Luminescence and defects creation at the relaxation of various electronic excitations in wide-gap materials

Aleksandr Lushchik

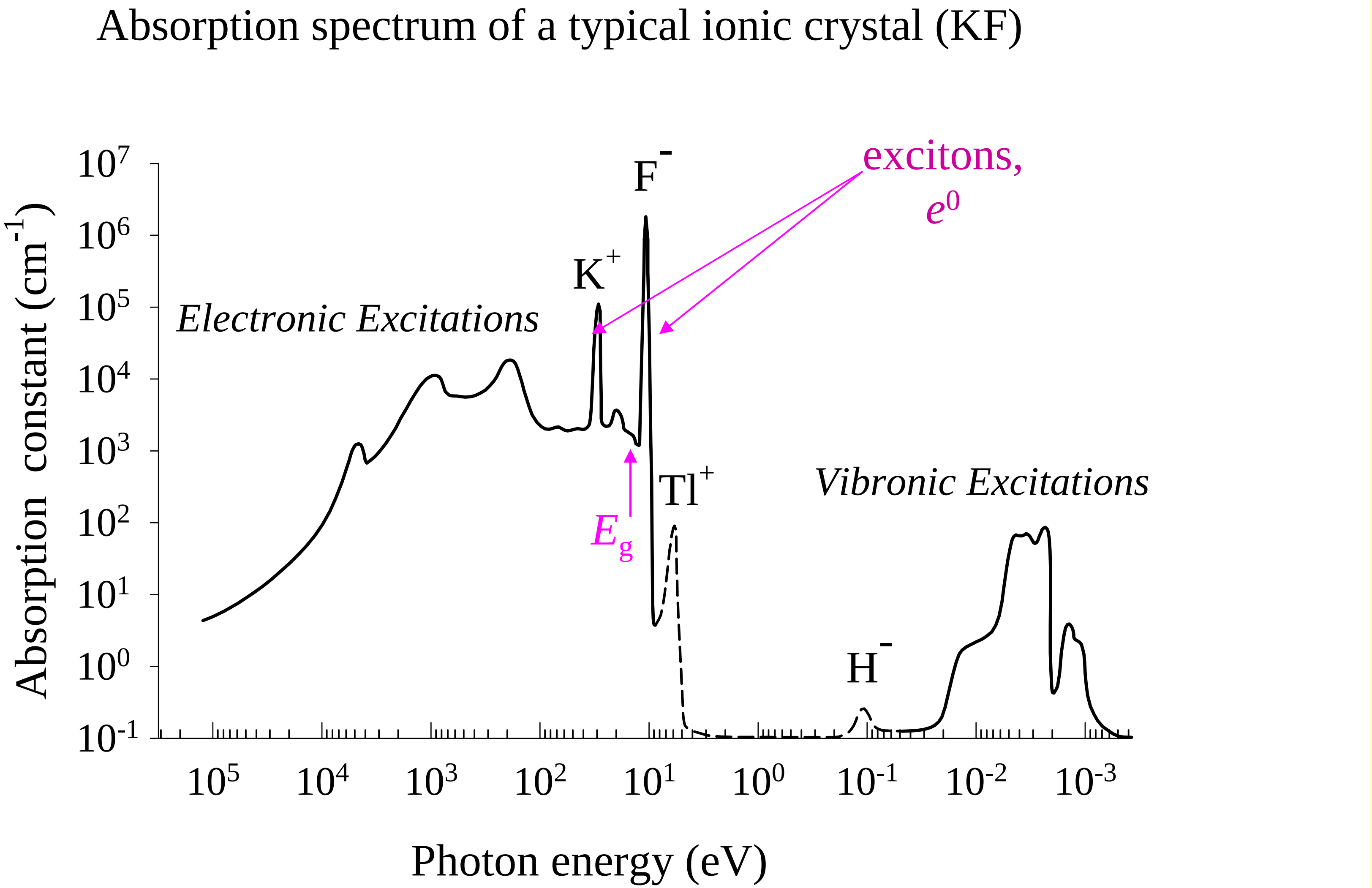
Institute of Physics
University of Tartu (Dorpat)
Estonia

Workshop “Scintillating Screen Applications in Beam Diagnostics”, GSI, Darmstadt, February 15, 2011

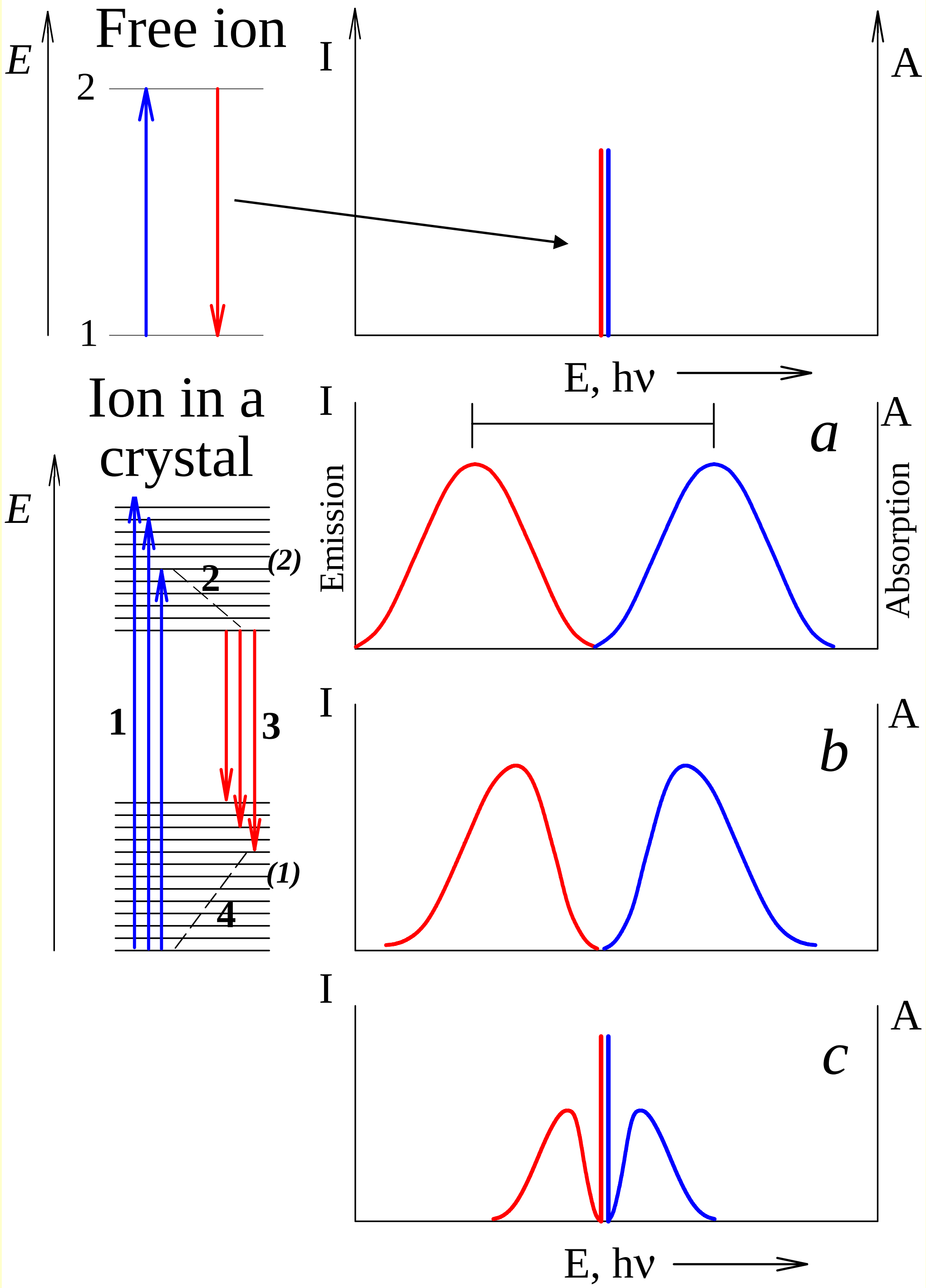
Outline

- Intracenter and recombination impurity luminescence. Thermal quenching
- Emission of free and self-trapped excitons in metal halides and oxides
- Core-valence luminescence (crossluminescence)
- Types of hot luminescence. Electron and hole intraband luminescence
- Multiplication of electronic excitations. Enhanced local density of EEs
- Creation spectra of Frenkel defects by synchrotron radiation. A role of hot *e*-*h* recombination in the materials with $E_g < E_{FD}$
- Competition between decay channels of EEs

Intrinsic and impurity excitations in a wide-gap crystal



Impurity luminescence



large Stokes shift

mercury-like ions

$1s^22s^22p^6\ldots ns^2np^6nd^{10}(n + 1)s^2$:

Ga^+, In^+, Tl^+

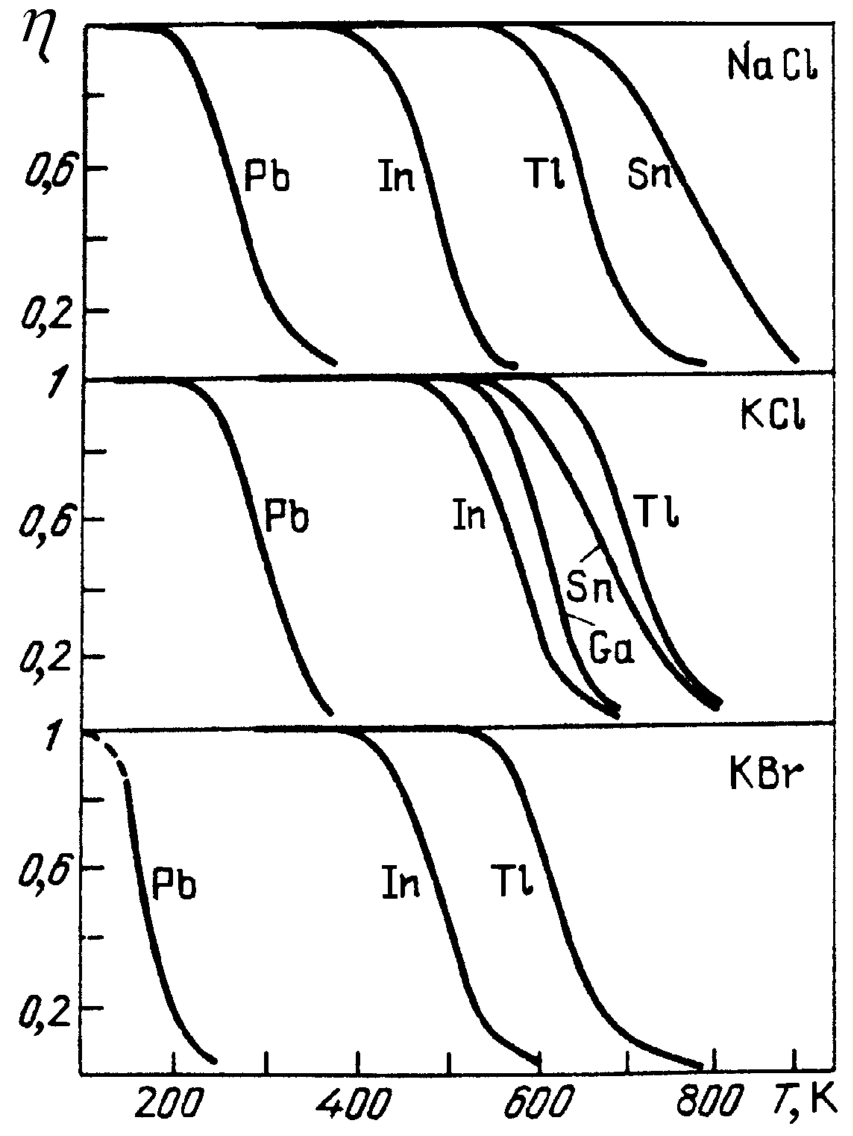
Ge^{2+}, Sn^{2+}, Pb^{2+}

intermediate Stokes shift

small Stokes shift

e.g., Eu^{2+} in CaF_2

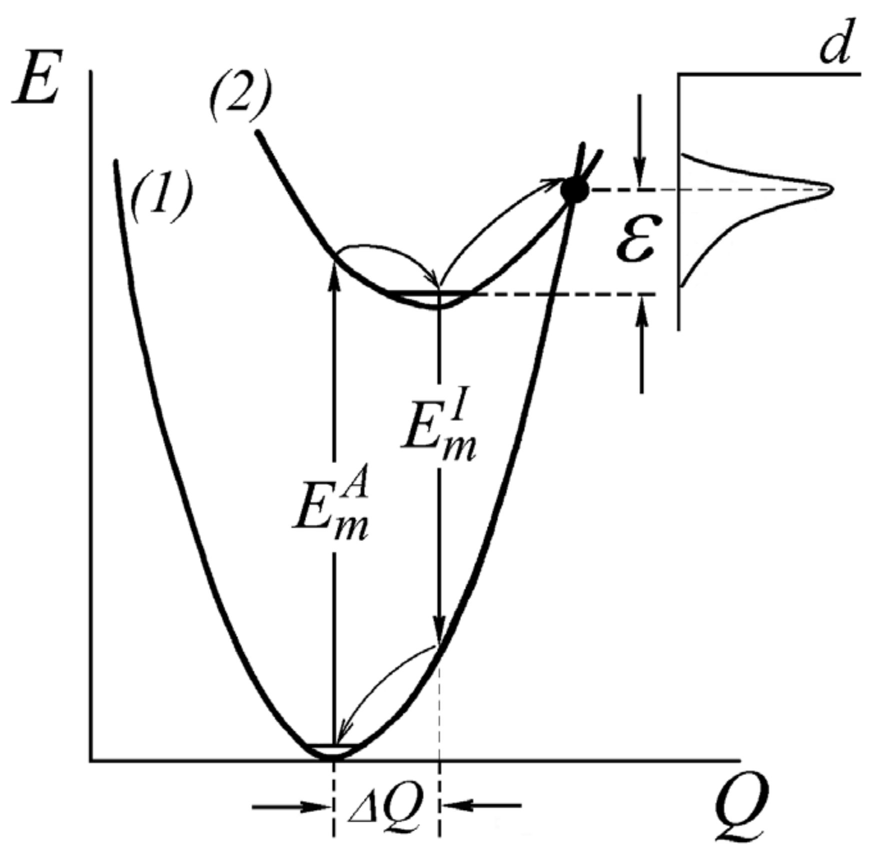
Thermal stability of impurity luminescence

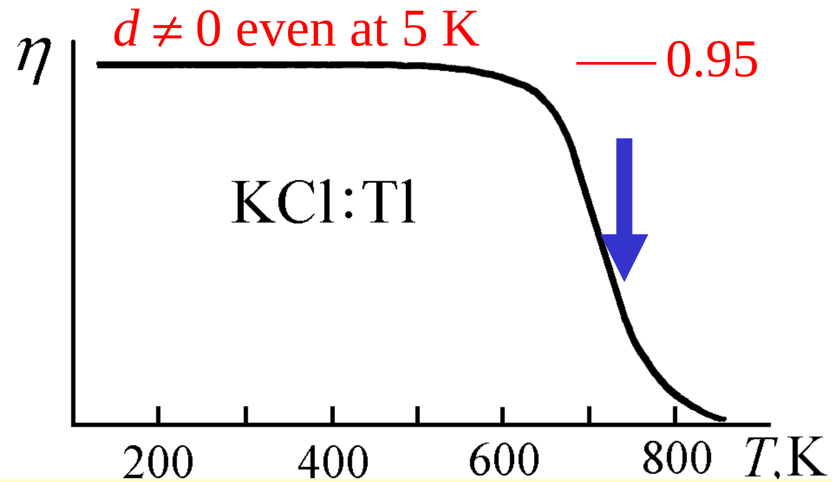


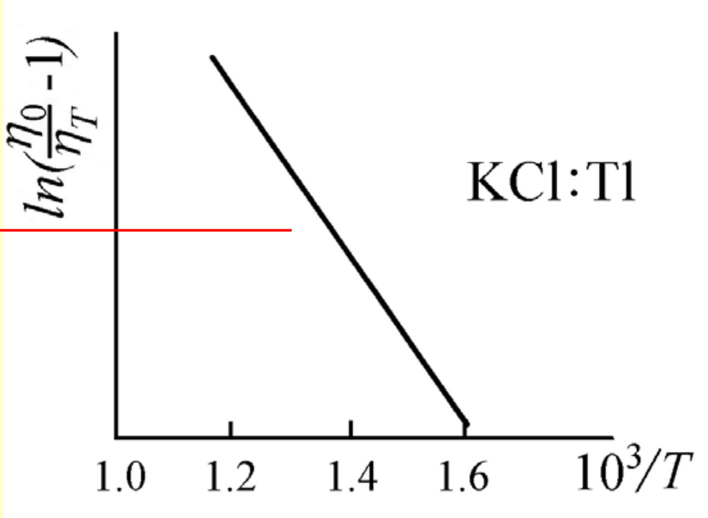
Thermal quenching of impurity luminescence

$$d = d_0 \exp(-\varepsilon/kT) \qquad f = \frac{1}{\tau}$$

$$\eta(T) = \eta(0)\frac{f}{f+d} = \frac{\eta_o}{1+d_0\tau\, exp(-\varepsilon/kT)}$$







For KCl:Tl $\varepsilon \approx 1.3$ eV

Usually, $d_0 \approx 10^{-13}\ s^{-1} \approx \varpi_{eff}$.

$\Delta n = \pm 1$ and even in case of 50 phonons

relaxation time $10^{-13} \times 50 < 10^{-11}$ s

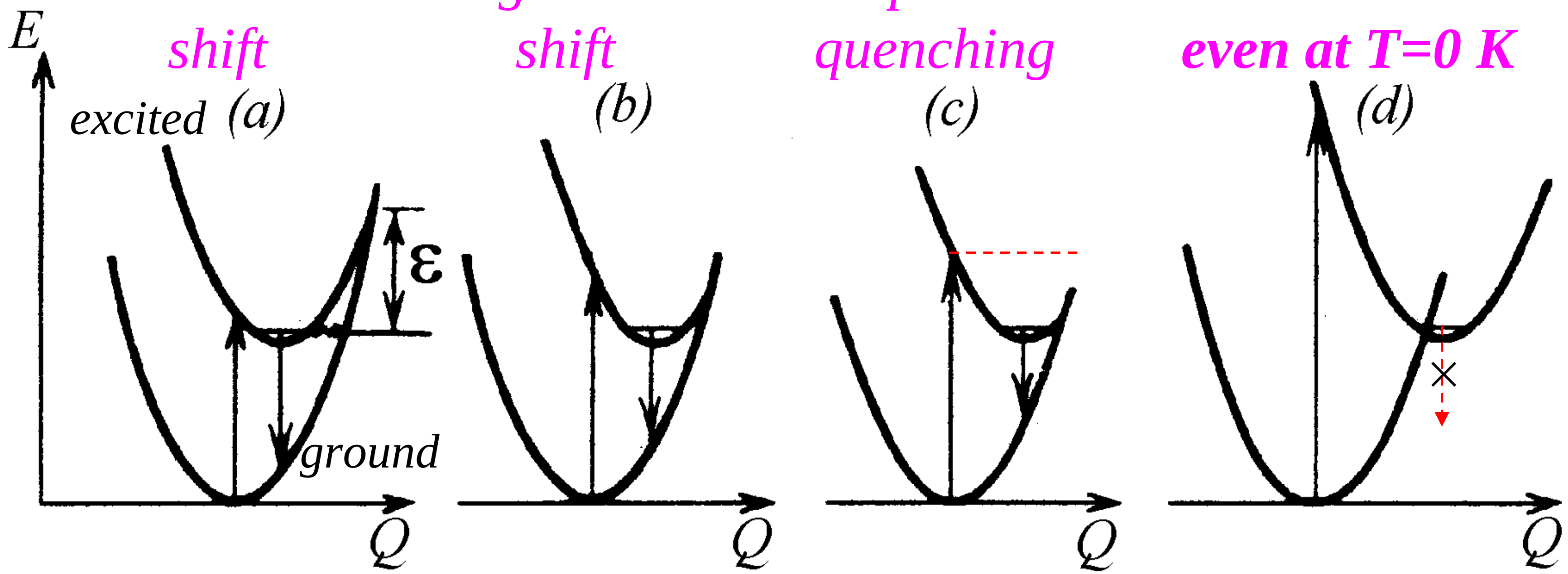
Potential curves for a ground and an excited state of different impurity centres

Small Stokes shift

Large Stokes shift

Optical quenching

No luminescence even at $T=0$ K



weak luminescence

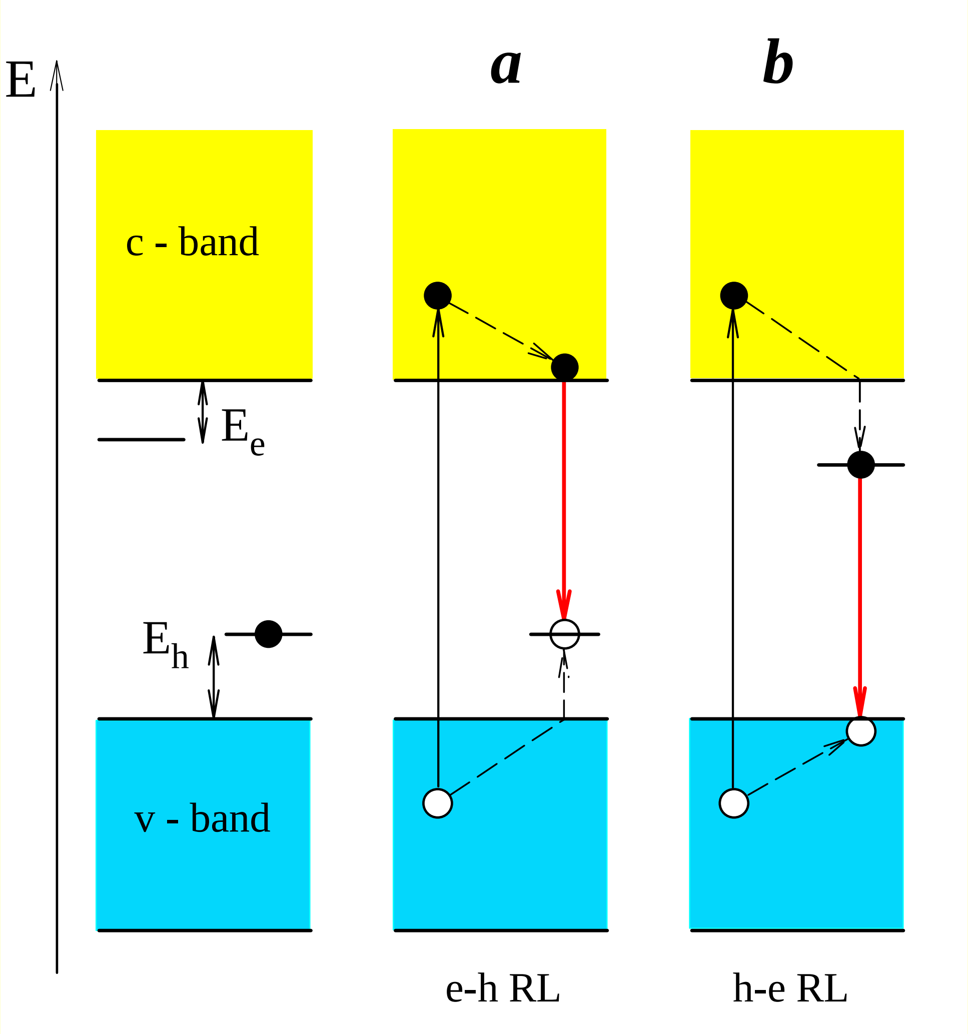
Introduction of RE^{3+} into binary and complex metal oxides with high resistance against radiation

Rare-earth ions with 1 to 14 4*f*-electrons:

Ce^{3+} Pr^{3+} Nd^{3+} Pm^{3+} Sm^{3+} Eu^{3+} Gd^{3+}
Tb^{3+} Dy^{3+} Ho^{3+} Er^{3+} Tm^{3+} Yb^{3+} Lu^{3+}

Line emission spectra, $f-f$ transitions, from IR to UV

Recombination luminescence (RL)



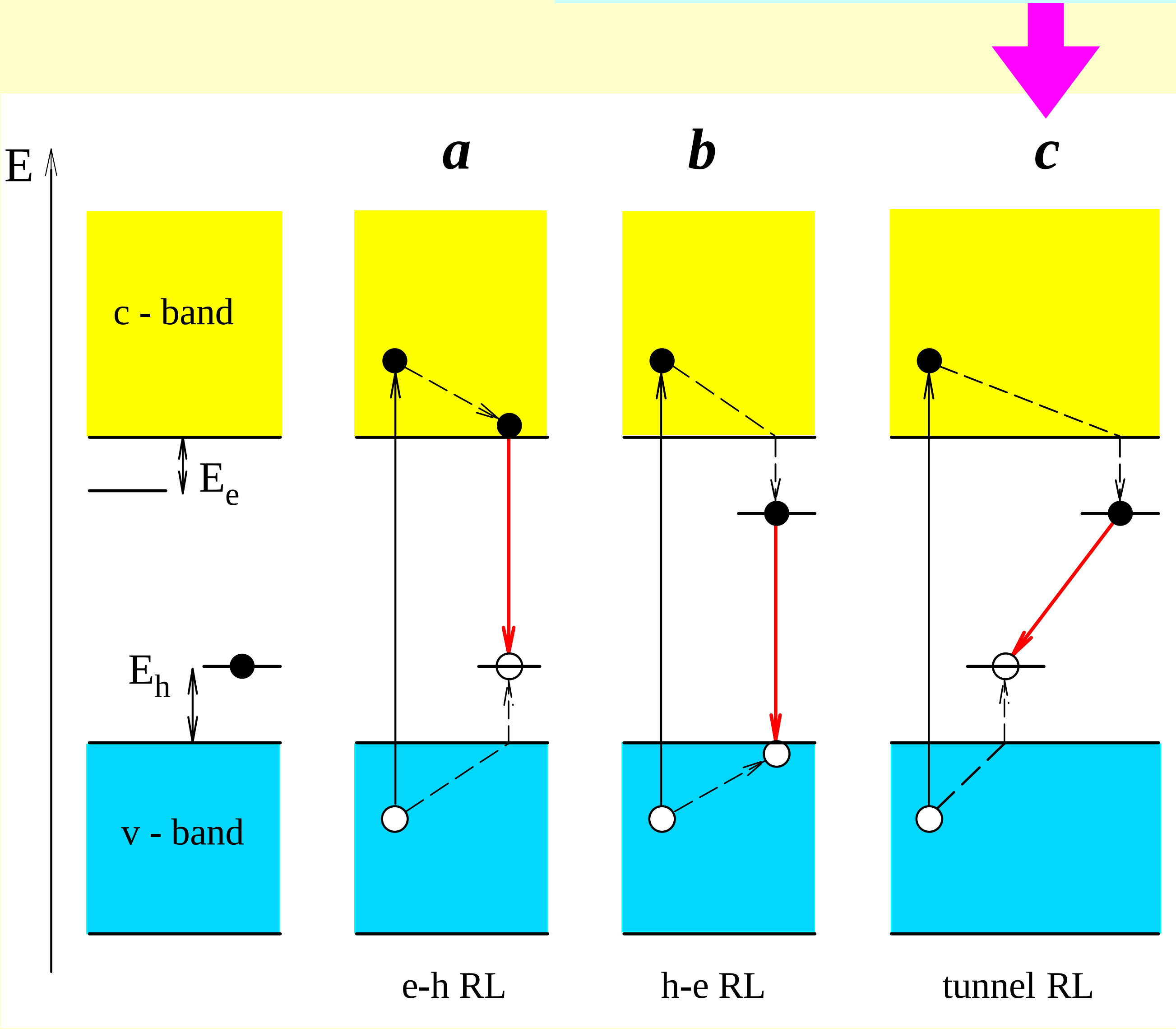
σ_r – recombination cross-section

<u>Two types of hole traps</u>: with an effective charge or neutral ones with respect to the crystal lattice

$$\sigma_r^{Coulomb} >> \sigma_r^{neutral}$$

Quenching of impurity recombination luminescence:
intracentre nonradiative transitions + external thermal quenching

Tunnel luminescence (TL)

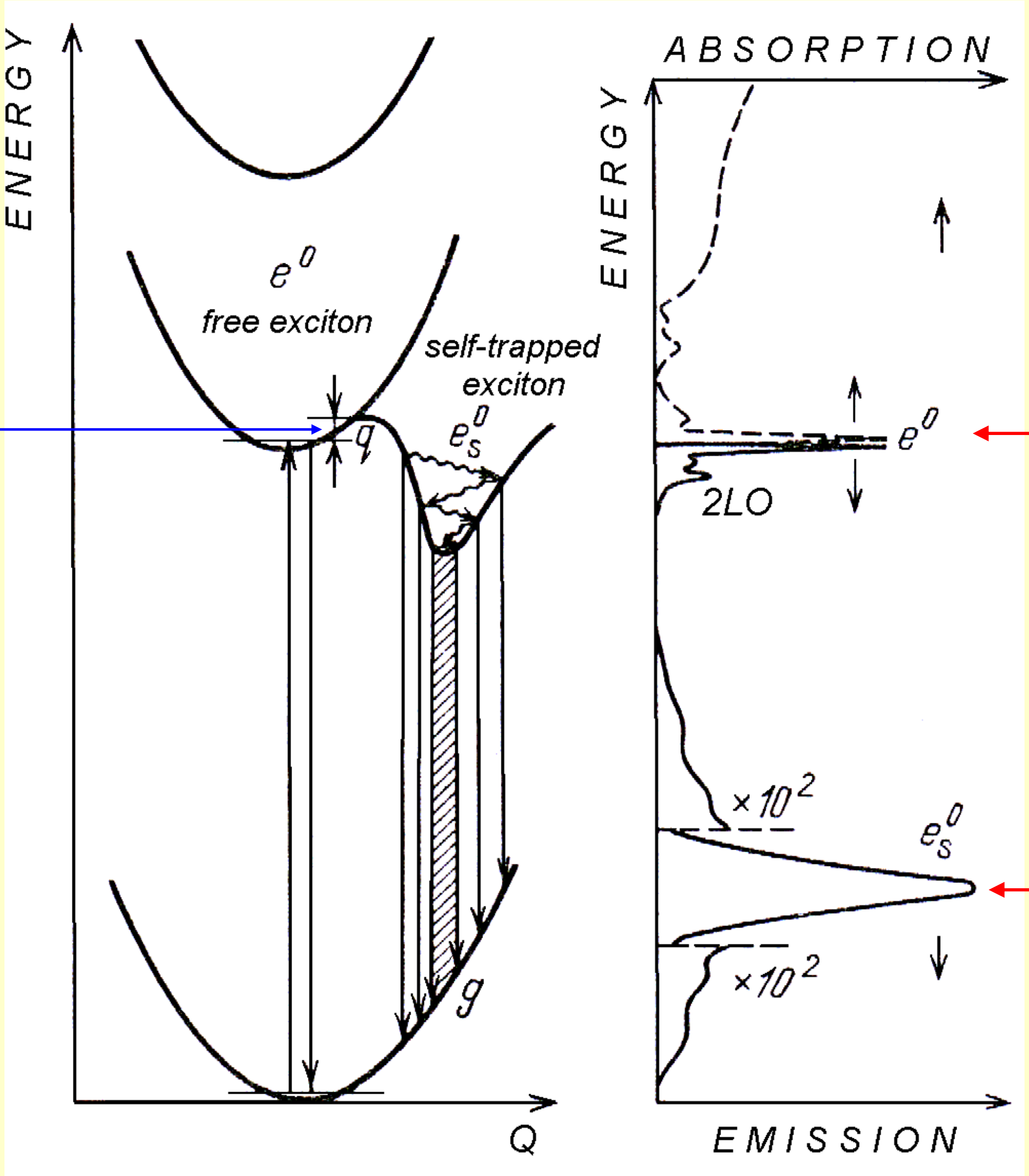


Deep electron and hole traps are needed to observe TL above RT.

In AHCs, E_e for an F centre equals 2-3 eV

<u>Self-trapping of holes</u> takes place in some WGMs

Free and self-trapped excitons *(FE and STE)* in AHC

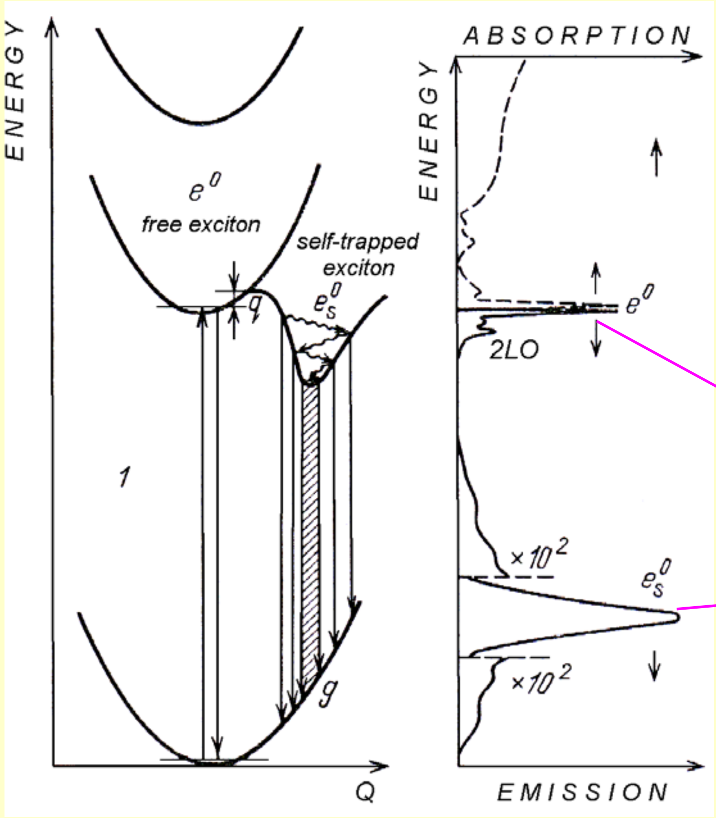


activation barrier *q*

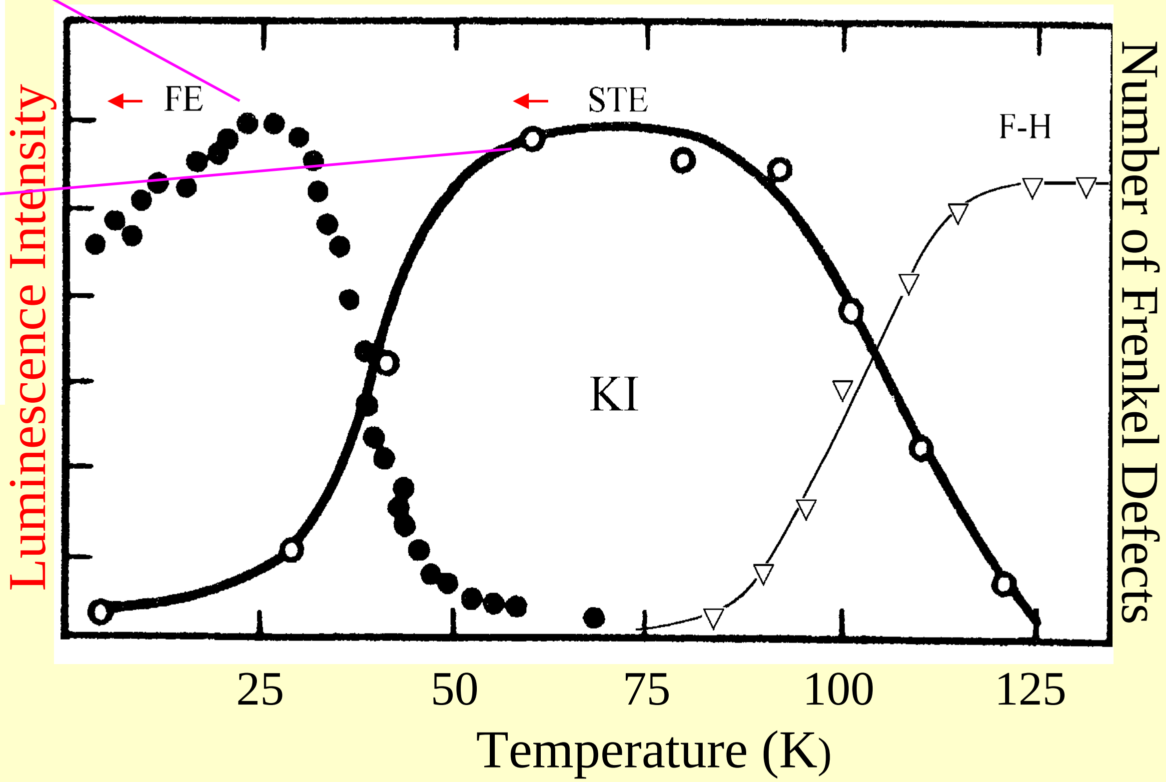
FE

$\tau \approx 10^{-8}$-10^{-3} s

STE



Free exciton → Self-trapped exciton → F-H pair

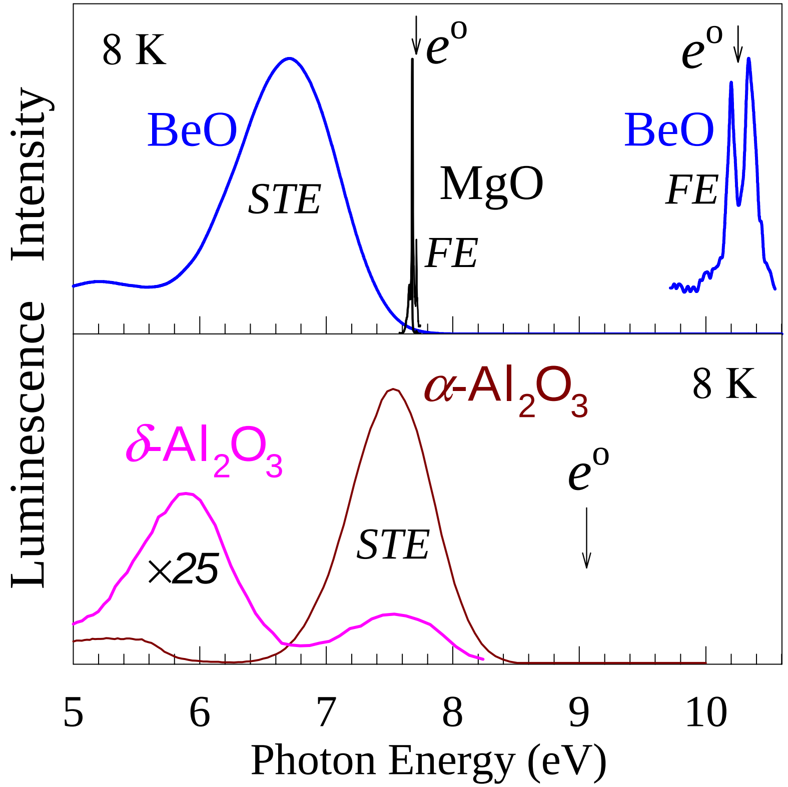


Free and self-trapped excitons (FE and STE) in metal oxides

Exciton-phonon interaction is responsible for the coexistence of FE and STE.

AHCs: NaI NaBr KI KBr

Free (FE) and self-trapped exciton (STE) emission.



MgO FE

BeO FE STE

α-Al_2O_3 STE

All the above-mentioned exciton emissions are low-temperature ones.

Emissions of bound excitons !!

Core-valence or crossluminescence (CL)

$\tau \approx 1$ ns = 10^{-9} s

energetic yield $\approx 10^{-1}$-10^{-2}

(*a*) We have both cross- and recombination luminescence

$E_{gc} < 2E_{ga}$

(*c*) Auger processes,

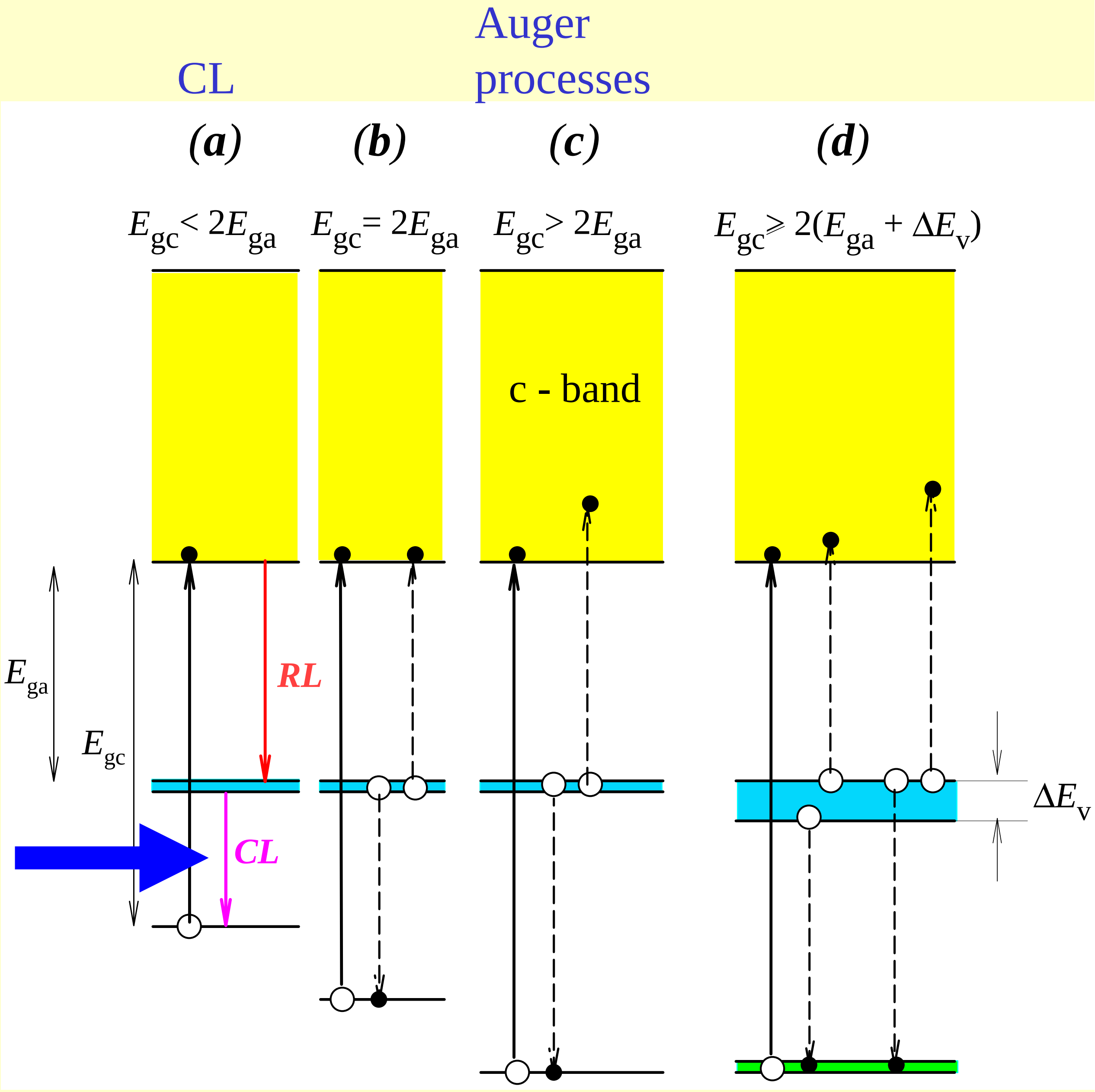
no CL at $E_{gc} > 2E_{ga}$

(*d*) We have CL at

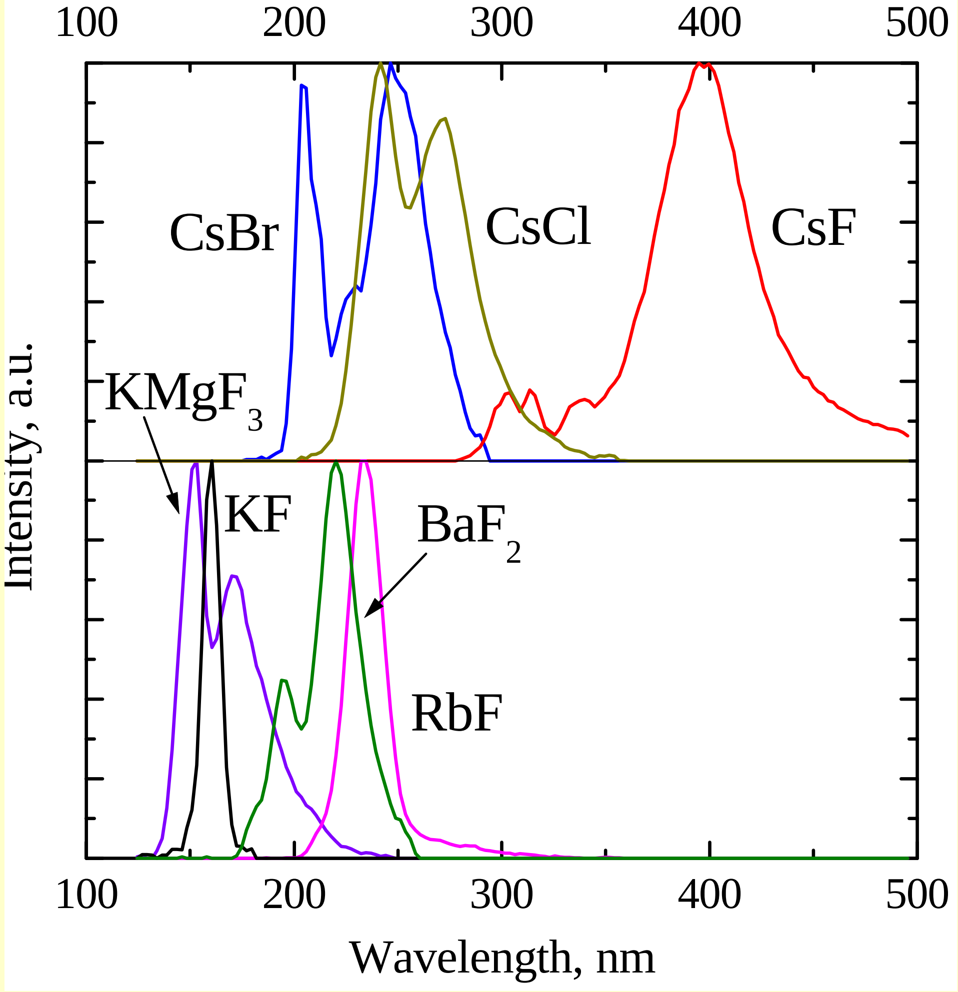
$2E_{ga} < E_{gc} < 2(E_{ga} + \Delta E_v)$

and no CL

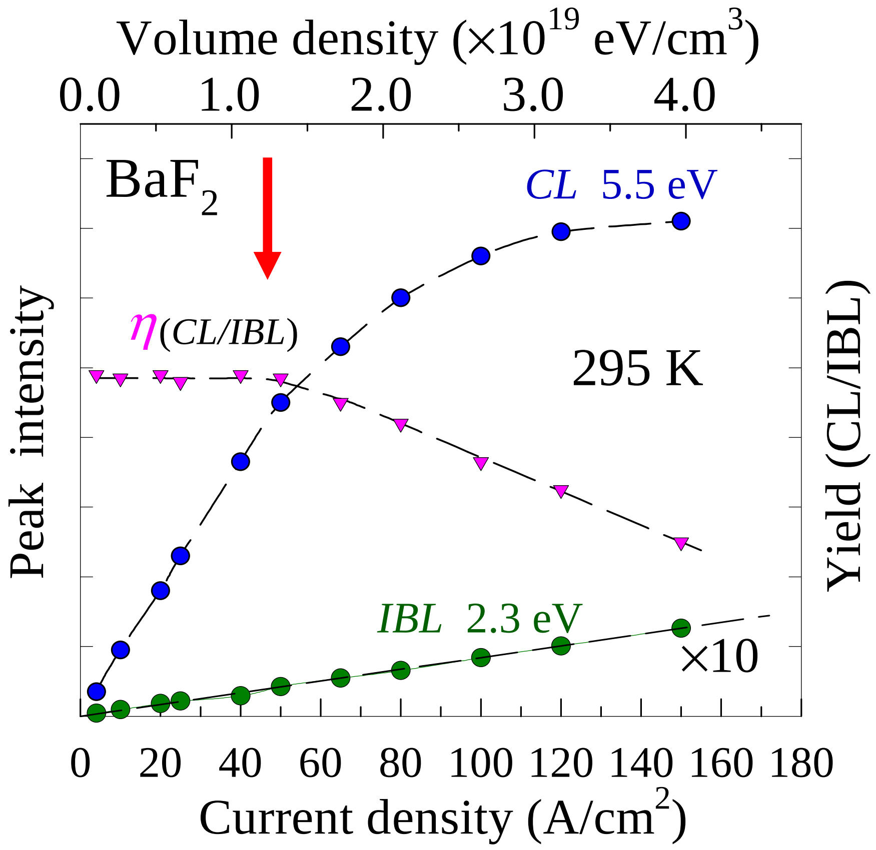
at $E_{gc} > 2(E_{ga} + \Delta E_v)$

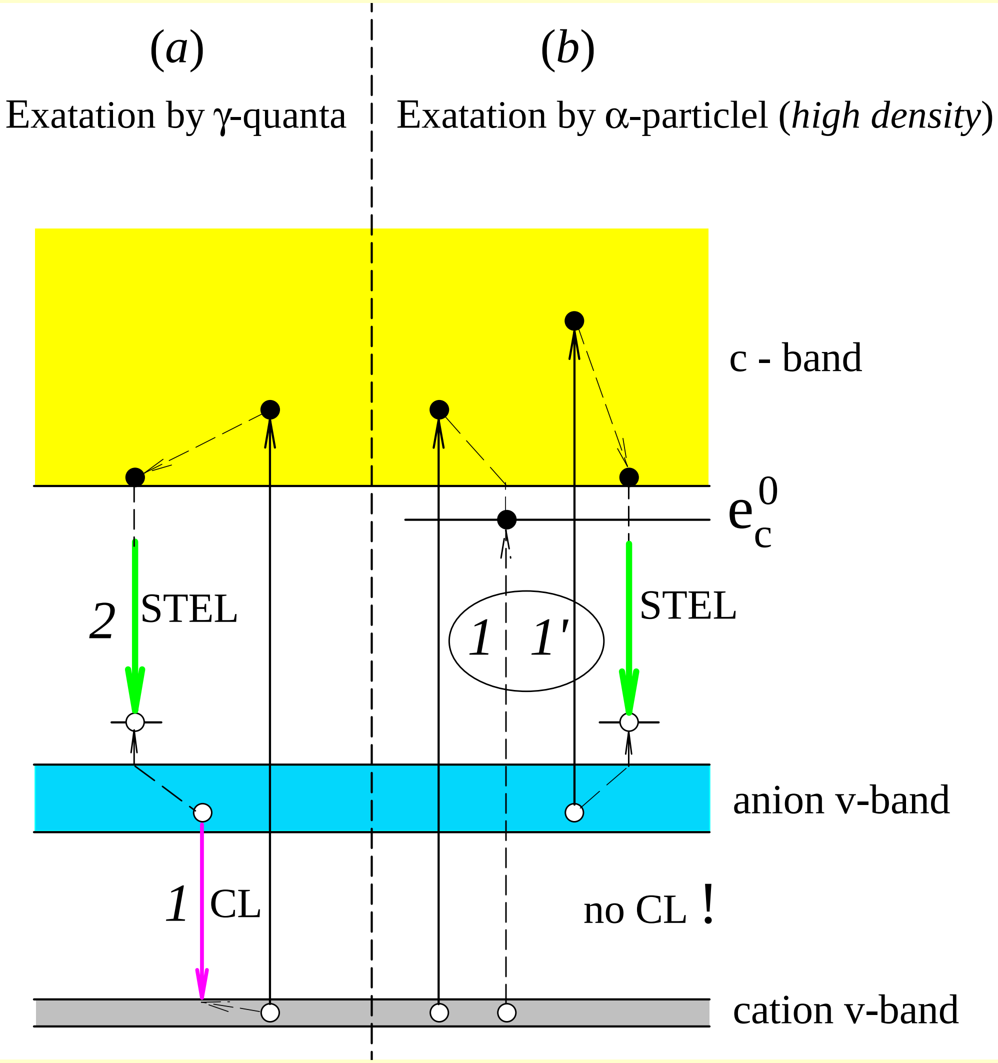


Core-valence or crossluminescence (CL)



Quenching of crossluminescence under high-dense irradiation more than 10^{18} *e-h* per 1cm^3 (>10^{19} eV)



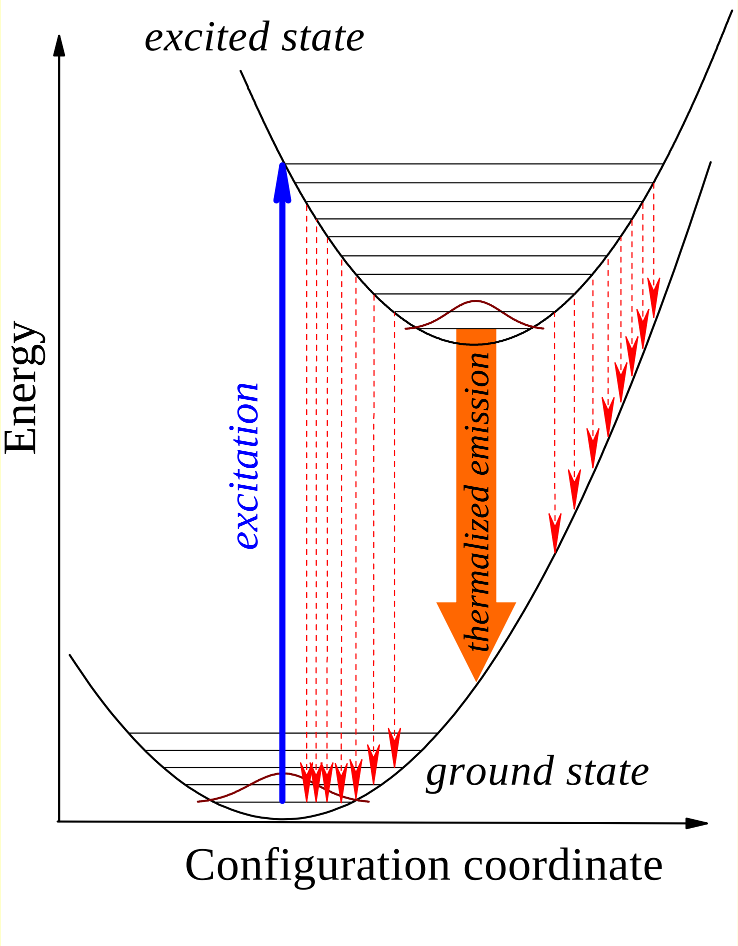


CL-crossluminescence,
IBL-(hole) intraband
luminescence
STEL- self-trapped exciton
luminescence

M. Kirm, A. Lushchik, Ch. Lushchik, A.I. Nepomnyashikh, F. Savikhin, Radiat. Meas. ***33*** *515 (2001)*

Hot luminescence

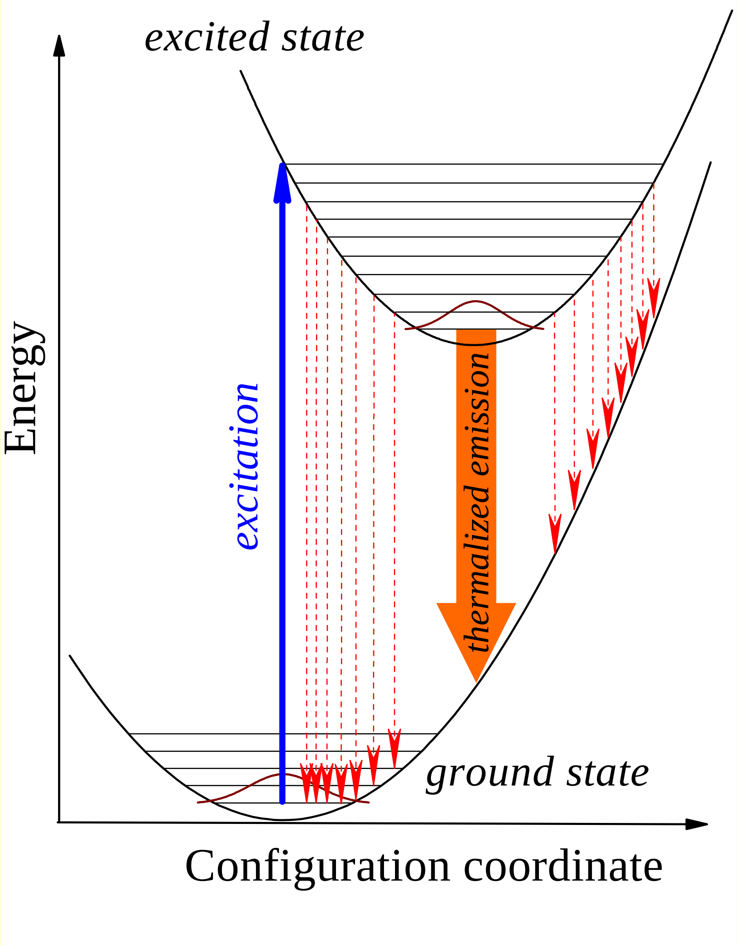
Hot luminescence of complex molecules in water solution (S.Vavilov's group)



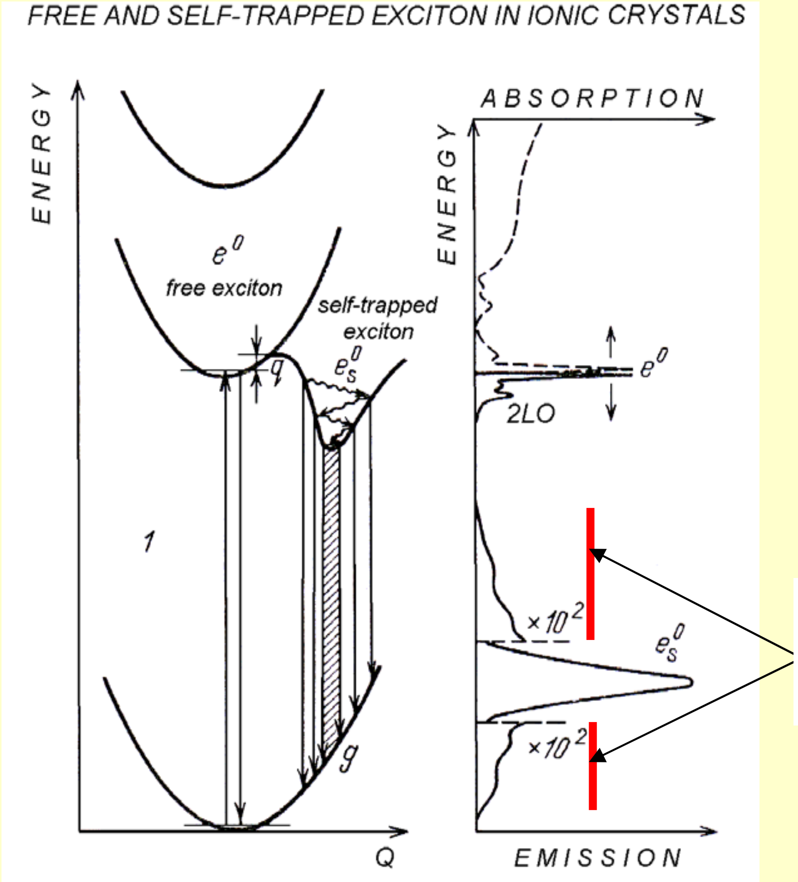
hot luminescence of impuriry centre

Hot luminescence

Hot luminescence of complex molecules in water solution (S.Vavilov’s group)

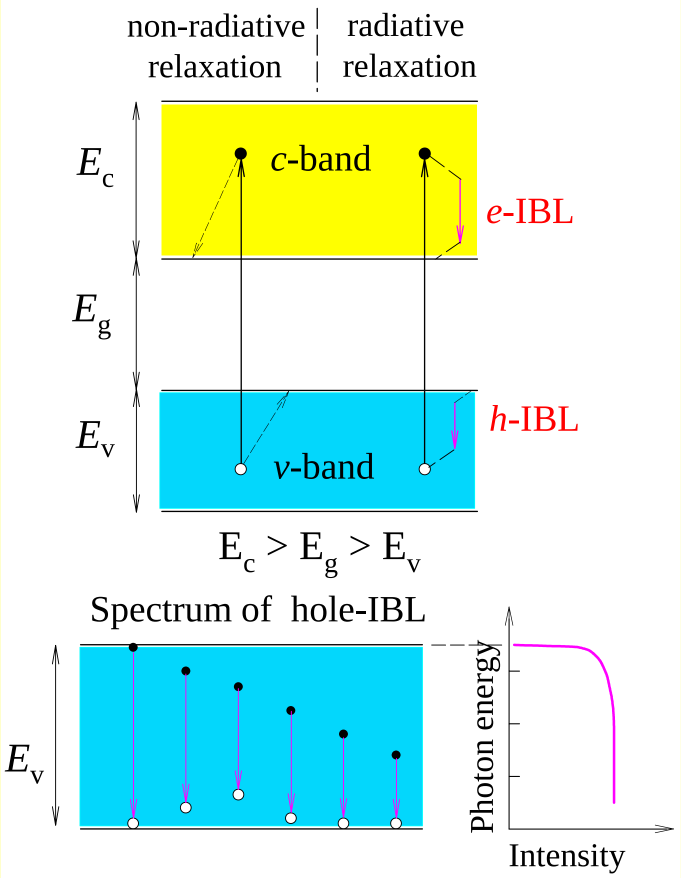


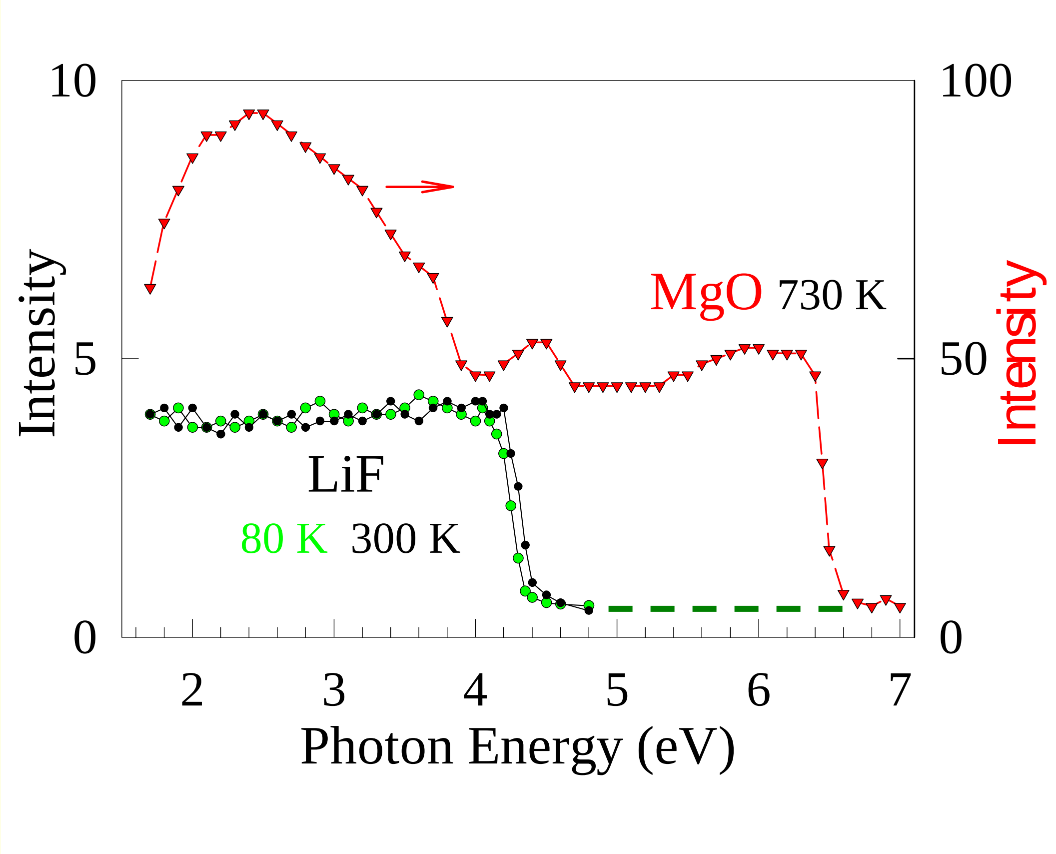
hot luminescence of impuriry centre



hot STE luminescence

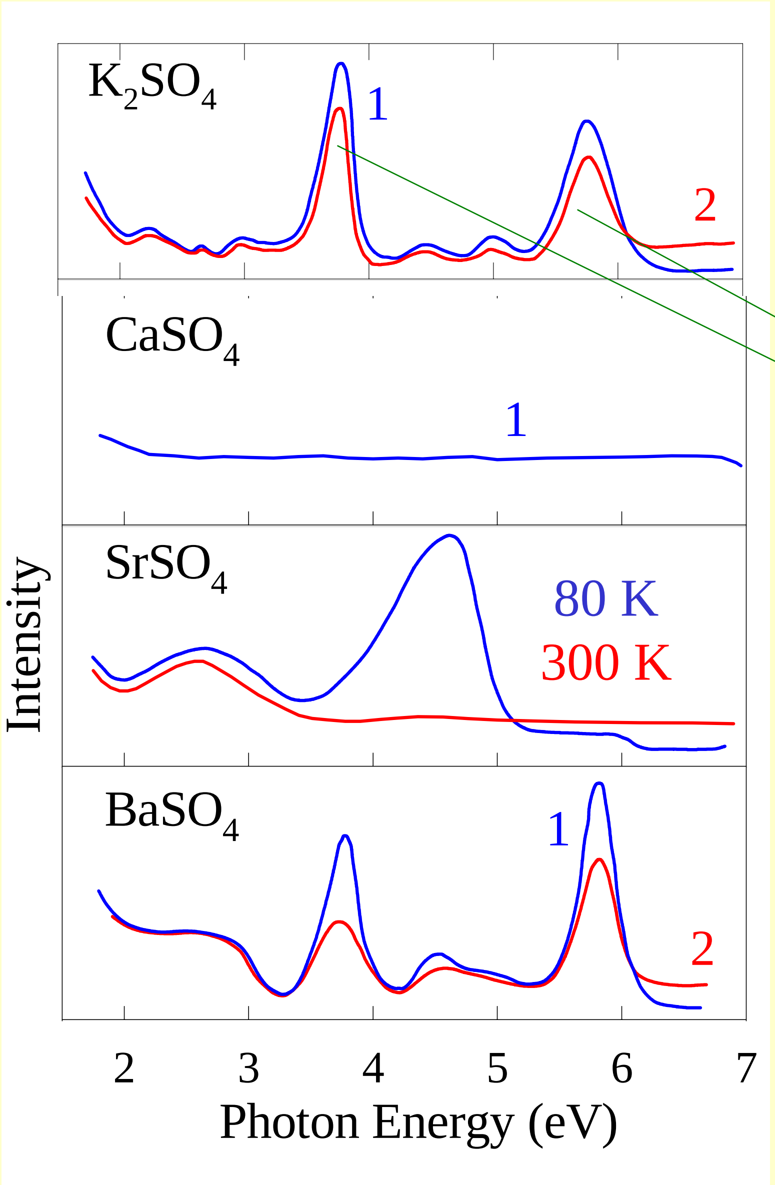
Intraband luminescence (IBL)

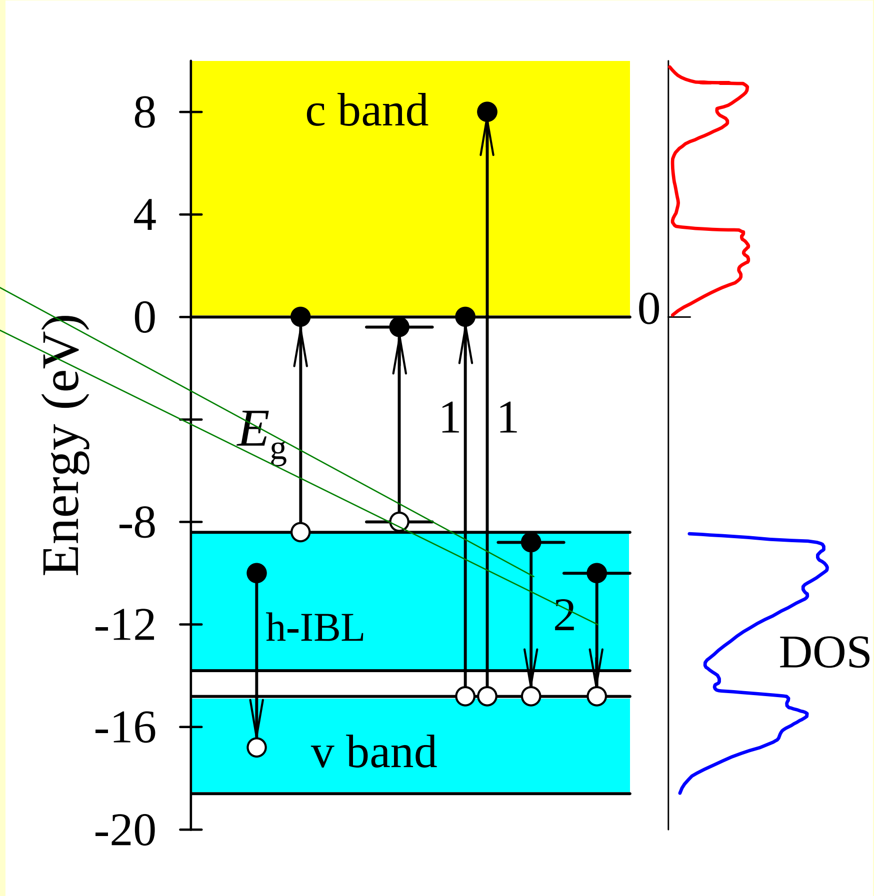




Spectra of fast ($\tau < 2$ ns) intraband (IBL) luminescence under irradiation by single nanosecond 300-keV electron pulses of the Kovalchuk-Mesyats-type generator

A. Lushchik, Ch. Lushchik, M. Kirm, V. Nagirnyi, F. Savikhin, E. Vasil'chenko, Nucl. Instr. and Meth. B ***250*** *330 (2006)*

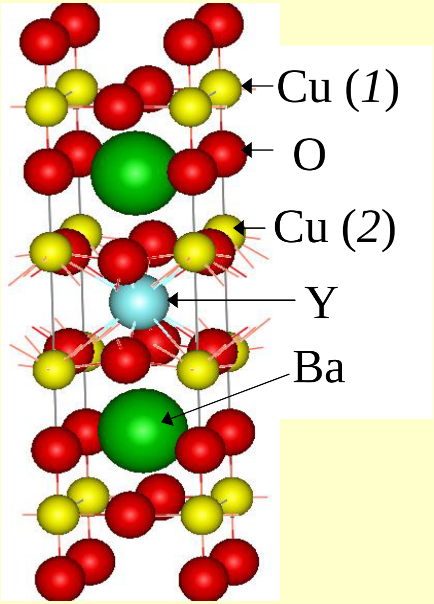


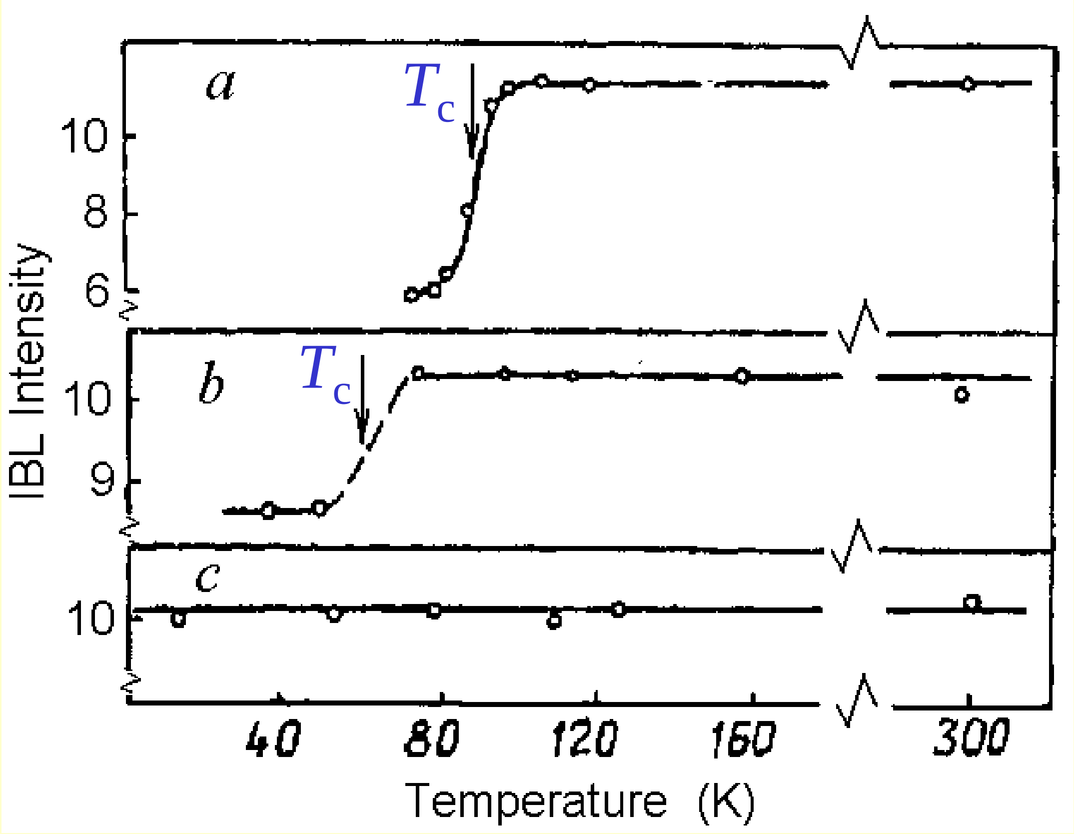


Schematic energy diagram of K$_2$SO$_4$

F. Savikhin, M. Kerikmäe, E. Feldbach, A. Lushchik, D. Onishchik, D. Rakhimov, I. Tokbergenov, "Phys. stat. sol. (c), ***2*** *252 (2005)*

Usage of fast IBL (excitation by single electron pulses, 300 keV, 2ns) for the investigation of high-temperature superconductivity in 1-2-3 ceramics





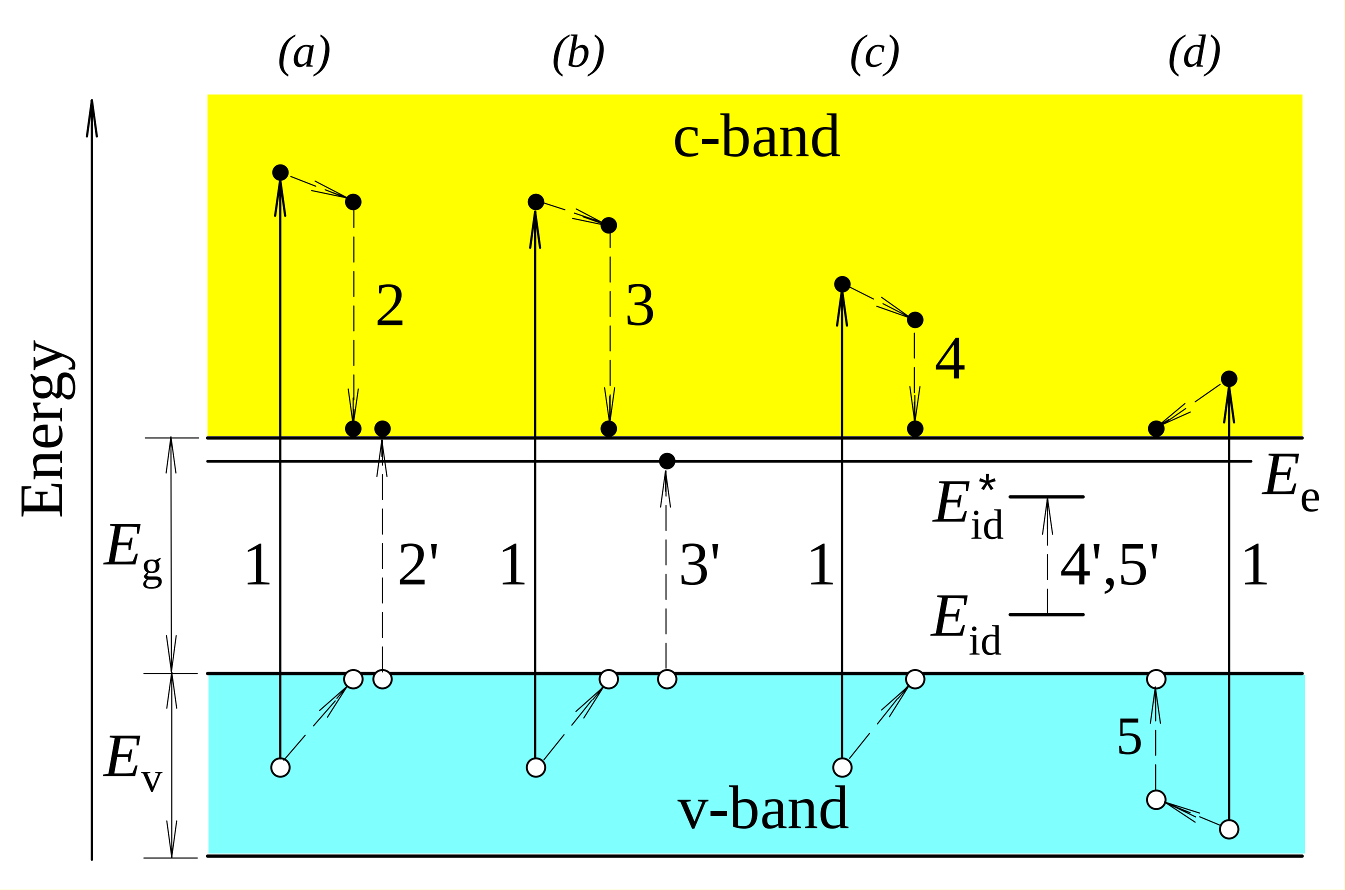
$YBa_2Cu_3O_{6.9}$
HTSC

$YBa_2Cu_3O_{6.6}$

$YBa_2Cu_3O_{6.2}$
no HTSC

Ch. Lushchik, F. Savikhin, E. Feldbach, I. Meriloo, Sov. J. Low. Temp. Phys. ***17*** *687 (1991)*

Multiplication of electronic excitations (MEE)

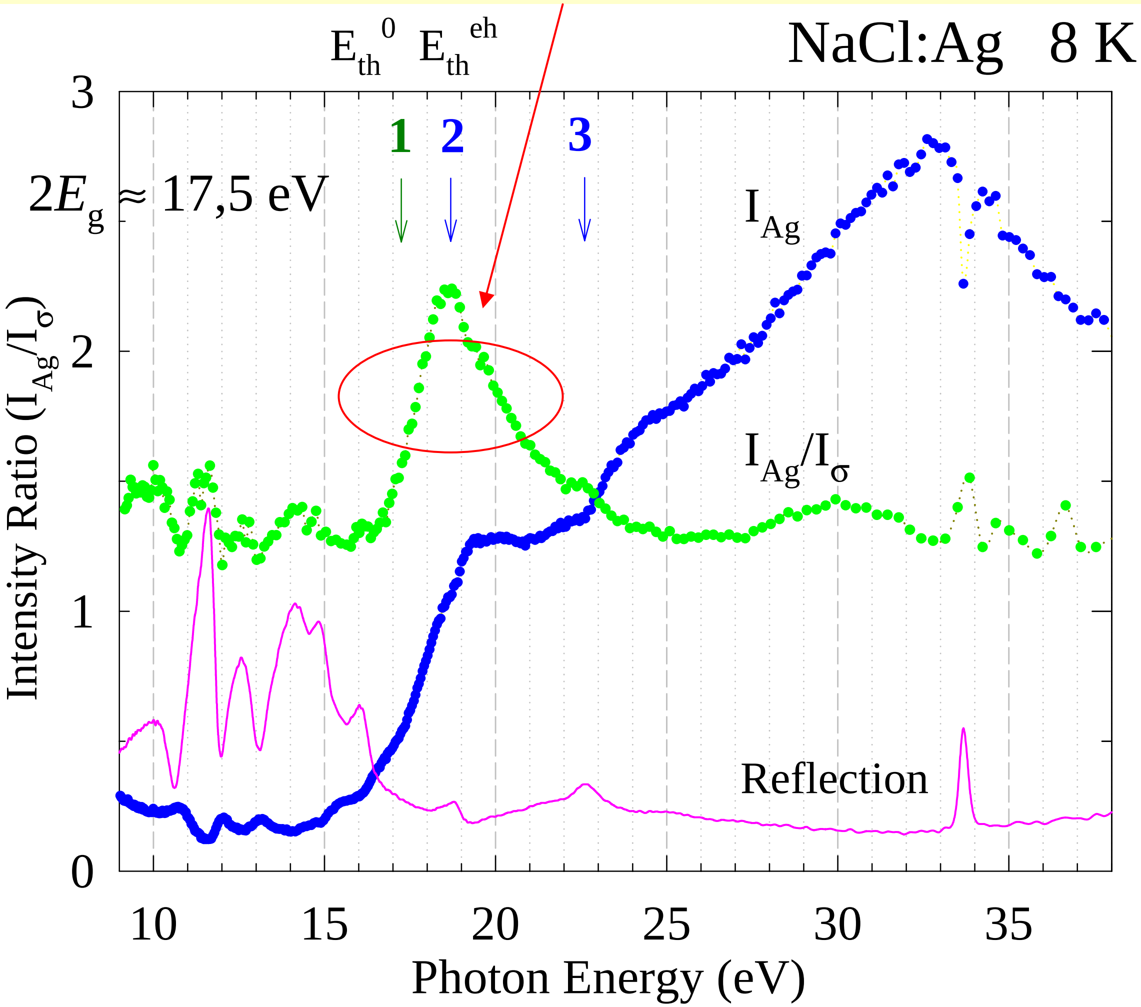


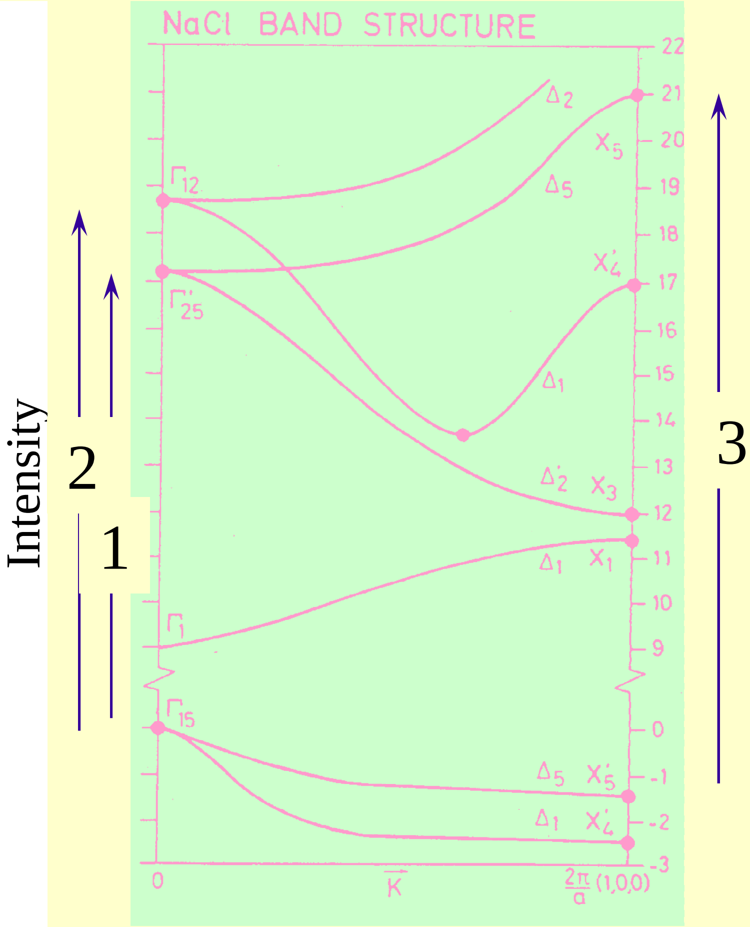
Three mechanisms of MEE in dielectrics:

(*a*) electron-hole, (*b*) excitonic and

(*c*, *d*) solid-state analogue of the Franck-Hertz effect in gases. QY >1

Excitonic mechanism of multiplication *(secondary excitons)*





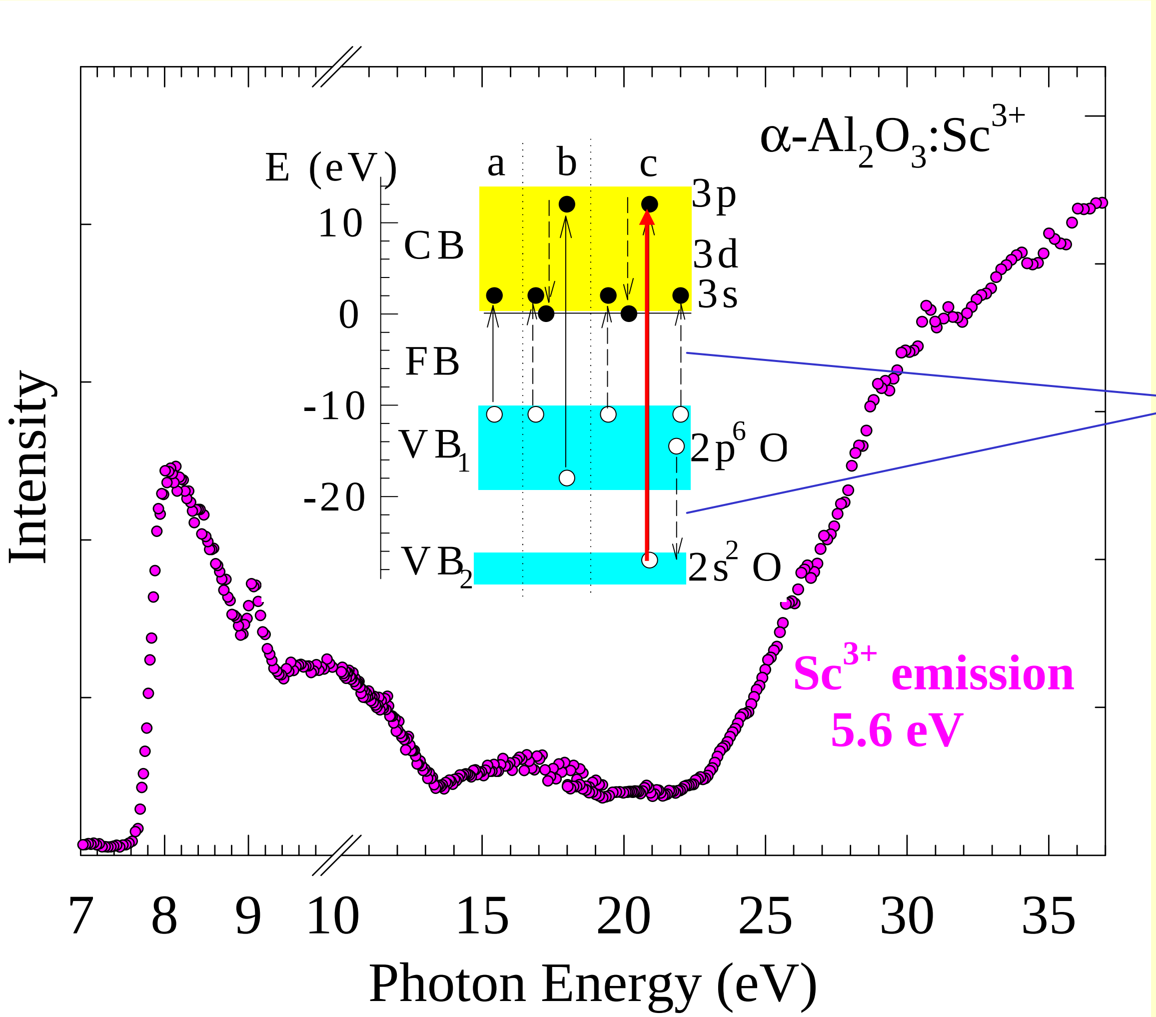
F.-J. Himpsel and W.Steinmann, Phys. Rev. B ***17*** *(1978) 2537.*

secondary excitons – see peak in intensity ratio spectrum at 17-22 eV

Ag^+ emission – e^0 are more efficient than e-h

σ-STE emission – due to $e + h$

E. Feldbach, M. Kirm, A. Lushchik, Ch. Lushchik, I. Martinson,
J. Phys: Condens. Matter ***<u>12</u>*** *1991 (2000)*

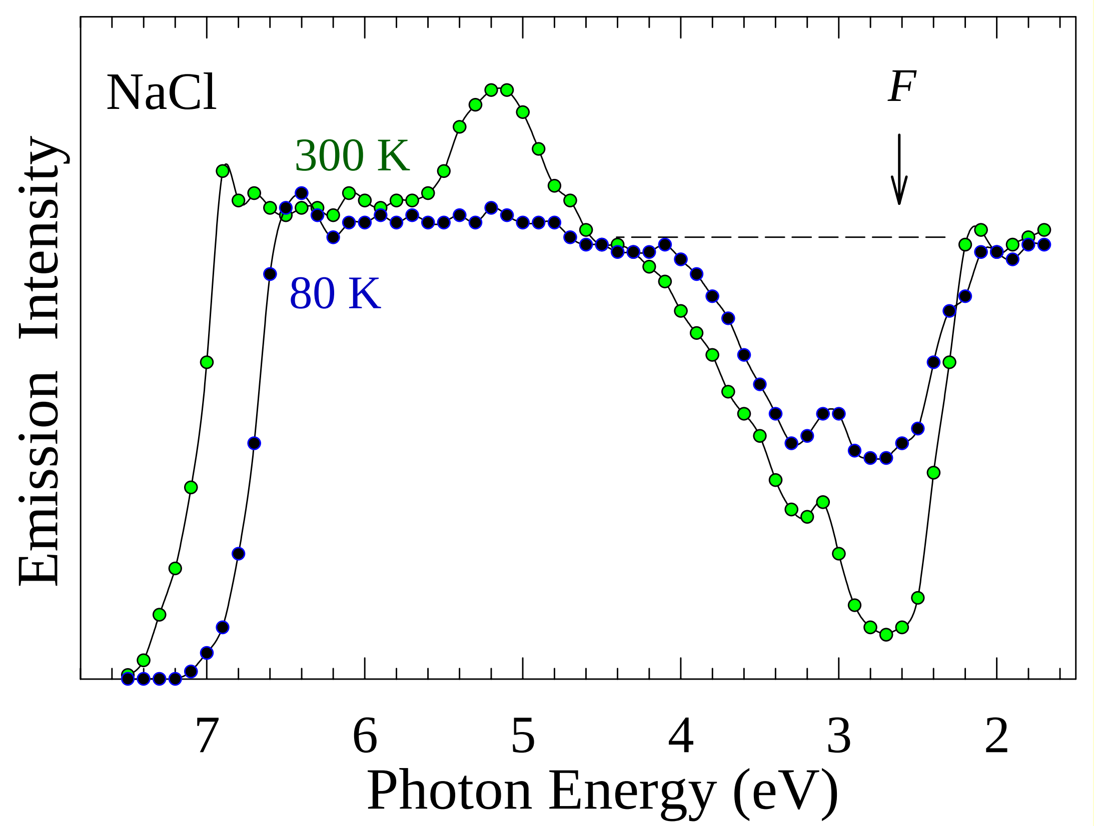


Auger process

One exciting photon of ~32 eV(start from 2s^2 oxygen shell) is able to form up to 3 *e*-*h* pairs

A. Lushchik, Ch. Lushchik, P. Liblik, A. Maaroos, V.N. Makhov, F. Savikhin, E. Vasil'chenko, J. Lumin. ***129*** *1894 (2009)*

	IBL	CL
Energetic yield	~10^{-5}	~10^{-3}
Lifetime	~0.1 ns	~ 1 ns



Reabsorption of IBL by short-lived Frenkel defects

Dielectric materials with high radiation resistance ($E_g < E_{FD}$)

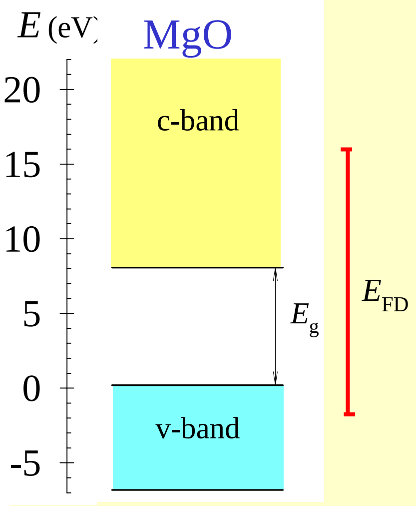
BeO
MgO
CaO
SrO

SiO_2
Al_2O_3
Sc_2O_3
Y_2O_3

$MgAl_2O_4$
$CaAl_2O_4$
$SrAl_2O_4$

ZrO_2
$Lu_3Al_5O_{12}$
$Y_3Al_5O_{12}$
Y_3SiO_5

NaCl (T = 4-80 K) NaBr NaI MgF_2



Dielectric materials with low radiation resistance ($E_g > E_{FD}$)

LiH
LiD

LiF
NaF
KF

NaCl (T > 200 K)
KCl
RbCl
CsCl

KBr
RbBr
CsBr

KI
RbI
CsI

CaF_2
SrF_2
BaF_2

Creation spectra of Frenkel defects by VUV radiation

In NaCl, the first creation spectrum of *F* centers was measured already in 1964 by Cheslav Lushchik and collaborators at room temperature (i.e. when $E_{\mathrm{FD}} < E_{\mathrm{g}}$).

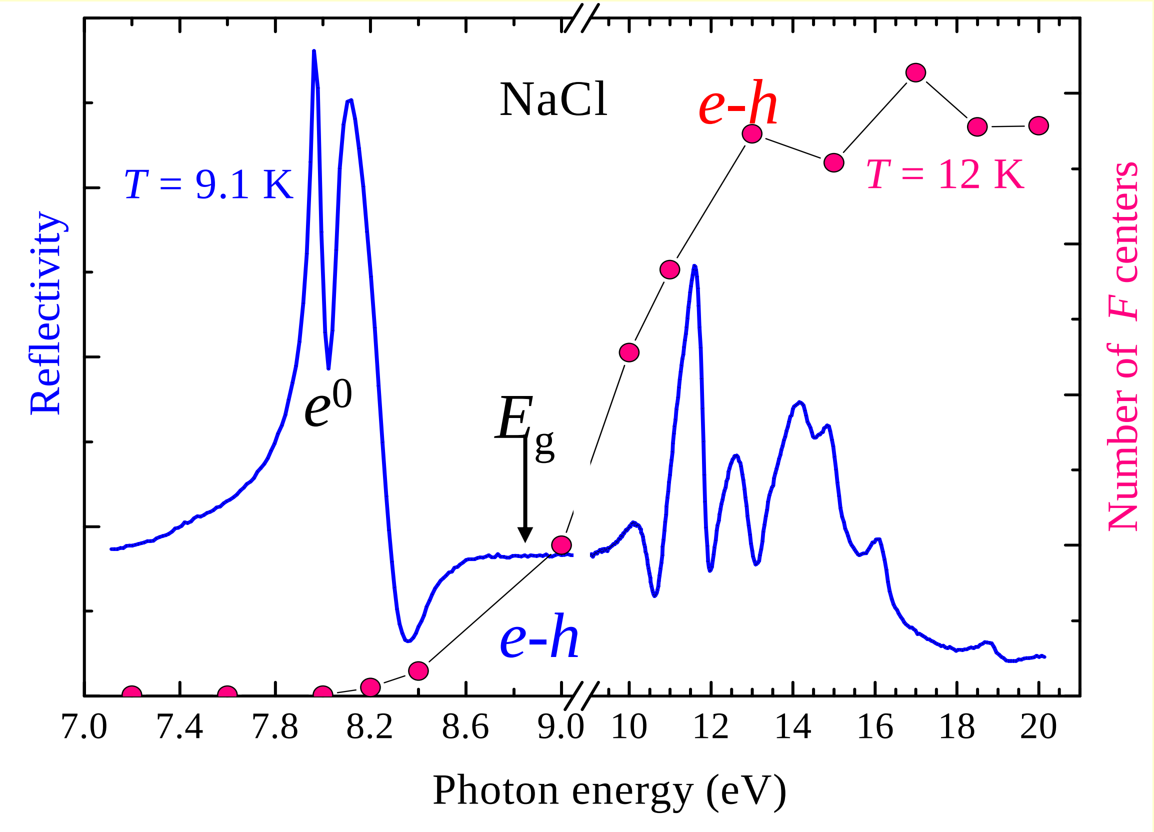
e^0 *and* *e-h* mechanisms of Frenkel defect creation –
stable F centers and complementary defects (halogen interstitials) are efficiently formed at the recombination of separated electrons and holes.

Ch.B. Lushchik, G.G. Liidya, M.A. Elango, "Electron-hole mechanism of color center creation in ionic crystals," Sov. Phys. Solid State, ***6****, pp. 1789-1794, 1965.*

KCl and KBr – efficient creation of stable radiation Frenkel defects
at both 10 and 300K

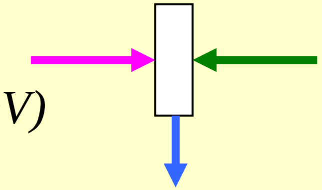
NaCl – highly resistant against radiation at $T \leq 80$ K

Low-temperature creation of long-lived *F-H* pairs in NaCl ($E_{FD} > E_g$)



N(*F*)~ light sum of (3-4 eV)-flash stimulated in the maximum of *F*-absorption band (2.75 eV).

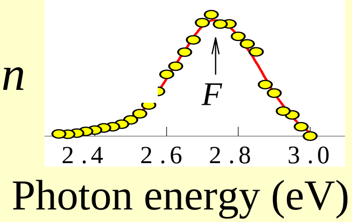
Synchrotron radiation - FINEST beamline with undulator, MAX-III, Lund



Synchrotron radiation (7-40 eV)

F-stimulation

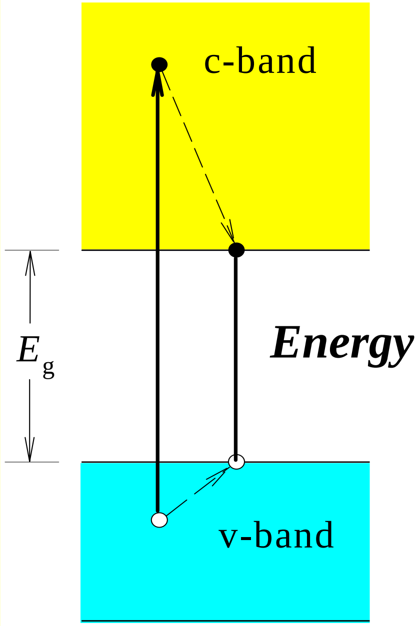
Lumisescence, ~ N(F)



$$F \ldots. H + h\nu_F \rightarrow F^* \ldots. H \rightarrow h\nu_{Lum} + \alpha \ldots. I \rightarrow R$$

$$v_a e \quad i_a^0 \qquad\qquad v_a \quad i_a^-$$

Three decay channels of electronic excitations (anion excitons or *e*-*h* pairs) in a typical wide-gap crystal



Energy ⇒

luminescence	$h\nu_L$
heat release	phonons, $n\hbar\omega$
Frenkel defects	$e_s^0 \rightarrow v_a e$ (F) + i_a^0 (H)

Competition between radiative and non-radiative (heat, defect creation) channels of STE decay

Dependence of STE luminescence quenching on high hydrostatic pressure in NaCl

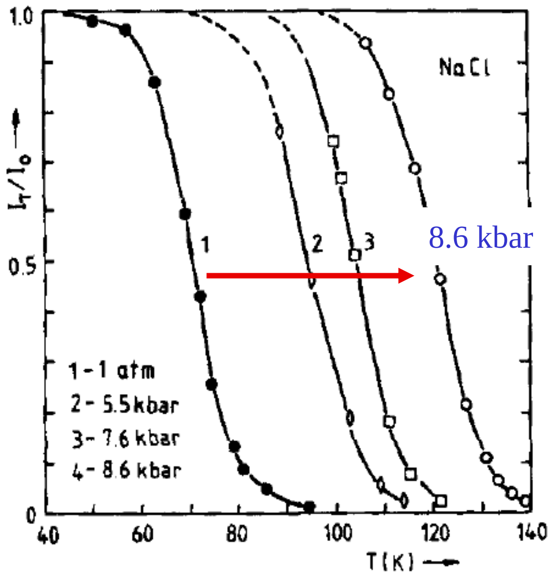


Fig. 2. Thermal quenching curves for the 3.47 eV XRL band of STE in NaCl at various pressures.

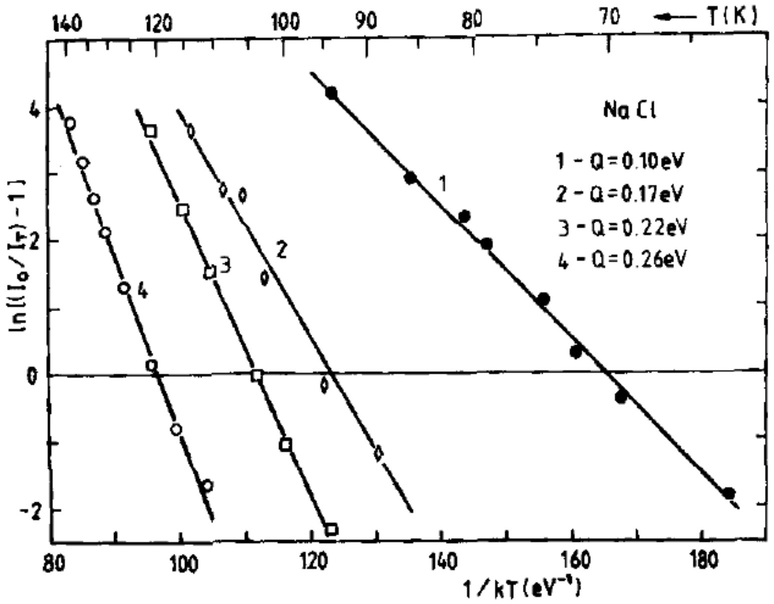


Fig. 3. The plots of $\ln[(I_o/I_T)-1]$ versus 1/T for thermal quenching curves 1-4 shown in Fig. 2.

__A.Laisaar__, V.Scherbakov, A.Kuznetsov, High Peressure Research ***3****, 78-80 (1990)*

Concluding Remarks

Radiation-hardened materials

Fast and temperature-stable electron or hole intraband luminescence

IBL under extremely high-dense irradiation?

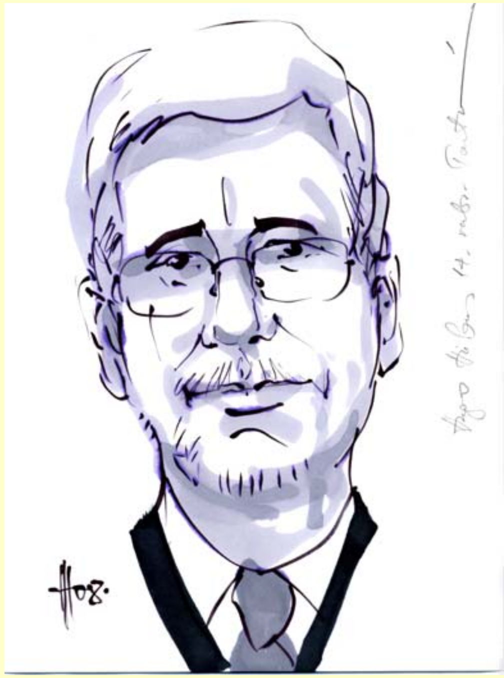
An obstacle – a pre-breakdown emission due to electron avalanches in the bulk of WGMs

Materials with additional gaps or at least pseudo-gaps (at certain wave vectors) inside energy bands should be preferred.

Acknowledgements

To all present and former colleagues from the Laboratory of Ionic Crystals

et al.



THANK YOU