Initial kinetics of material excitation and relaxation in swift heavy ion tracks

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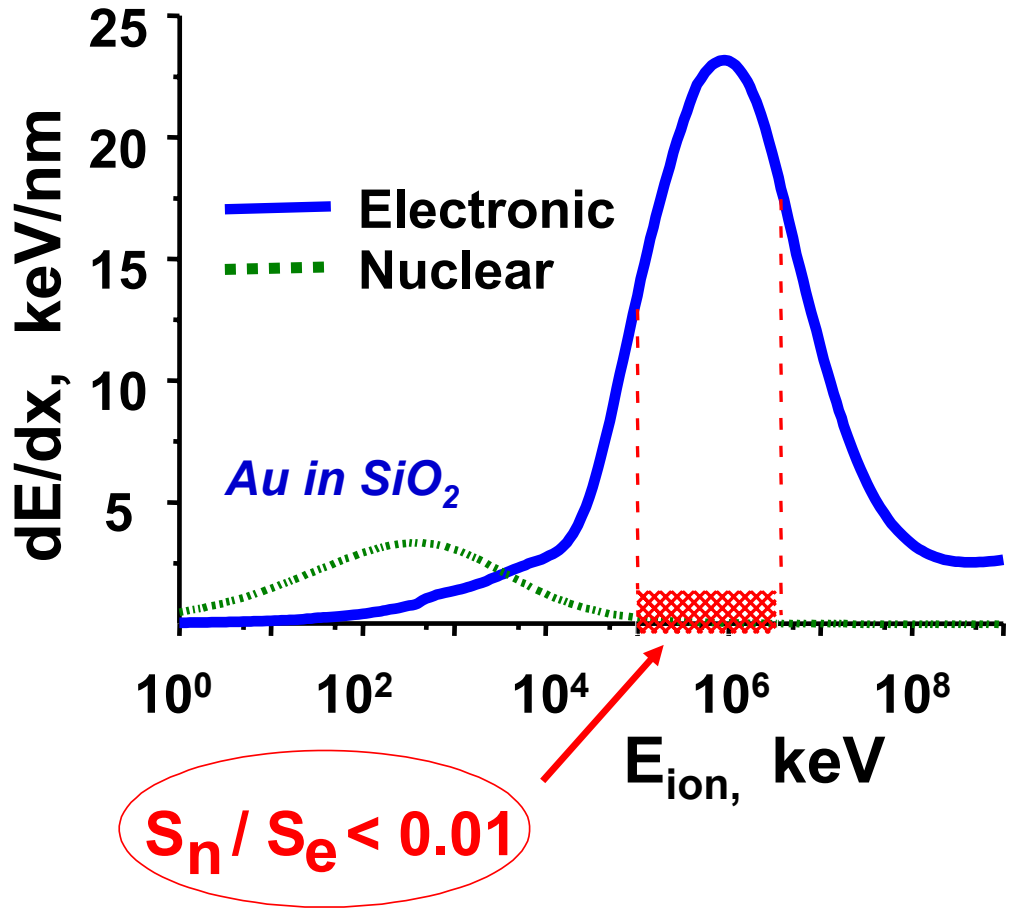
Swift Heavy Ions

E_{ion} > 1 MeV/u

M_{ion} > 20 m_p

Se > 1 keV/nm

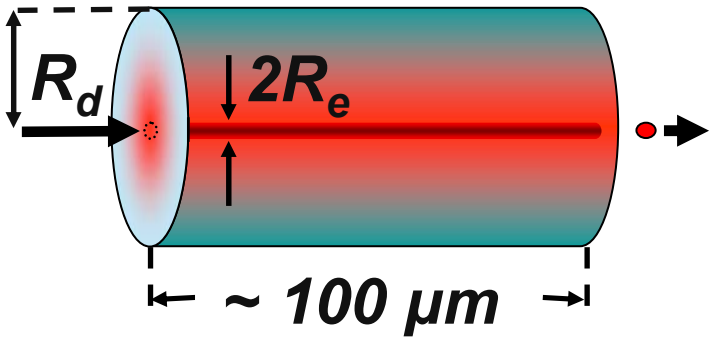
O^+	>20 MeV
Xe^+	100 – 300 MeV
U^+	1 – 2 GeV

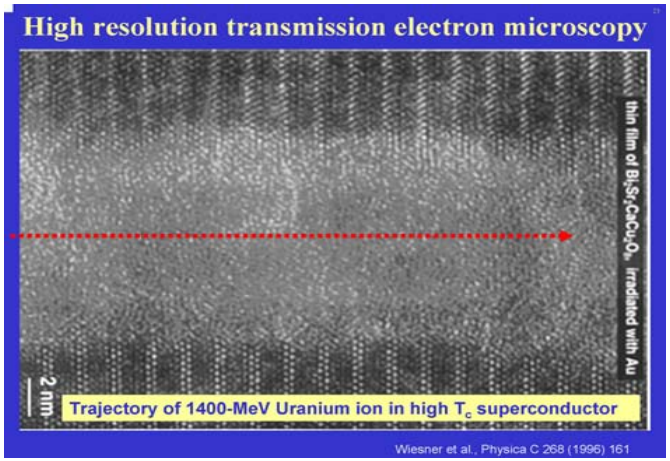


The electronic energy losses are more than two orders larger than the elastic losses

Why SHI are interesting ?

I. A new tool for nanostructuring





Initial excitation: $R_e < 5$ Å

Structure transformations: $R_d \sim 10 nm$

The energy losses due to elastic collisions are too small to produce detected damage

Why SHI are interesting ?

II. Fundamentals

Nanometric spatial and

Femto-picosecond temporal scales

Extremely high levels of initial excitations

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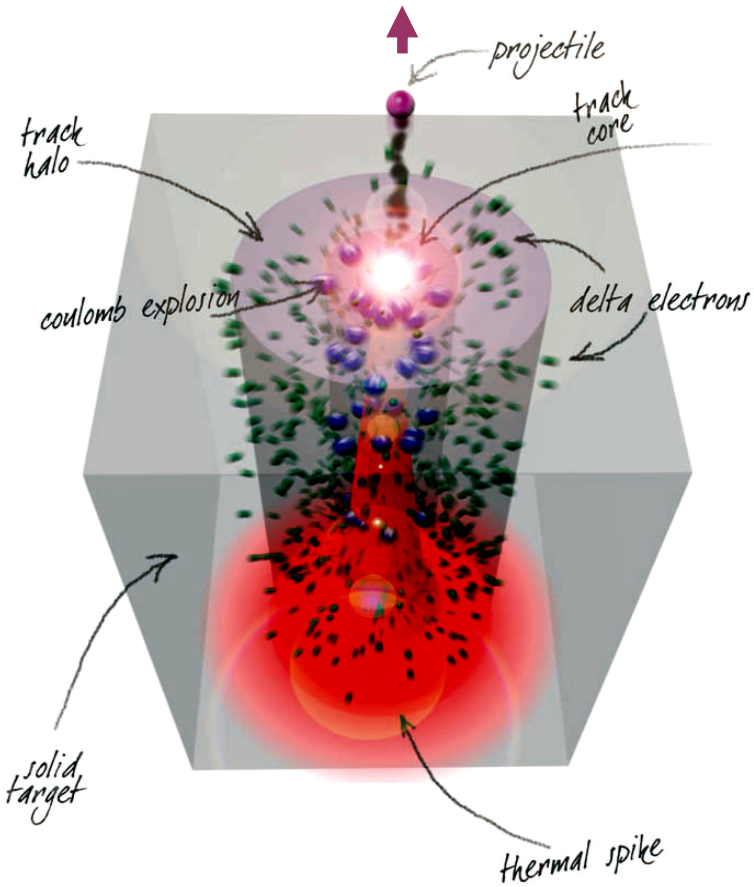
Unusual kinetics pathways of track relaxation

Which can not be described by macroscopic models

Models are necessary

which form the basis for controlling the technological processes based on SHI irradiations

Time Scales



Marek Skupinski (Uppsala)

1. Initial electronic excitations 10^{-17} s
2. Plasmon screening 10^{-16} s
3. Thermalization of electrons 10^{-15} s
4. Cooling down of electrons 10^{-14} s
5. Energy transfer to lattice up to 10^{-11} s
6. Track cooling down 10^{-9} s
7. Stress relaxation $> 10^{-9}$ s

Why the Thermal Spike is popular?

Temperature

Easier description of structure and phase transformations

Macroscopic models with local equilibrium ⟷ **Thermo activated mechanisms**

Heat Diffusion

Diffusion

Phase transformations

How to produce Two Temperatures Thermal Spike

1. Thermalization of both subsystem of a target (electronic and ionic) at different temperatures. Local equilibrium
2. A difference between electronic and ionic temperatures forms the driving force for energy transfer
3. Parabolic equations of heat diffusion

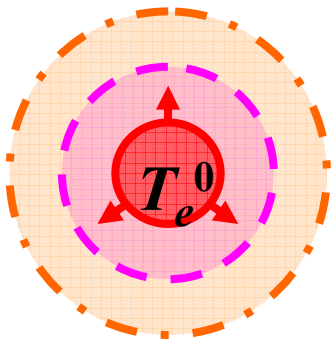
$$\frac{\partial T_e}{\partial t} = div(\chi_e \nabla T_e) + q_{ei}$$

$$\frac{\partial T_i}{\partial t} = div(\chi_i \nabla T_i) - q_{ei}$$

$$t_i^c = \left(R_i^0\right)^2 / 4\chi_i$$ Lattice cooling down

$$t_e^c = \left(R_e^0\right)^2 / 4\chi_e$$ Electronic cooling down

$$t_{ei}^E = q_{ei}^{-1} T_i$$ Electrons to ions energy transfer



$t_e^c > t^E{}_{ei}$ ⇨ lattice is heated

$t_e^c < t^E{}_{ei}$ ⇨ lattice is not heated

Electron – phonon coupling

$$e - i \equiv e - ph$$

$$t_{os} = 10^{-13}\, s$$

$$t^{E}_{e-ph} = 10^{-12} - 10^{-11}\, s$$

Ginzburg et al (1956)

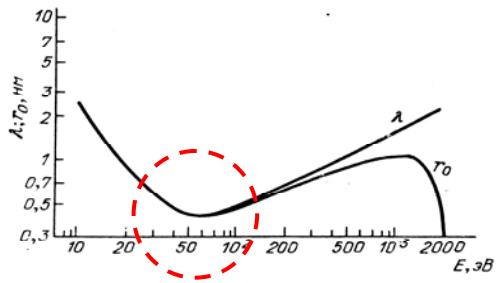
$$\chi_e > 10\ cm^{2} s^{-1}$$

$$t_e^{c} < 10^{-14}\, s << t^{E}_{e\text{-}ph}$$

$$\Delta T_i = 10 \text{ to } 100\ K$$

No heating

Martynenko and Yavlinskii (1983)



$$\chi_e = 1\ cm^{2} s^{-1}$$

when

$$T_e = 1 \text{ to } 10\ \varepsilon_f$$

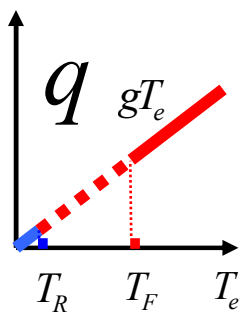
$$t_e^{c} < t^{E}_{e\text{-}ph}$$

$\Delta T_i =$ **a few handreds** K

$$q = gT_e$$

$$g = 3.6\ s^{-1}$$

room temperature experiments in *Fe*



Toulemonde et al. (1992)

$$\Delta T_i > 2000\ K$$

Above the melting point

Electron-lattice interaction in a SHI track

Cooling down time of electrons is much shorter that the atomic vibration time.

$$t^c_e = (R^0_e)^2 / 4\chi_e < 10^{-14}\, s << t_{os} = 10^{-13}\, s$$

Lattice dynamic can not be ascribed by phonons

Frozen ionic structure with the ideal gas dynamics

(L. van Hove 1952)

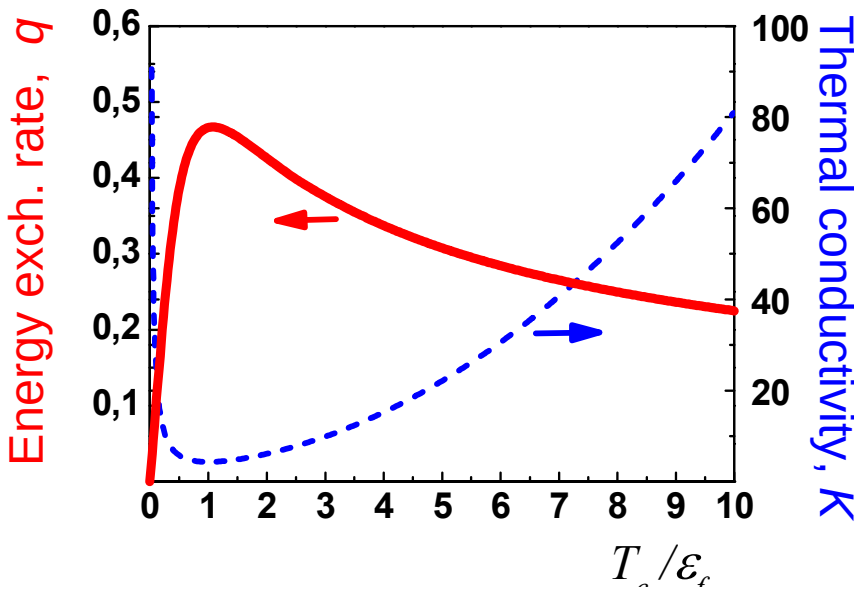
Dynamically isolated atoms : $\varepsilon(\mathbf{k}) \sim \mathbf{k}^2$

Phonons $\varepsilon(\mathbf{k}) \sim \mathbf{k}$, $(k << \pi/a)$

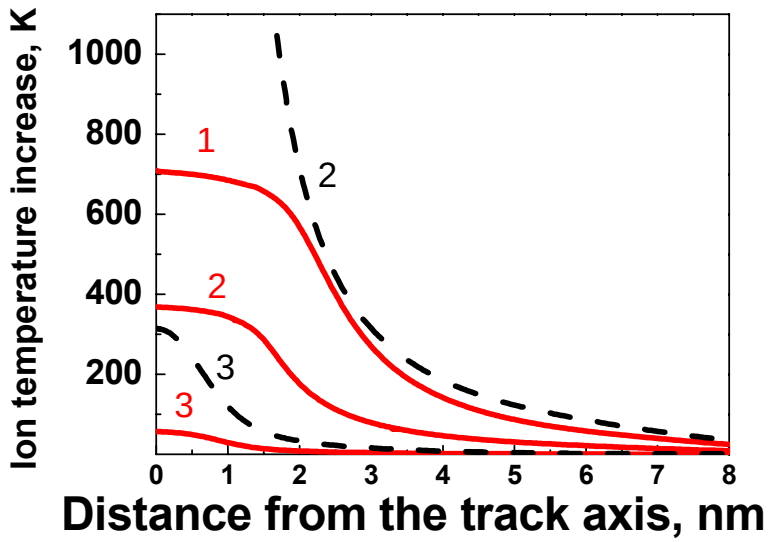
Electron – phonon coupling mechanism can not be applied before 10^{-13}s in SHI tracks

Electron-to-Lattice heat transfer rate

$$q = \frac{4LZne^4m^2}{\pi M\hbar^3\left[1+\exp(-\mu/T_e)\right]}\left\{\frac{T_i}{1+\exp(\mu/T_e)} - T_e\right\}$$



Classical limit at high energies : electron – ion interaction in two component plasma



Dash lines - e-ph coupling.
The maximum initial electronic temperatures:
(1) $10\varepsilon_f$ **, (2)** $5\varepsilon_f$ **and (3)** ε_f

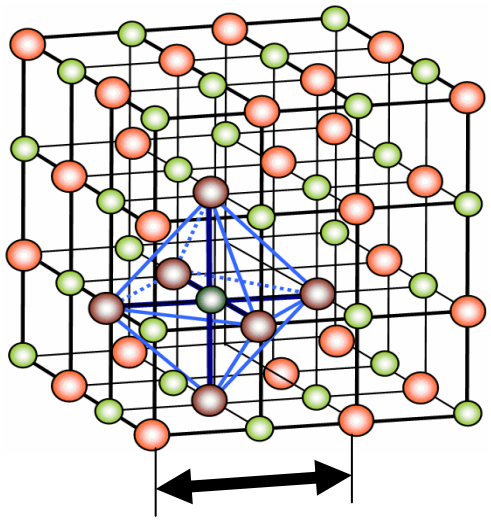
No large heating

“Thermometer” and “tool” for defect kinetics investigations

Examination of different temperature-based models of track excitation needs a natural “thermometer” – a system where :

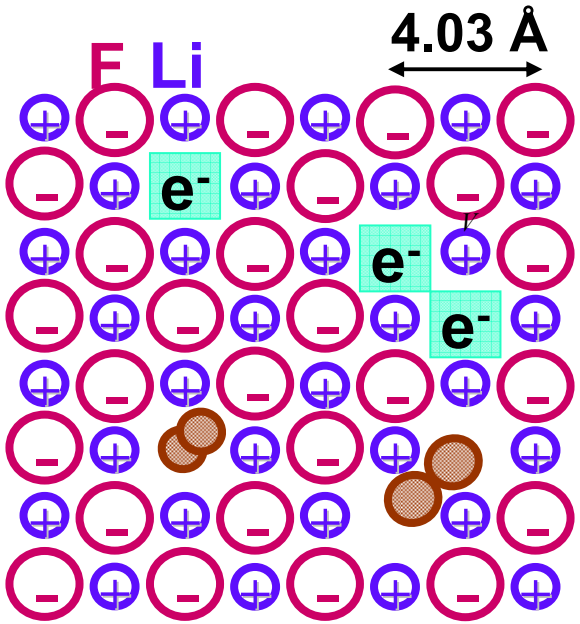
a) Relaxation of electronic excitations results in well detected changes

b) Temperature considerably affects to these changes that also must be easy detected



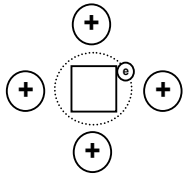
Alkali – Halides
(LiF, NaCl)

Defects in alkali – halides



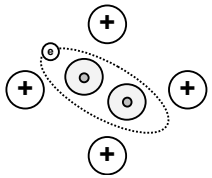
fcc lattice, (100) plane

Electron centers

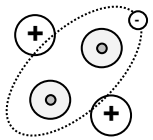


$v_a^+ e^-$ **F-center (stable at RT)**

Hole centers



X_2^- / X^- **H-center (T<80K)**



$X_2^- / 2X^-$ **V_K- self-trapped hole (T<140K)**

Electro-neutrality. Vacancies and interstitials must capture charge carriers

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New electronic levels due to localization of carriers

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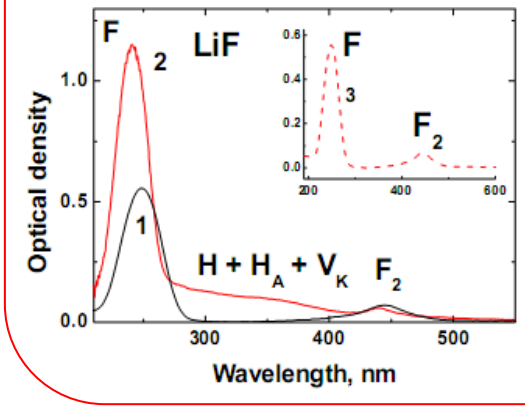
Color Centers

1. Well separated by Spectroscopy



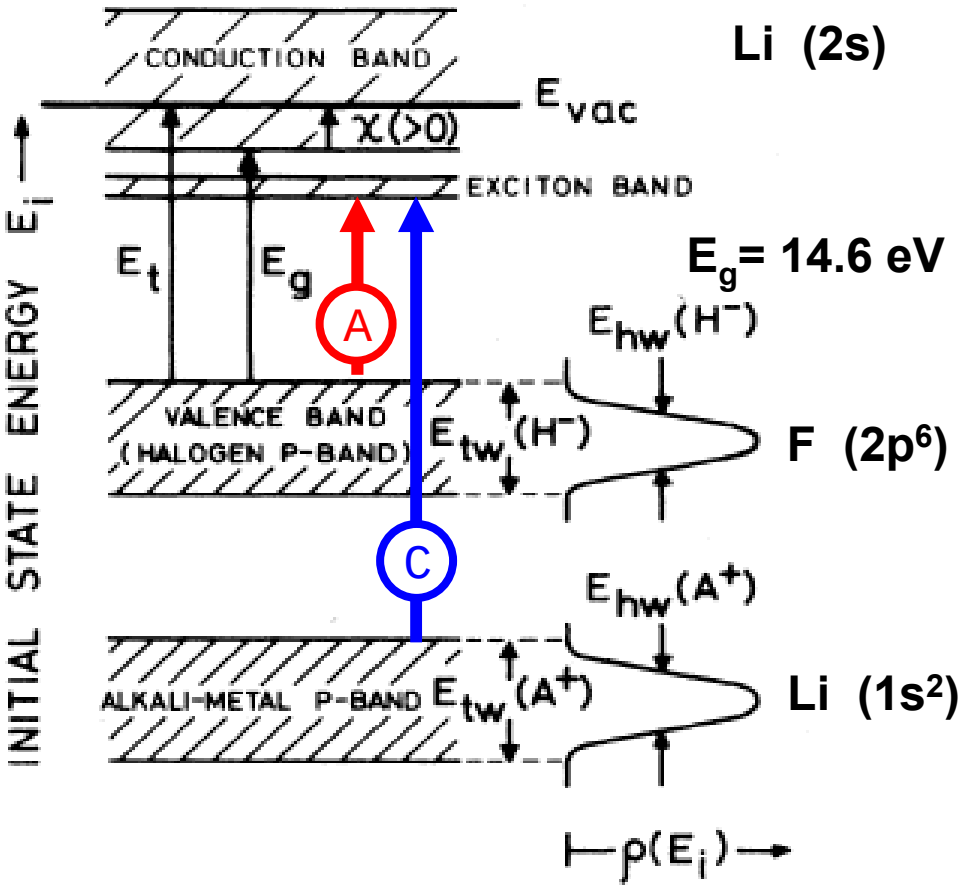
2. Different temperatures of stability

F	1000K
V_k	140K
H	80K
I	10-25K

Exciton mechanism of defect creation

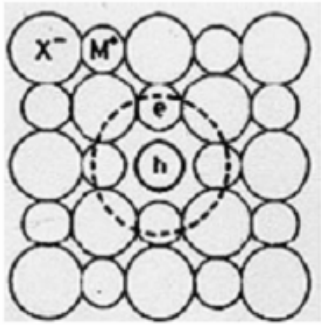
Excitons in LiF

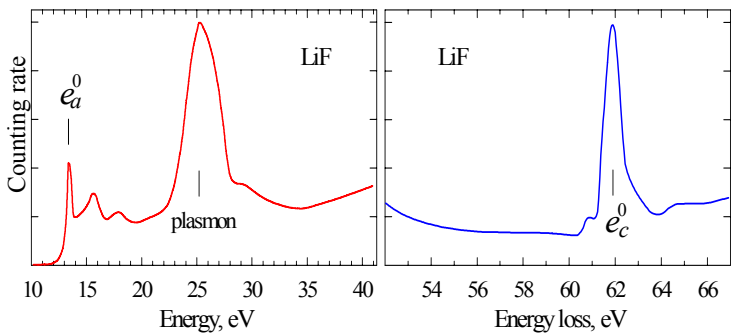
R. T. Poole et al., PRB 11 (1975) 5179; J. R. Fields et al. PRL 38 (1977) 430



A **Anion exciton 13.6 eV**

C **Cation exciton 62 eV**





Plasmons 25 eV

In-situ spectroscopy at UNILAC GSI

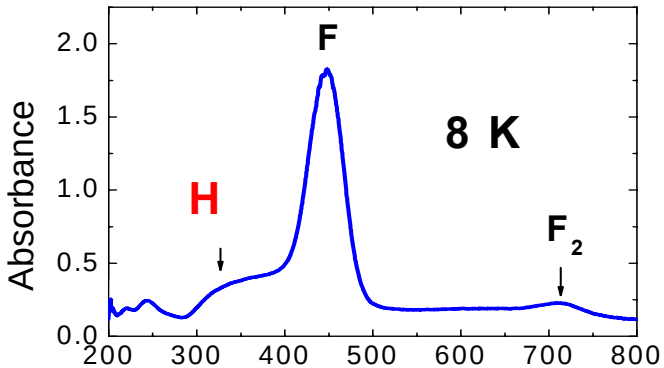
Prof. Kurt Schwartz

1. LiF and NaCl
2. The ion energies 11 Mev/u (50 - 2600 MeV)
3. Ions
   - a) Light C, Ti, Ni
   - b) Kr, Sm
   - c) Heavy Au, Pb, U
4. The electronic energy losses 0.7 - 26 keV/nm
5. Fluences from 10^8 to 10^{12} ions/cm^2

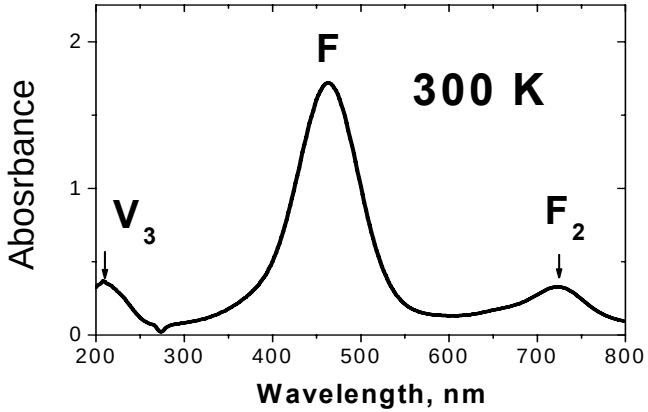
6. Irradiation temperatures 8 K and 300 K

Detection of defects having low thermal stability

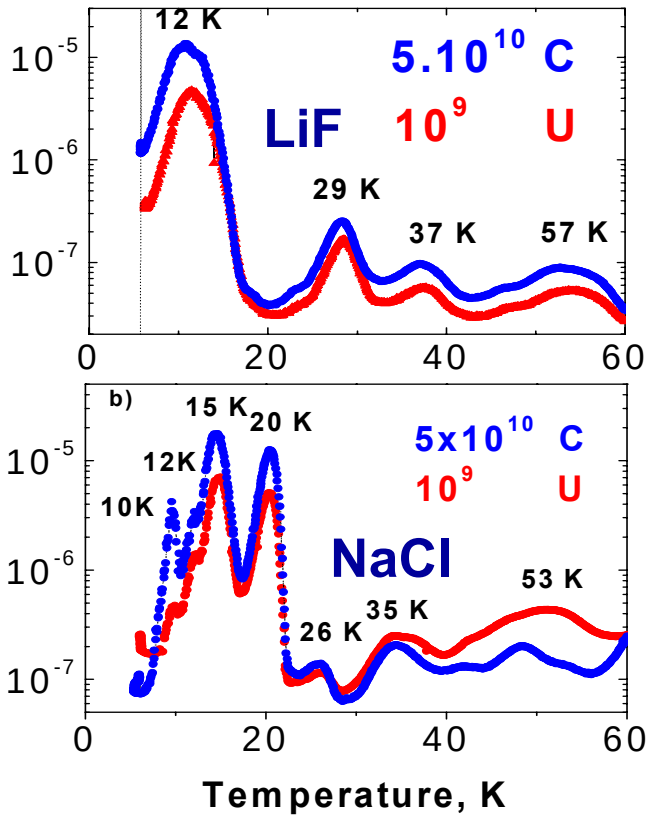
«Low temperature» defects



^{238}U in LiF



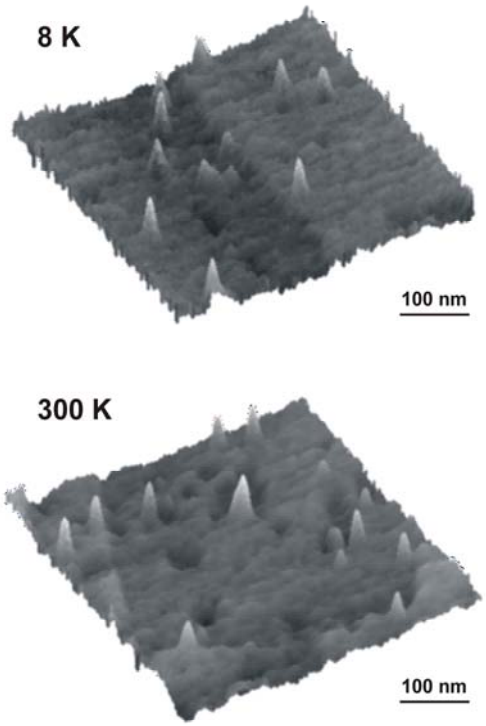
H centers are not stable at T > 70 K



I centers are stable only before 10 – 25 K

No dependence on the electronic energy loss

Hillocks in LiF
1400 Pb ions at 8 K and 300 K

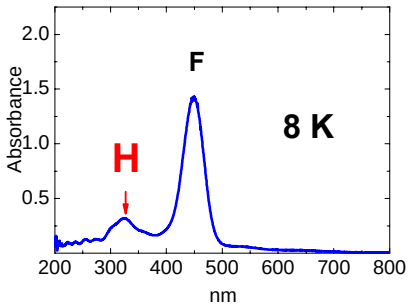


1. Core damage
2. Threshold dE/dx ~ 6 keV/nm
3. **No dependence on T_{irr}**

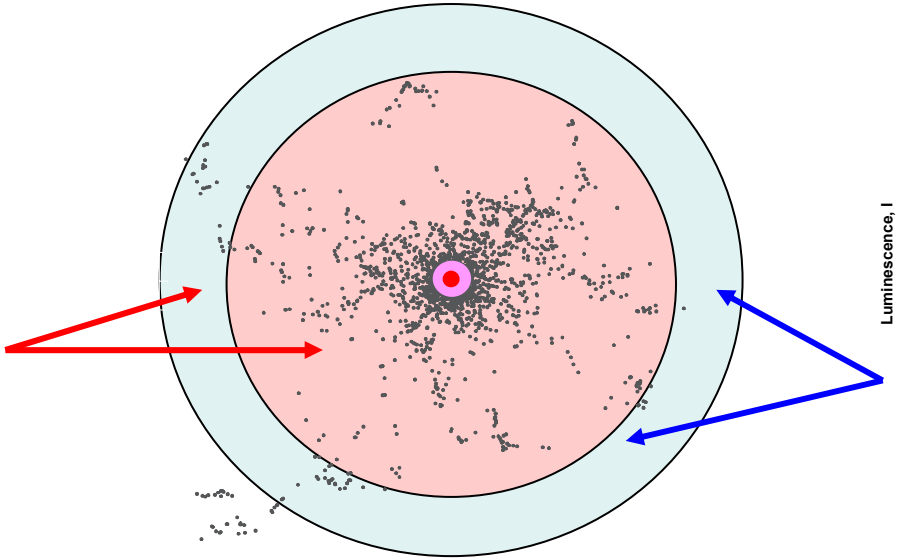
	8 K	300 K
d, nm	19.5 ± 3	18.3 ± 3
h, nm	0.9 ± 0.2	0.8 ± 0.2

Athermic process ??

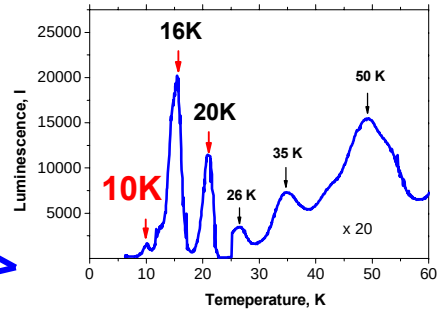
Different spatial scales of the thermal spike and damage creation region



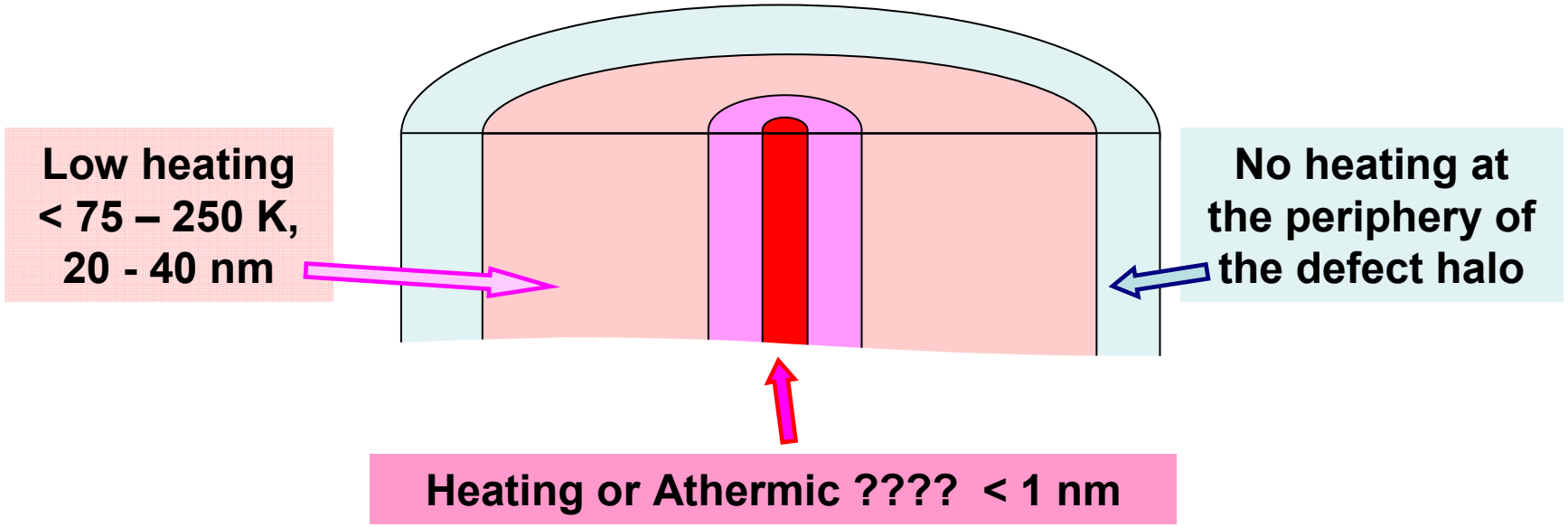
H centers



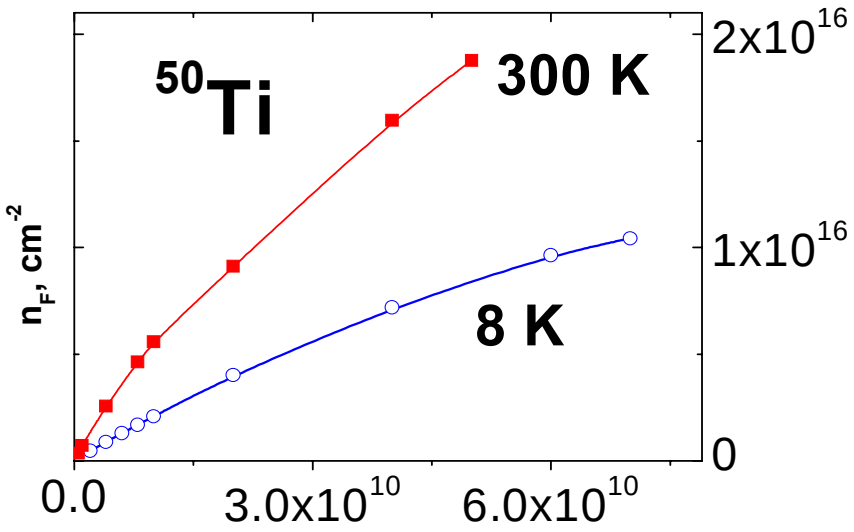
Ionization, MC by S. Bouffard

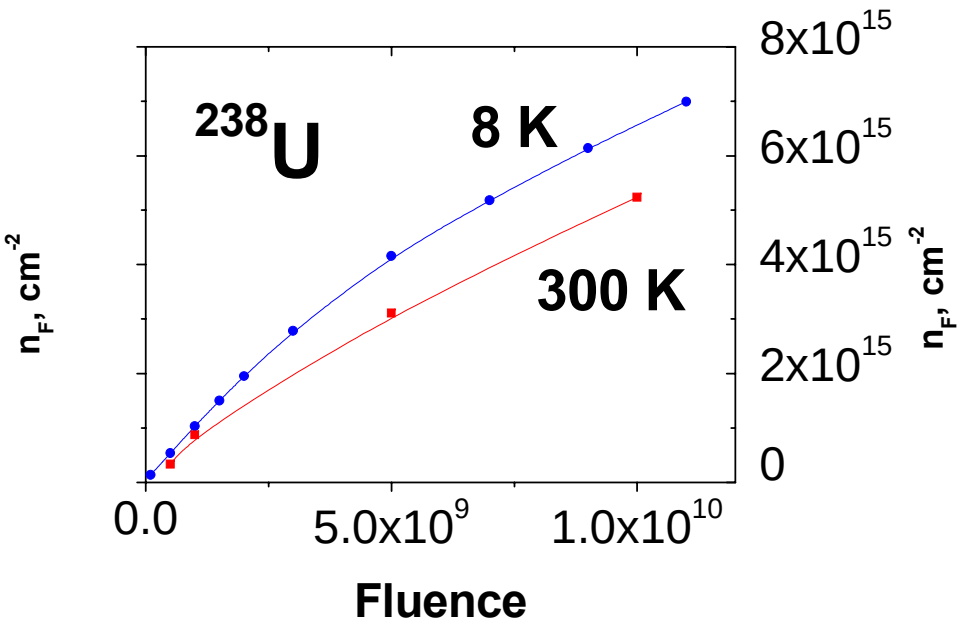


"10 K" defects



Irradiation temperature effects on fluence dependences of F- center production for light and heavy ions



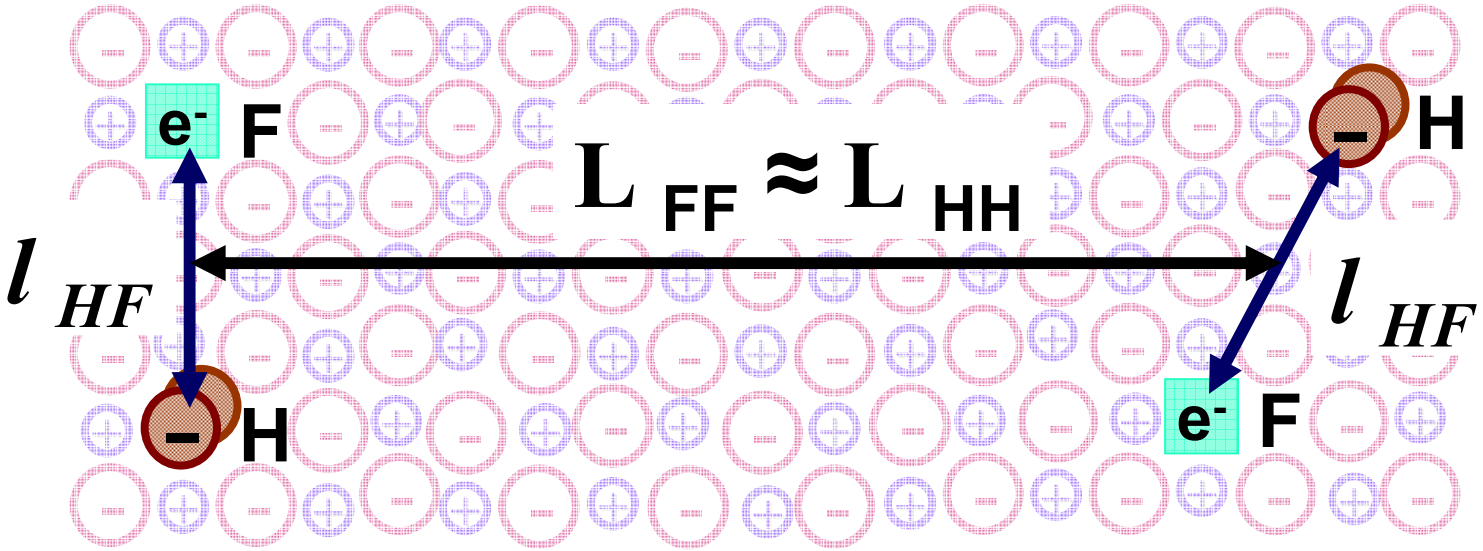


Increase of defect production rate at 8 K for heavy ions

Decrease of defect production rate at 8 K for light ions

Formation of stable Frenkel pairs (F and H centers)

Two lengths govern defect separation and recombination



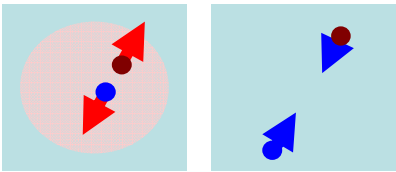
Good separation in a pair:

$$l_{HF} \geq l_{HF}^{\min} = 5a = 1.4 \quad nm$$

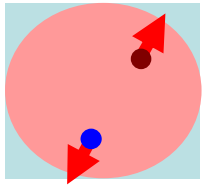
Separation of F and H centers in Frenkel pairs depends on the local temporal temperature increase

Local heating and the defect production rate

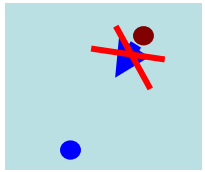
$$l_{HF}\,[\,T(r,\tau)\,] = l_{HF}\,[\,\Delta T(r,\tau) + T_{irr}\,]$$



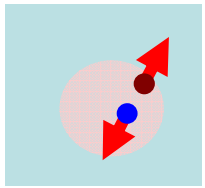
Separation at hot stage and recombination after track cooling down



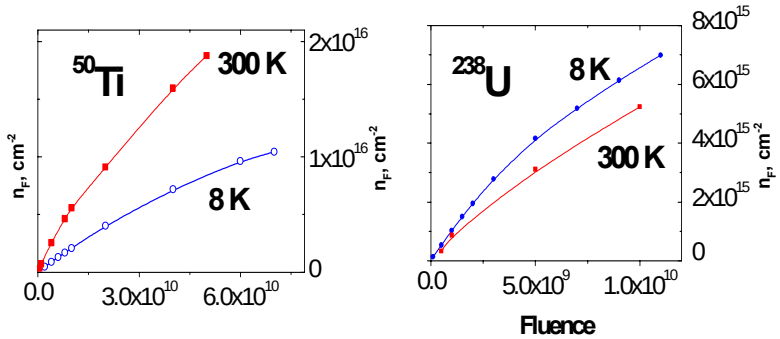
ΔT from heavy ions provides good separation and a similar number of stable pairs at 8 K and 300 K



Recombination of H and F centers is suppressed at 8 K



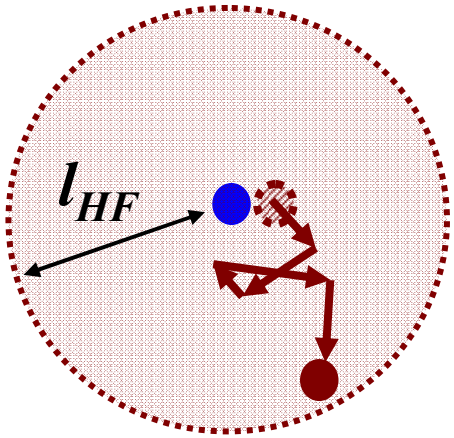
For light ions a local temperature is too week for effective separation of defects at 8K



Estimations of the temperature increase in the defect halo

$$l_{HF}\,[\,T(r,\tau)\,] = l_{HF}\,[\,\Delta T(r,\tau) + T_{irr}\,]$$

Separation due to Diffusion



$$6D_0\,exp(\,-\,U_H\,/\,T)\,t_i^c \approx l^2_{HF}$$

$D_0 = 10^{-2}\ cm^2/s$, $U_H = 0.05 - 0.1\ eV$ $t_i^c = 10 - 100\ ps$

T_{irr} = 8K

Heavy Ions
Good sep.

$l_{HF} \approx$ 2 nm ⇒ $\Delta T \approx$ 100 K – 250 K

Light Ions
Weak sep.

$l_{HF} \approx$ 1 nm ⇒ $\Delta T \approx$ 50 K – 100 K

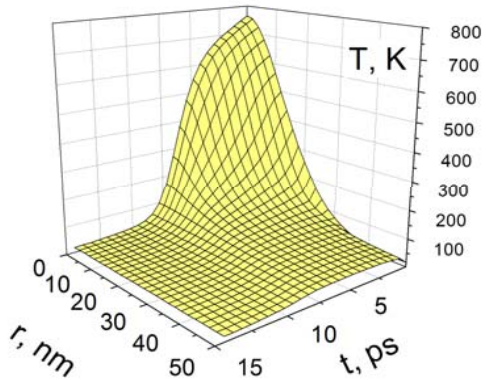
Difficulties of the classical model of heat diffusion

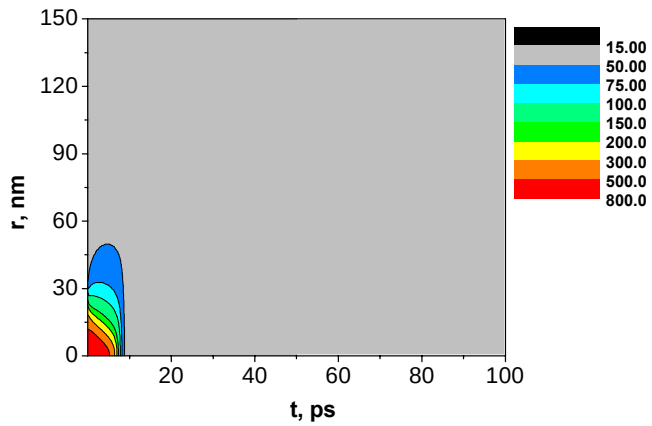
$$J_F = -K \quad \partial T / \partial r$$

$$\frac{\partial T}{\partial t} = \frac{K}{\rho C} \frac{1}{r} \frac{\partial}{\partial r} \left(r \quad \frac{\partial T}{\partial r} \right)$$

Extremely fast cooling down at cryogenic temperatures

$$\chi = K/\rho C \sim 10^2 \, cm^2/s \quad \Longrightarrow r_i^2 / \chi \ll 10^{-12} s$$





No enough time for good defect separation in the defect halo

Origin : An infinite velocity of heat propagation assumed by the model

Cattaneo equation

For spatial and temporal scales of track relaxation we have to take into account the finite velocity of heat propagation.

For the phonon mechanism - the velocity of sound

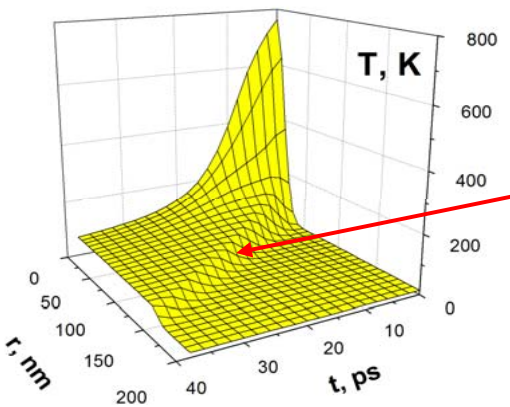
A finite velocity ⇨ the wave equation

$$\tau \frac{\partial J_C}{\partial t} + J_C = -K \frac{\partial T}{\partial r}$$

$$\frac{\partial^2 T}{\partial^2 t} + \frac{1}{\tau}\frac{\partial T}{\partial t} - \frac{K}{\tau \rho C}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) = 0$$

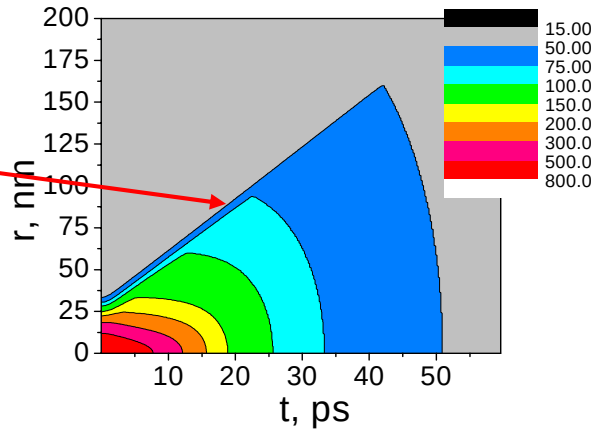
v^2

$$v^2 = K/(\tau\rho C) = v_s^2/3$$



Heat front

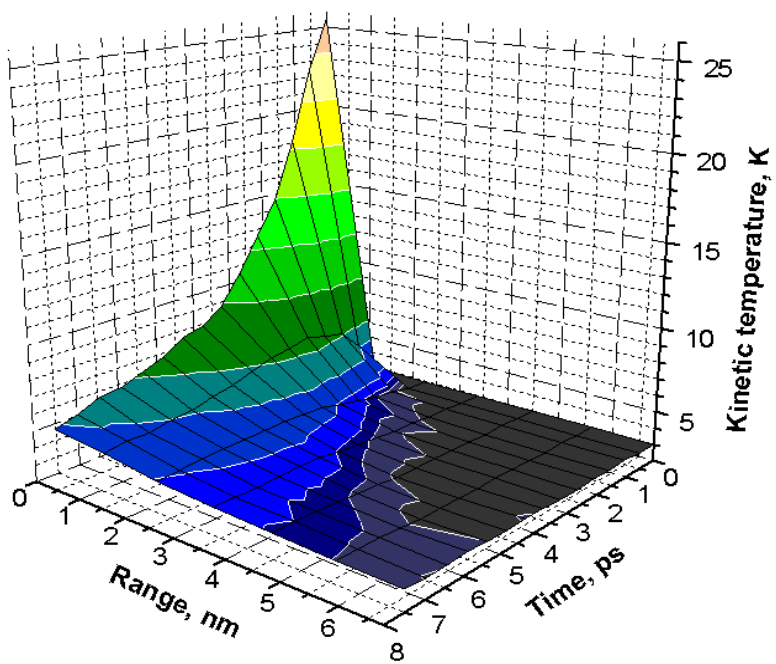
$v_s \sim 10^5$ cm/s

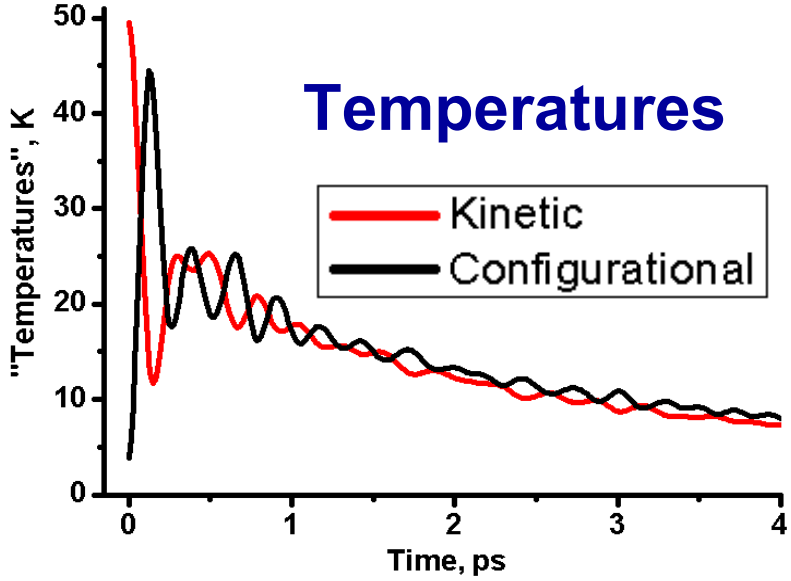


Enough time for defect separation

MD Investigations of the lattice kinetics

Crystal argon with fcc lattice and L - J pair potential



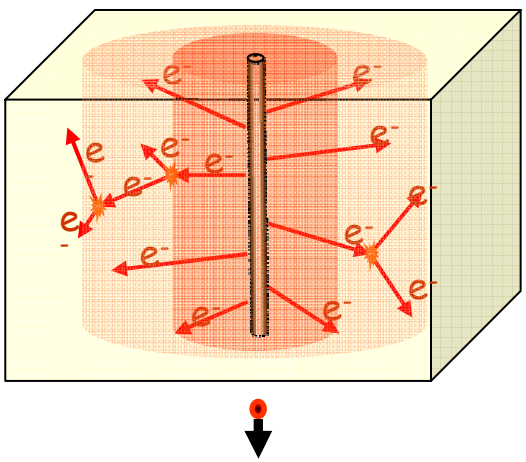


Front of Excitation

Temperature based approach is questionable till 1 - 4 ps

Monte-Carlo simulations of the initial electronic kinetics

$t = 10^{-17}$ s – 10^{-14} s



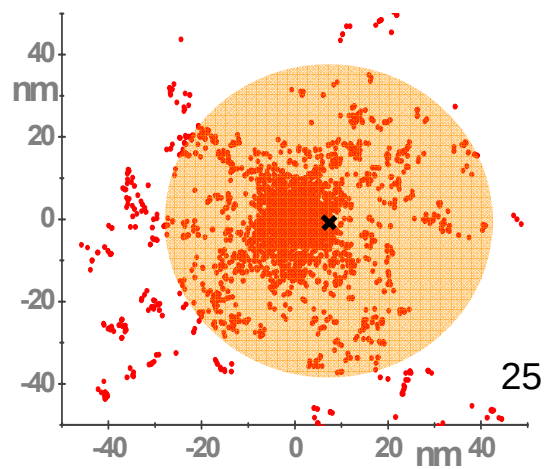
1. Creation of 1st generation of delta-electrons and holes by SHI

2. Propagation of primarily electrons. Creation of secondary electrons and holes

3. Auger decays of holes creating free electrons

Spatial and temporal distributions of

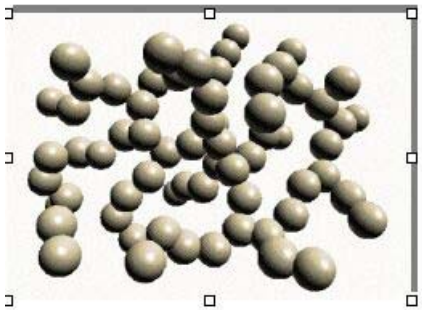
- delta-electrons
- electronic vacancies at different shells
- excess energy of electronic subsystem
- excess energy of lattice



Experiments which are able to touch the shortest times of of electronic relaxations in a track ($t < 10^{-14}$s)

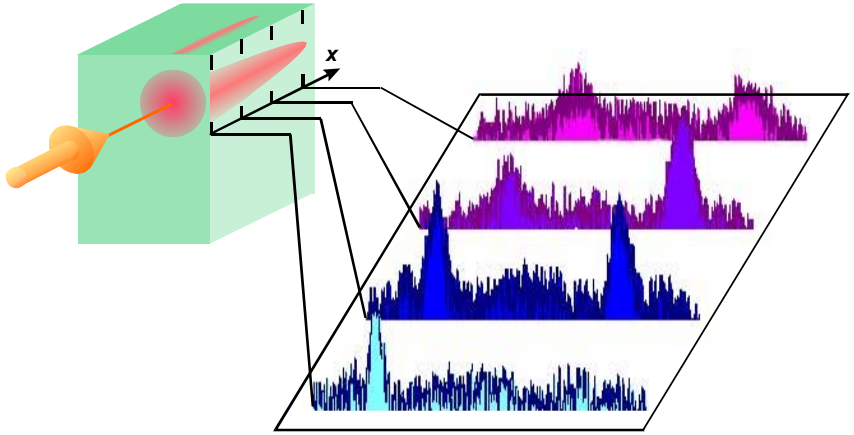
Dr. Olga Rosmej et al.

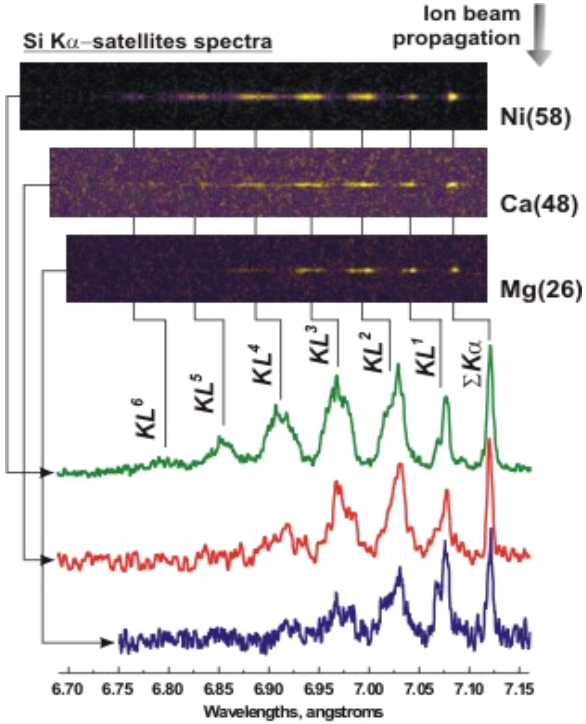
X-rays spectroscopy. Spatially resolved measurements of the K-shell projectile and target radiation along the ion trajectory



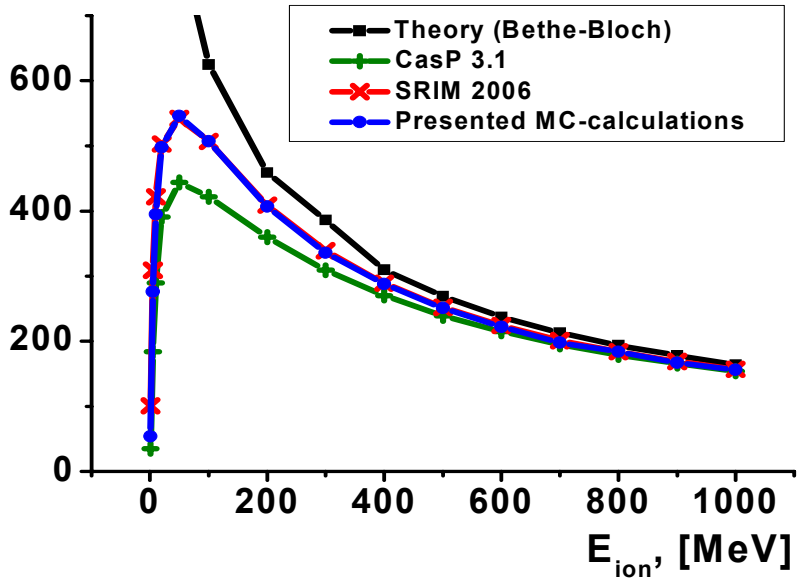
SiO_2 Aerogel Targets **Ca^{+19}** **(E = 5 - 11.4 MeV/u)**

3-D network:
3 nm - solid beads
20 - 50 nm - pore





Disadvantage of the first attempt to fit



Only Ionizations

1. Quantitative agreement

Ion energy losses/ deposited dose

2. No success with fitting of $K_\alpha L_n$ (n) spectra

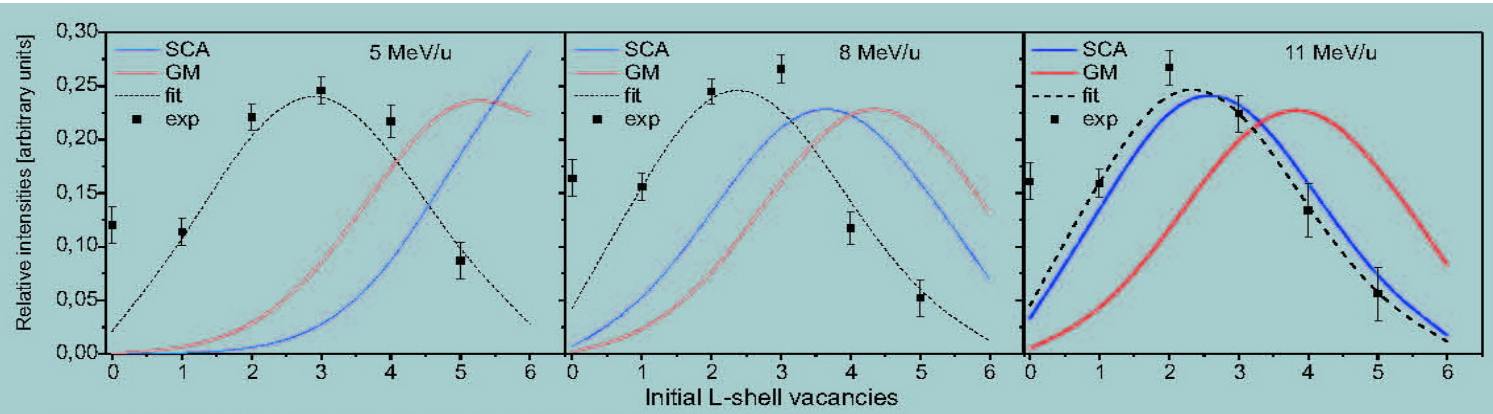
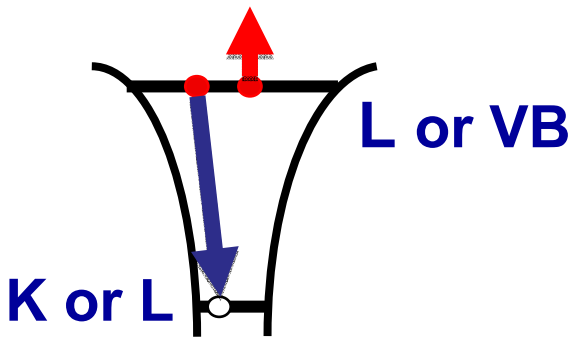


Fig.4. The experimental and theoretical L-shell vacancy distribution

O.Rosmej ey al.

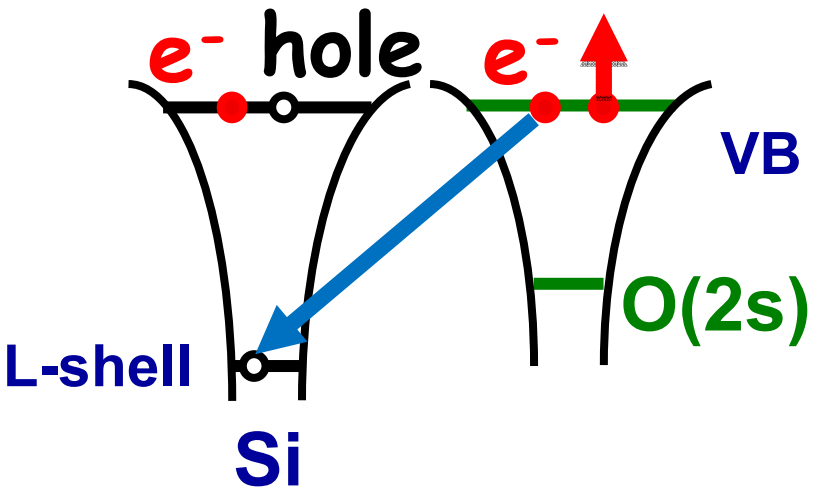
Decay of holes



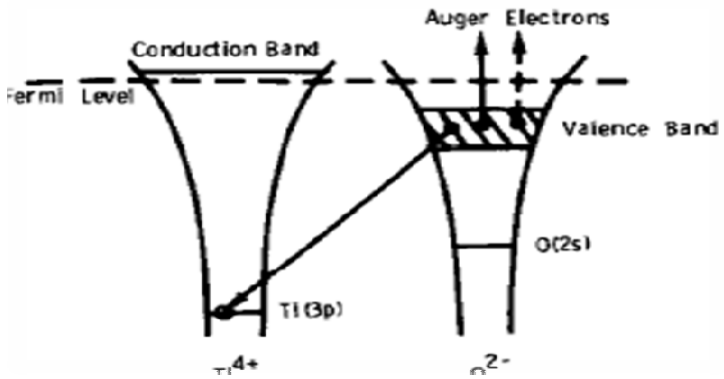
(a) radiative decay

(b) Auger process

(c) Due to solid-like density - Inter-atomic Auger processes



M.L. Knotek and P.J. Feibelman, Surface Science 90 (1979) 78-90

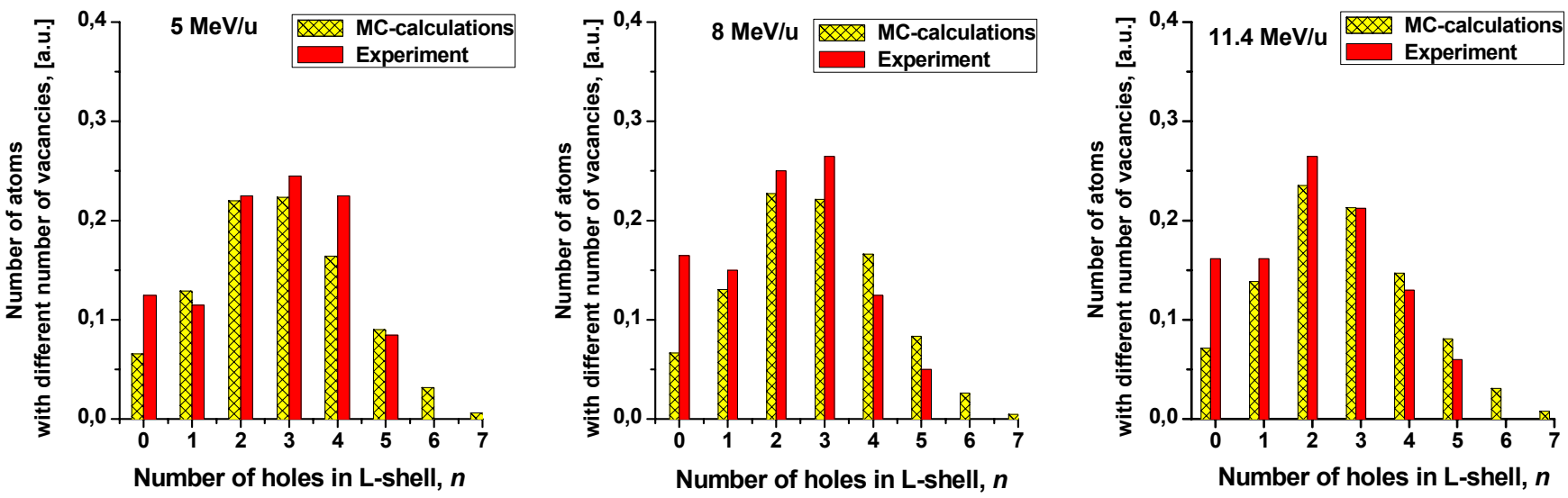


Verification of the MC model

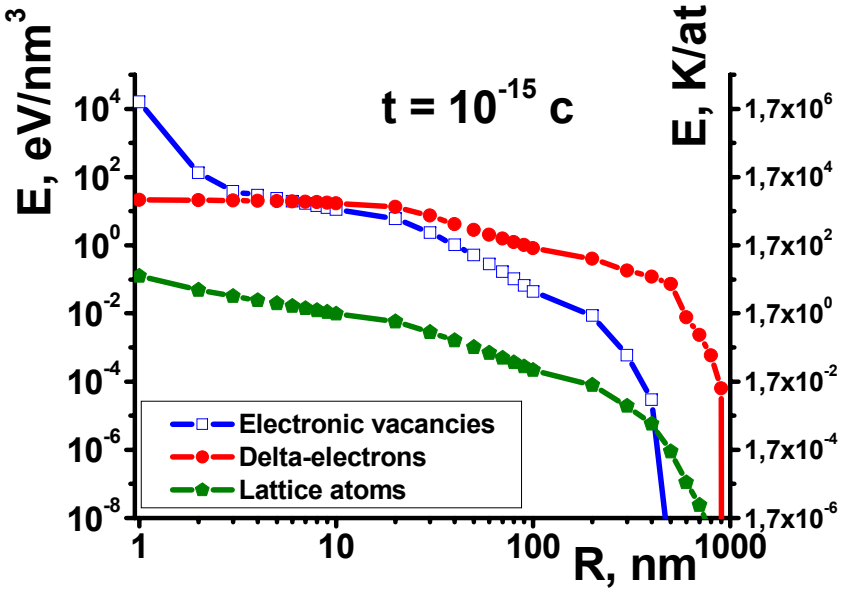
X-ray KαL^n Si-spectra can be described for different ion energies by using

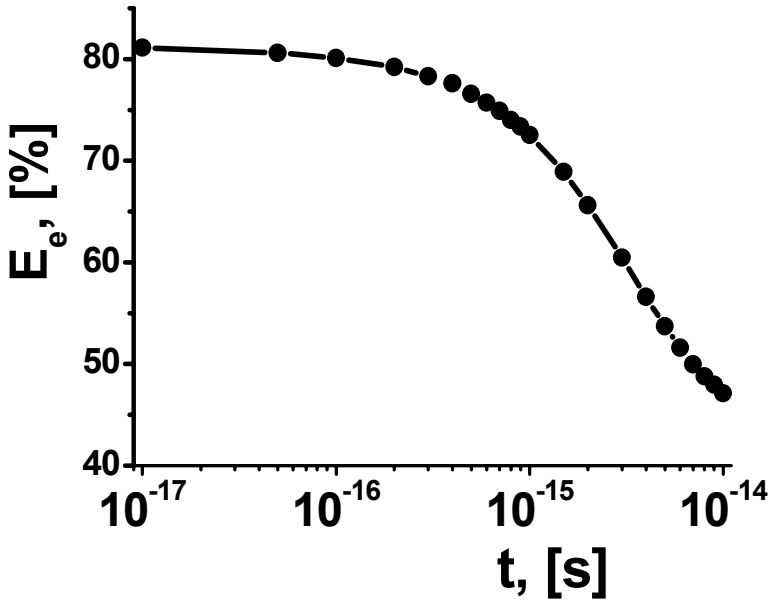
only the one (!) free parameter: the time of the inter-atomic Auger process

which fills holes in L-shells of silicon atoms



Excess energy





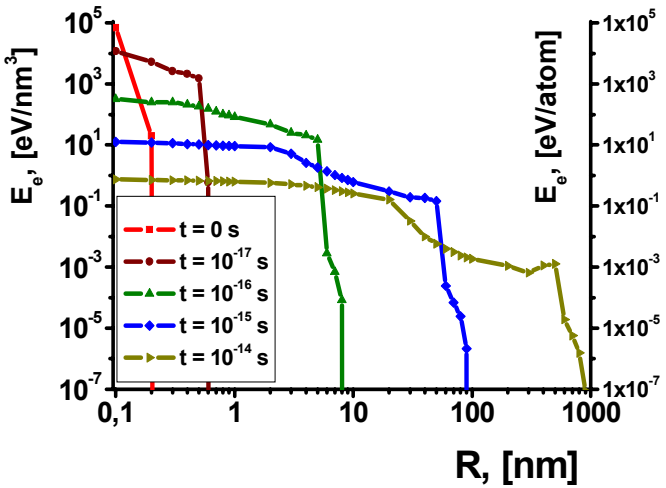
The excess energy densities of *δ*-electrons, electronic vacancies and lattice atoms.

Decrease of the energy of *δ*-electrons due to secondary ionization.

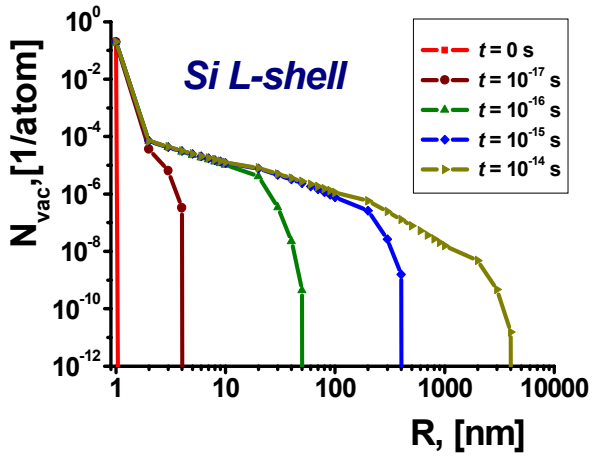
1. The energy of vacancies can not be neglected (55%)

2. Lattice excitation at times < 10^{-14} s (before phonons)

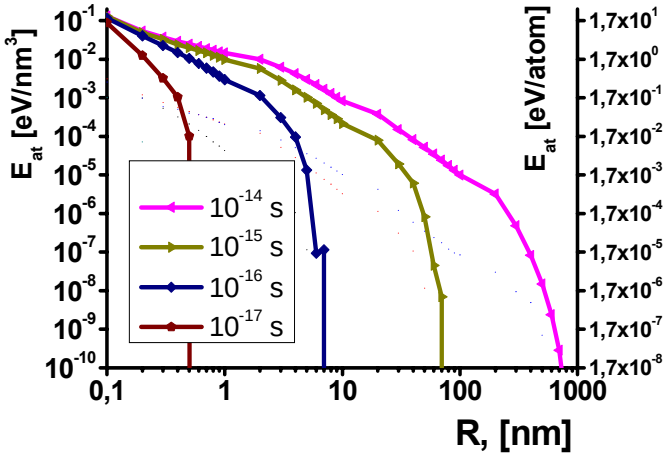
Ballistic propagation of the excess energy



δ- electrons



Electronic vacancies

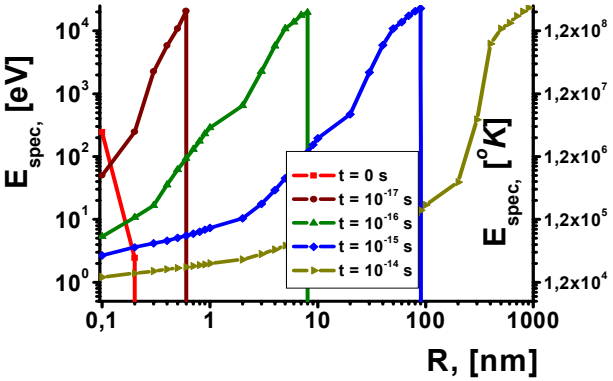


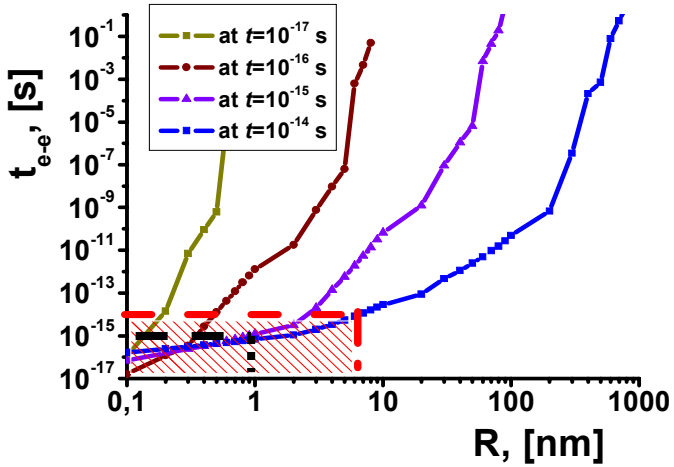
Lattice atoms

Can not be described by heat diffusion

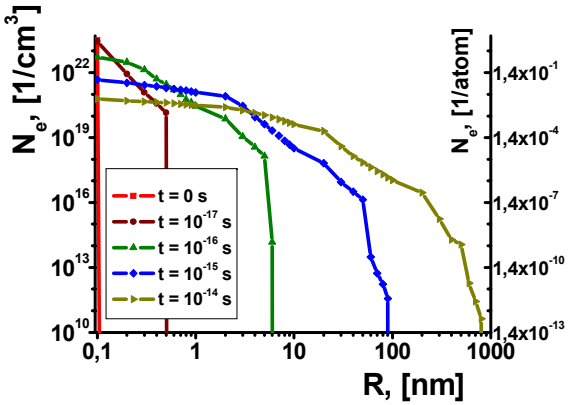
Delocalized electrons

Energetic and spatial separations.





Ballistic propagation



Thermalization only

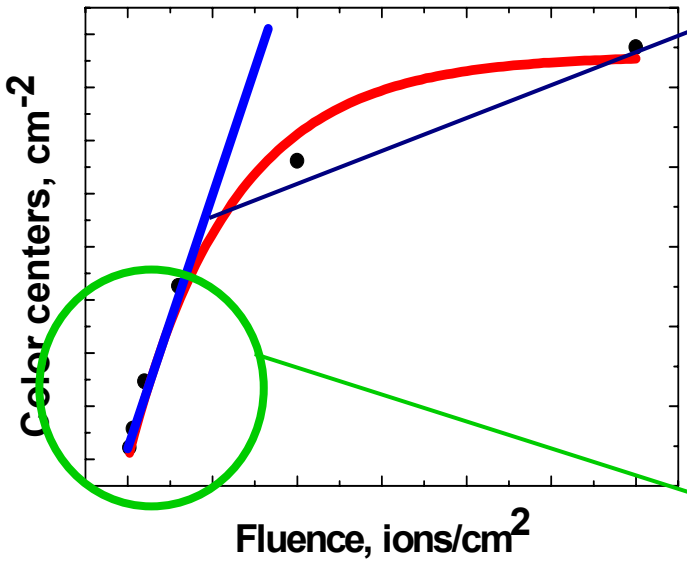
2 % of the excess energy in R < 1 nm at 10^{-15}s

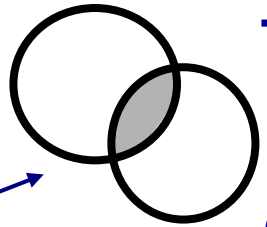
6 % of the excess energy in R < 6 nm at 10^{-14}s

"fragments of a grenade"

Application of the local temperature approach and heat diffusion model (thermal spike) is questinable

Track parameters



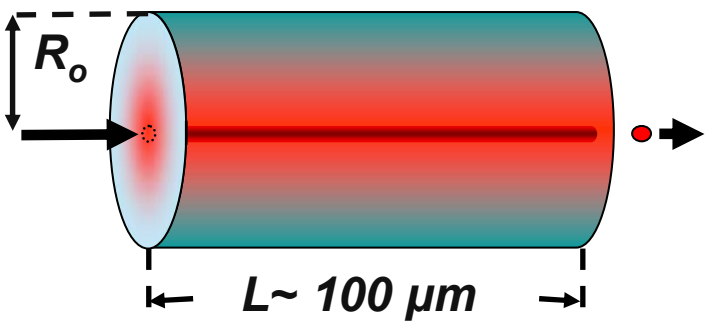


Track overlapping results in deviation from the linear growth of the concentration

$$R_d = (\pi\, \Phi_d)^{-0.5} = 10 - 30 \text{ nm}$$

Number of defects produced per a single track

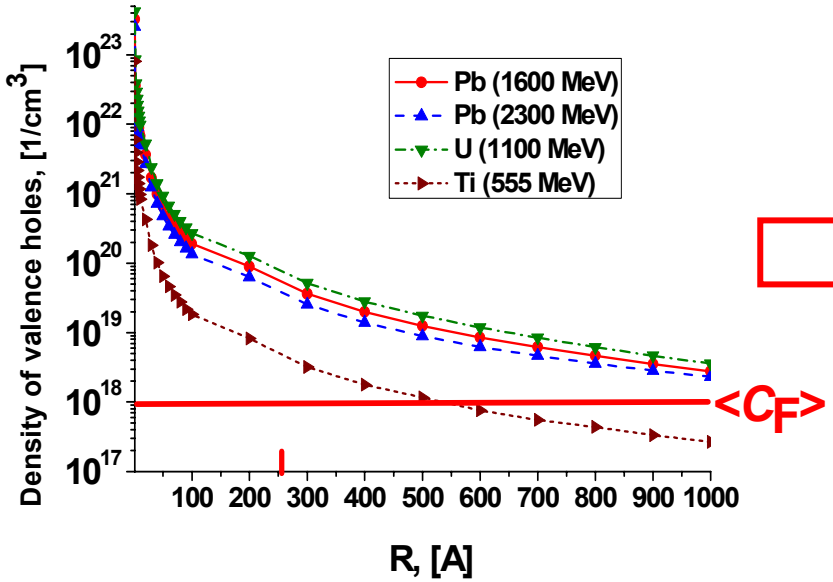
$$\Delta N_F = dn_F^{linear} / d\Phi$$

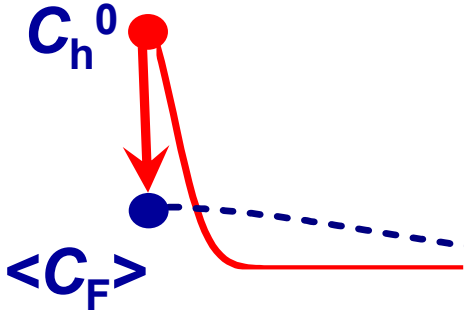


Average defect concentration in a track

$$< C_F > = \Delta N_F / (\pi R^2_0\, L)$$

Diffusion coefficient of valence holes in SHI tracks



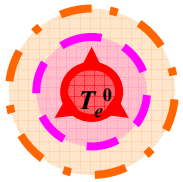


Spatial redistribution of valence holes is necessary before self-trapping (10^{-12}s)

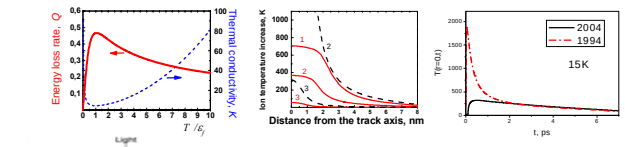
$$D_h = \frac{C_h^o R_h^2}{4\tau_h \langle C_F \rangle}$$

Ion / energy (MeV)	D_h cm^{2}s^{-1}	Ion / energy (MeV)	D_h cm^{2}s^{-1}
Pb 1600 MeV	9.4	Ti 555 MeV	3.4
Pb 2300 MeV	11.4	C 57.6 MeV	0.3
U 1100 MeV	16.3	C 133 MeV	0.4

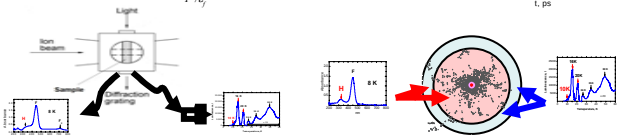
Conclusions

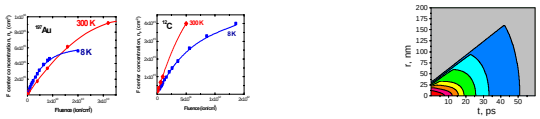


Thermal Spike Model

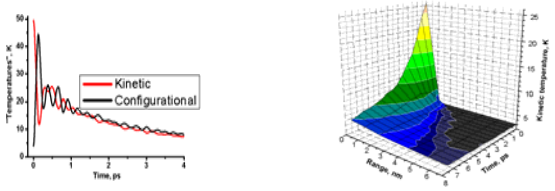


Electron to ion coupling . No large heating

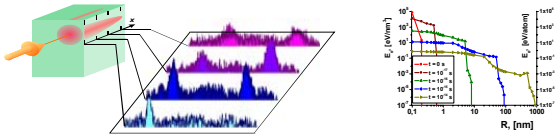




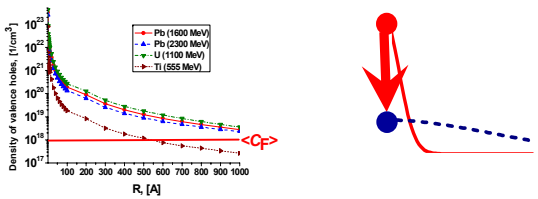
Spectroscopy experiments. Low temperatures in the defect halo



MD of lattice excitation. Problems with thermalization. Excitation front



Monte-Carlo of electronic excitations. Ballistic front. No thermalization. Interatomic Auger



Considerable spatial redistributions of valence holes is necessary before self-trapping. Diffusion coefficient of holes

Conceptions of temperature, local equilibrium, heat diffusion, phonons etc. are applied hardly for the most important stages of track kinetics

Acknowledgements

K. Schwartz

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