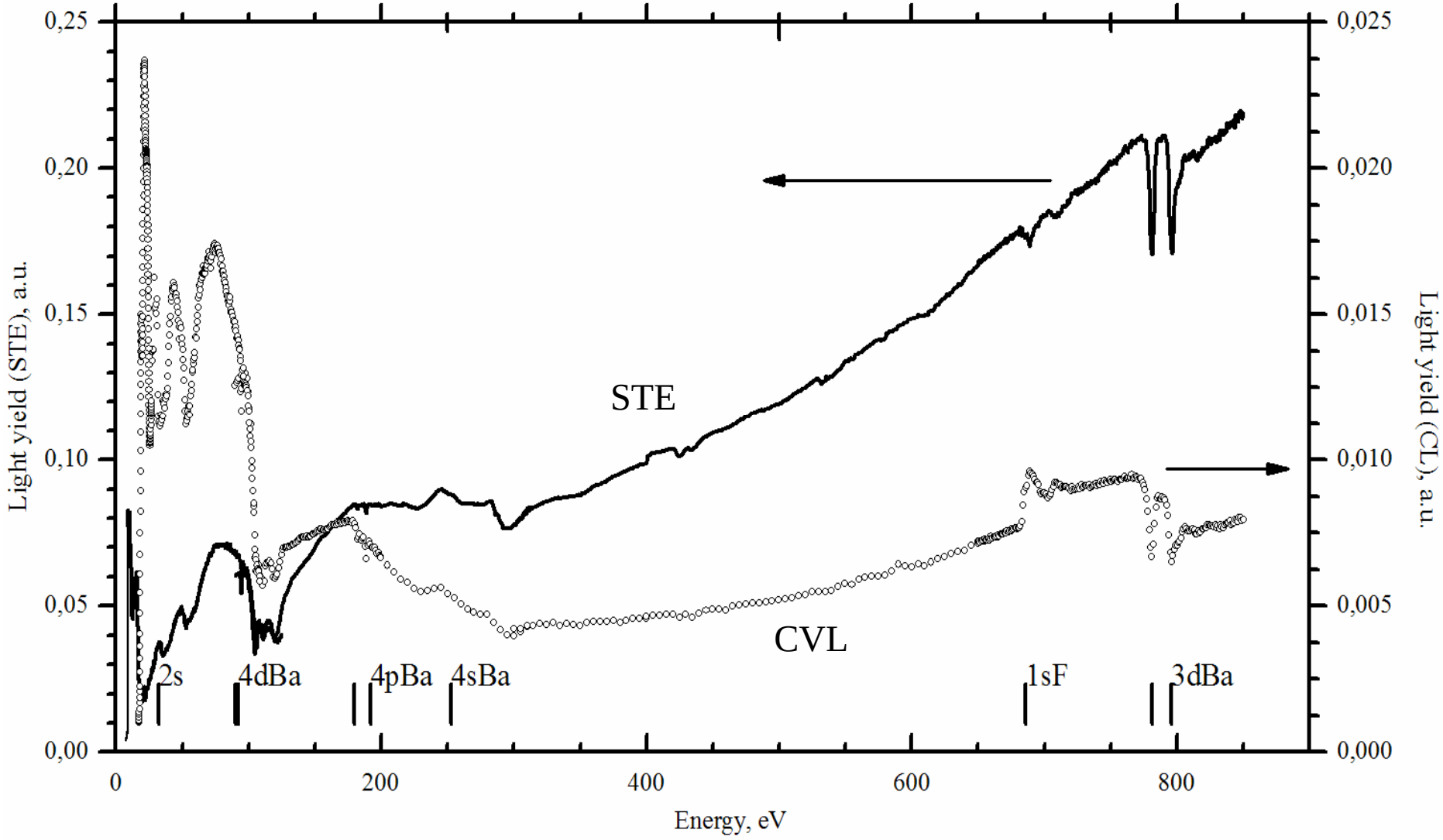


Energy relaxation processes which can are studied using synchrotron radiation

	Excitation range	Types of electronic excitations	Relaxation processes
Visible	$h\nu \le E_g$ $h\nu$ = 3÷10 eV	Excited and ionized states of defects and impurities. Self-trapped excitons	Scintillator and phosphor emission. Energy transfer between centers. Defect creation after exciton annihilation. Intrincic defect quenching.
UV			
VUV	$E_g \le h\nu \le (2\div3)E_g$ $h\nu$ = 5÷20 eV	Electron-hole pairs with energies below the threshold of secondary excitation creation. Free excitons.	Electron-phonon interaction resulting in thermalization and migration quenching (separation of electron-holee pair components). Diffusion of excitations. Trapping of excitations. Specific types of core hole relaxation (core-valence luminescence).
XUV Soft X X	$(2\div3)E_g \le h\nu \le (5\div10)E_g$, $h\nu$ = 15÷100 eV	Hot excitations with energy higher than the threshold of secondary excitation creation. Excitation of outermost core bands.	Electron-electron inelastic scattering and Auger processes resulting in multiplication of electronic excitations.
	$h\nu \ge (5\div10)E_g$, $h\nu$ > 50 eV	Core excitations.	X-ray fluorescence. Auger processes.
		Excited region which contains a hundreds of excitations. Tracks of ionizing particles.	Interaction of large number of electronic excitations.

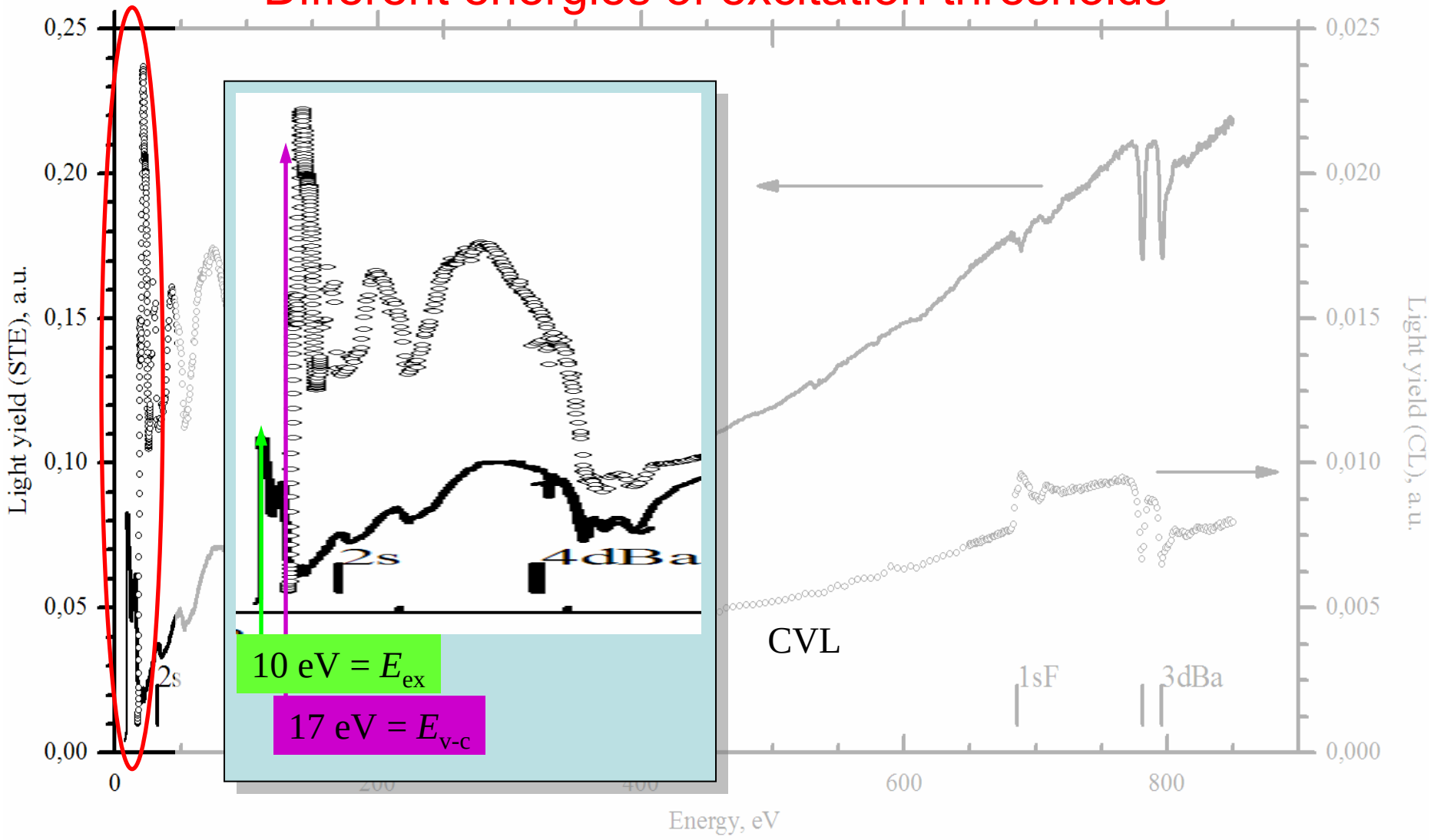
An example of excitation spectrum in which all of mentioned above effects are observed

Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points) [A.Belsky et al., LURE (France) + ELETRA (Italy)]



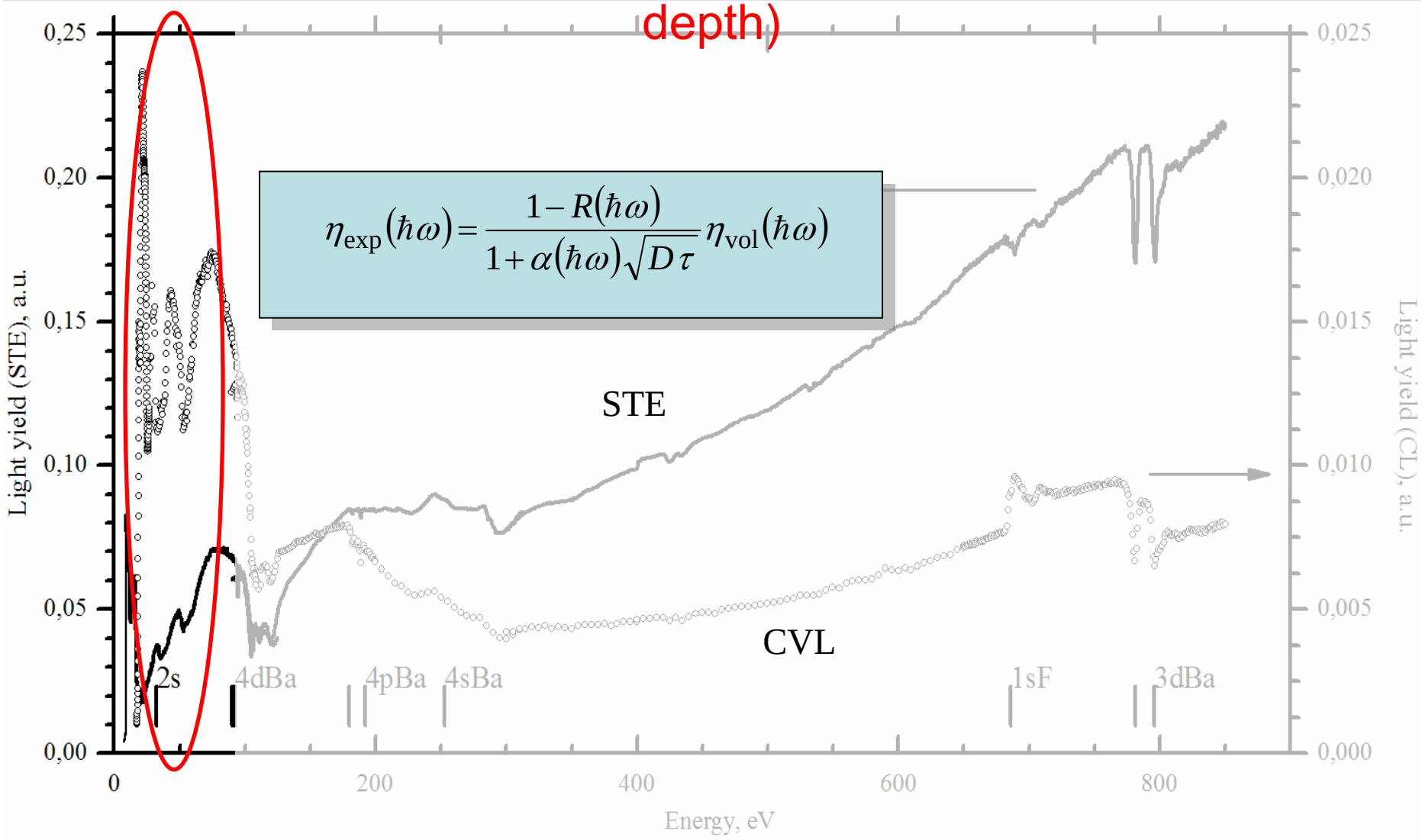
Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points)

Different energies of excitation thresholds



Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points)

Surface losses (pecularities due to radiation penetration depth)



Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points)

Local density effects

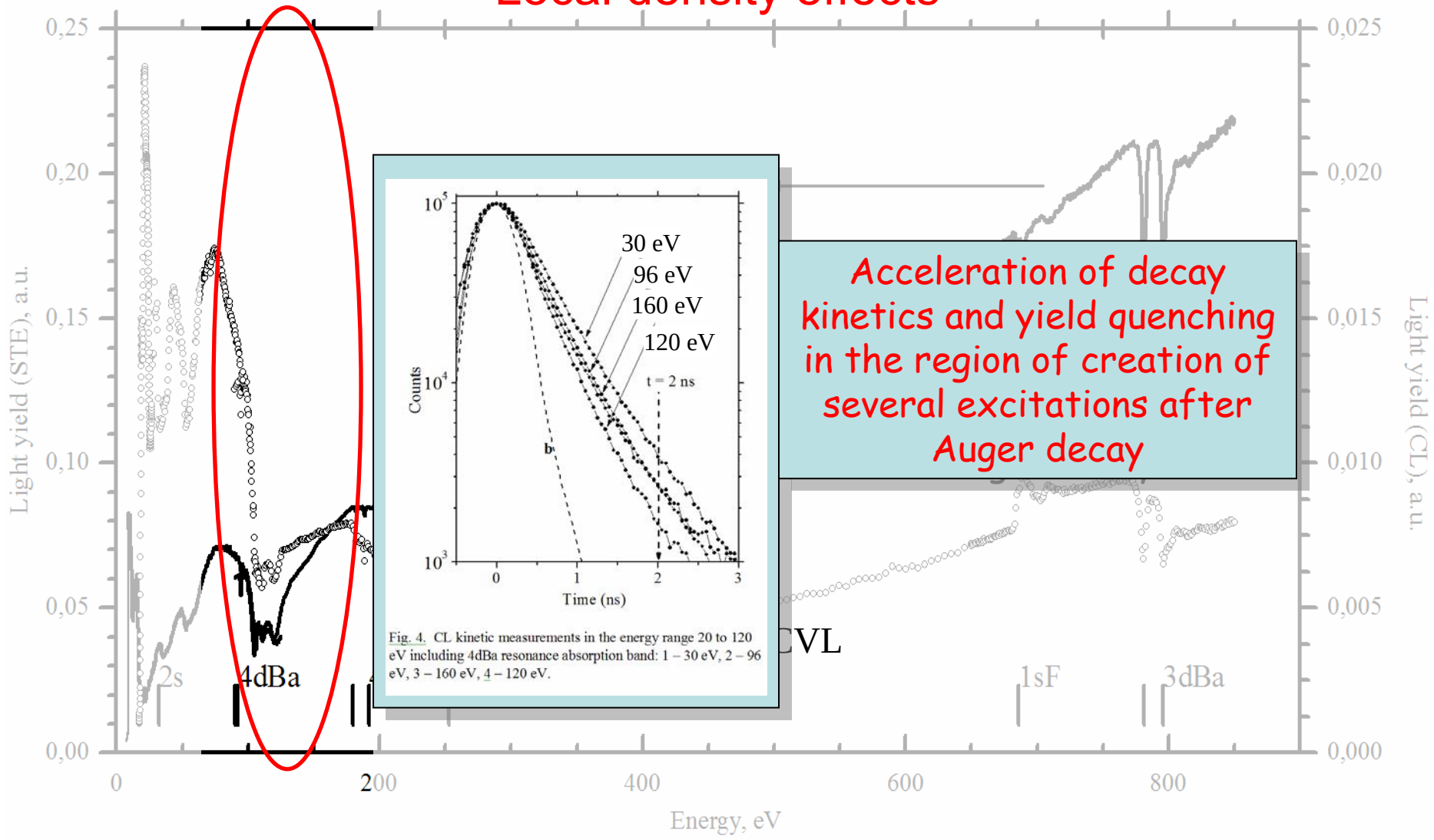
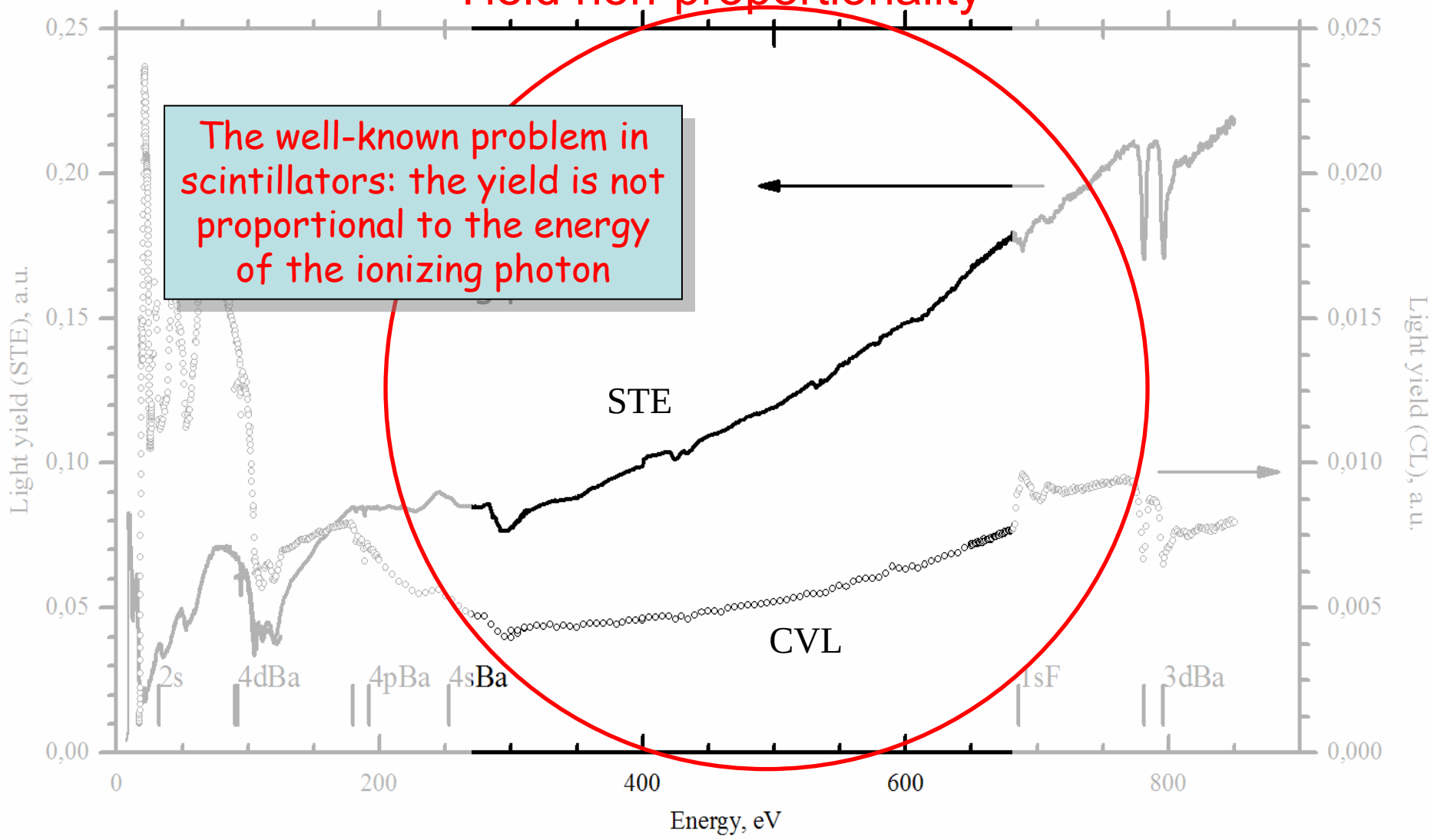


Fig. 4. CL kinetic measurements in the energy range 20 to 120 eV including 4dBa resonance absorption band: 1 – 30 eV, 2 – 96 eV, 3 – 160 eV, 4 – 120 eV.

Acceleration of decay kinetics and yield quenching in the region of creation of several excitations after Auger decay

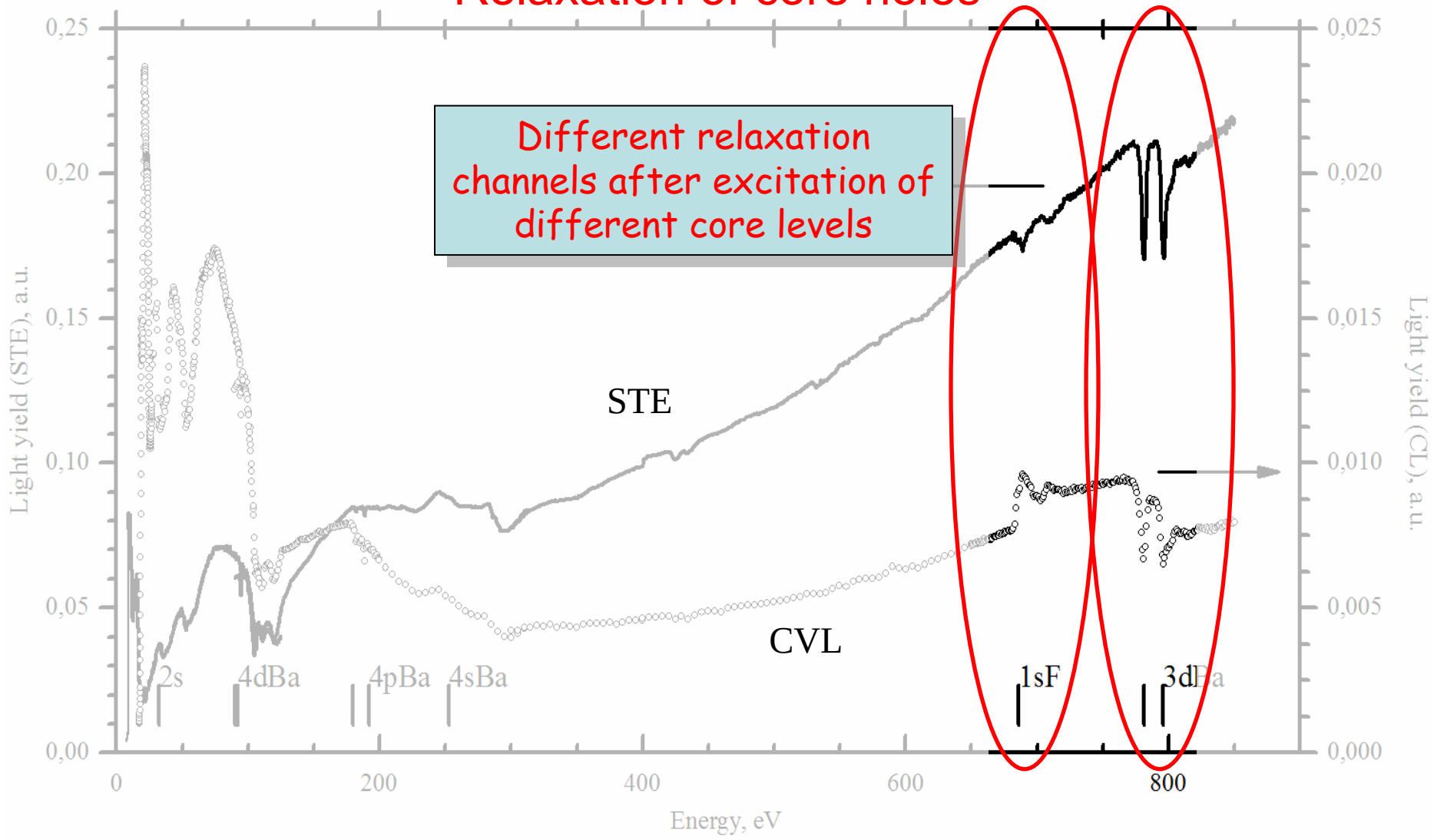
Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points)

Yield non-proportionality

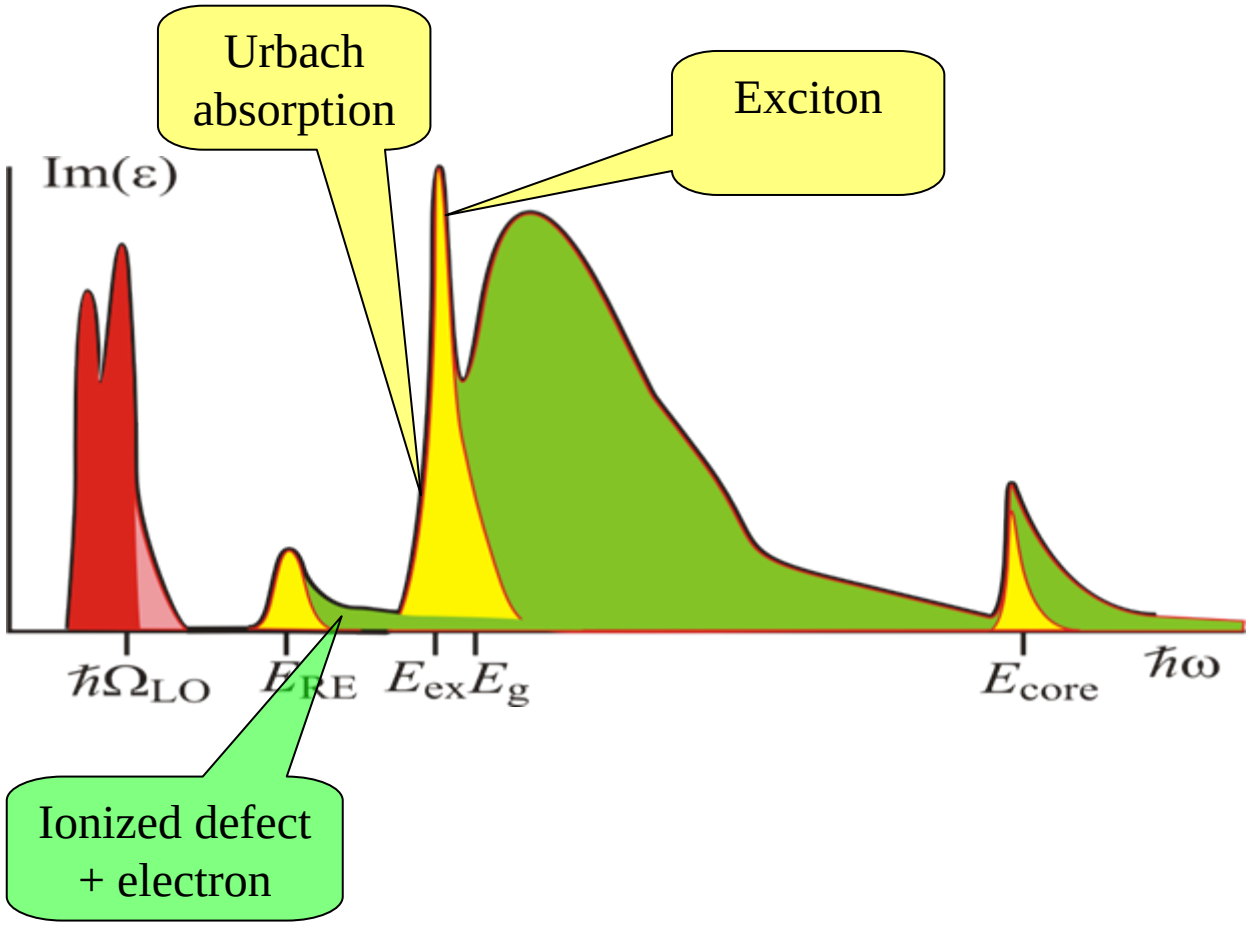


Excitation spectra for two emission bands in BaF_2: self-trapped exciton emission (solid) and core-valence transitions (points)

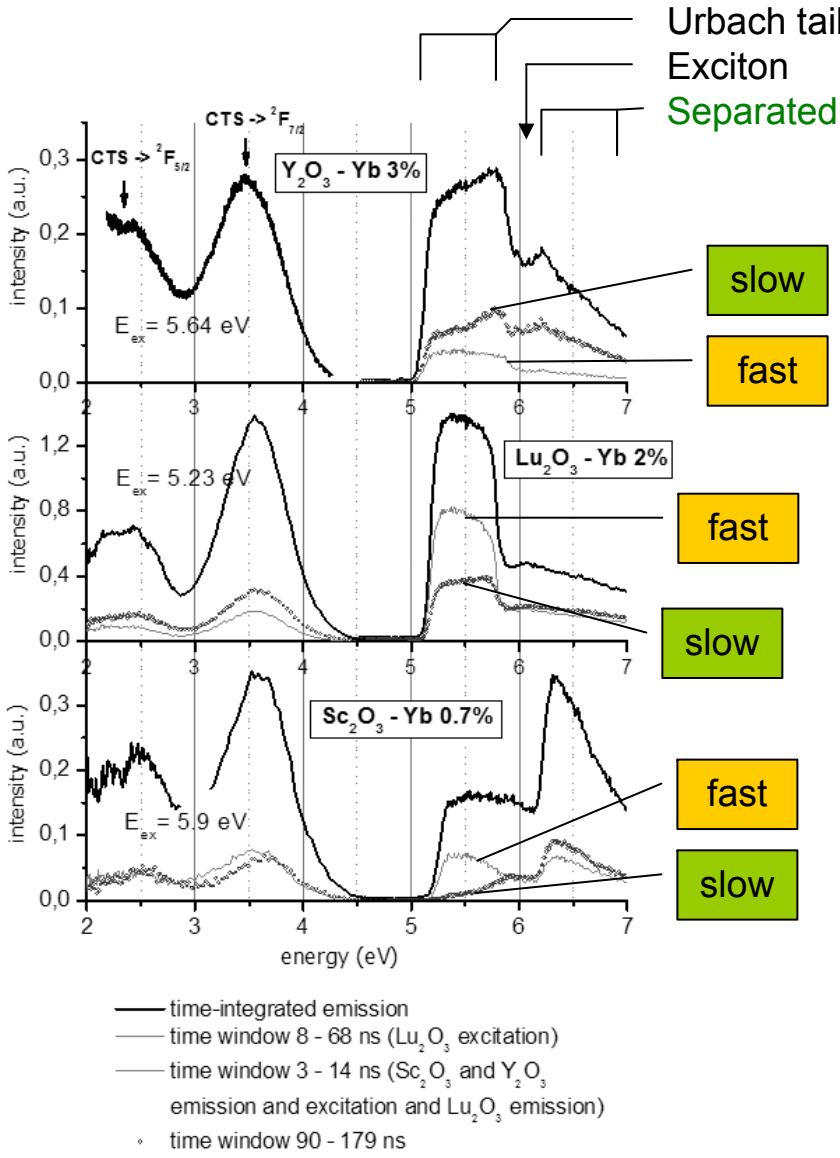
Relaxation of core holes

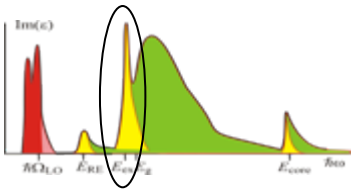


- Ionization of defects by photons with energy below the matrix forbidden gap
- Excitation of matrix Urbach tail



Yb^{3+} charge transfer luminescence (CTL) excitation (Guerassimova et al)

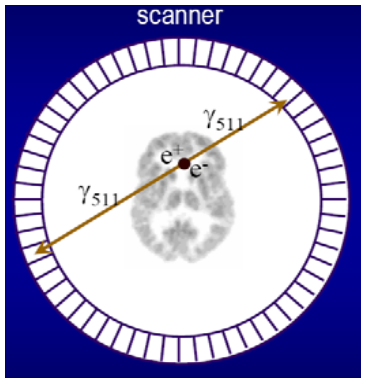




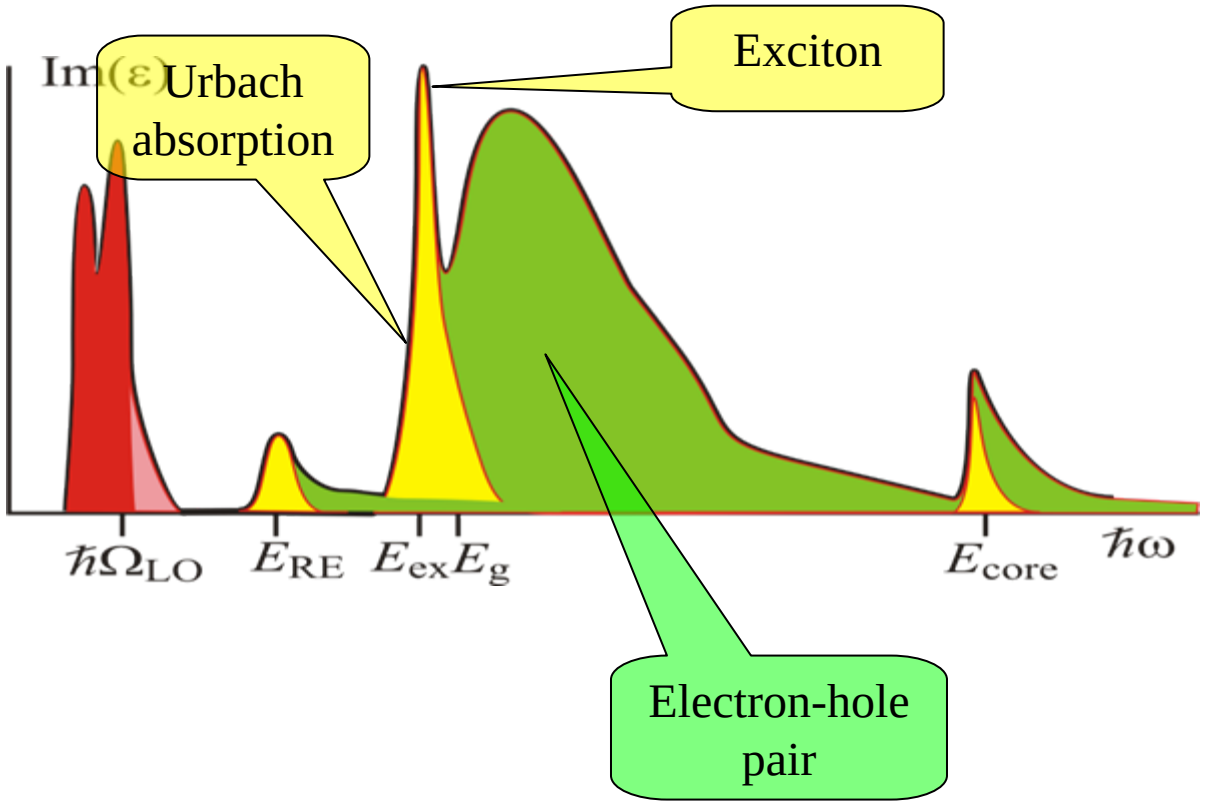
CTL spectra and excitation of CTL spectra of sesquioxides measured with different time windows, temperature 10 K.

Slow/fast emission ratio increases with energy in Urbach tail region, i.e. slow component increases with delocalization.

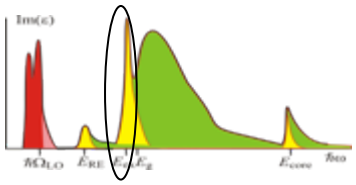
Crystals with Yb^{3+} CTL (e.g. LuAP:Yb) are used in PET scanners for small animals

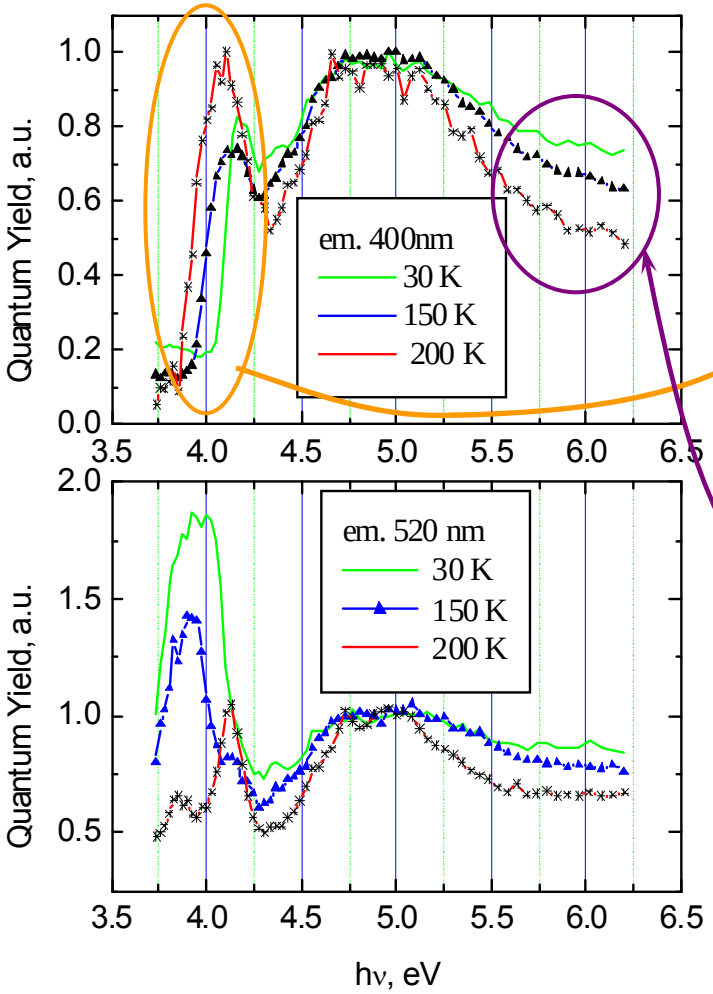


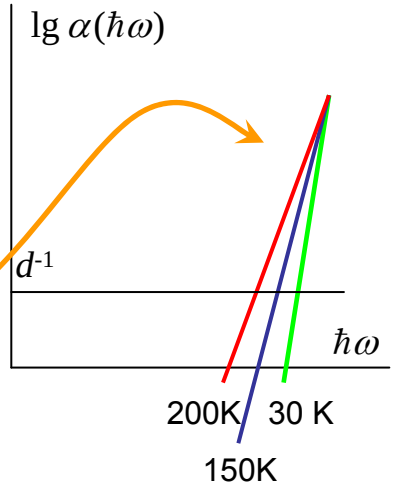
- Excitation of matrix Urbach tail
- Excitation of excitons
- Production of separated low-energy electron-hole pairs



Urbach tail effect in $PbWO_4$ excitation spectra







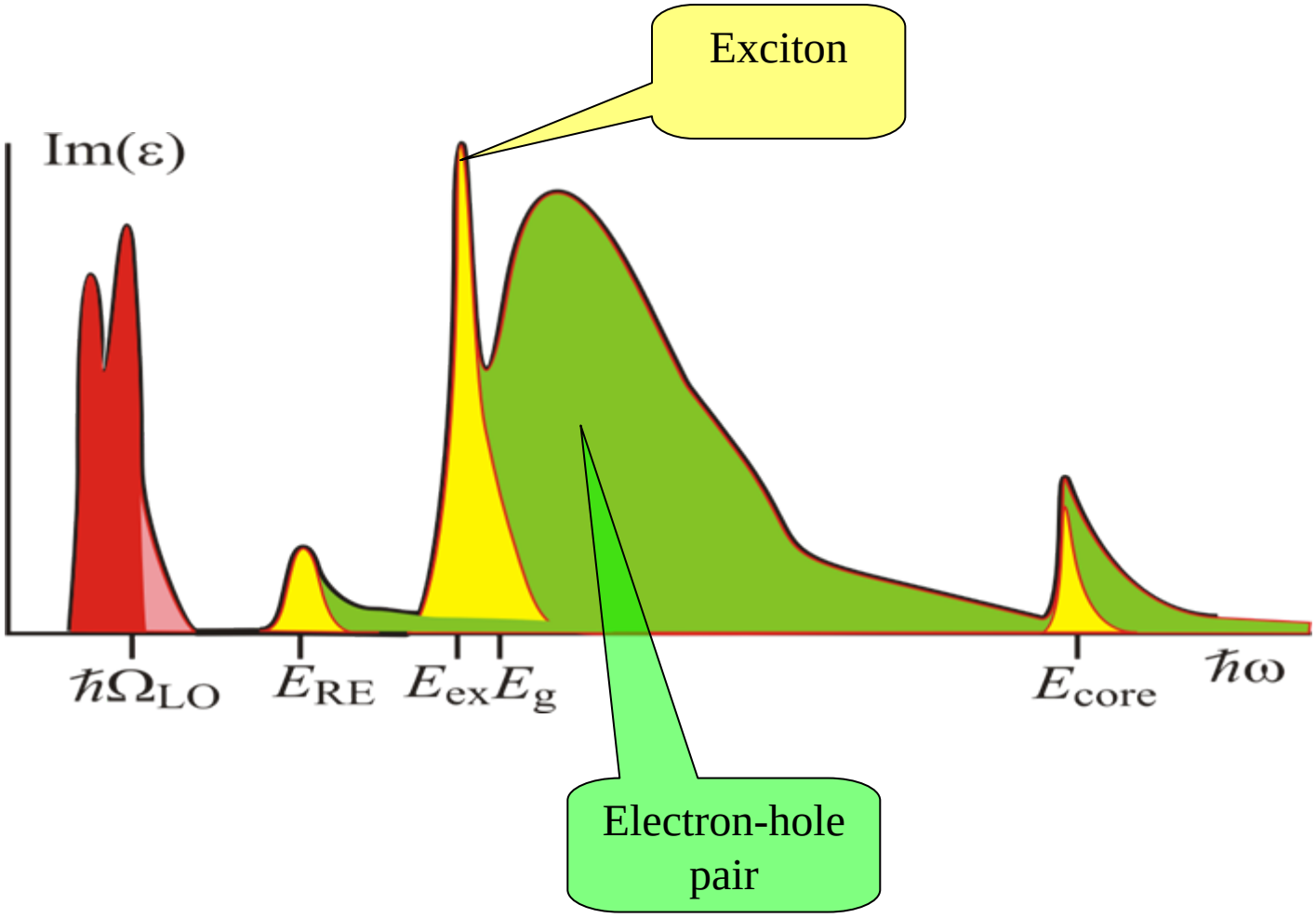
Temperature dependence of PWO excitation spectra shows two phenomena:

(1) dependence of excitation spectrum in Urbach absorption region due to change of the fraction of absorbed radiation in the sample and

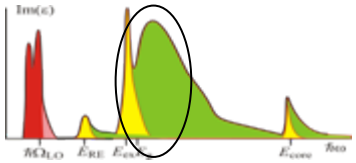
(2) increasing of the slope of quantum yield with T in the region of separated e-h pairs (see below)

PWO excitation spectra for blue (top) and green (bottom) emission bands

- Production of separated low-energy electron-hole pairs

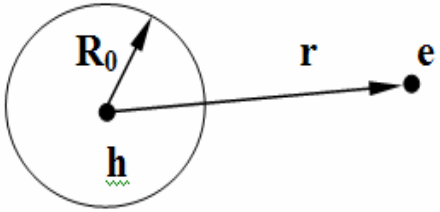


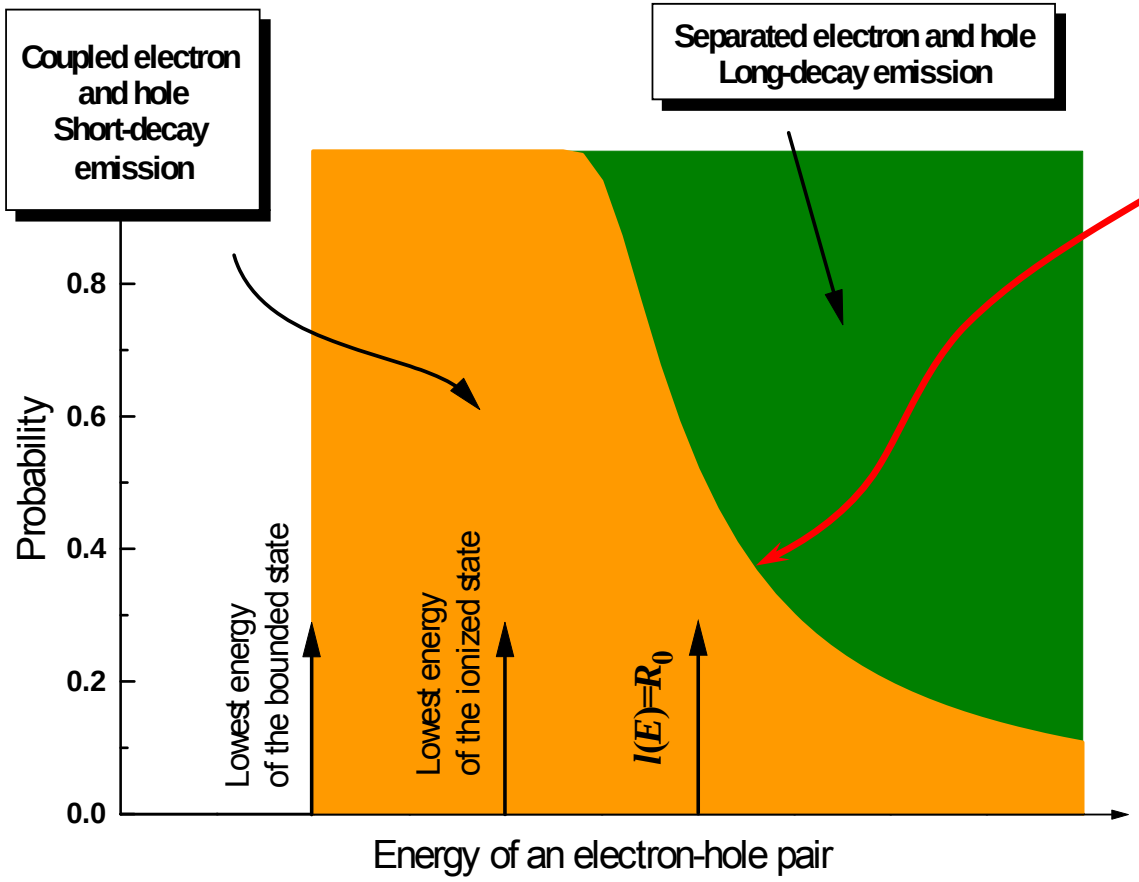
Probability of binding or separation of the components of an electron-hole pair vs their energy



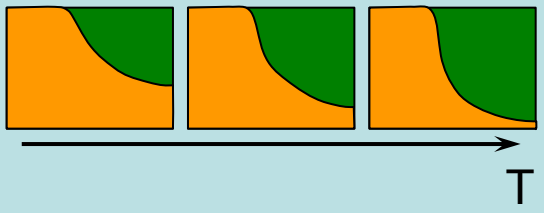
The nature of this curve is the increase of electron-hole separation with pair energy and the decrease of direct recombination with this separation:

$$\text{Probability of recombination} = \begin{cases} 1, & r < R_0 \\ R_0/r, & r \geq R_0 \end{cases}$$

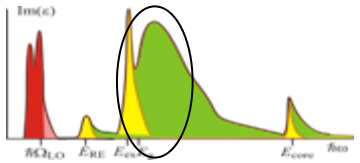


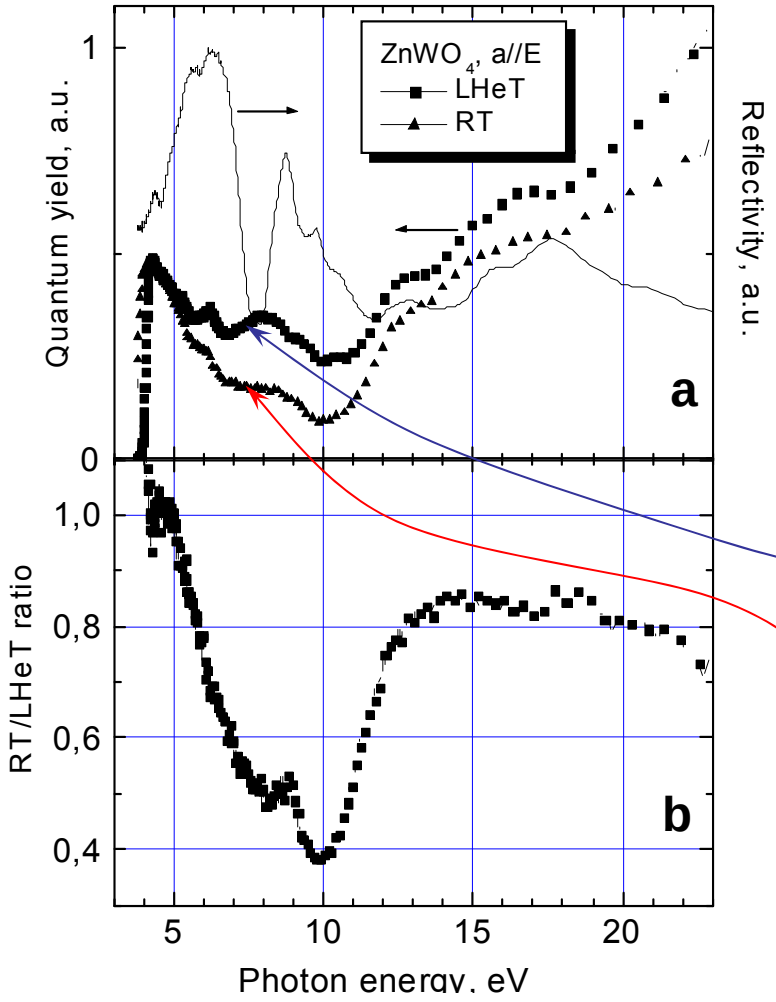


R_0 increases with decrease of temperature, therefore this probability is temperature dependent:

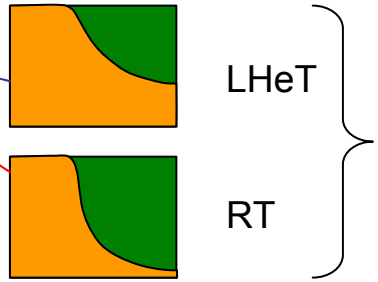


The effect of electron kinetic energy on the efficiency of energy transfer to the luminescence center as a function of temperature (Spassky et al)





$ZnWO_4$:
(a) –quantum yield spectra at RT and LHeT and reflectivity (thin curve);
(b) – the ratio of the above quantum yield spectra.

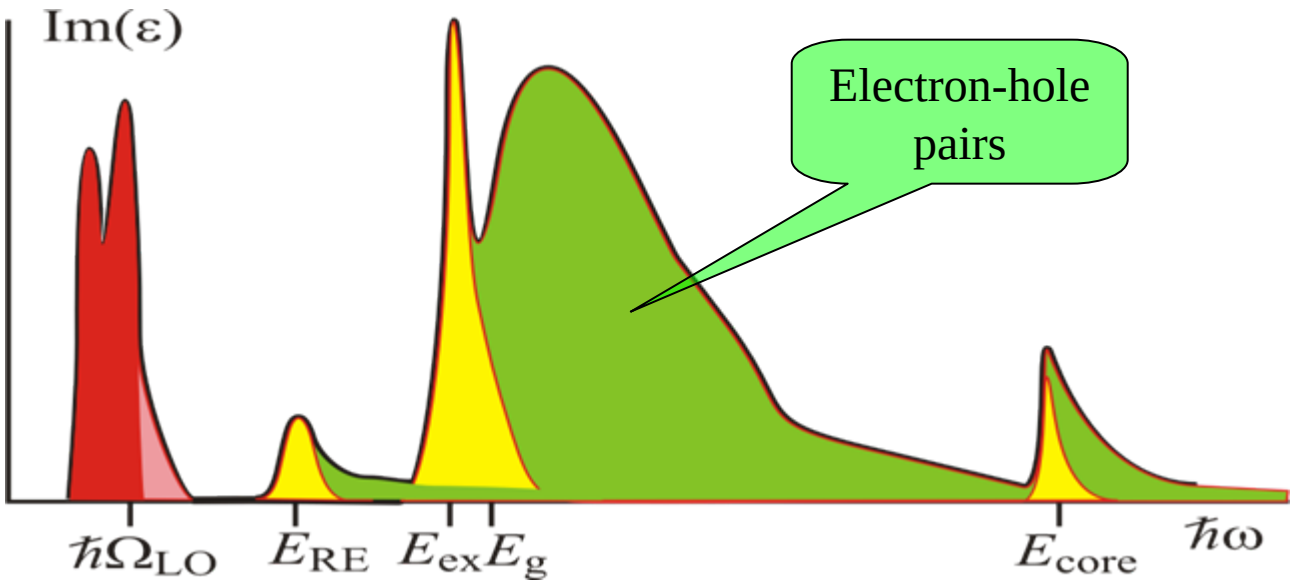


LHeT

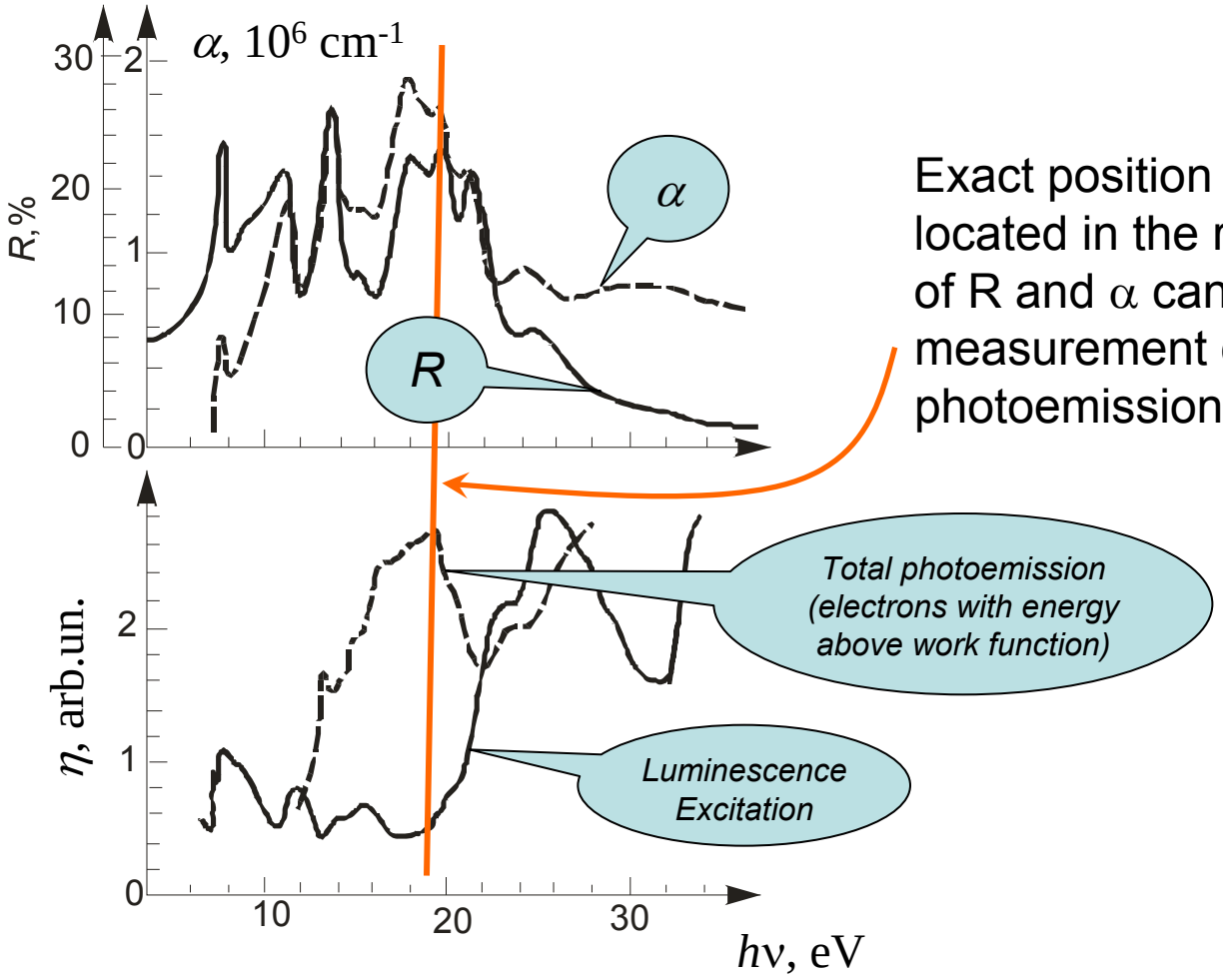
RT

Excitation spectrum temperature dependence is described in previous slide

- Production of high-energy electron-hole pairs followed by impact excitation/ionization of defects

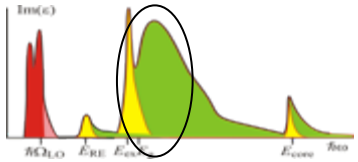


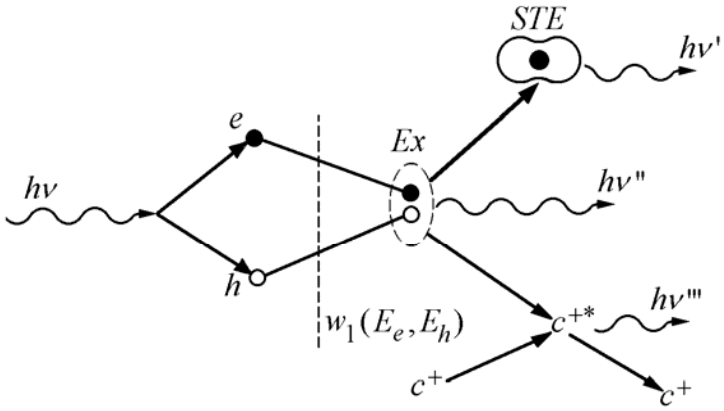
MgO:Al – threshold of multiplication of electronic excitations (Ch. Lushchik, Mikhailin et al)

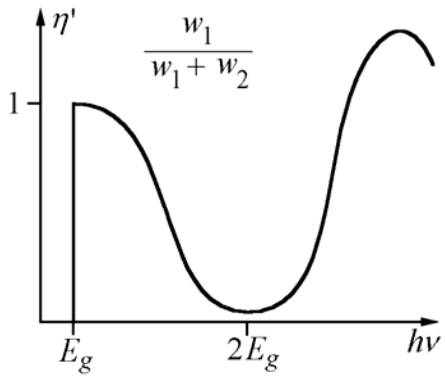


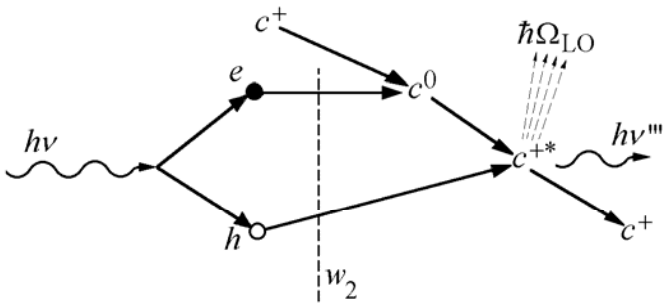
Exact position of e-e scattering threshold located in the region of abrupt decrease of R and α can be estimated using measurement of luminescence and total photoemission excitation spectra

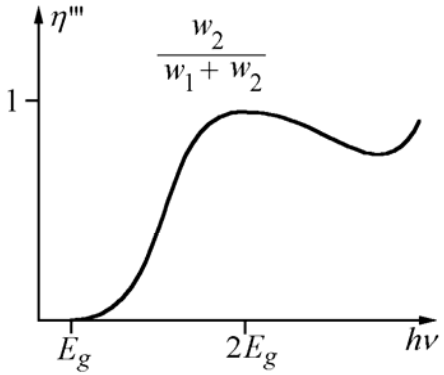
Two types of recombination channels:
excitonic one (upper part) and recombination on a centre (lower part).
Figures on the right display typical energy dependence of the quantum yield of these channels



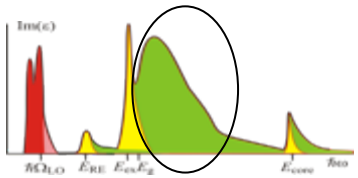


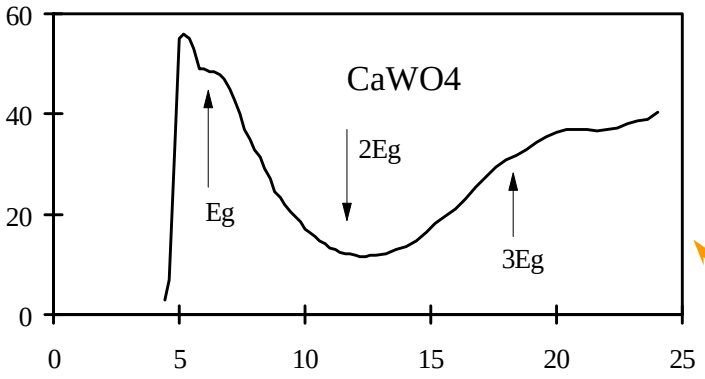


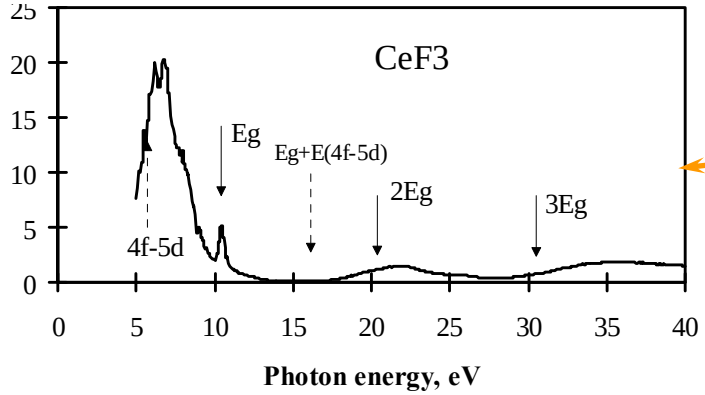


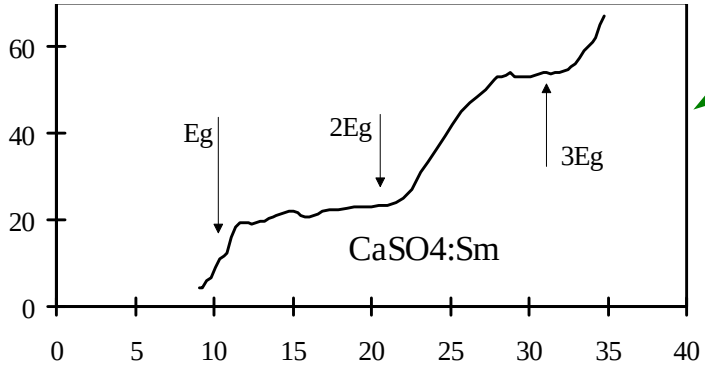


Experimentally observed two types of recombination channels



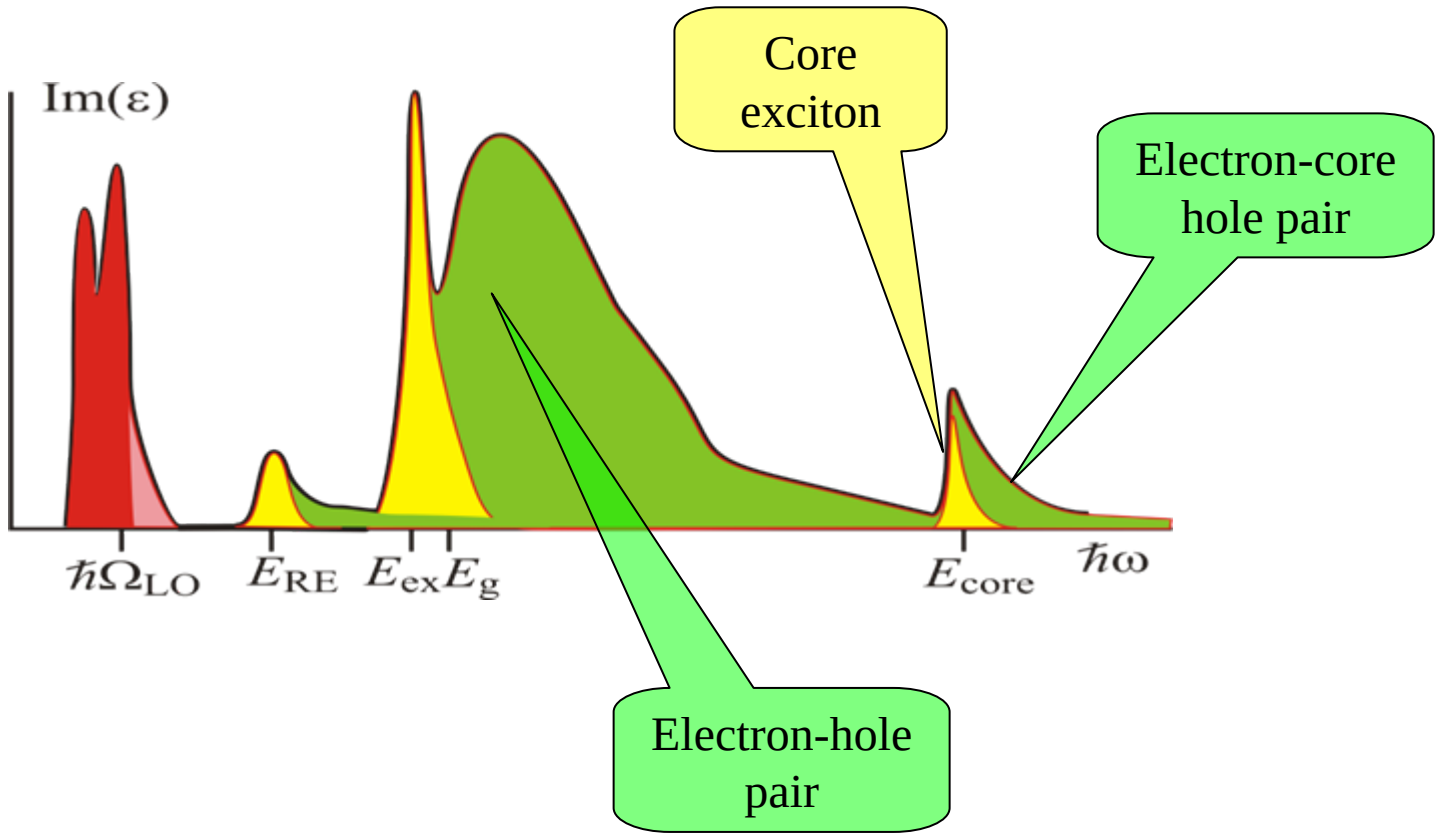






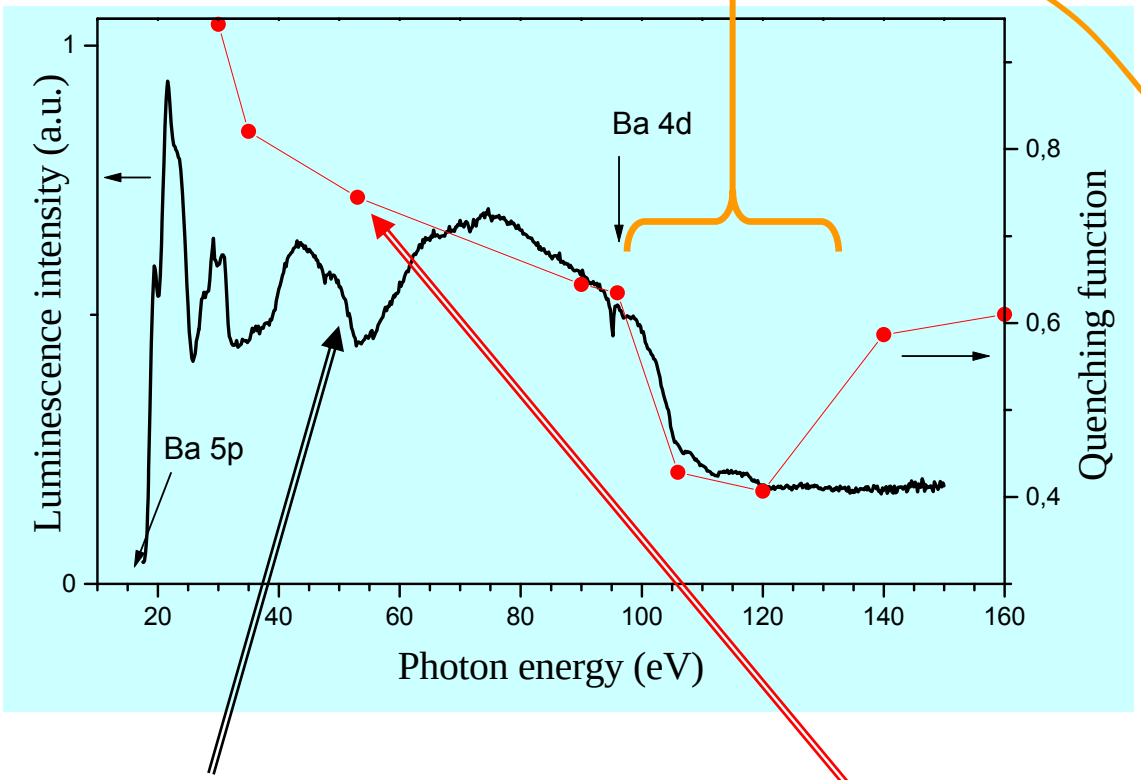
Luminescence excitation spectra of intrinsic luminescence of **$CaWO_4$** (upper panel) [S. I. Golovkova, A. M. Gurvich, A. I. Kravchenko, V. V. Mikhailin, A. N. Vasil'ev, Phys. Stat. Sol. (a), 77 (1983) 375] and **CeF_3** [C. Pedrini, A. N. Belsky, A. N. Vasil'ev, D. Bouttet, C. Dujardin, B. Moine, P. Martin, M. J. Weber, Material Research Society Symposium Proceedings, v. 348, pp. 225–234, 1994] (lower panel) and activator luminescence of **$CaSO_4$:Sm** [I. A. Kamenskikh, V. V. Mikhailin, I. N. Shpinkov and A. N. Vasil'ev, Nucl. Instr. and Meth., A282 (1989) 599] (middle panel)

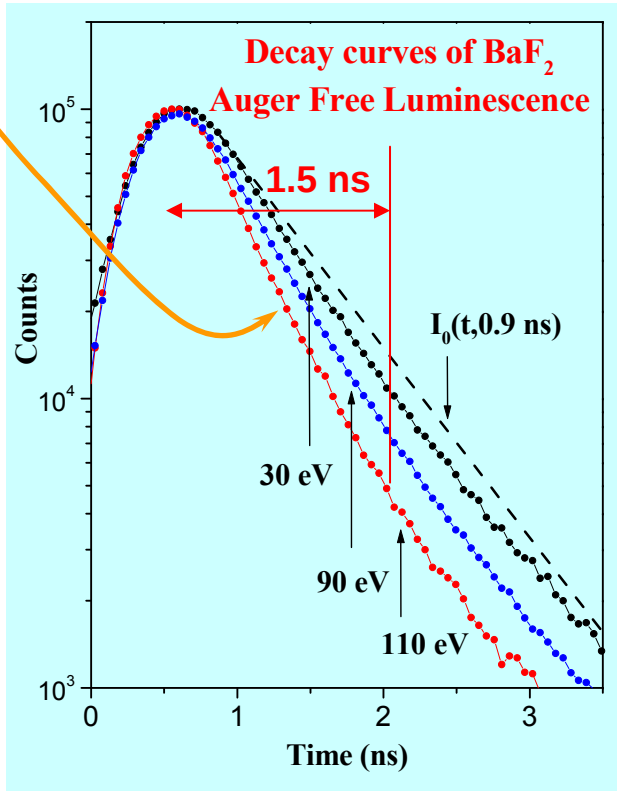
- More complicated case: an example of crossluminescence quenching at 4d Ba^{2+} core level



5p core hole interaction with excitons and conduction electrons in BaF_2 (Belsky et al)

Decay is fastest and yield is quenched in the region of 4d Ba2+ absorption region due to interaction of several excitations

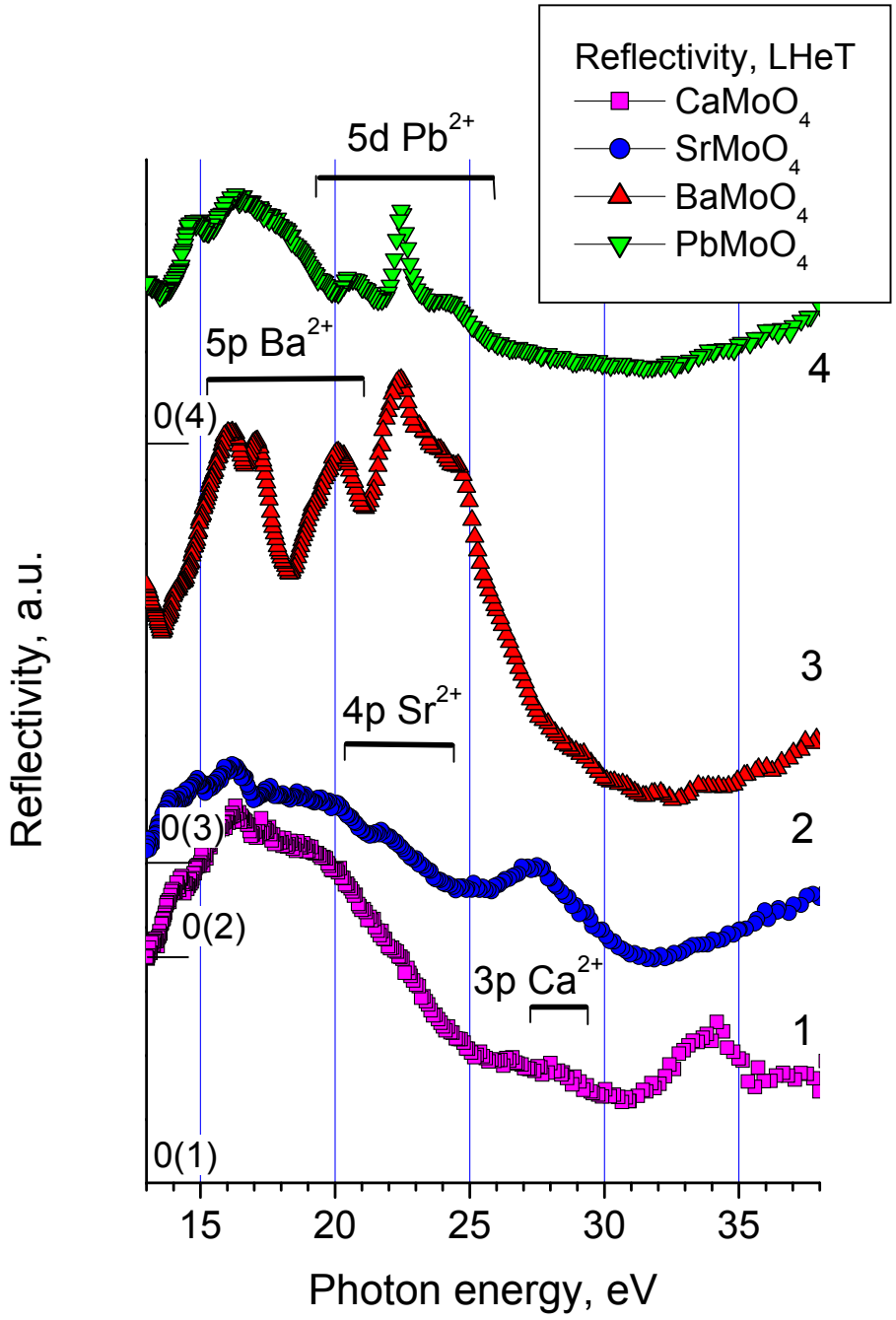




Crossluminescence excitation spectrum

Quenching factor at 1.5 ns after excitation pulse maximum

CL decay curves at different excitation energies

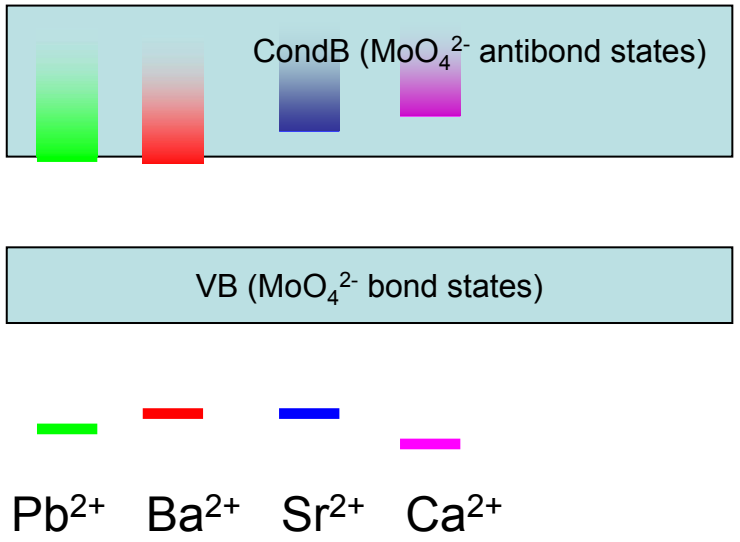


Manifestation of core excitons in in optical functions in VUV reguion

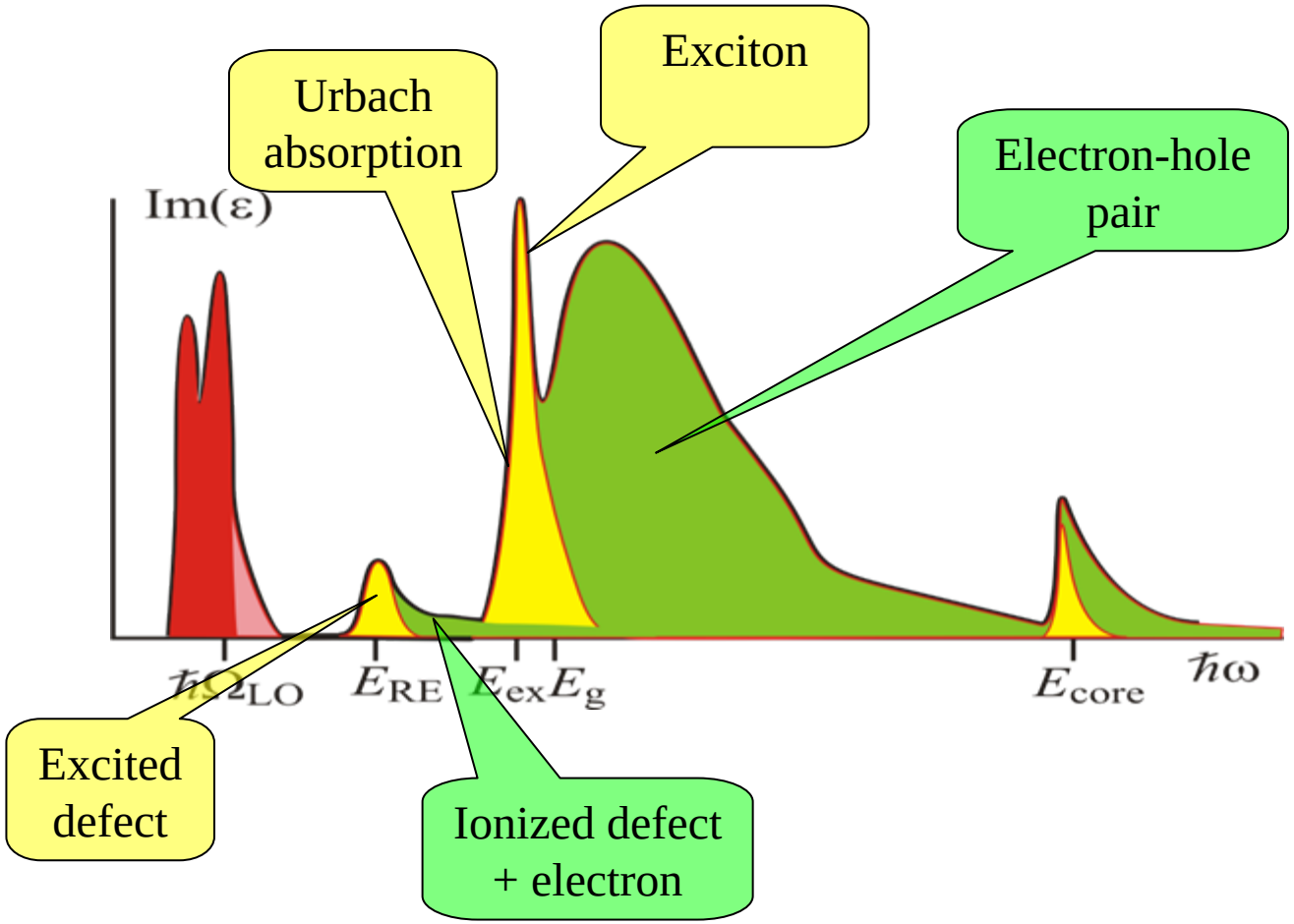
Intensity of core exciton peaks correlates with the nature of the bottom of the conduction band (Kolobanov, Spassky et al).

Cation core excitons are visible only if the lowest states of conduction band are formed from cation states (Pb and Ba molibdates).

Reflectivity shows no structure in core exciton region if the lowest states are formed from complex anion states (Sr and Ca molibdates).

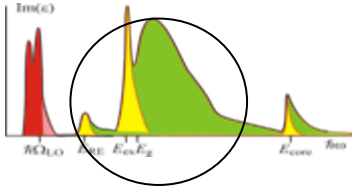


- An example of study of energy transfer in wide range in a crystal with complicated electronic structure

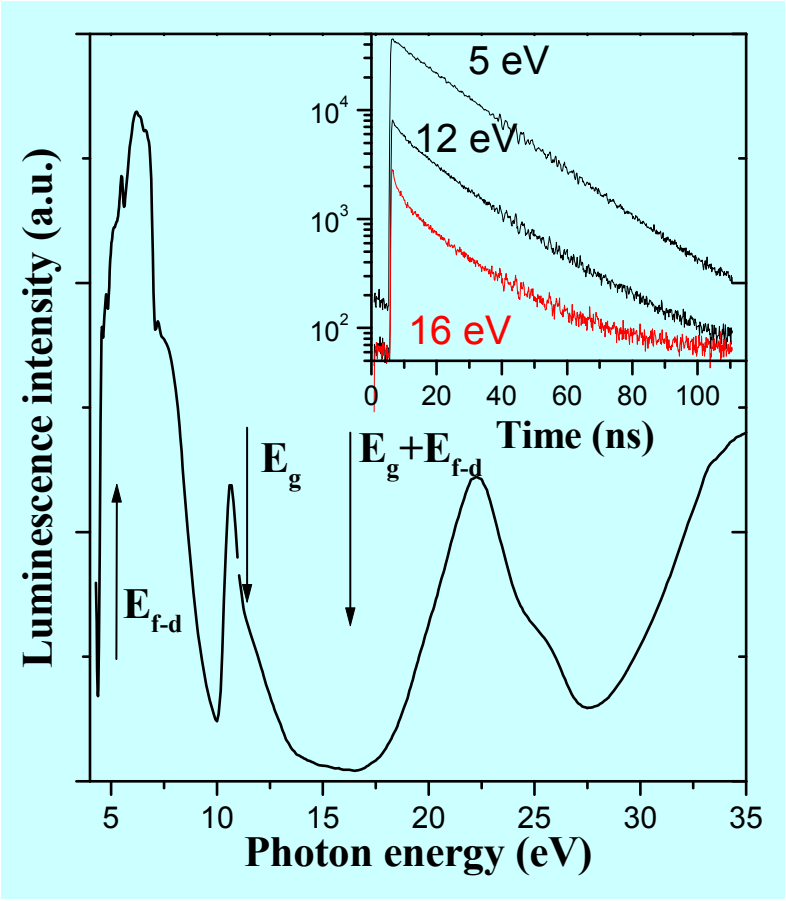


Interaction of cerium excitons in CeF_3 (energy transfer) The elementary region of high local density of excitations

(Belsky et al)



An example of study of luminescence excitation spectra in wide region of processes



At high energy excitation luminescence decay of CeF_3 is non exponential and show a strong acceleration

Energy threshold of decay acceleration in CeF_3 is at 16 eV

Above 16 eV inelastic scattering of the primary photoelectron can create two excited ions $(Ce^{3+})^*$ in close vicinity.

The result of their interaction can be written as

$$(Ce^{3+})^* + (Ce^{3+})^* \rightarrow Ce^{4+} + e + Ce^{3+}$$

From simulation of interaction the acceleration of decay is from picosecond range

The reasons of light yield instability induced by radiation

- Creation of the reversible damage:

a) transient defects - close *F*-*H* pairs

b) Change of electronic state of deep defect levels in the forbidden energy gap

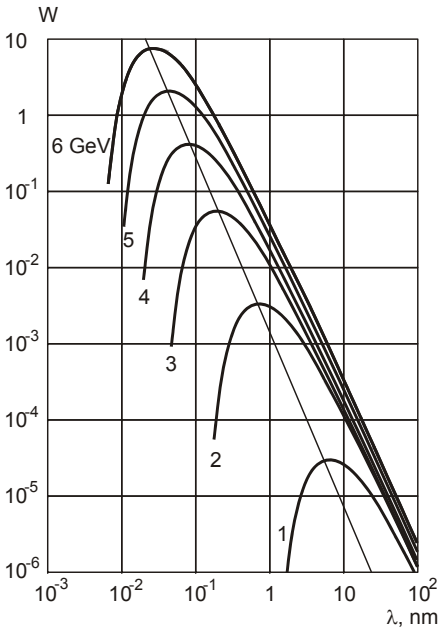
- Creation of the irreversible damage:

a) stable *F*-*H* pairs

b) defect conglomerates

Benefits of VUV and X-ray SR in radiation damage study

- VUV (especially XUV) and X-ray photons produce the same spectrum of elementary electronic excitations (electron-hole pairs, excitons, core level excitations, initial defect formation stages) as high-energy ionizing particle
- Absorption coefficient in XUV and X-ray region is extremely high (10^4 to 10^6 cm^{-1}), therefore accumulated dose in the thin absorption layer becomes huge
- Unique spectral features and time structure, and high intensity of synchrotron radiation allow one to use this kind of excitation in investigation of defects and their creation in insulators with wide band gap.



SR spectral distribution for various electron energy (R=32 m)

How to study radiation effects using luminescence spectroscopy

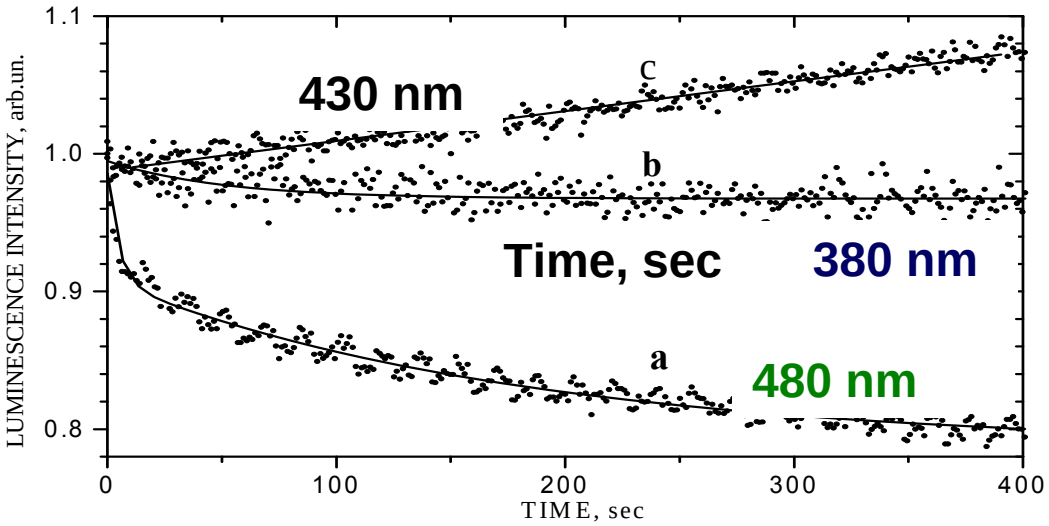
- Changes of luminescence emission spectra (additional emission bands)
- Changes of decay kinetics (radiation defects can result in sharpening of initial stages of decay and increasing of slow component)
- Changes of energy transfer (radiation defects can change ratio of several relaxation channels)

Usage of SR in X-ray region in the study of PWO radiation hardness

- VEPP-3 (Budker INP): Flux of 10^{16} ph/s with energy from 2 to 100 KeV ("white" X-rays)
- DCI (Lure, Orsay): Flux of 10^{12} ph/s of monochromatized 15 KeV X-ray photons

Dose dependence for different regions of PWO emission spectrum excited by X-ray SR

- Dose rate is about 1 kGy/sec (in thin absorption layer, d~10^{-5} cm)
- Degradation / enhancing of emission under irradiation depends on the emission spectral region
- Fast and slow recovering of radiation defects



(a) Green emission (480 nm) – fast degradation at first 10 sec followed by much slower degradation

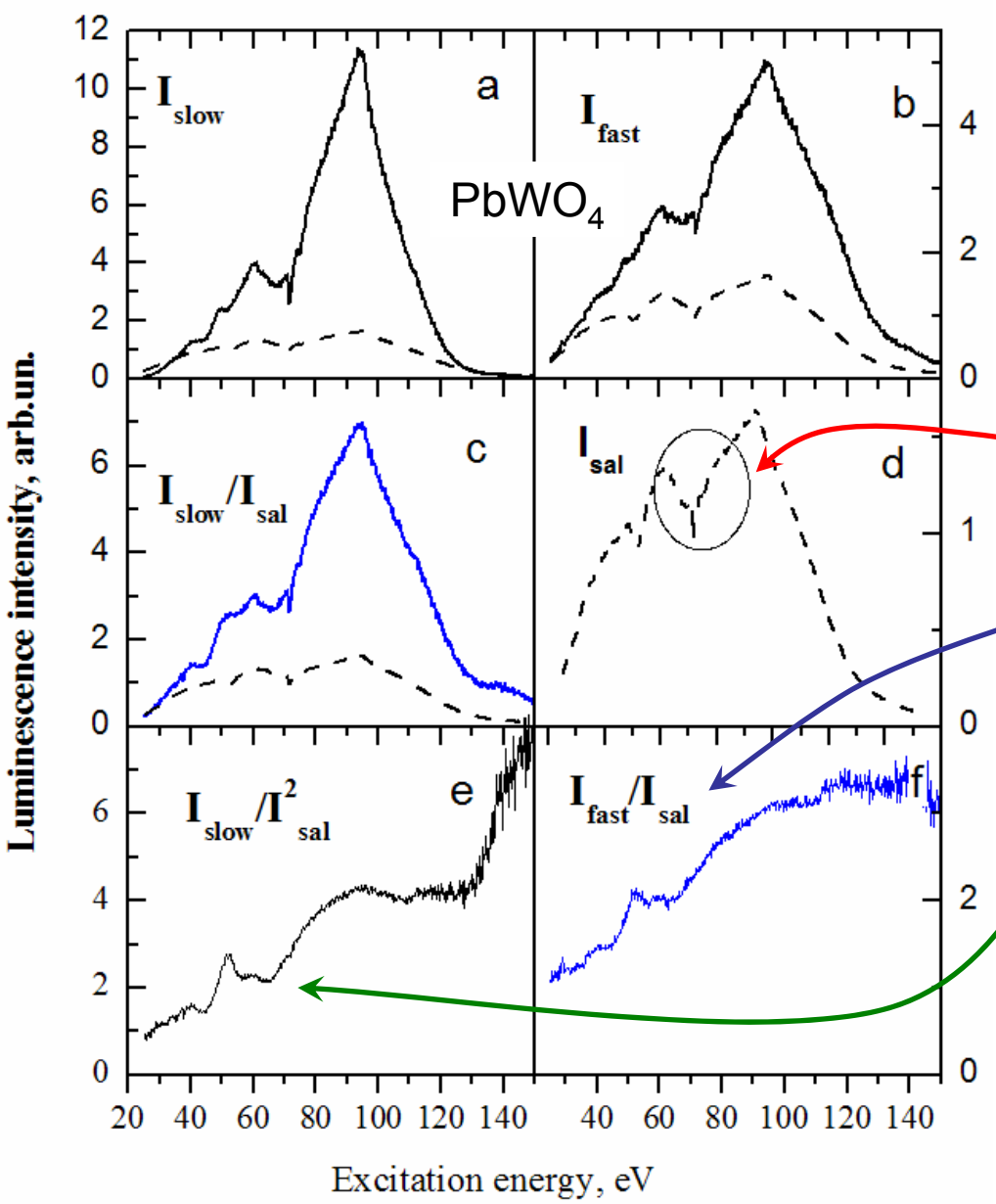
(b) Blue emission (380 nm) is more stable under irradiation

(c) Few cases of increase of emission in intermediate range (430 nm) under irradiation – the evidence of new emission center production

PWO emission spectrum explanation

- Fast (blue) component – excitonic (Pb) emission, (should be linear with excitation intensity)
- Slow (green) component – defect recombination emission, (should be non-linear (quadratic?) with excitation intensity)

How to measure nonlinear excitation efficiency?



Modulation of SR spectrum by the grating spectral efficiency with sharp peculiarities allows one to estimate the order of the process

Sharp structure due to Pt covering of the grating dissapiars in

1st order fast PWO emission

and

2nd order slow PWO emission

Conclusions

Fundamental mechanisms of electronic relaxation in large bandgap solids and energy transfer can be studied by analysis of luminescence excitation spectra and kinetics excited by VUV-X synchrotron radiation photons, especially using Time-Resolved Luminescence VUV Spectroscopy.

High flux of SR enables to simulate and investigate radiation damage effects.