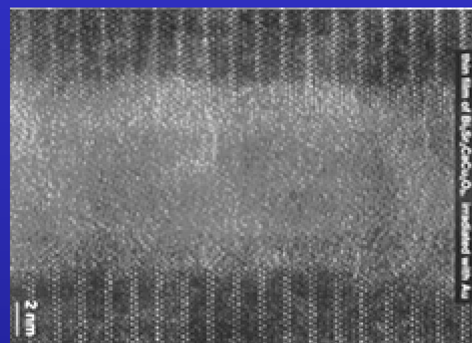
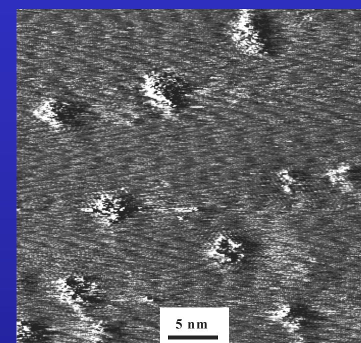
Materials research with ion beams

❒ beam-induced material modifications

- track formation
- damage analysis
- threshold
- sputtering



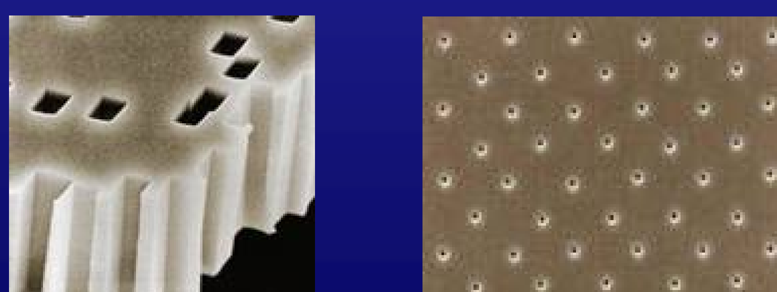
single ion track



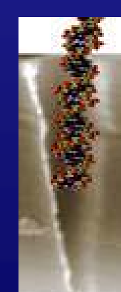
surface tracks

irradiated epoxy foils

❒ nanotechnology



nanopores



biosensors

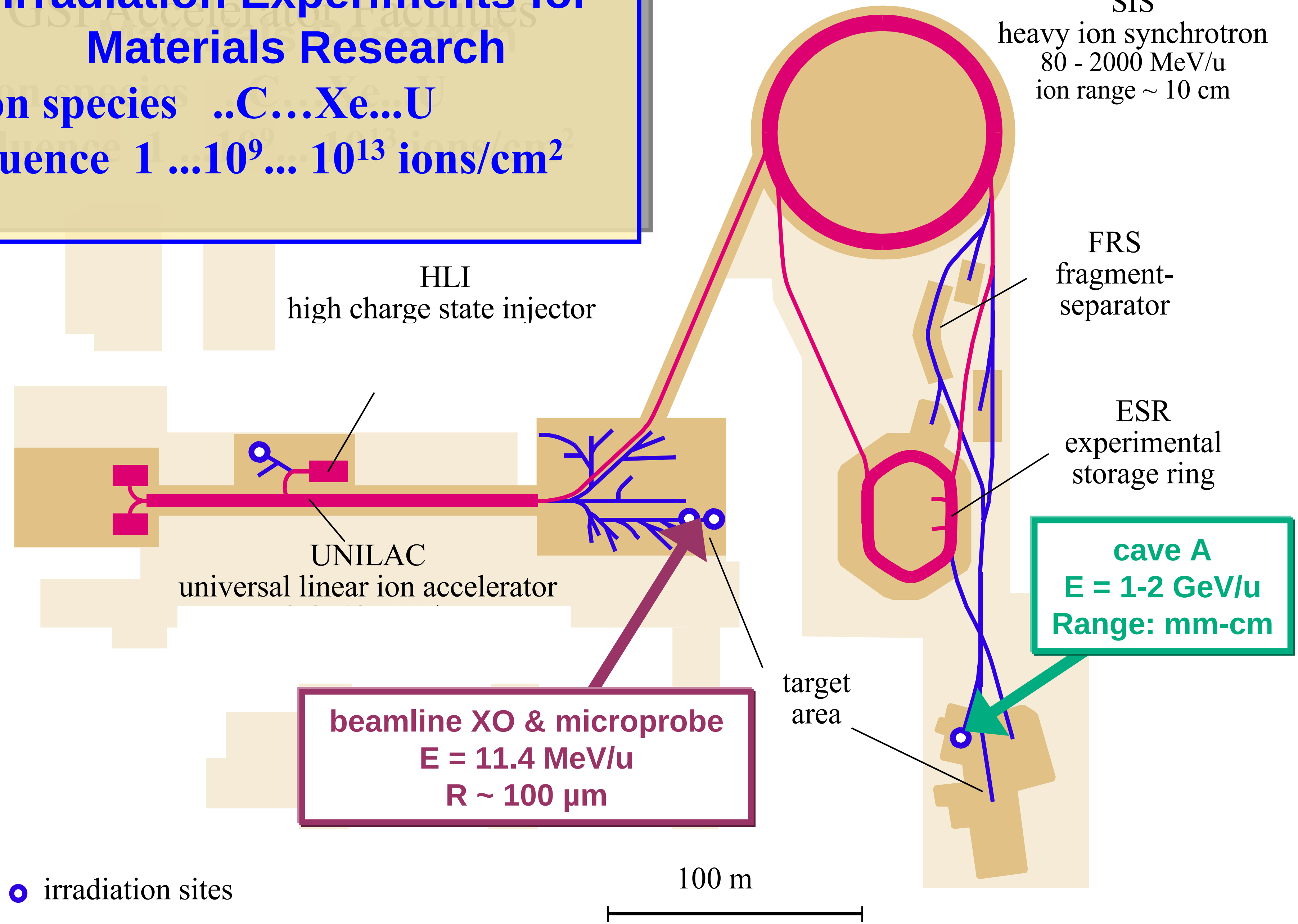
nanowires

Christina Trautmann, Materialforschung, GSI

Irradiation Experiments for Materials Research

ion species ..C…Xe…U

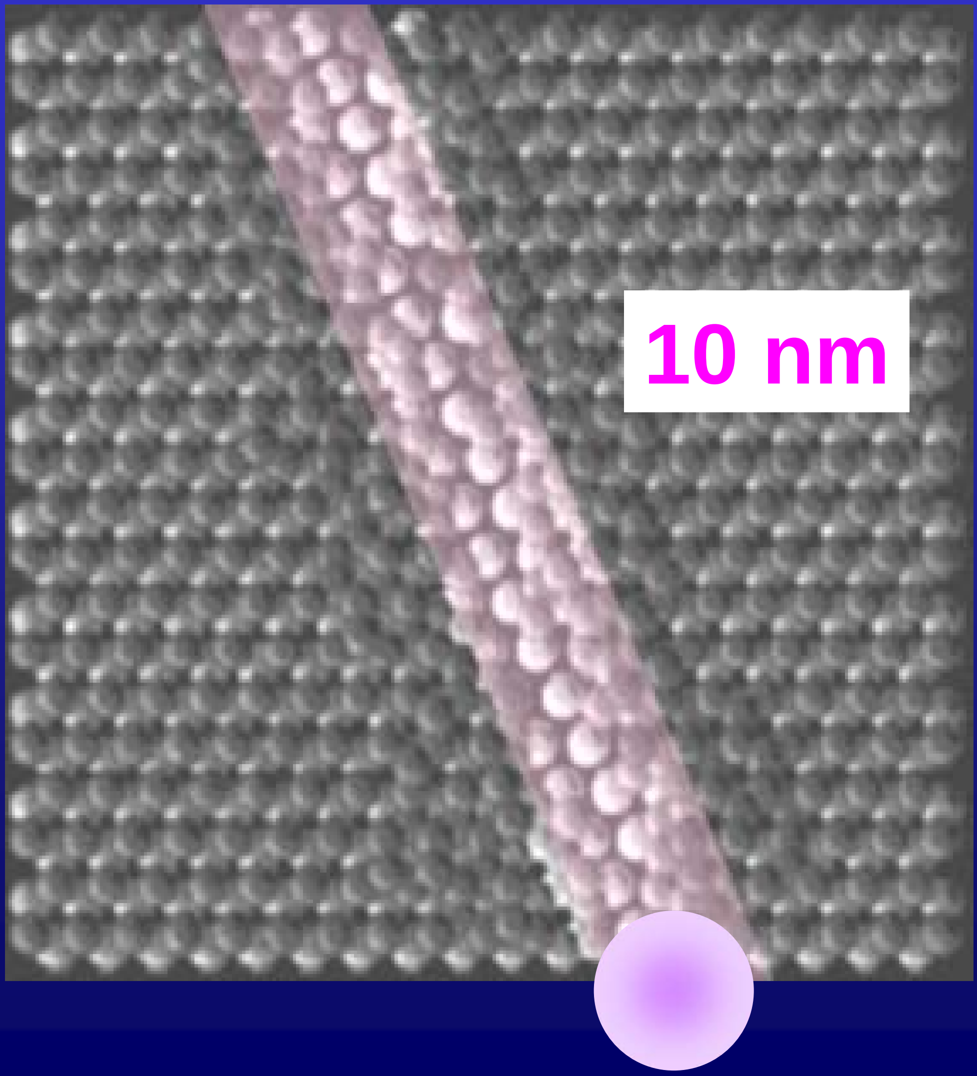
fluence 1 …10^9… 10^{13} ions/cm^2



ion beams

kinetic energy: MeV- GeV

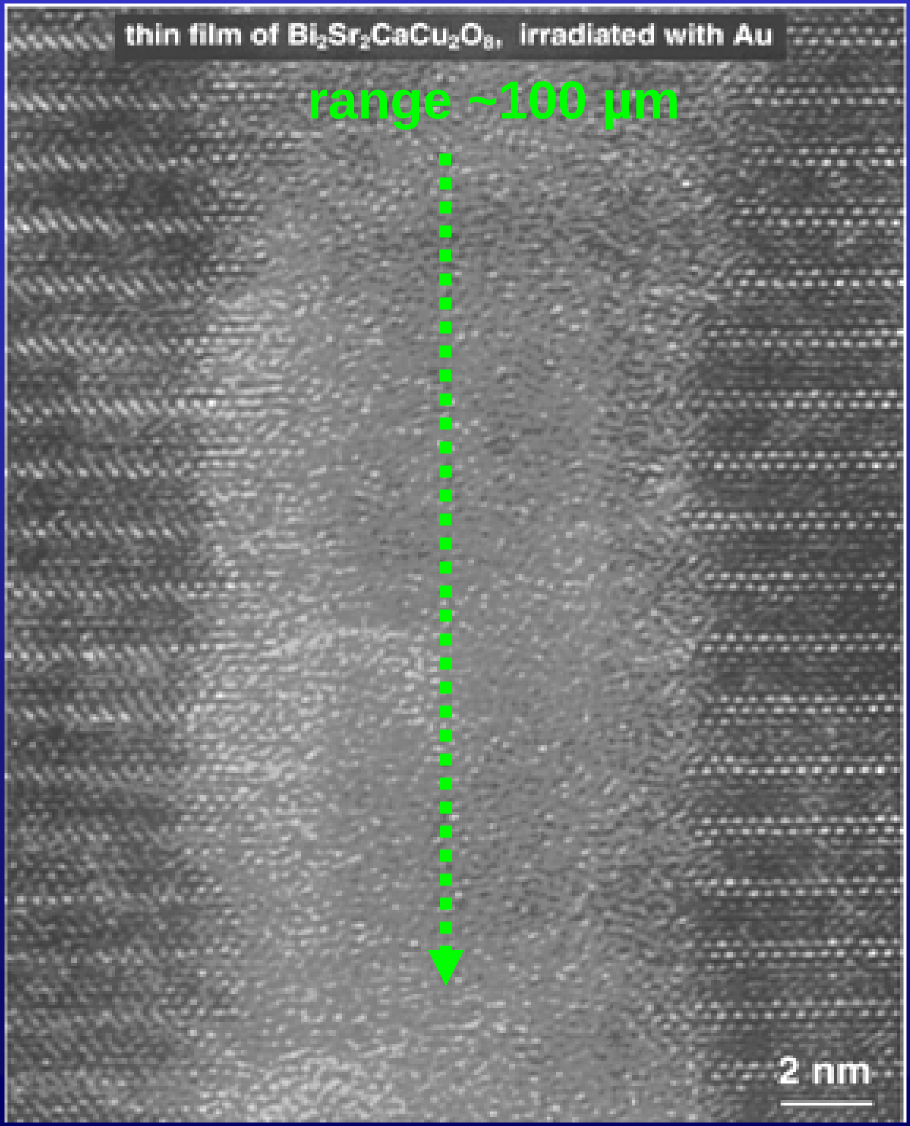
10% of velocity of light



Single ion tracks produced in amorphisable insulators

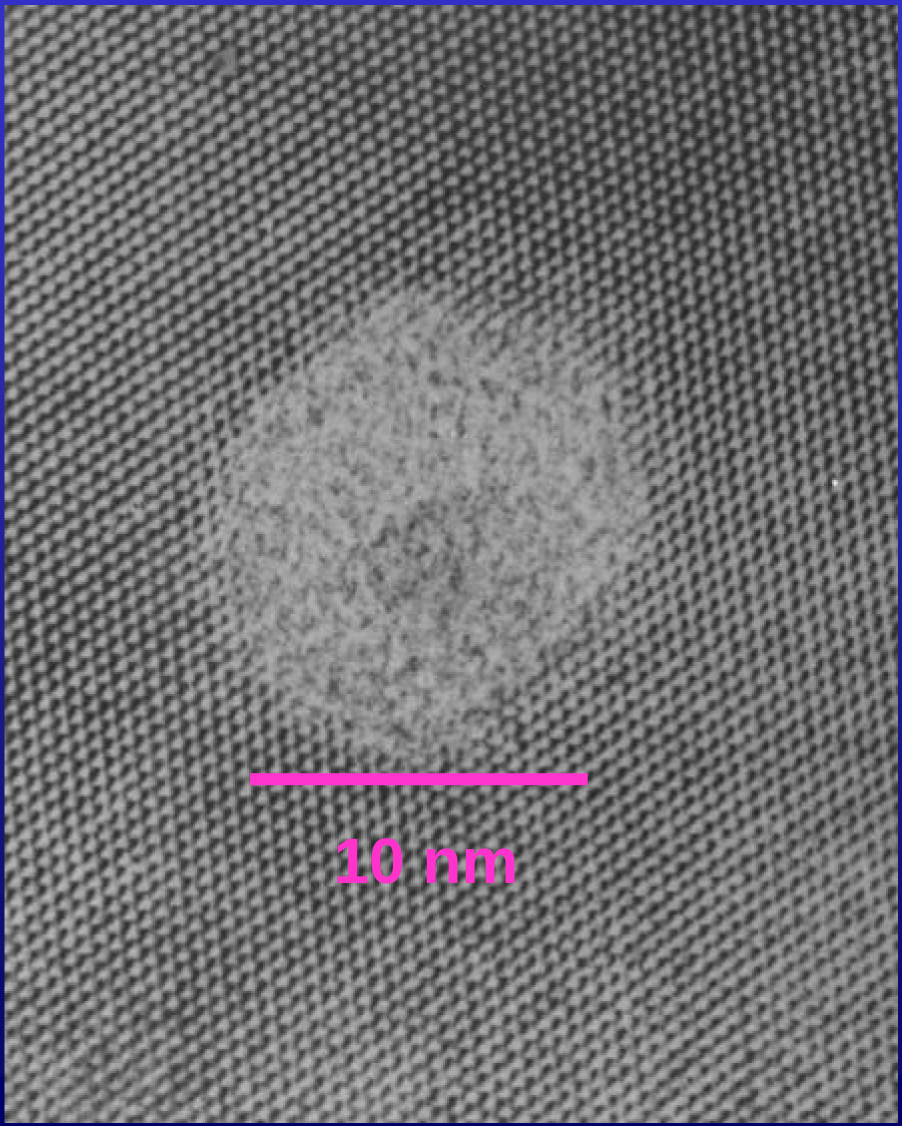
@ ~ 10 MeV/u heavy ions

Au-ion trajectory in high T_c superconductor



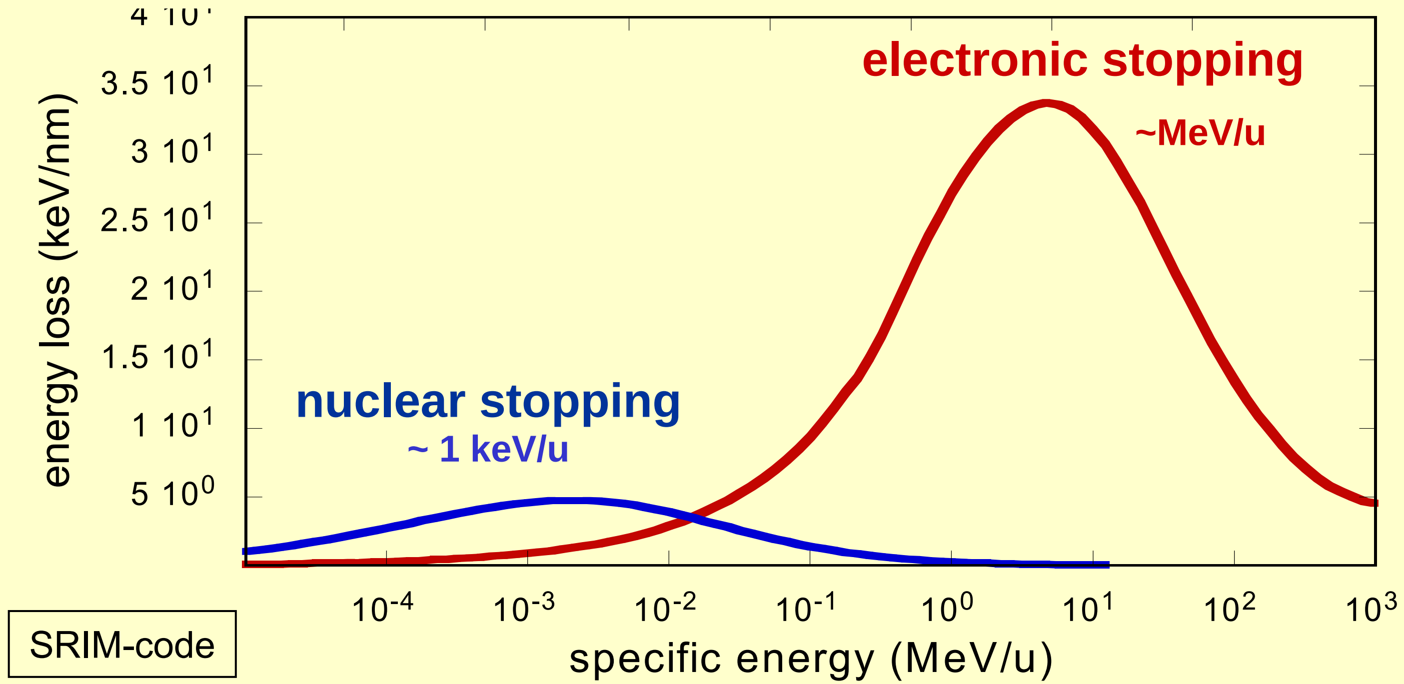
J. Wiesner et al., Physica C 268 (1996) 161

cross section of Pb-ion track in mica



J. Vetter et al., NIMB 141 (1998) 747

energy deposition



target atoms → atomic collision cascade → defects

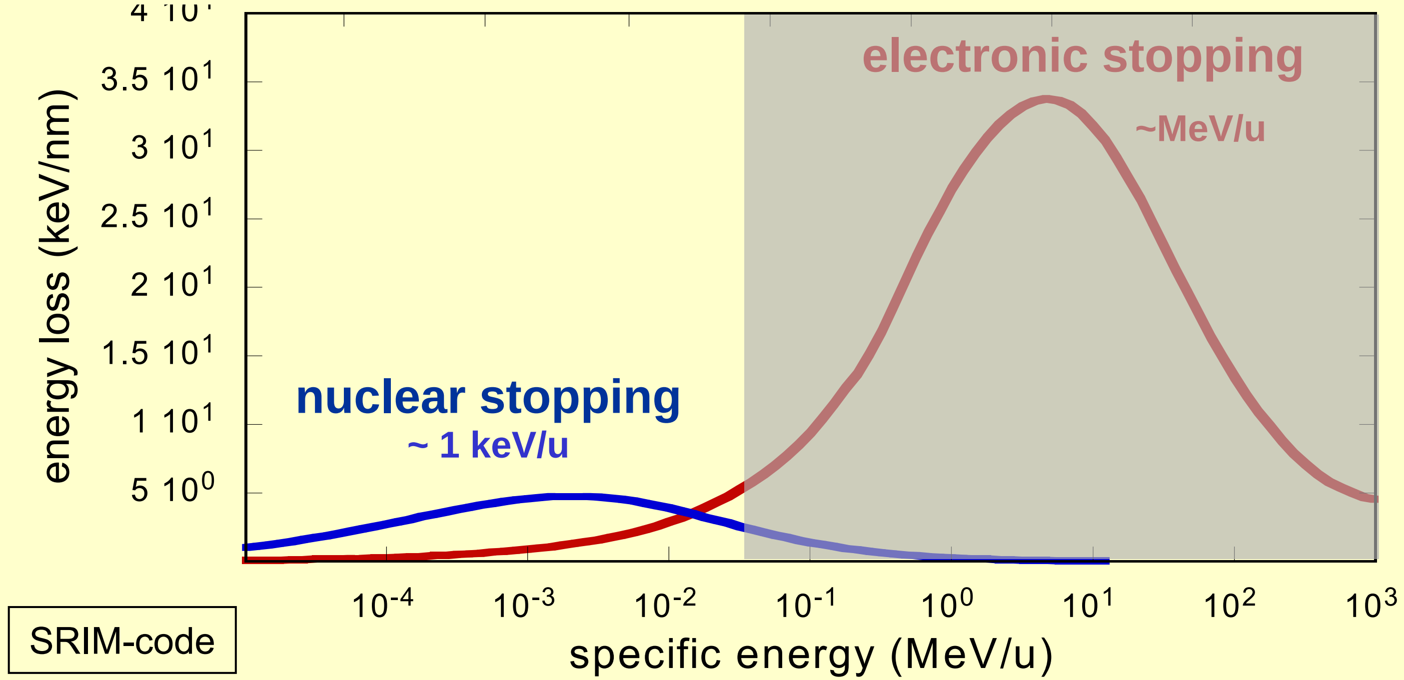
target electrons 10^{-17} - 10^{-16} s

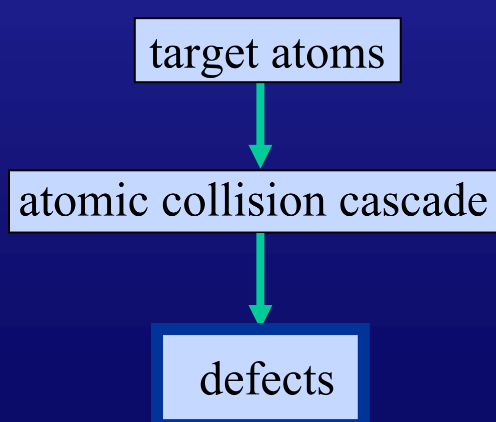
→ electron cascade 10^{-15} - 10^{-14} s

→ coupling to lattice 10^{-13} - 10^{-11} s

→ **track**
defect clusters - amorphisation

energy deposition





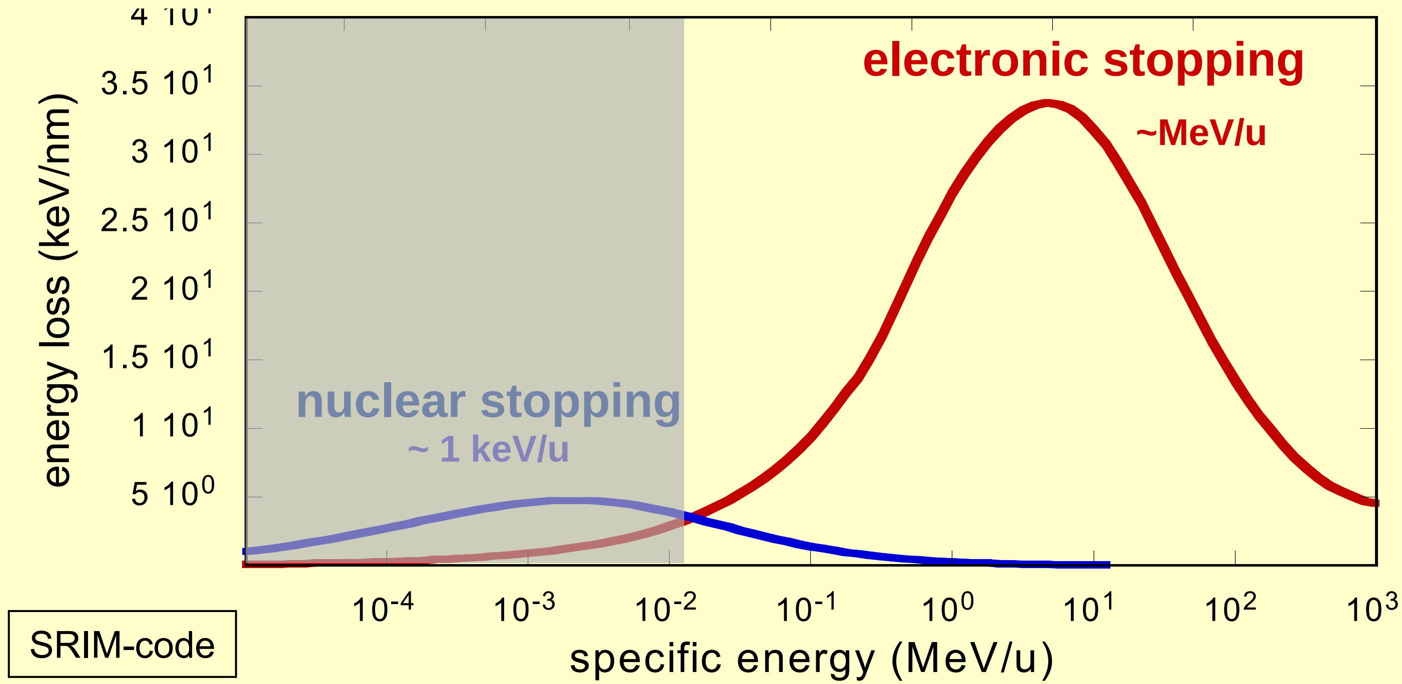
elastic collisions

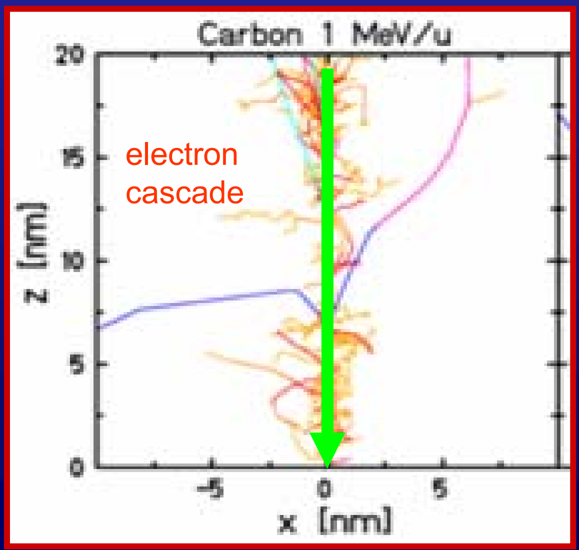
↓

vacancies & interstitials

important material parameter = displacement energy

energy deposition





target electrons — 10^{-17} - 10^{-16} s

↓

electron cascade — 10^{-15} - 10^{-14} s

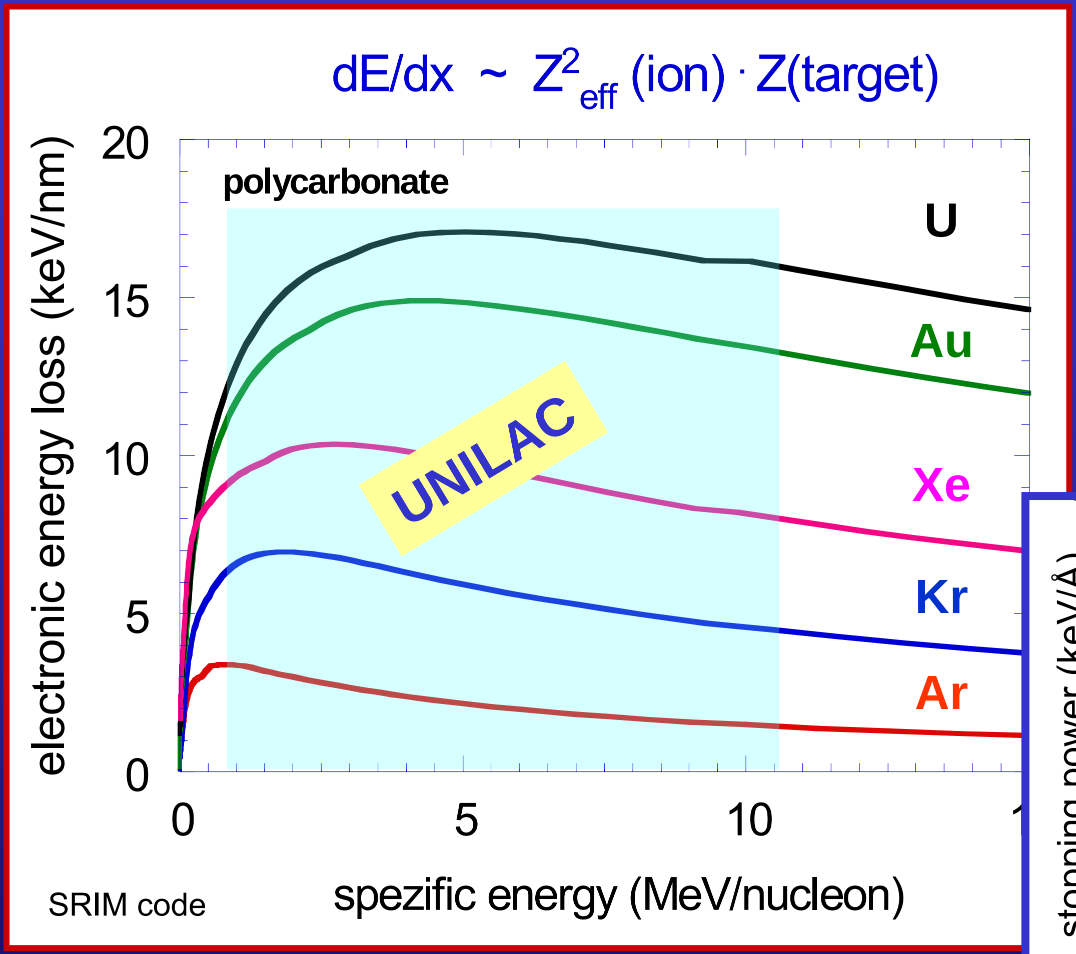
↓

coupling to lattice — 10^{-13} - 10^{-11} s

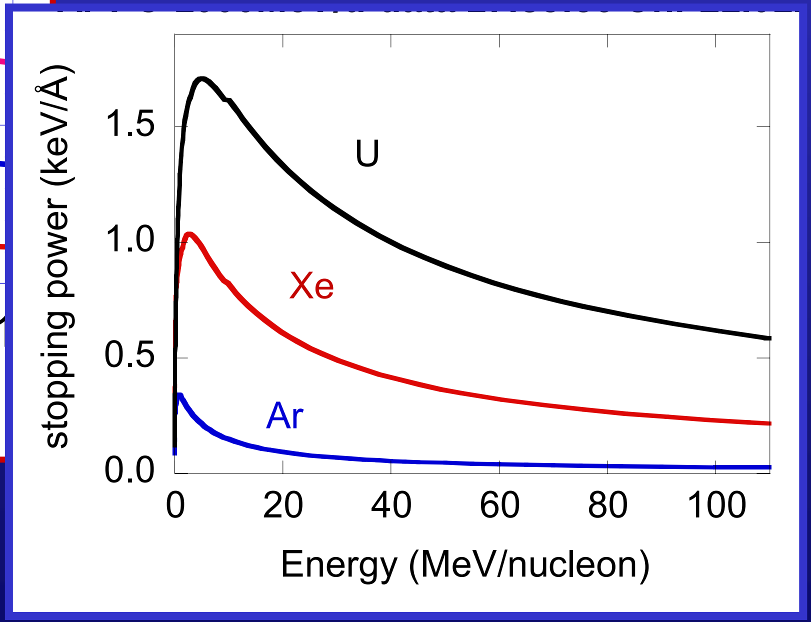
↓

track
defect clusters - amorphisation

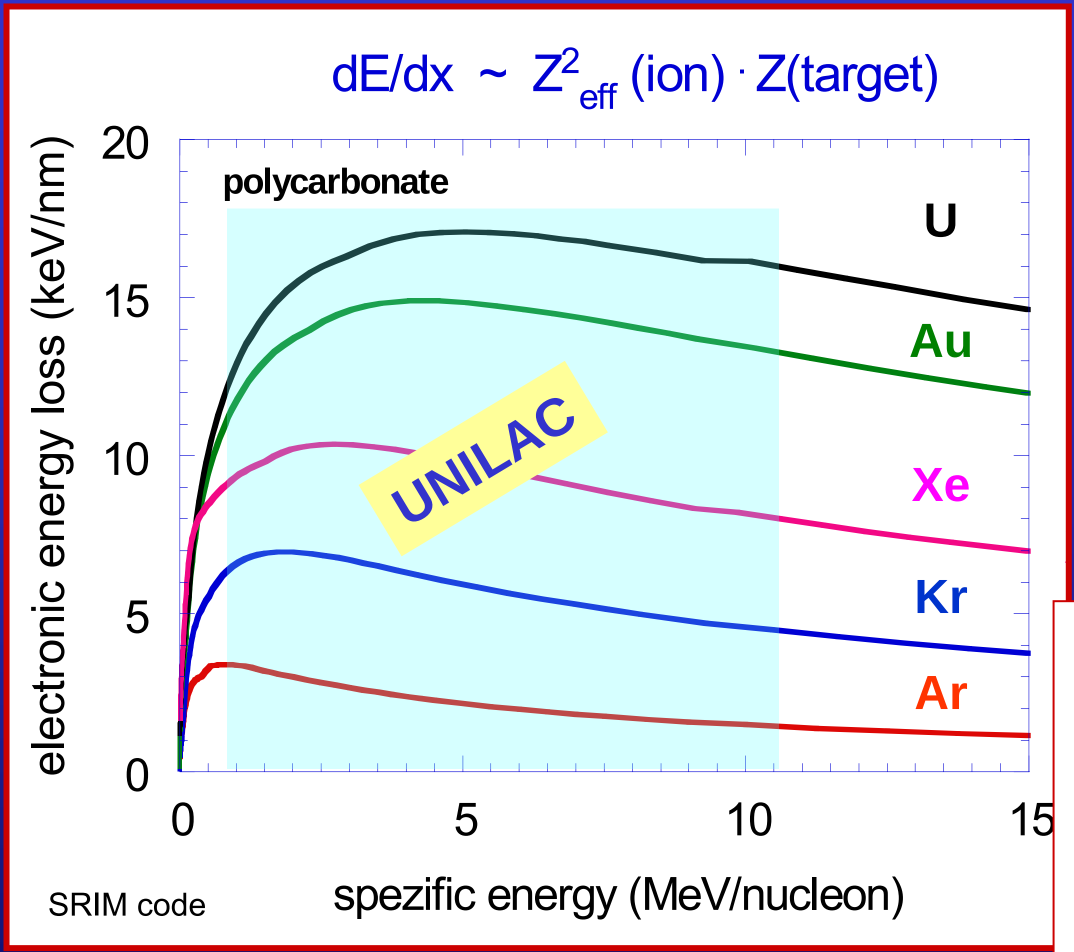
linear energy loss of different ions

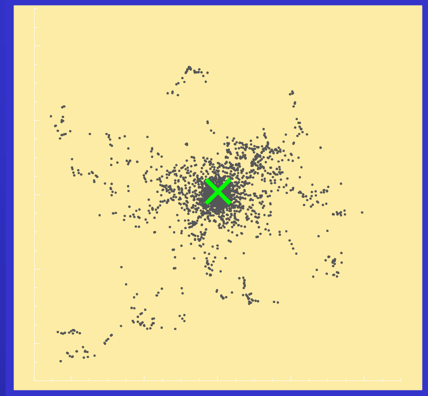


high energy

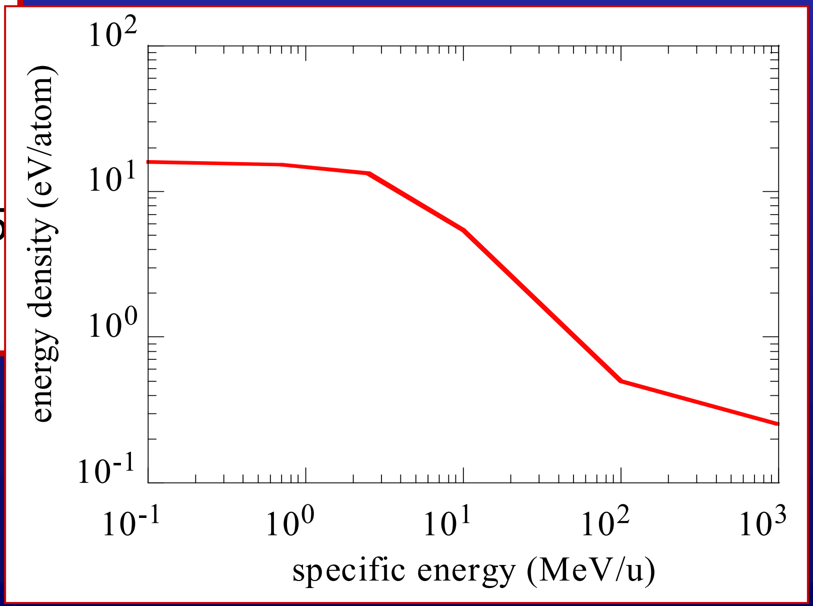


linear energy loss of different ions





energy density

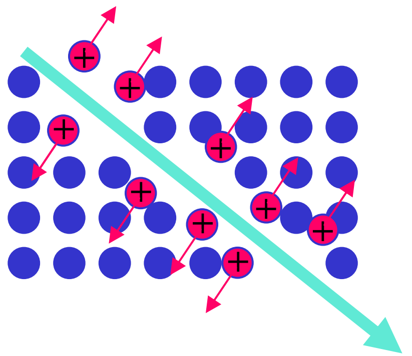


Track formation models

macroscopic

❒ **Coulomb explosion:** screening time by electrons

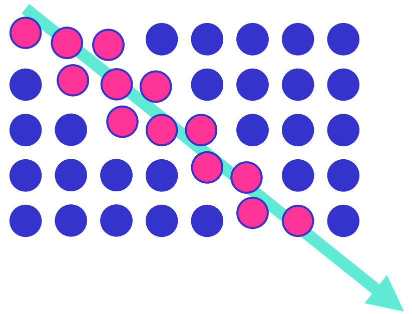
few quantitative calculations



[Fleischer et al., J. Appl. Phys. 36 (1965) 3645]
[Lesueur et al., Rad. Eff. Def. Sol. 126 (1993) 135]

❒ **thermal spike:** local melting and quenching

transient thermodynamics?



[Desauer, Z. Physik 38 (1923) 12]
[Seitz and Köhler Sol. St. Phys. 2 (1956) 305]
[Lifshitz et al. J. Nucl. Ener. A12 (1960) 69]

microscopic

❒ **molecular dynamic calculations:** ab initio lattice calculations

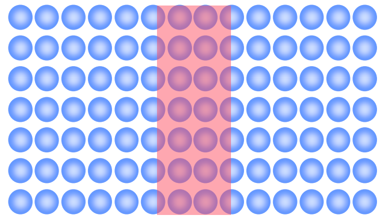
- electron subsystem not included
- interatomic potential?
- large computing times!

[Beuve et al.PRB 68 (2003) 125423]
[Bringa NIMB 203 (2003) 1]

Scheme of two-step process for track formation

energy deposition

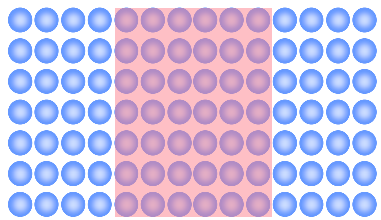
10^{-17} - 10^{-16} s



electronic excitation & ionization
'hot' electrons

electron cascade

10^{-15} - 10^{-14} s

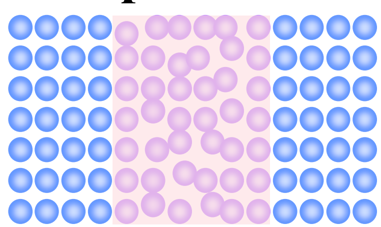


energy diffusion in electronic subsystem
cooling of hot electrons
'cold' lattice

Coulomb explosion

electron-phonon interaction

10^{-13} - 10^{-12} s

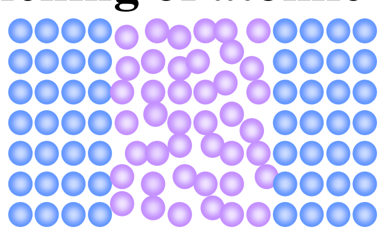


energy diffusion to atoms
lattice heating
melting

thermal spike

quenching of atomic disorder

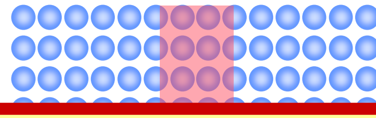
metals ~ 10^{-12} s
insulators ~ 10^{-10} s



fast cooling of atoms
defect formation

Scheme of two-step process for track formation

energy deposition



10^-17 – 10^-16 s

electronic excitation & ionization

electronic energy loss regime

important material properties:

- electric (number & mobility of electrons)
- thermal conductivity
- electron – phonon coupling

10

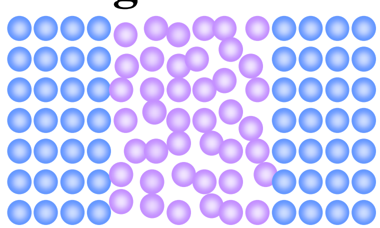
subsystem

ns

10

thermal spike

quenching of atomic disorder



metals ~ 10^{-12} s
insulators ~ 10^{-10} s

fast cooling of atoms
defect formation

Inelastic Thermal Spike Model

two-temperature model

~ ion energy loss

Electrons $$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[rK_e(T_e)\frac{\partial T_e}{\partial r}\right] - g(T_e - T_a) + A(r,t)$$

Atoms $$C_a(T_a)\frac{\partial T_a}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[rK_a(T_a)\frac{\partial T_a}{\partial r}\right] + g(T_e - T_a)$$

electron-phonon coupling

C = specific heat capacity
K = thermal conductivity

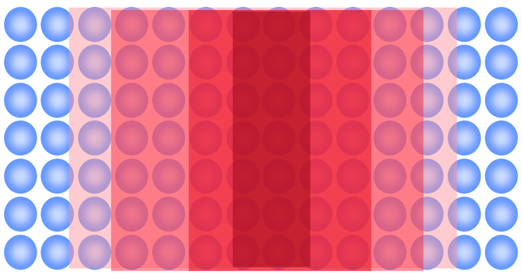
metals: Wang et al., J. Phys. : Condens. Matter 6 (1994) 6733
Dufour et al. Bull. Mater. Sci. 22 (1999) 671

insulators: Toulemonde et al., Nucl. Instr. Meth. B166-167 (2000) 903

Thermal Spike Code available: Toulemonde (CIMAP, Caen) or Stoquert (PHASE, Strasbourg)

Diffusion & Transfer of Energy - Thermal Spike

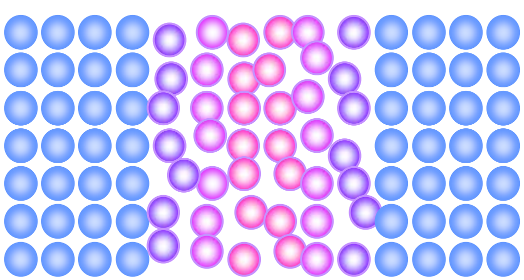
electronic subsystem



$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rK_e(T_e)\frac{\partial T_e}{\partial r}\right) - g\cdot(T_e - T) + A(r,t)$$

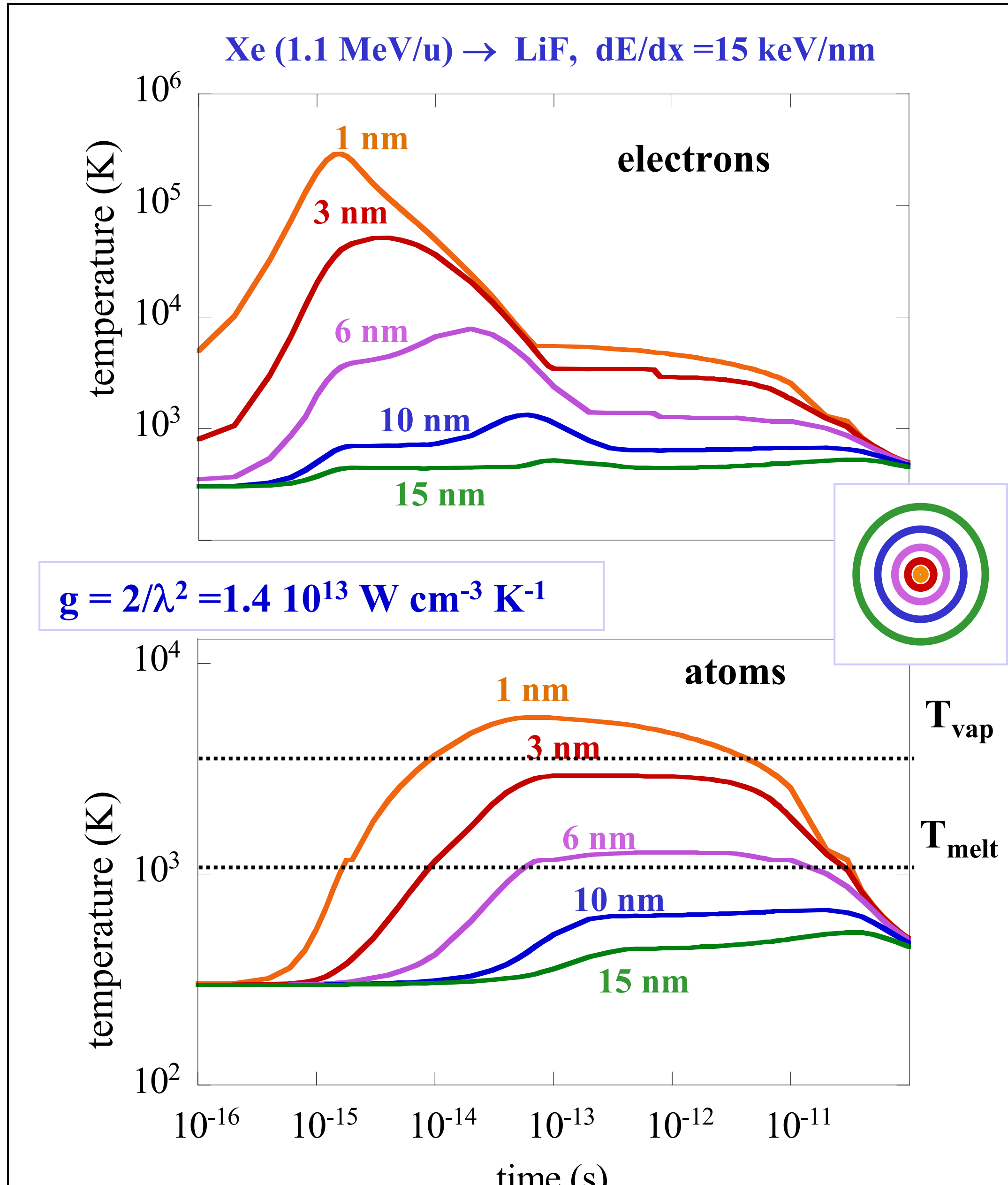
electron-phonon interaction

$$C(T)\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\,K(T)\frac{\partial T}{\partial r}\right) + g\cdot(T_e - T)$$



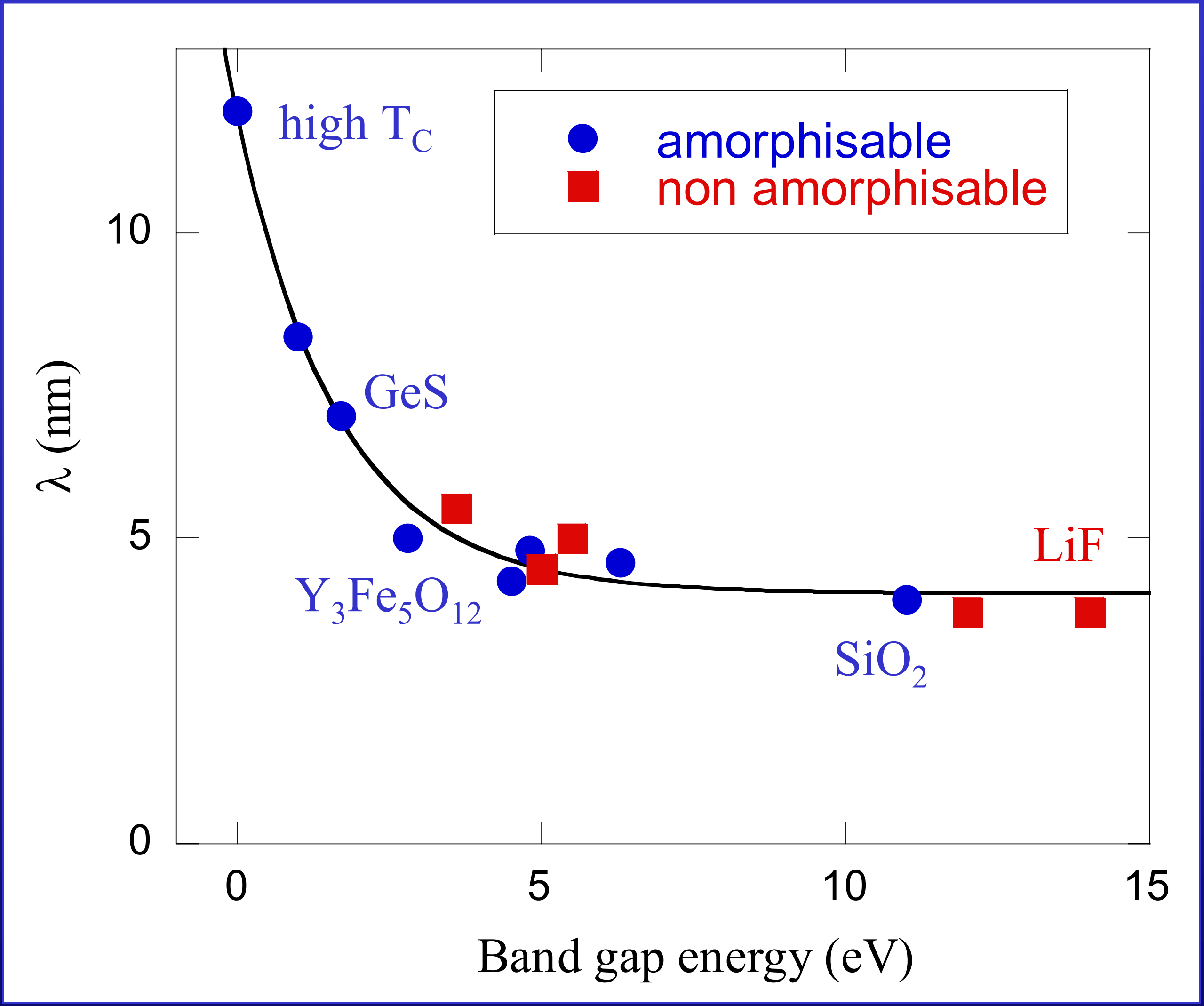
atomic subsystem

Toulemonde et al. NIMB 167-167 (2000) 903



Electron-phonon coupling: λ

High T_c
$BaFe_{12}O_{19}$
GeS
$Y_3Fe_5O_{12}$
SnO_2
$LiNbO_3$
$Gd_3Ga_5O_{12}$
UO_2
Y_2O_3
$Y_3Al_5O_{12}$
SiO_2
CaF_2
LiF



Toulemonde, Dufour, Paumier, Meftah, NIM B166-167 (2000) 903

Track formation and defects in different materials

- metals
- semiconductors
- insulators

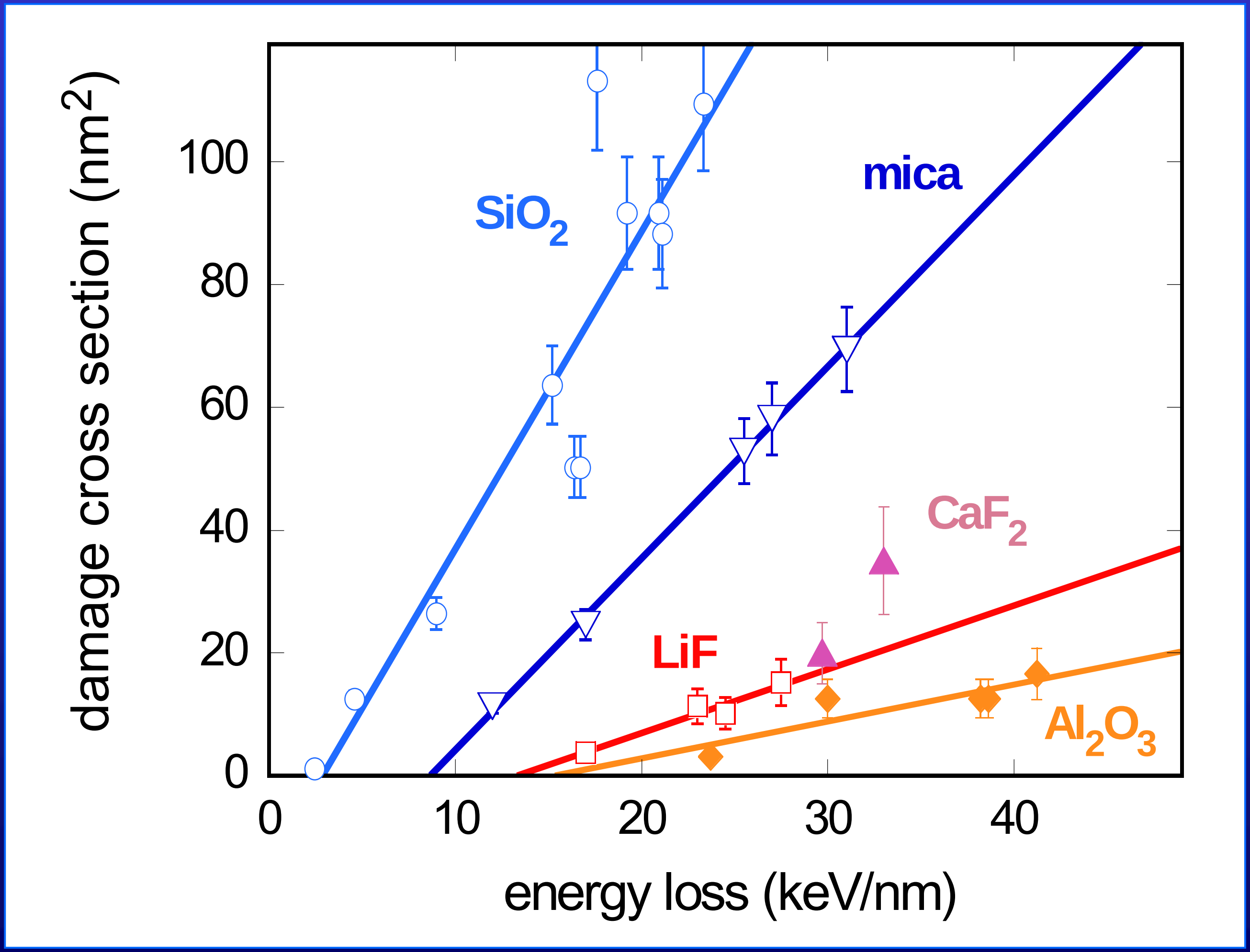
Material sensitivity
(phenomenological)

high sensitivity — **low sensitivity**

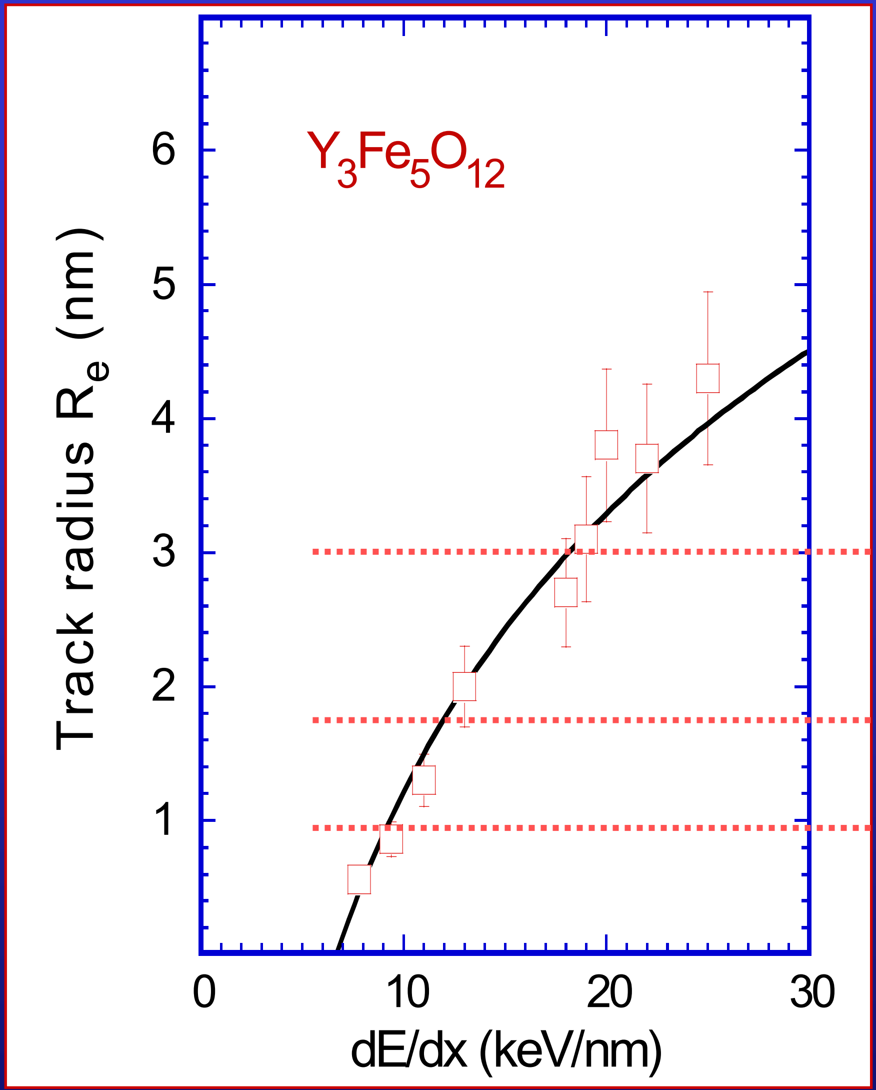
dE/dx threshold	~1 keV/nm	~20 keV/nm	~50 keV/nm

insulators	semi-conductors	metals
☺ polymers	☺ amorphous Si	☺ amorphous alloys
☺ oxides, spinels	☺ GeS, InP, $Si_{1-x}Ge_x$	😐 Fe, Bi, Ti, Co, Zr
☺ ionic crystals	☹ Si, Ge	☹ Au, Cu, Ag…
☹ diamond		

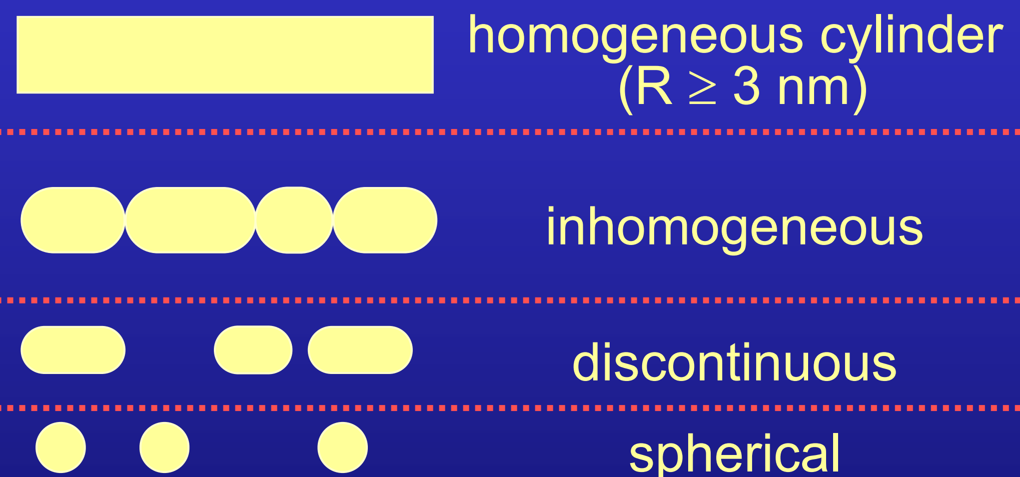
track size and energy loss threshold

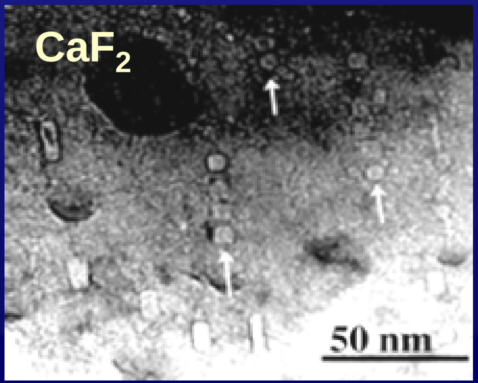


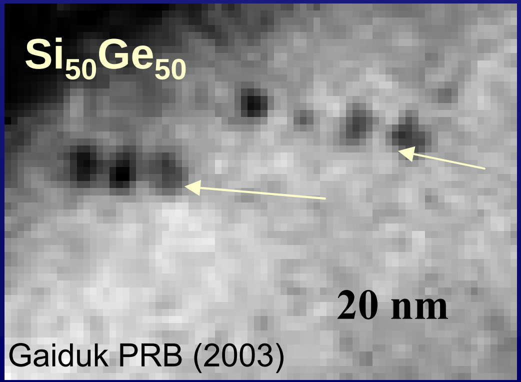
Damage morphology



Toulemonde et al., Sol. State Phen. 30/31 (1993) 477

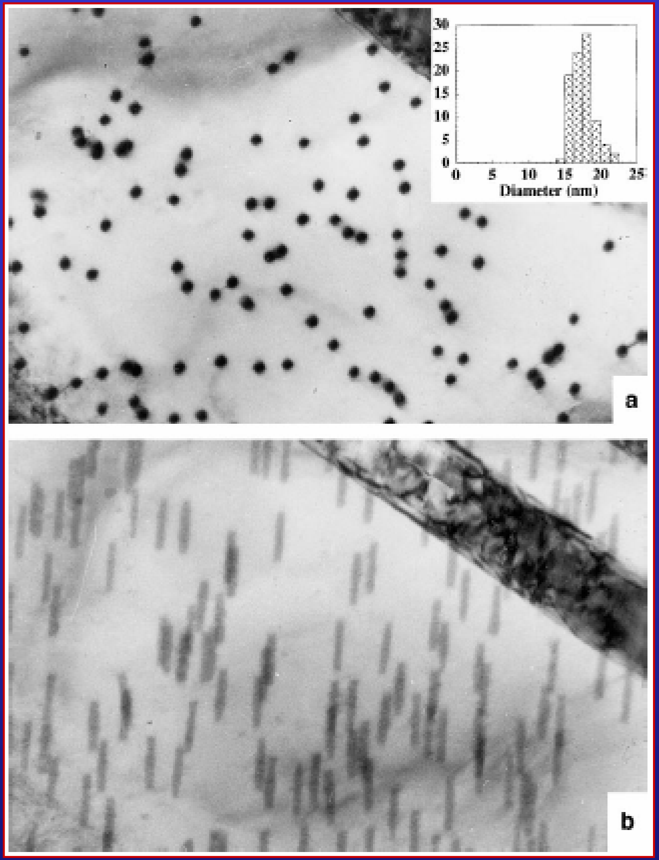






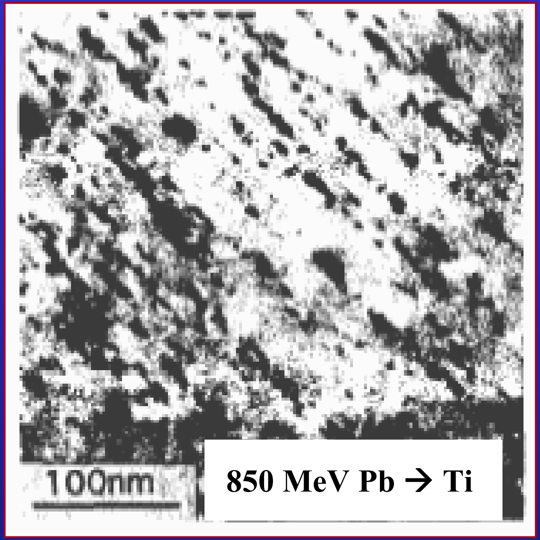
Tracks in metals

structural changes in intermetallic compound NiTi



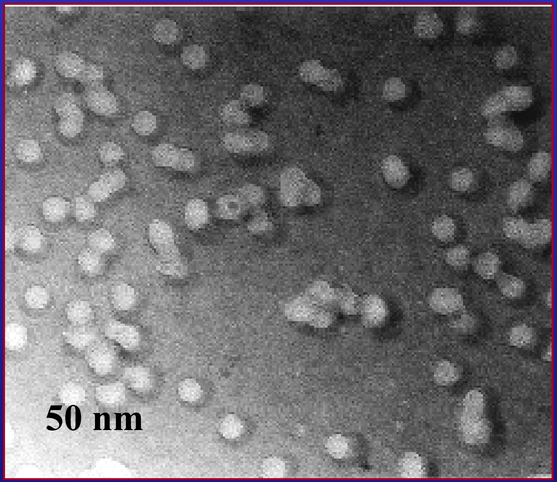
Barbu et al., NIMB 145 (1998) 354

discontinuous tracks in Ti



Dunlop et al. NIM B 112 (1996) 23

30 MeV C_{60} → Ni_3B amorphous tracks



Dunlop et al. NIM B 146 (1998) 222

sensitive metals

pure metals: Fe, Ti, Co, Zr, Bi

metallic compounds: NiB, FeCrNi, TiNi, etc

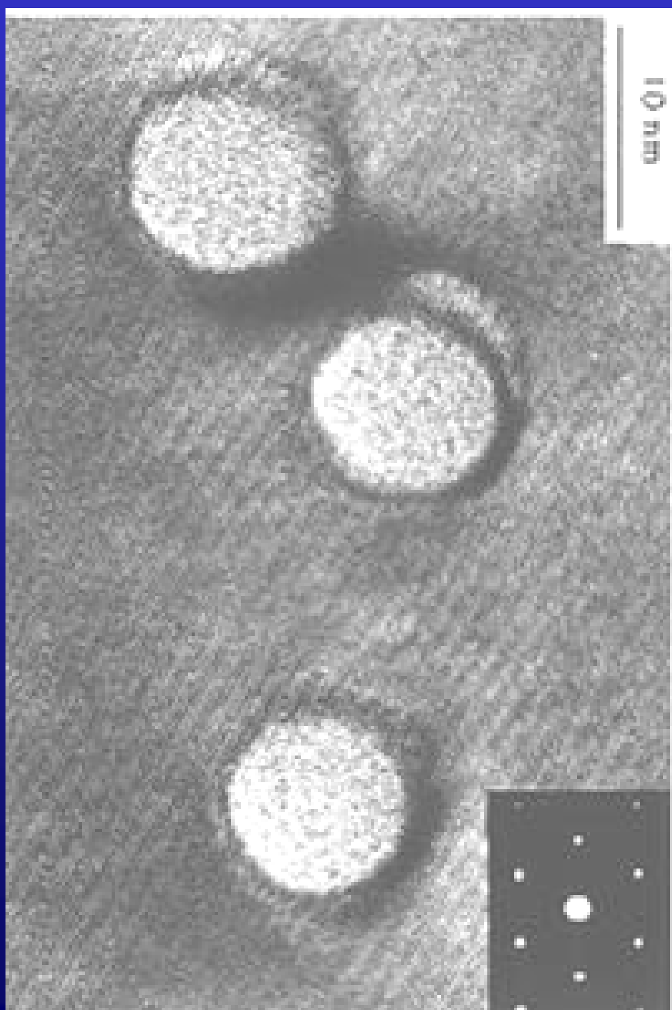
metallic glasses: PdSi, FeB, etc

insensitive metals

Nb, Cu, Ni, Pt, W, Ag, Pd, Au

Tracks in semiconductors

no tracks in Si by monoatomic ions (up to U ions)
but amorphous tracks by C_{60} clusters



30 MeV C_{60} clusters ⇨ (111) Si

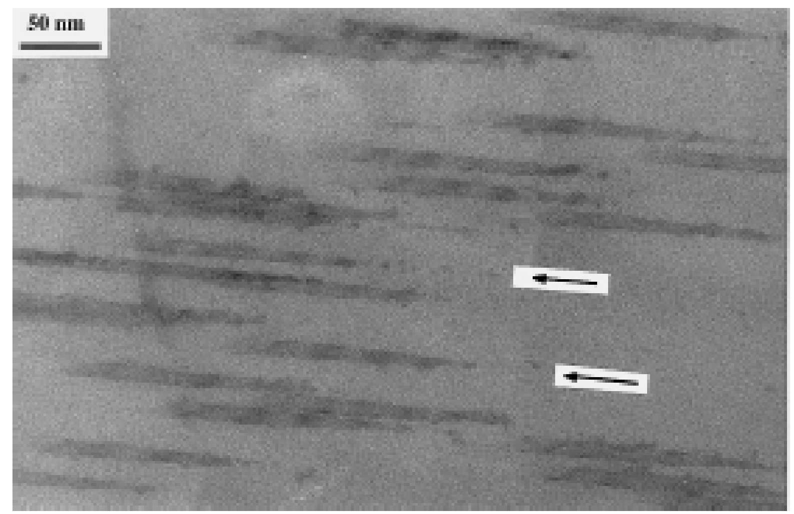
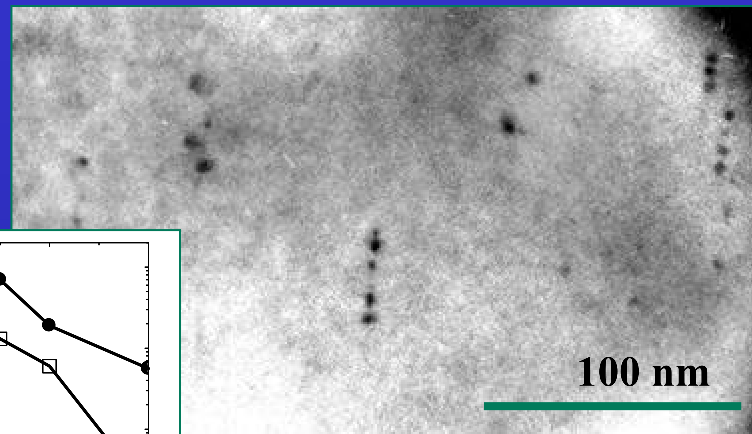


Fig. 3. Bright field electron micrograph of a monocrystalline silicon target irradiated at grazing incidence (≈80° of normal incidence) with 30 MeV C_{60} cluster ions. The micrograph is taken without any reflection strongly excited.

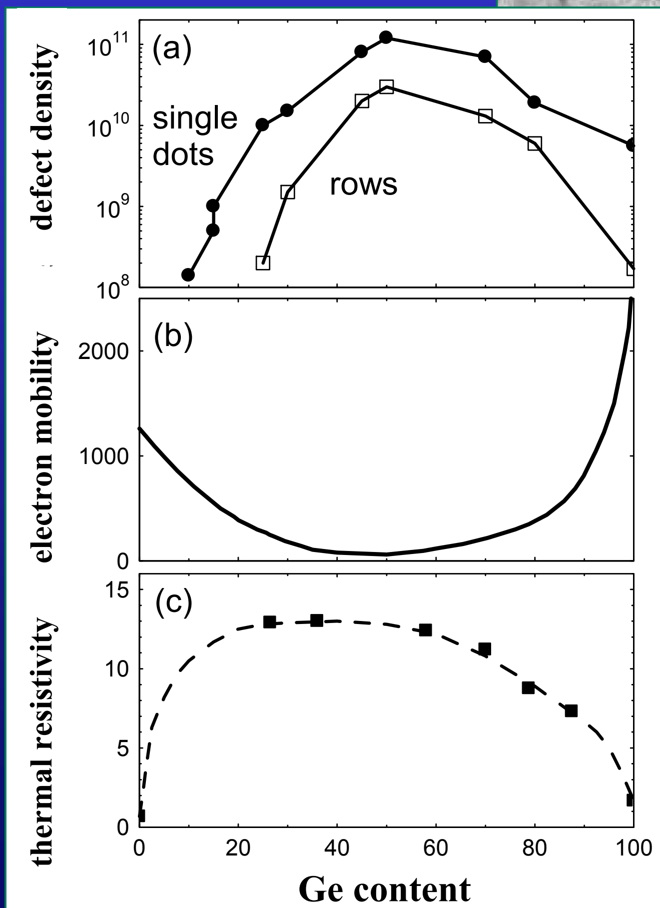
Dunlop et al., NIMB 146 (1998) 302
Canut et al., NIMB 146 (1998) 296

discontinuous tracks in semiconducting compounds

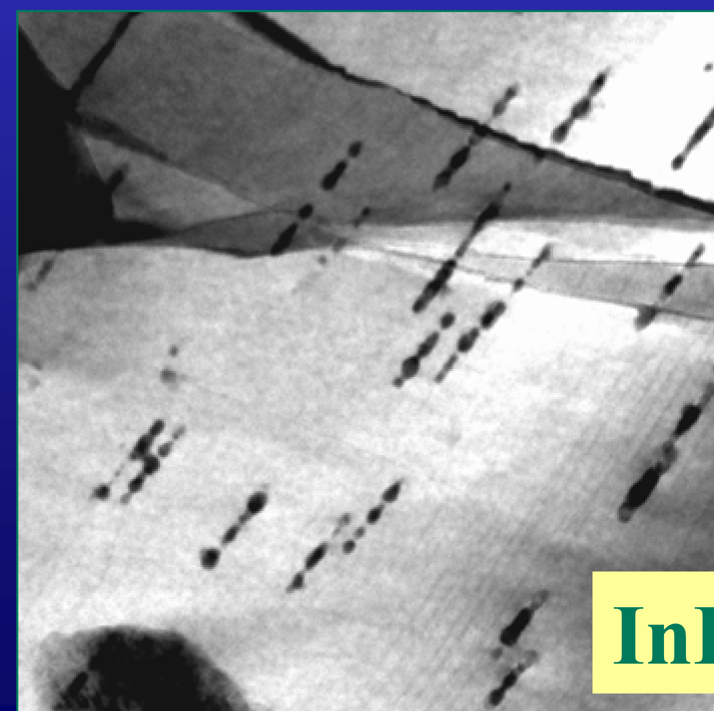
Si_xGe_{1-x}



$Si_{50}Ge_{50}$



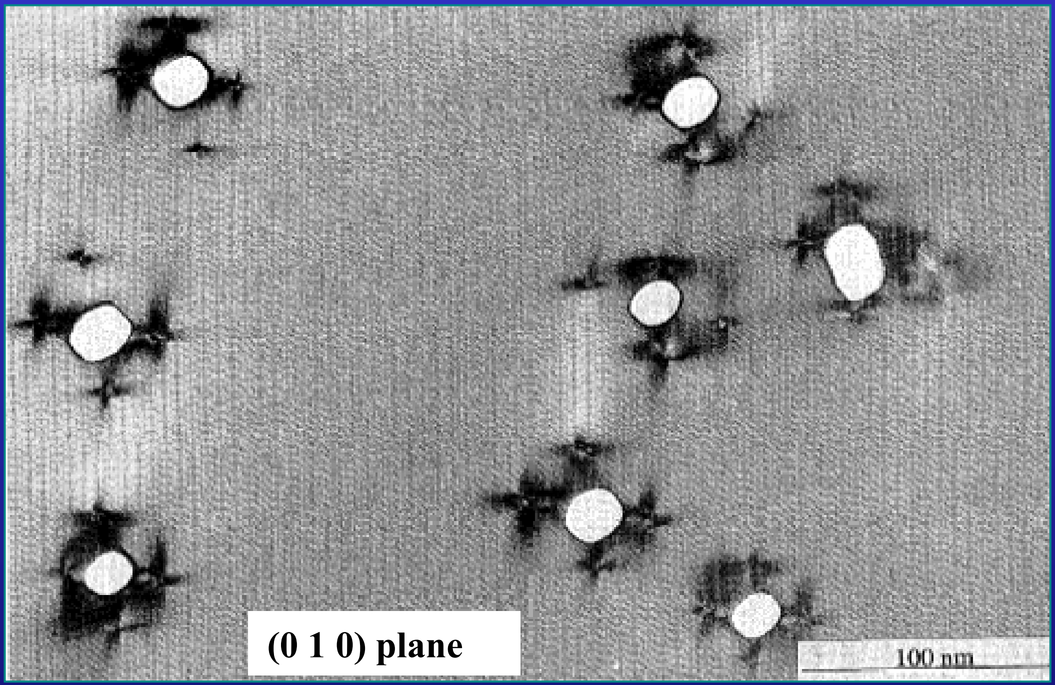
Gaiduk et al, PRB 66 (2002) 045316
Physica B 340 (2003) 808

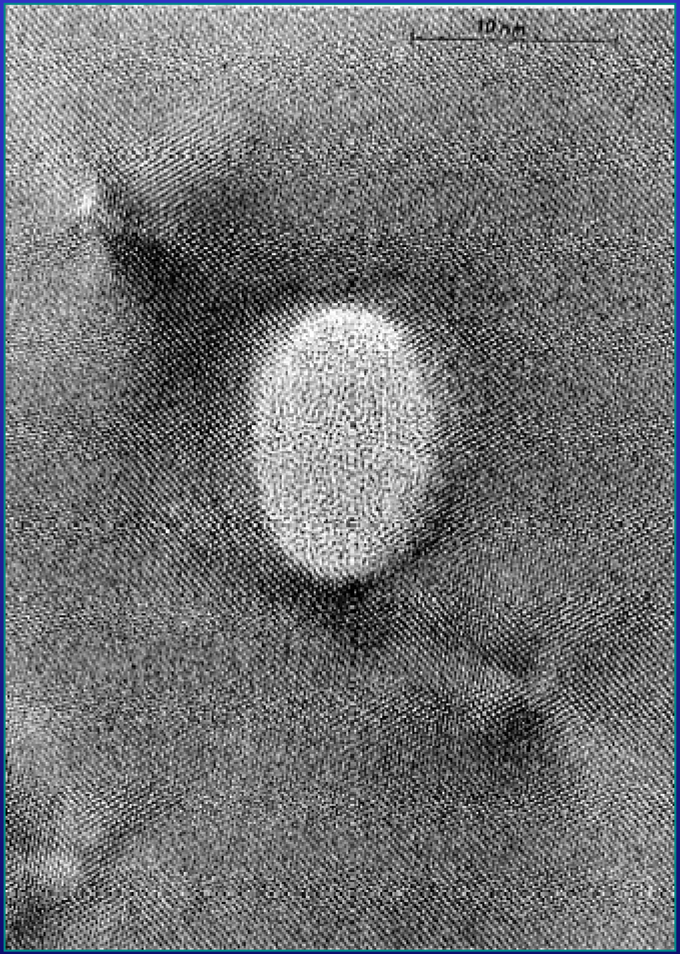


InP

L. Chadderton

amorphous tracks in narrow bandgap GeS





layered structure, E_g = 1.65 eV

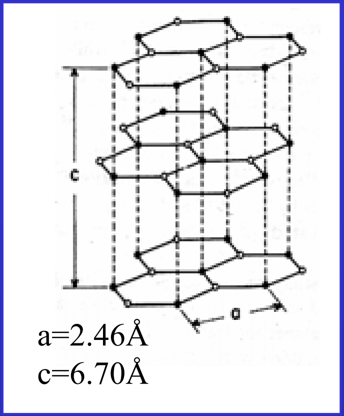
lattice constants: a = 0.429 nm
c = 0.365 nm

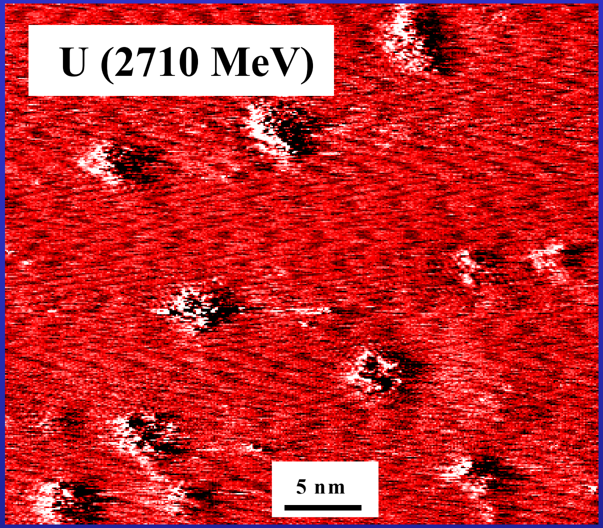
2.7 GeV U → GeS

Vetter et al., NIMB 91(1994) 129

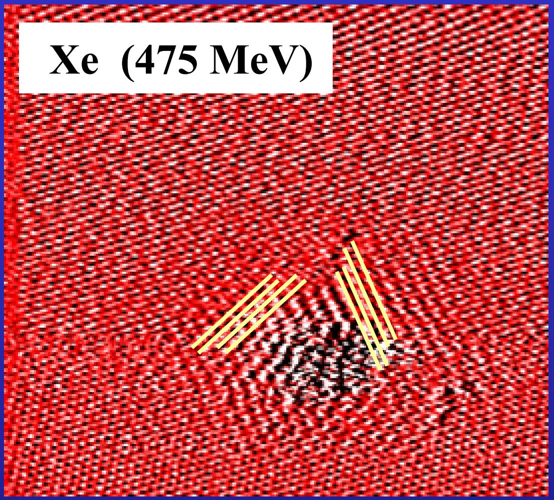
Tracks in carbon-based materials

Graphite (highly oriented pyrolytic, HOPG)

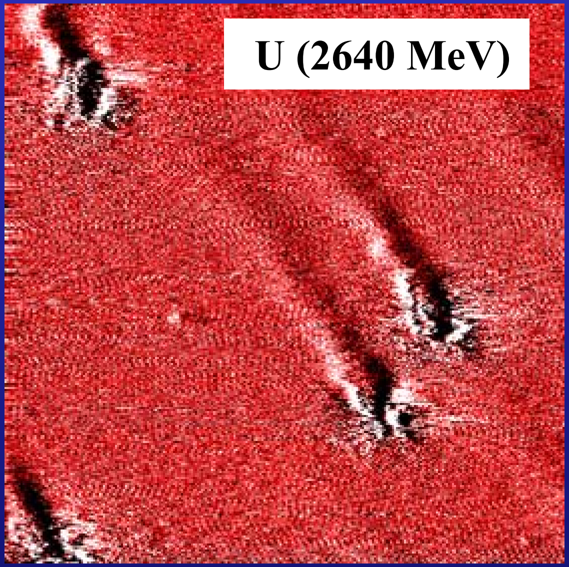




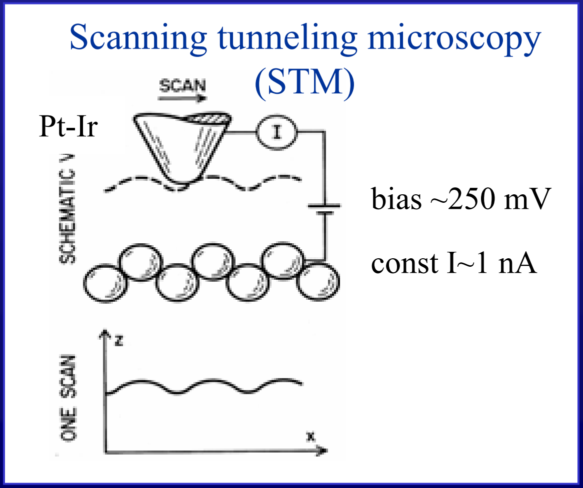
30 nm x 30 nm



15 nm x 15 nm

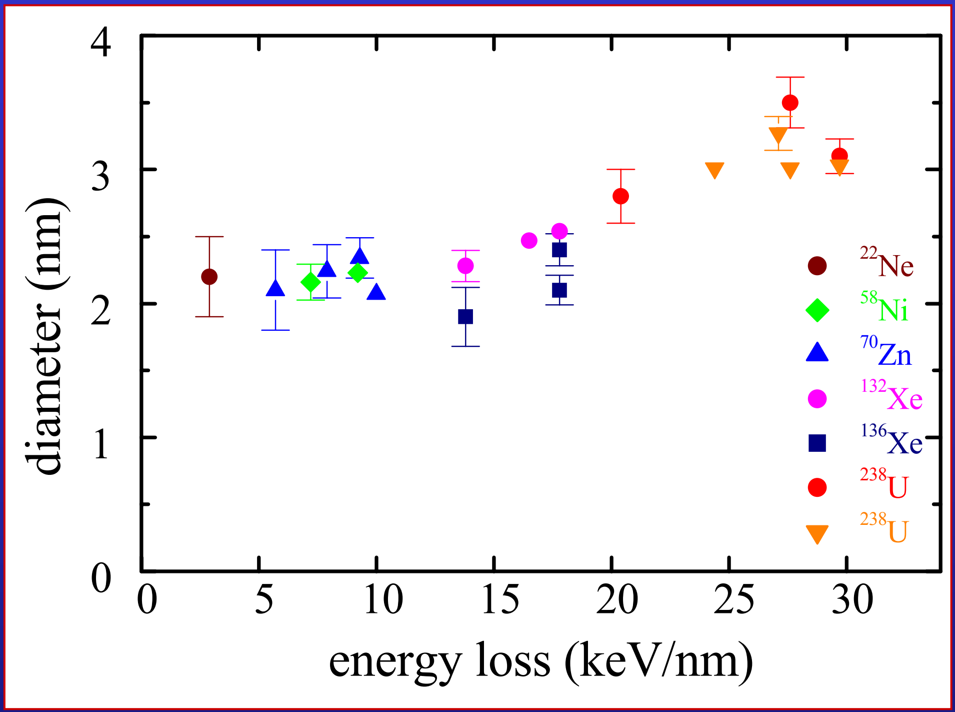


50 nm x 50 nm

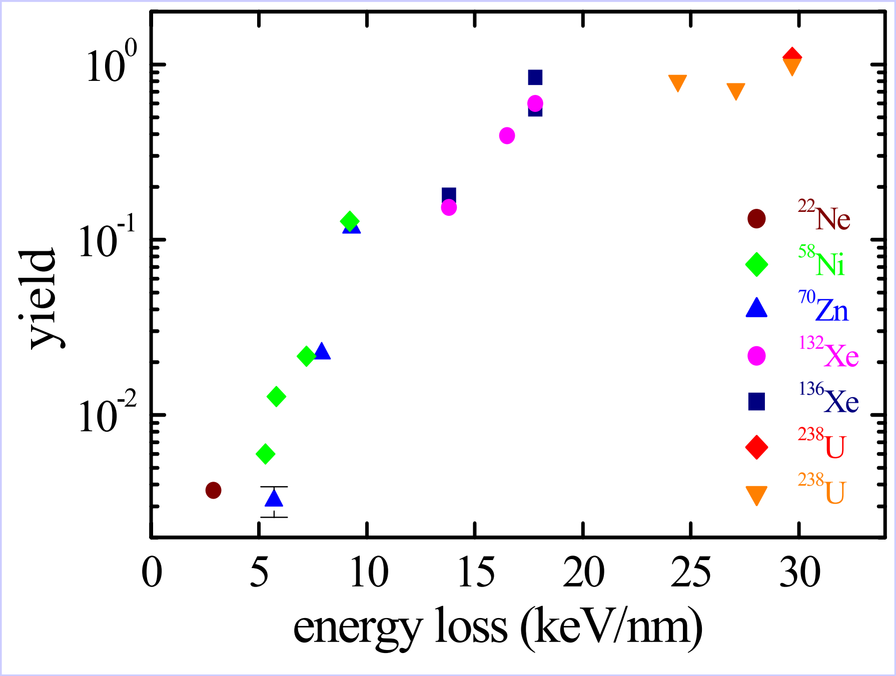


Liu et al, PRB 64 (2001) 184115
NIMB 212 (2003) 303

track diameter in HOPG



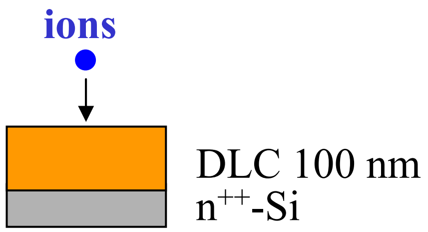
track formation efficiency



- **extremely small track diameters**
- **100% track efficiency only above ~18 keV/nm**

Ion tracks diameter in DLC

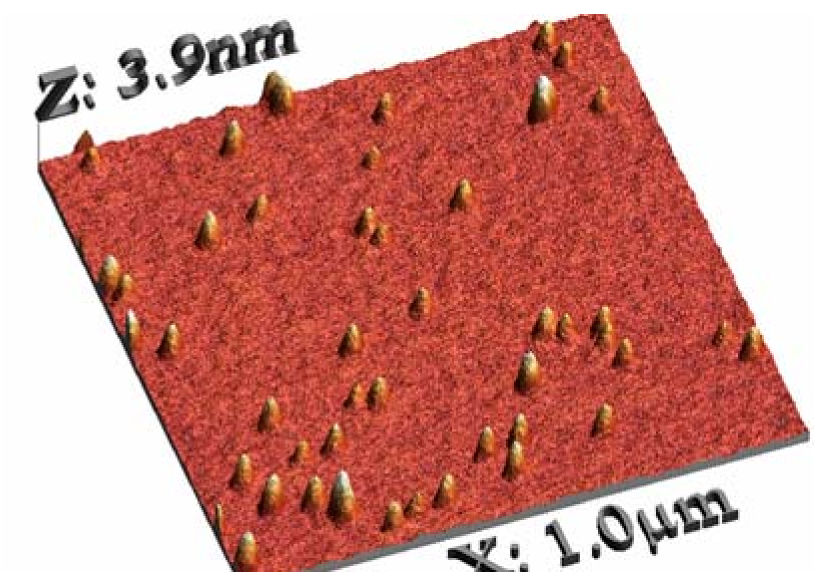
1 GeV U-ions ($5x10^9$ cm^{-2}) → DLC



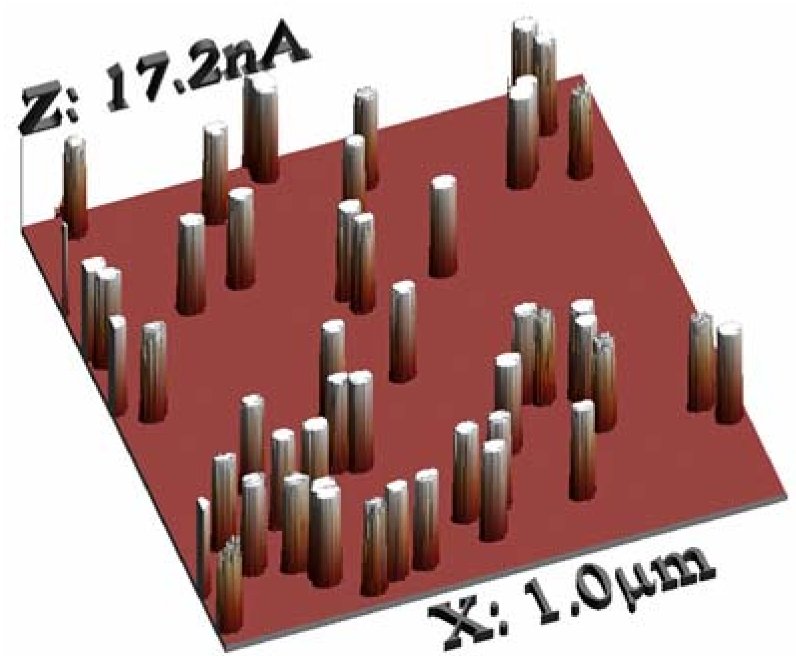
sp^3-bonds: 70 - 80 %

AFM measurements

topography

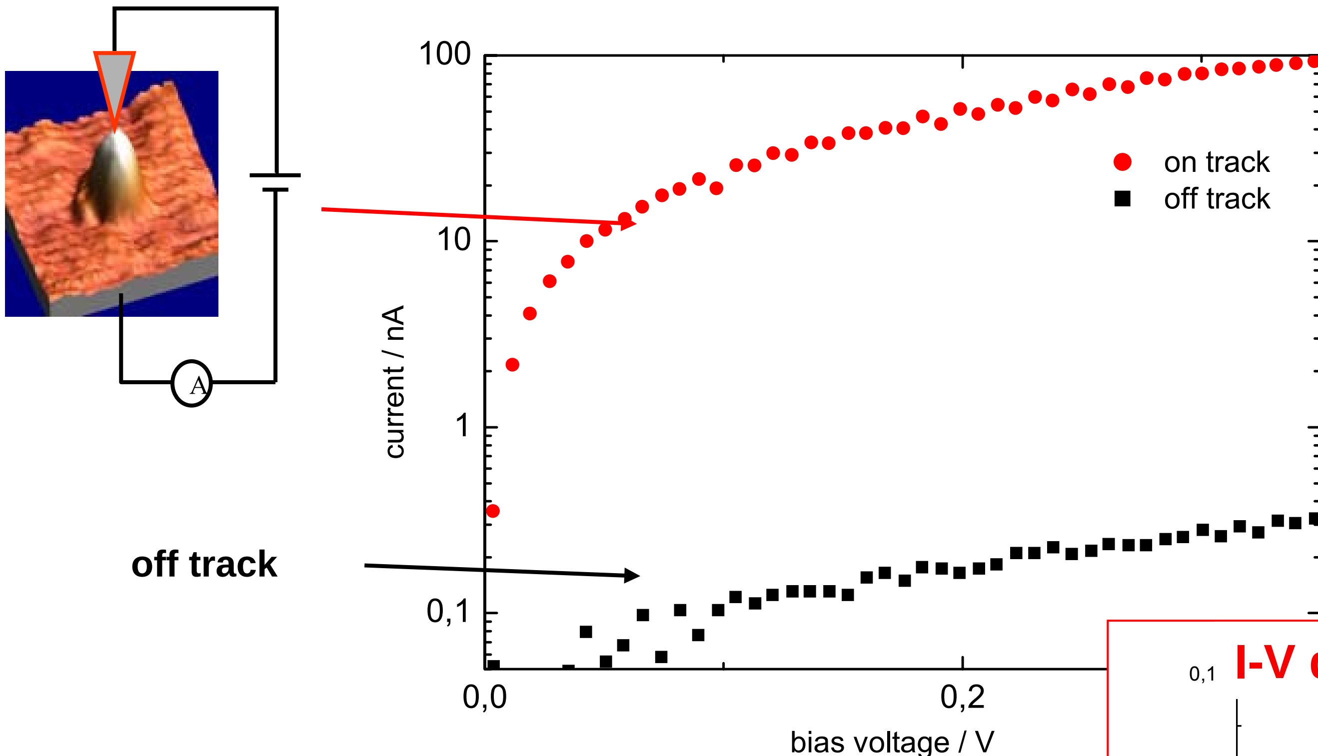


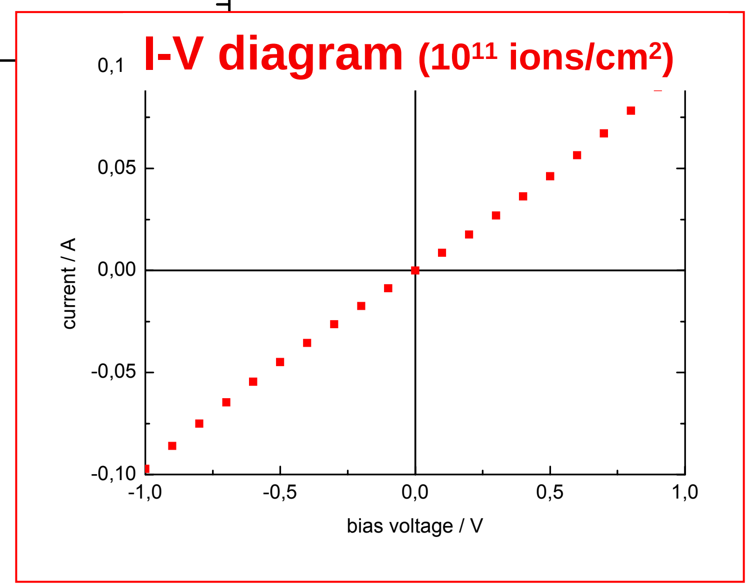
current mapping



U = 150 mV

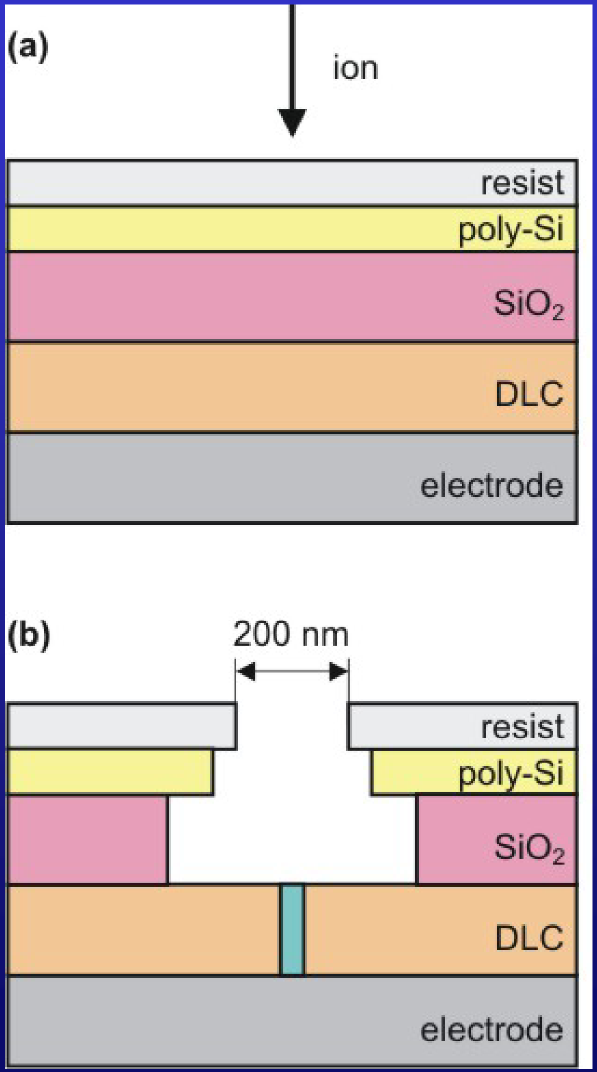
I-V diagram of single track and off-track regions





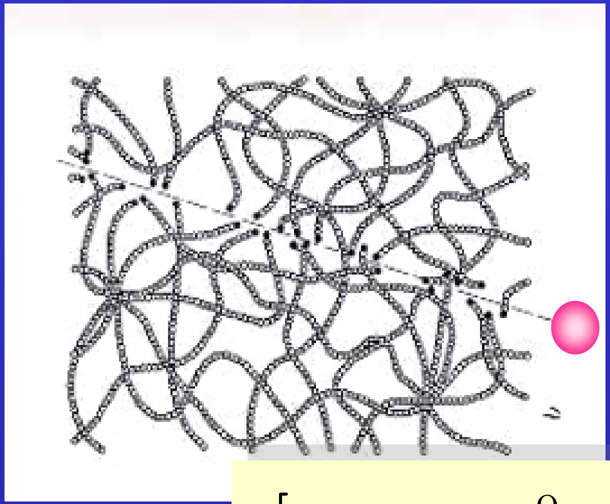
(U = 0.35 V (AFM tip – substrate)
max. current = 98 nA
current density ~ 1x10^5 A/cm^2
conductivity ~ 2.8 S/cm.

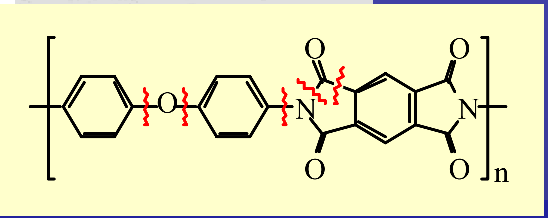
possible field emitting device



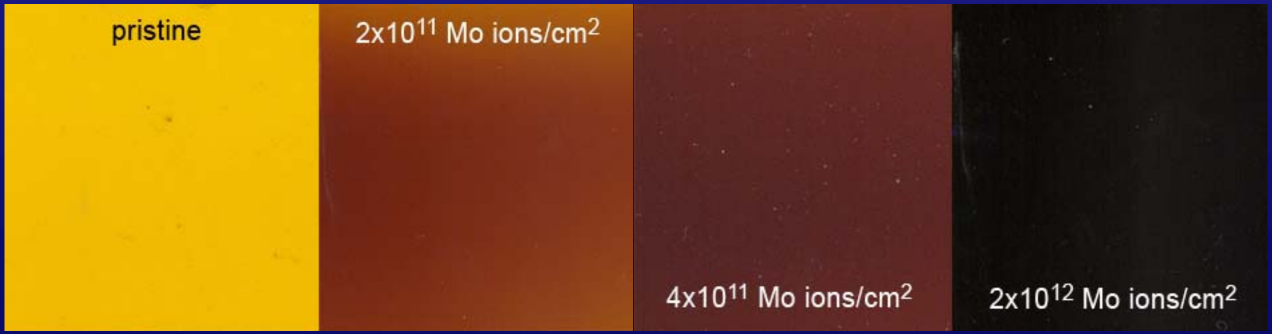
Polymers

- chain scission
- cross linking
- formation of radicals
- amorphisation etc





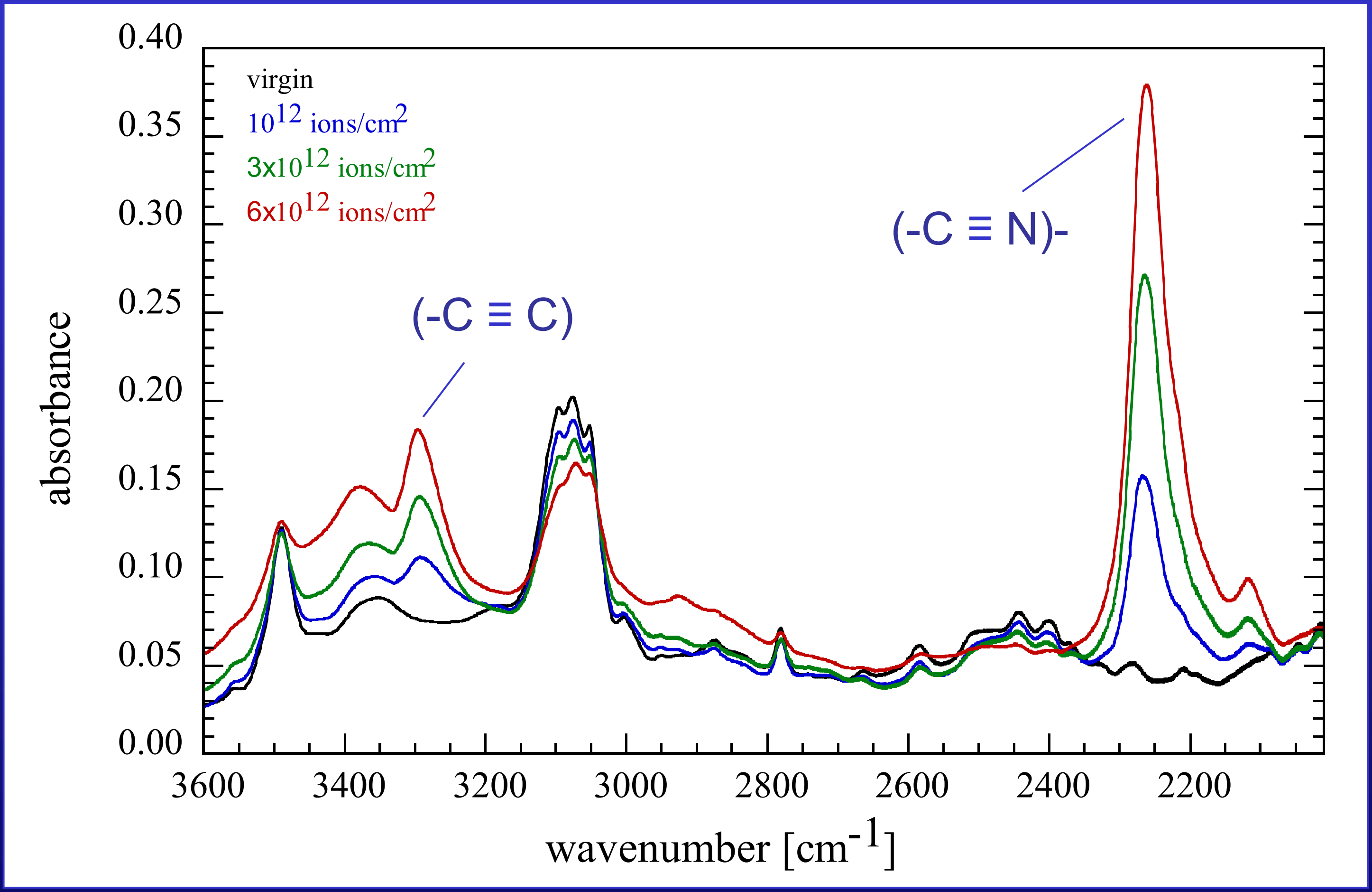
- **outgassing of small molecules (CO_n, C_nH_m,...)**
- **creation of unsaturated bonds (e.g. -C ≡ C, -C=C)**
- **graphitization**



graphitization of Kapton increasing as a function of ion fluence

Infrared spectroscopy: unsaturated bonds

Kr (720 MeV) → Kapton



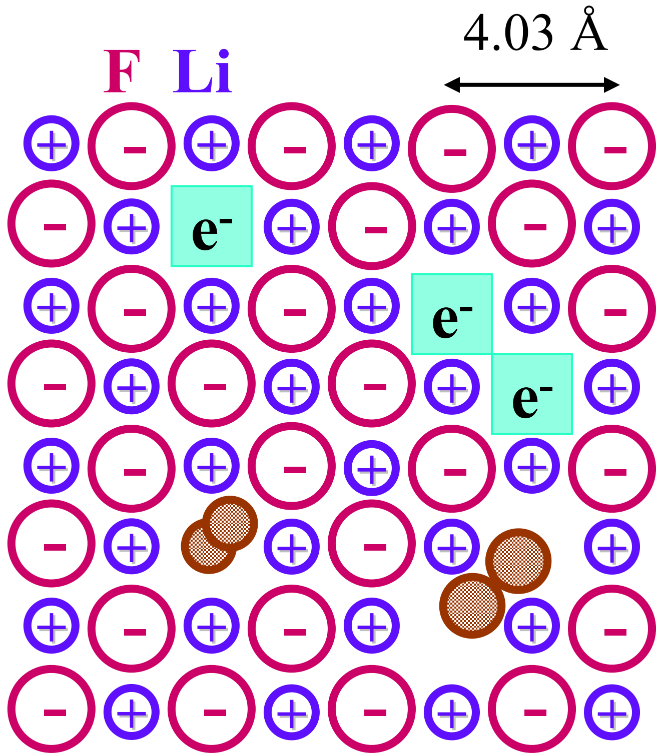
Steckenreiter et al. J. Polym. Sci. A37 (1999) 4318

Defect creation in ionic crystals

LiF, NaCl, KCl, MgF_2, CaF_2, BaF_2

non-amorphisable !!

lithium fluoride



fcc lattice, E_g=14.6 eV
cleaving along (100) plane

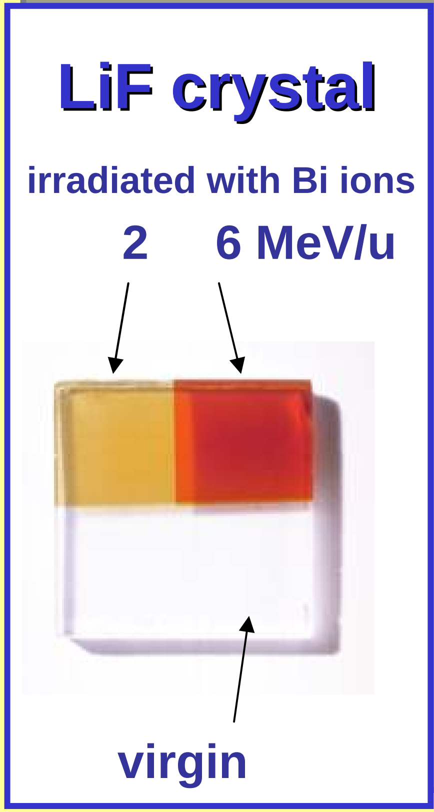
color centers

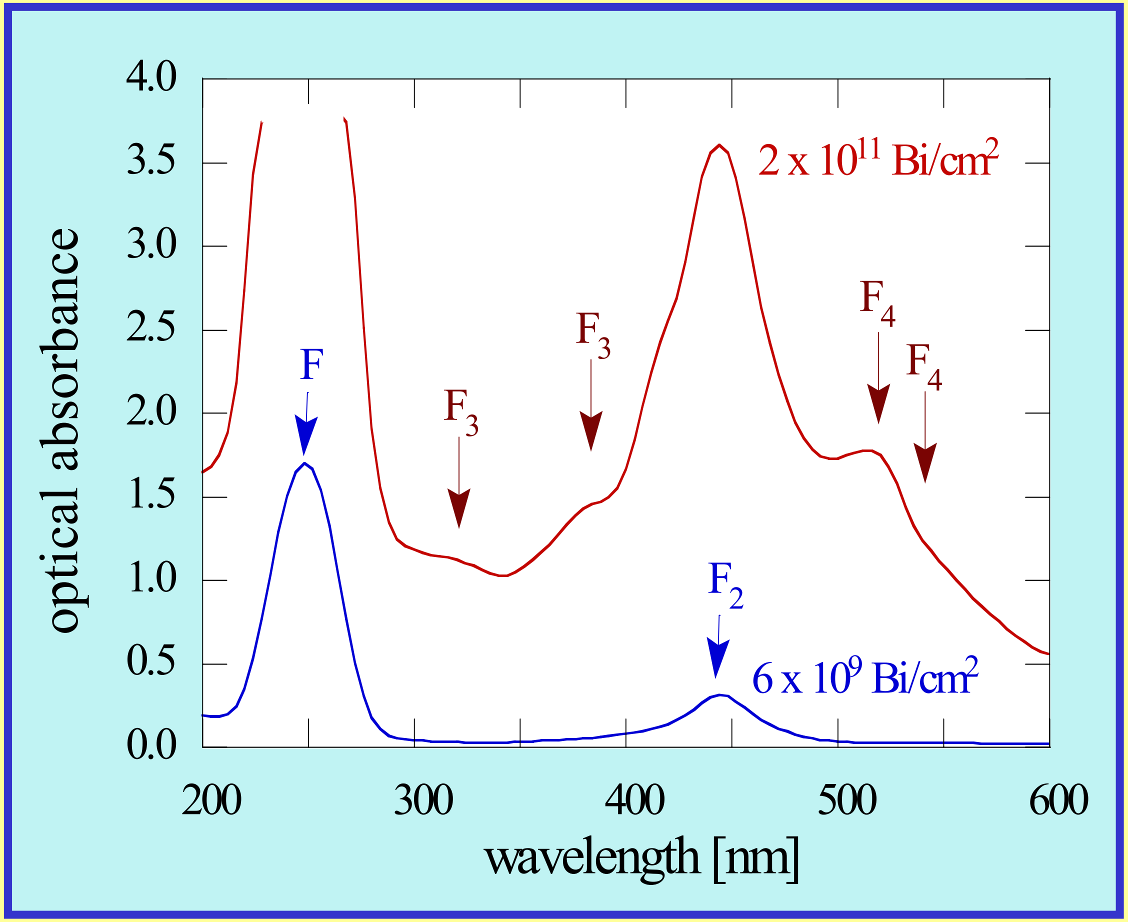
F-center
F_2-center
} electron centers

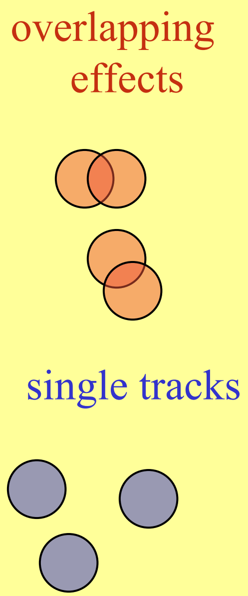
Frenkel pair

H-center
V_K-center
} hole centers

Spectroscopy of color centers

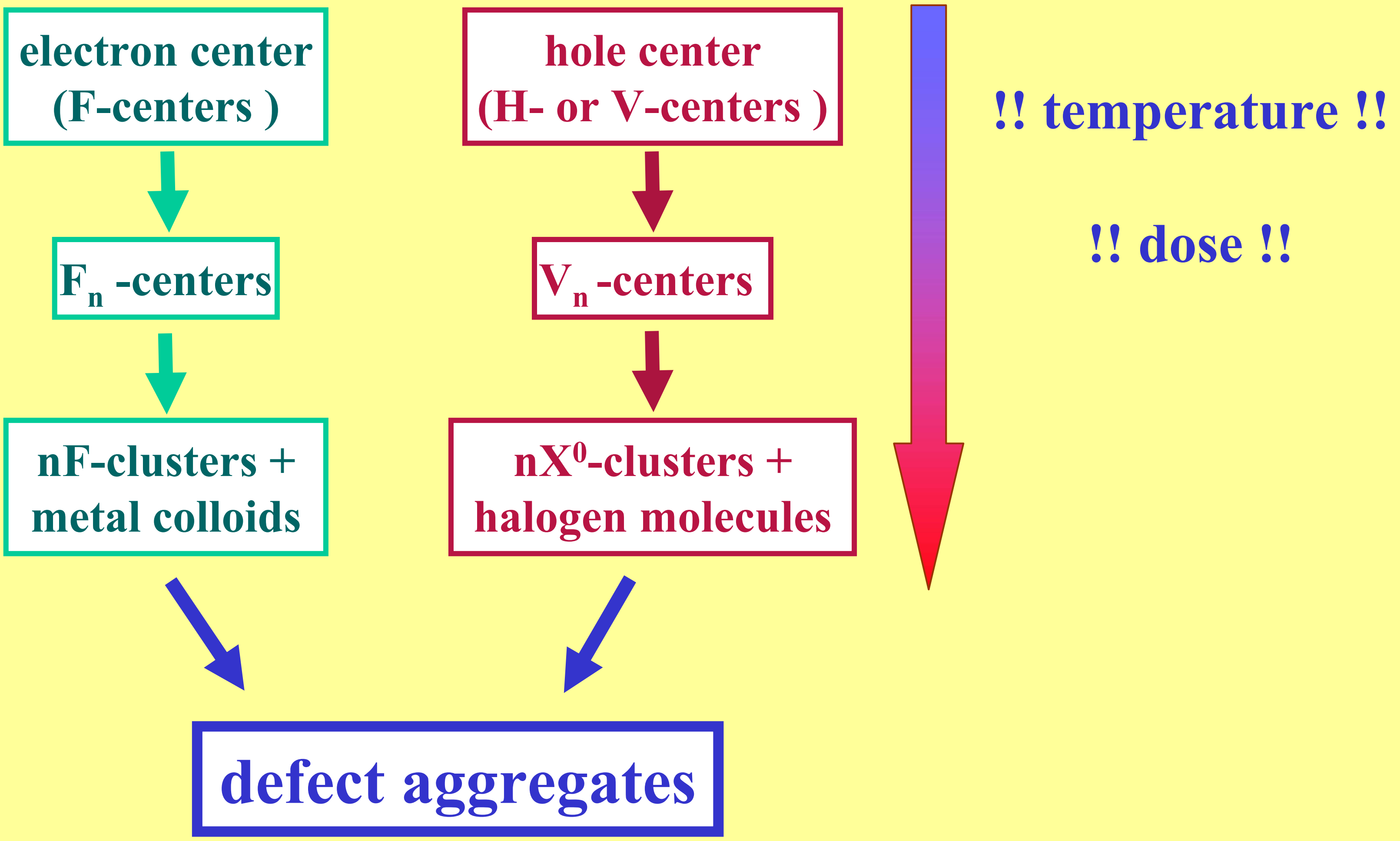




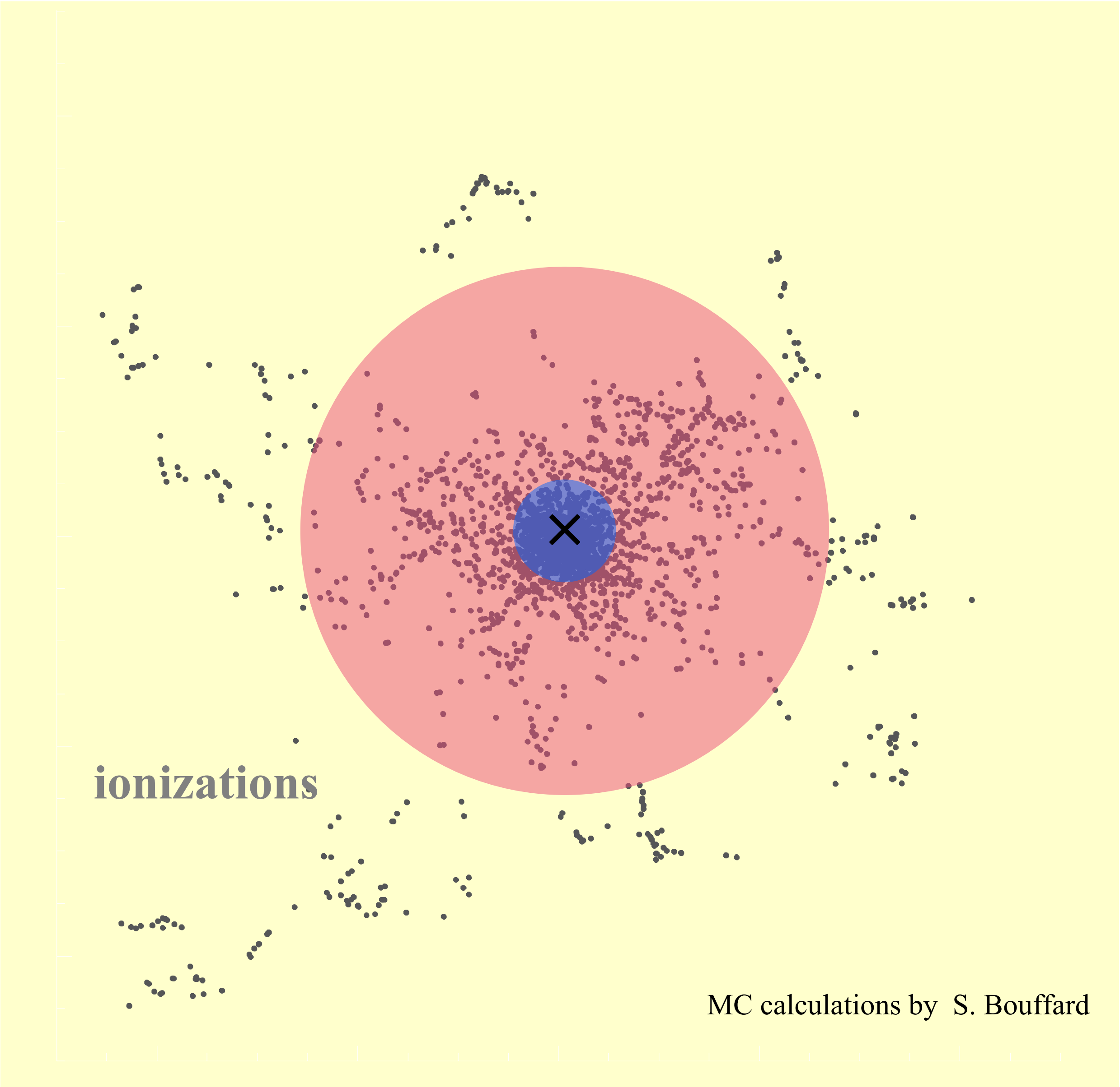


Schwartz et al. Phys. Rev. B 58 (1998) 11232

Aggregation of single defects



Scheme of track damage in LiF



core (aggregates)

radius **1-2 nm**

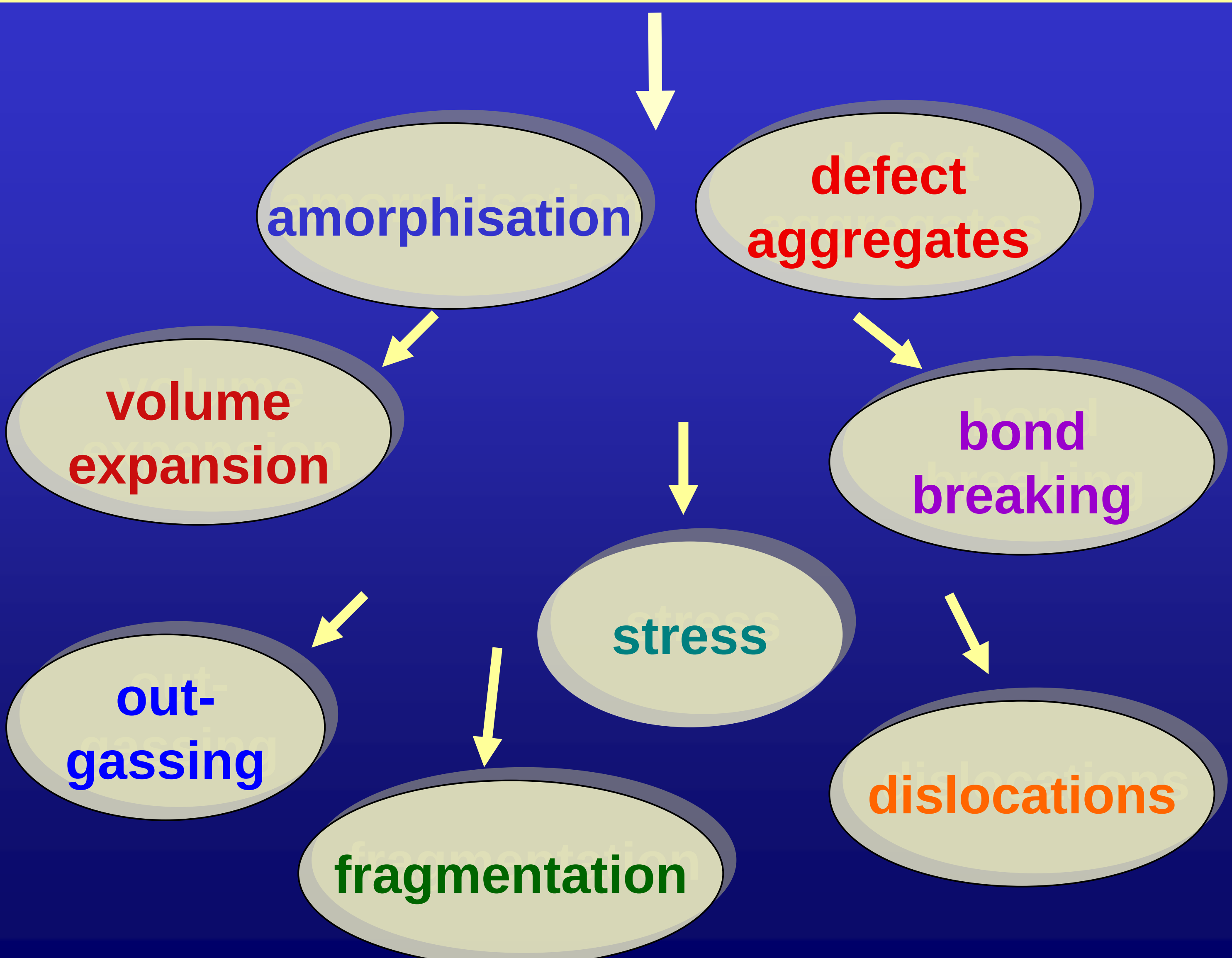
energy **~ 0.3 E_{tot}**

halo (single defects)

radius **10-40 nm**

energy **~ 0.7 E_{tot}**

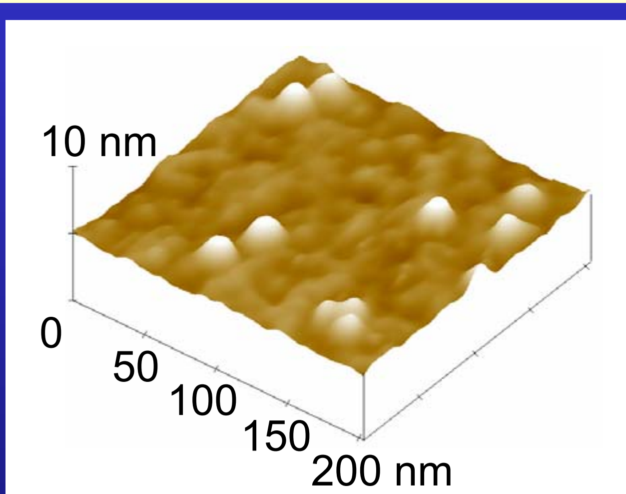
Ion-induced bulk modifications



Ion-induced surface processes

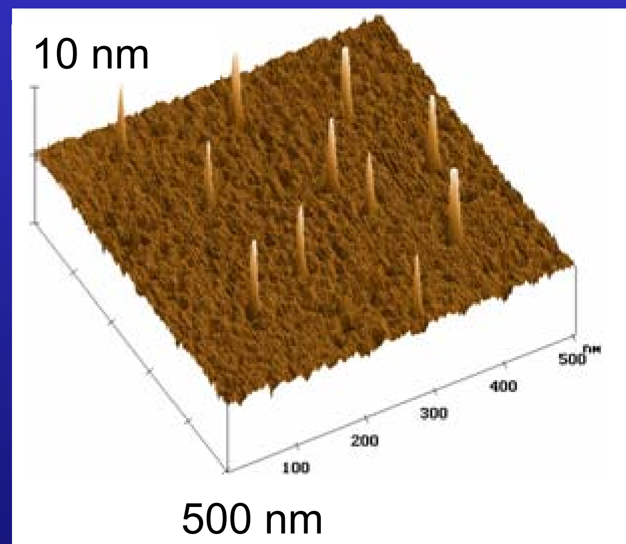
scanning force microscopy

amorphous metallic alloy $Fe_{85}B_{15}$



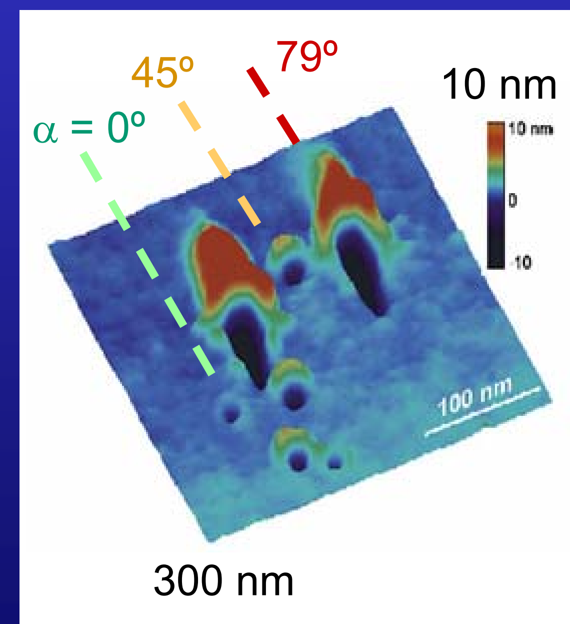
Audouard, NIMB 146 (1998)

ionic crystal CaF_2



Khalfaoui NIMB (2005)

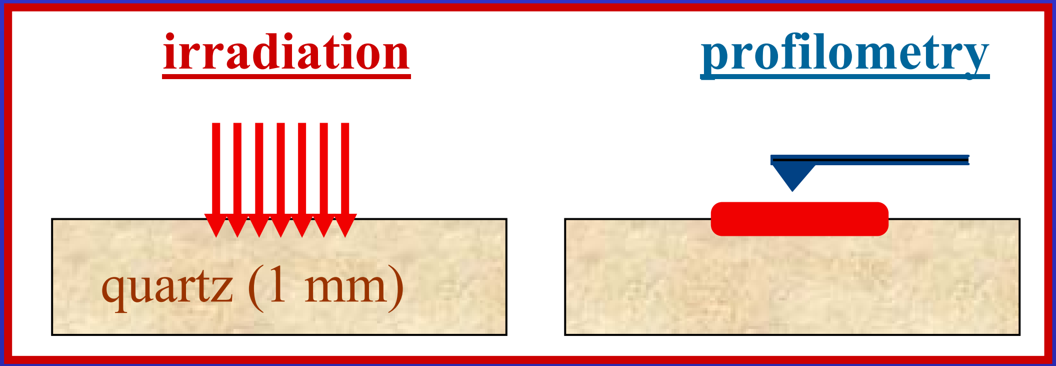
polymer (PMMA)



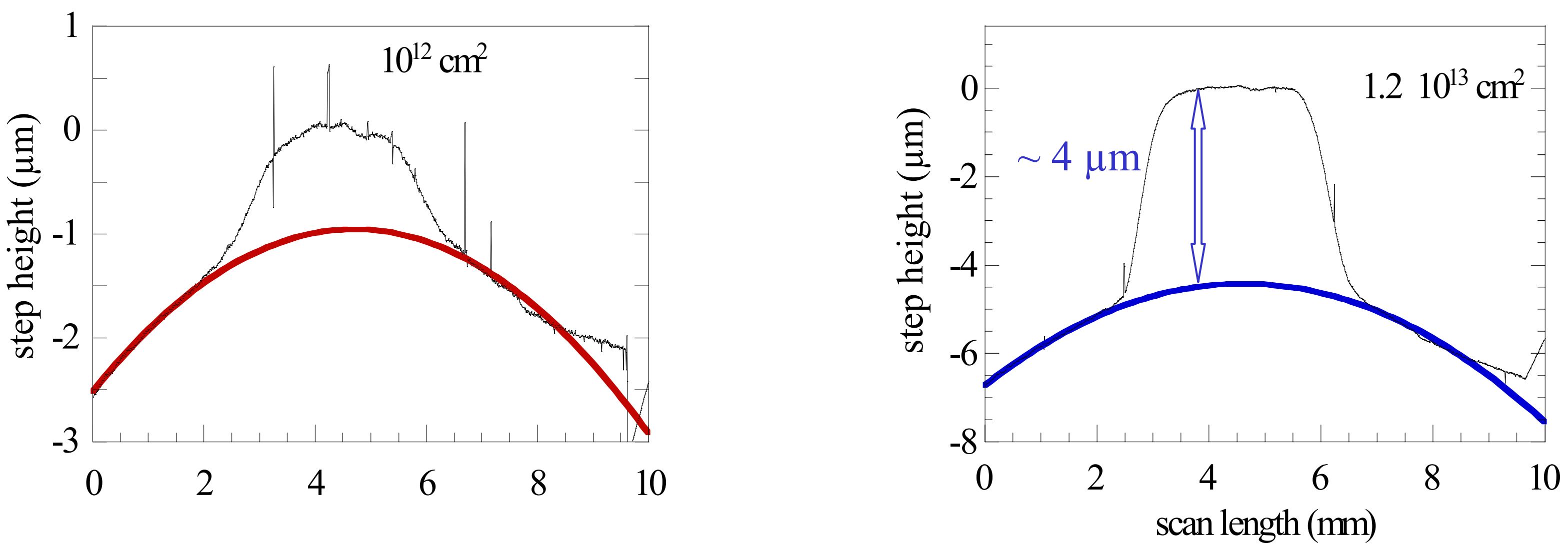
Papaléo, NIMB 206 (2001)

$\rho_{matrix} > \rho_{track}$

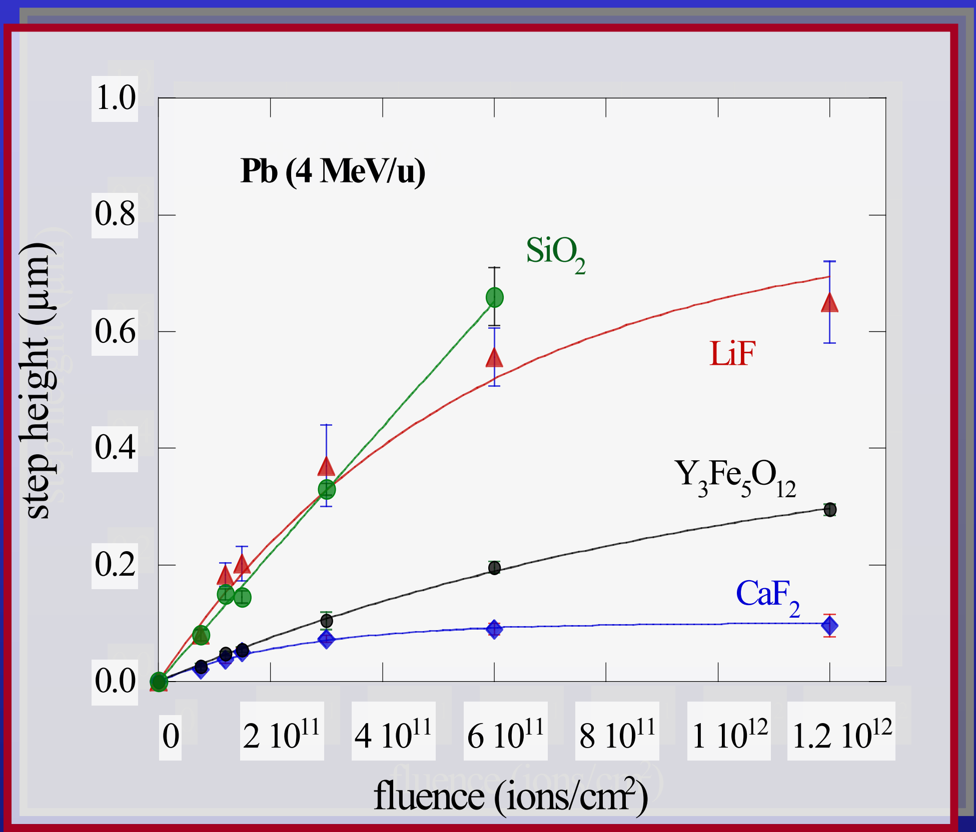
Swelling and stress due to phase change and/or defects



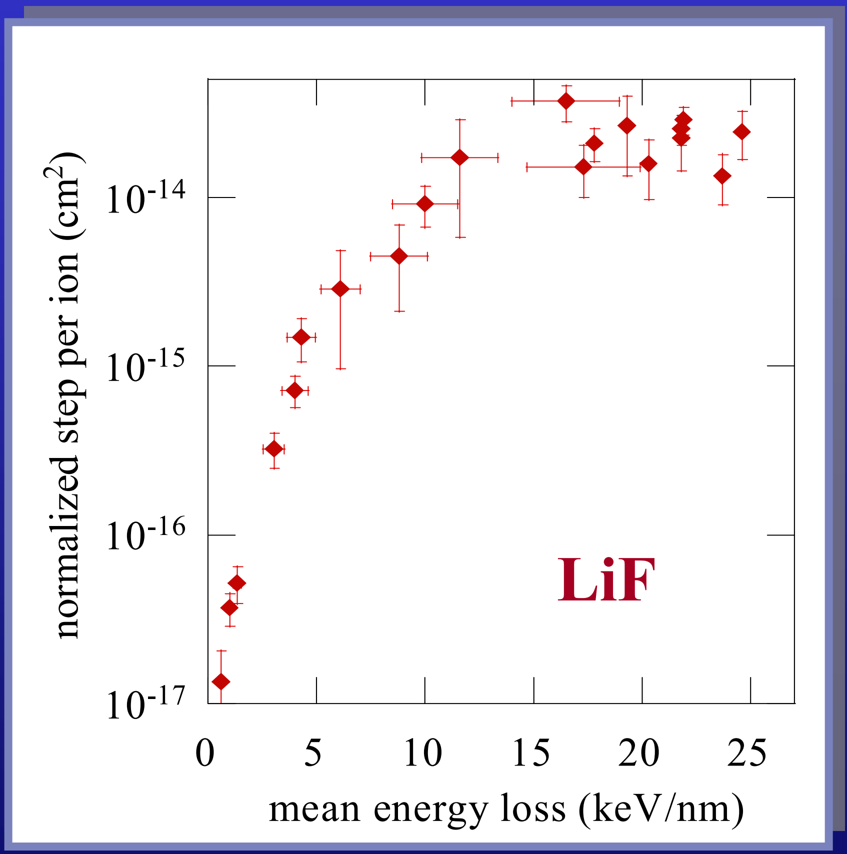
Xe (450 MeV) → quartz (range = 30 μm)



ion-induced swelling



threshold effect

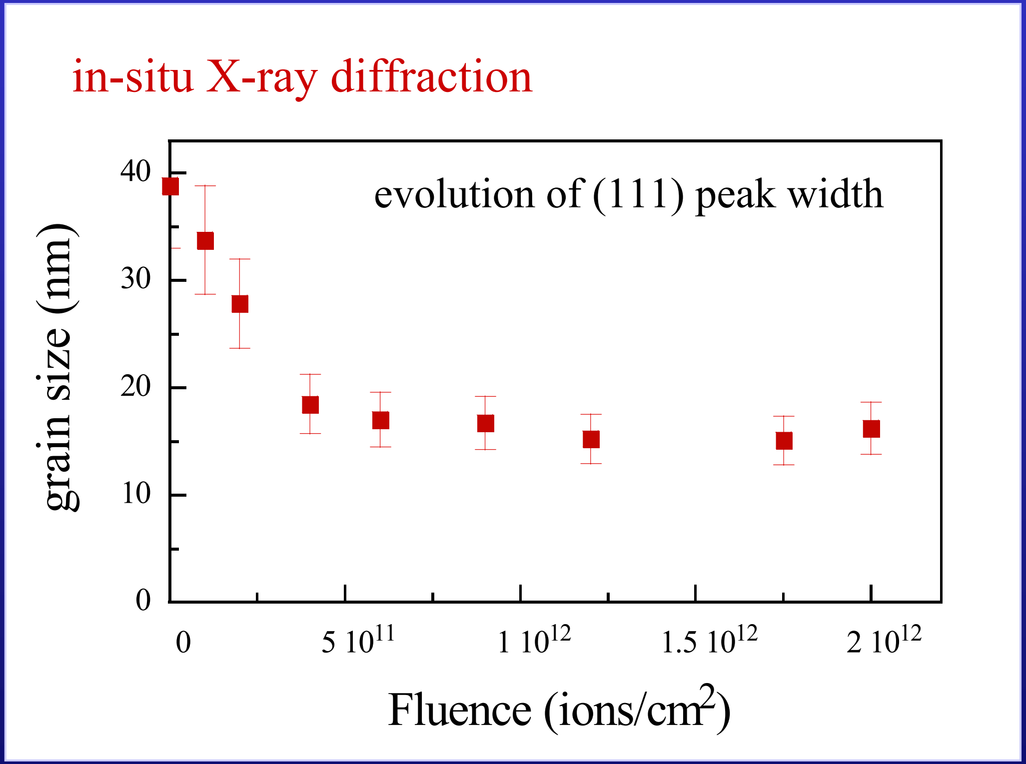


- ➔ scales with range of ions
- ➔ saturates at high fluences
- ➔ increases with electronic energy loss
- ➔ occurs above a dE/dx threshold

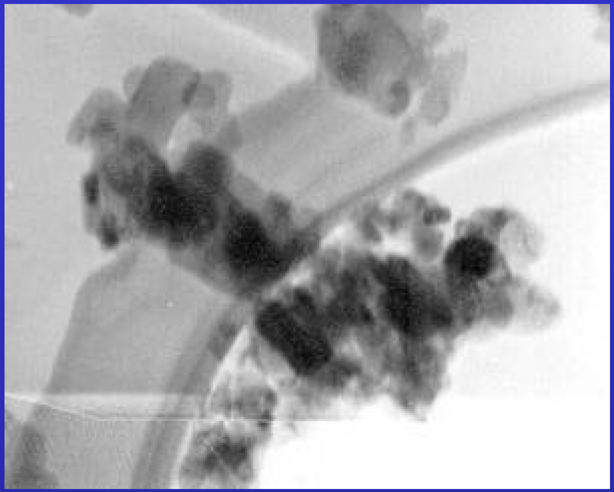
Trautmann et al., PRB 62 (2000)13

Beam-induced grain breaking

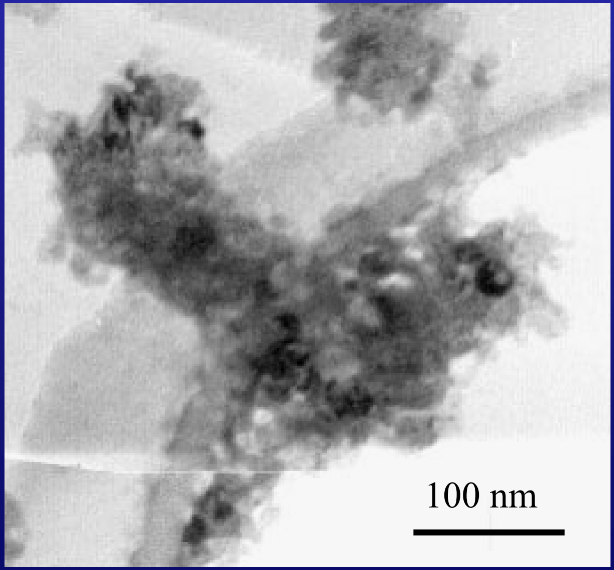
4 MeV/u Pb → CaF_2 powder



before irradiation



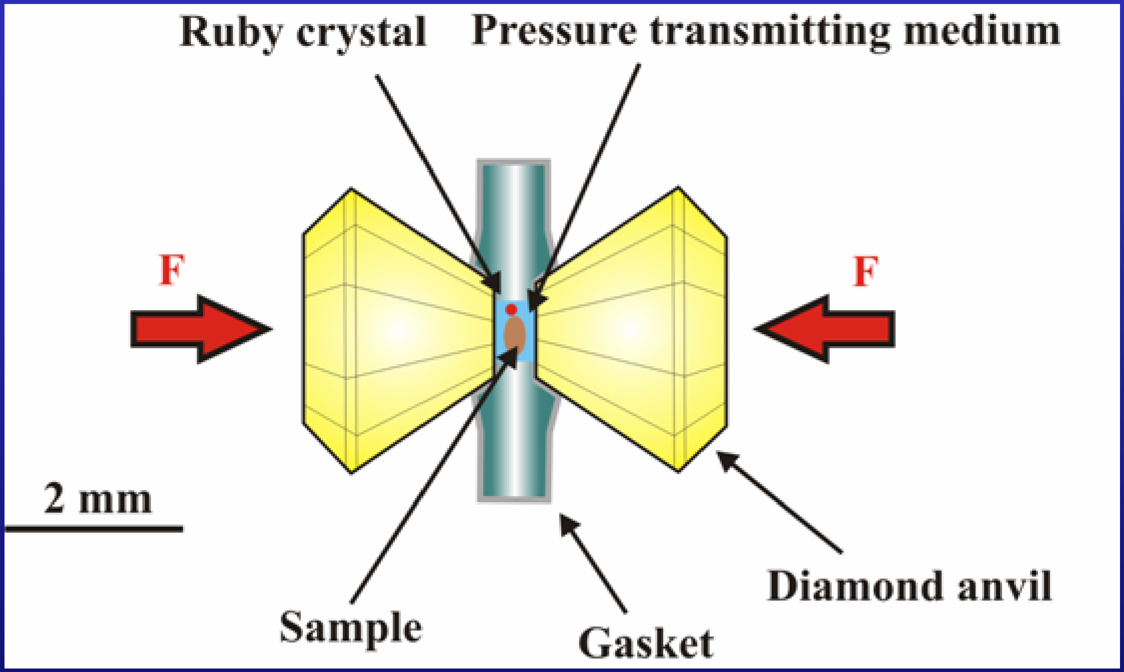
10^{12} cm^{-2}



40 nm → 20 nm grains

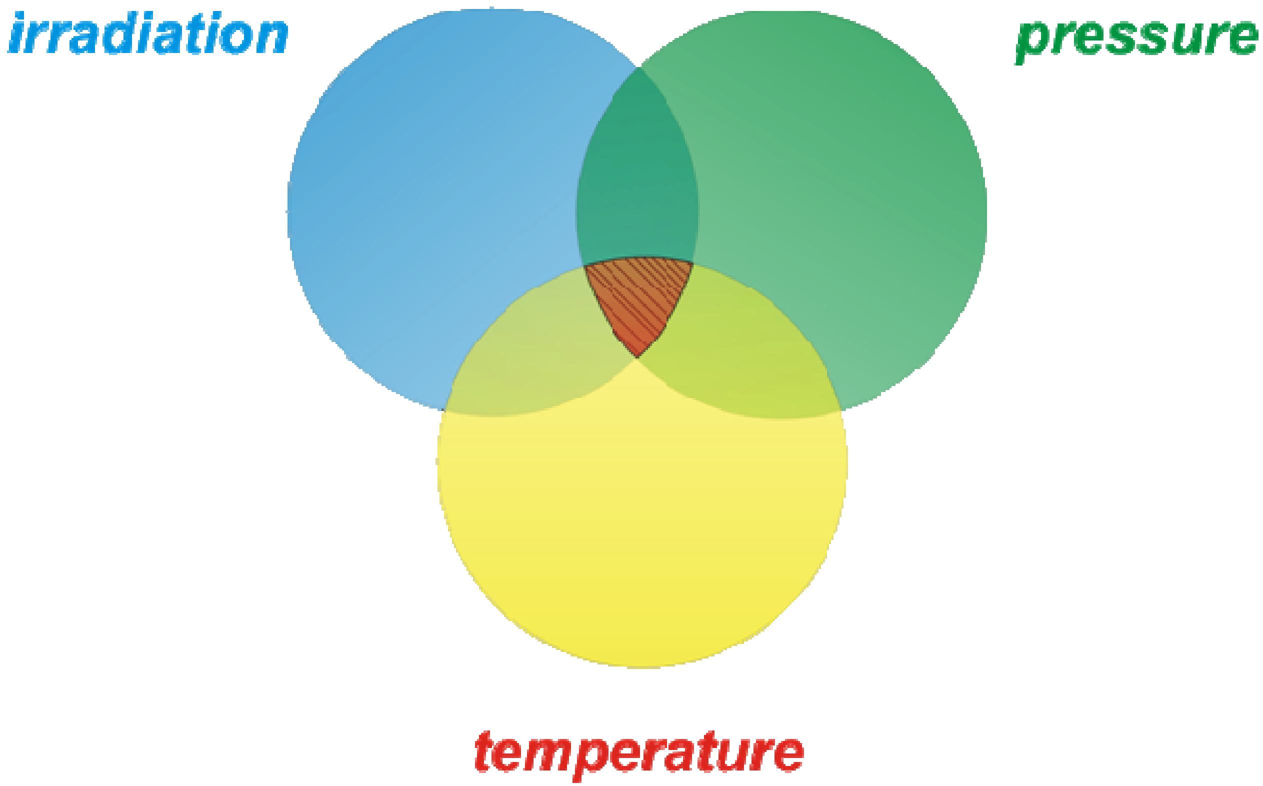
Boccanfuso, thesis CIRIL

Use of diamonds in irradiation experiments



Solids under extreme conditions

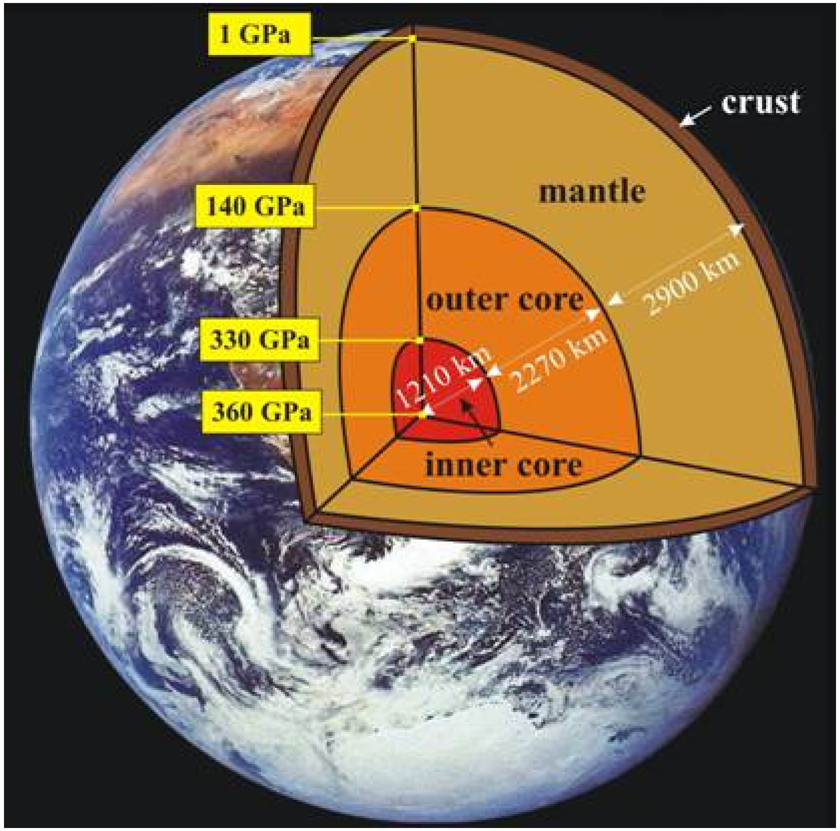
simultaneous or sequential exposure



Motivation: Materials Science & Geosciences

Geo- and thermochronology

Minerals exposed to high pressure and temperature



Earth's interior:

25 °C/km and 50 MPa/km

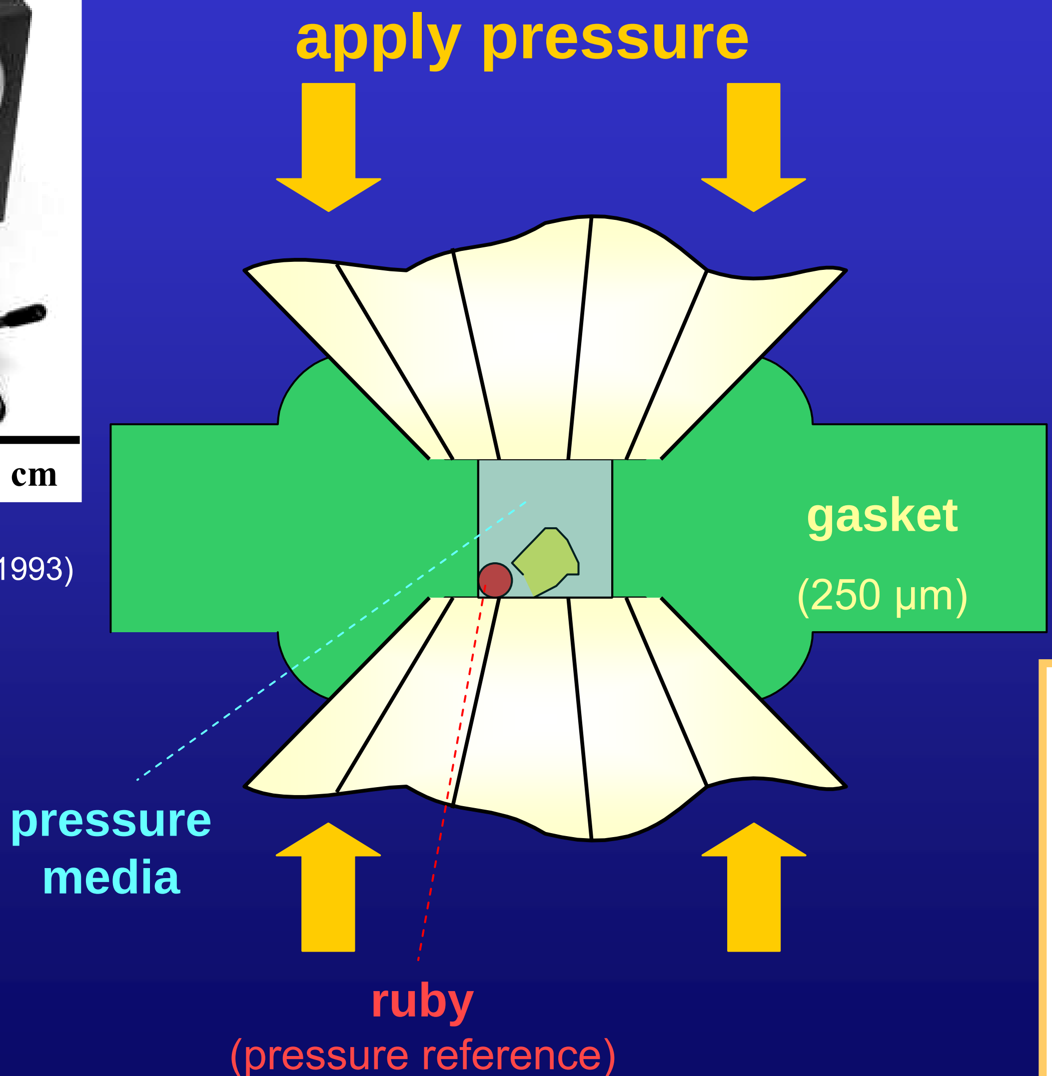
★ influence of pressure on fission track formation?
(e.g. track length → dating)

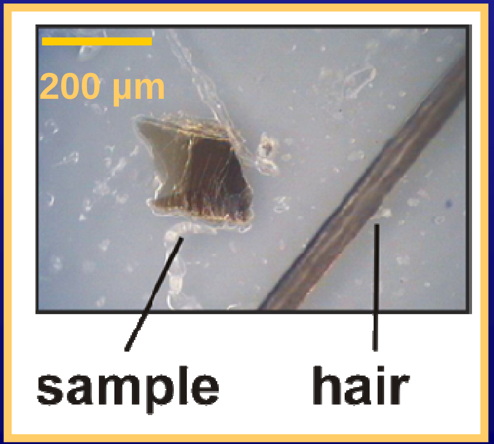
★ can fission fragments induce specific phase transitions?

1 GPa = 10 kbar

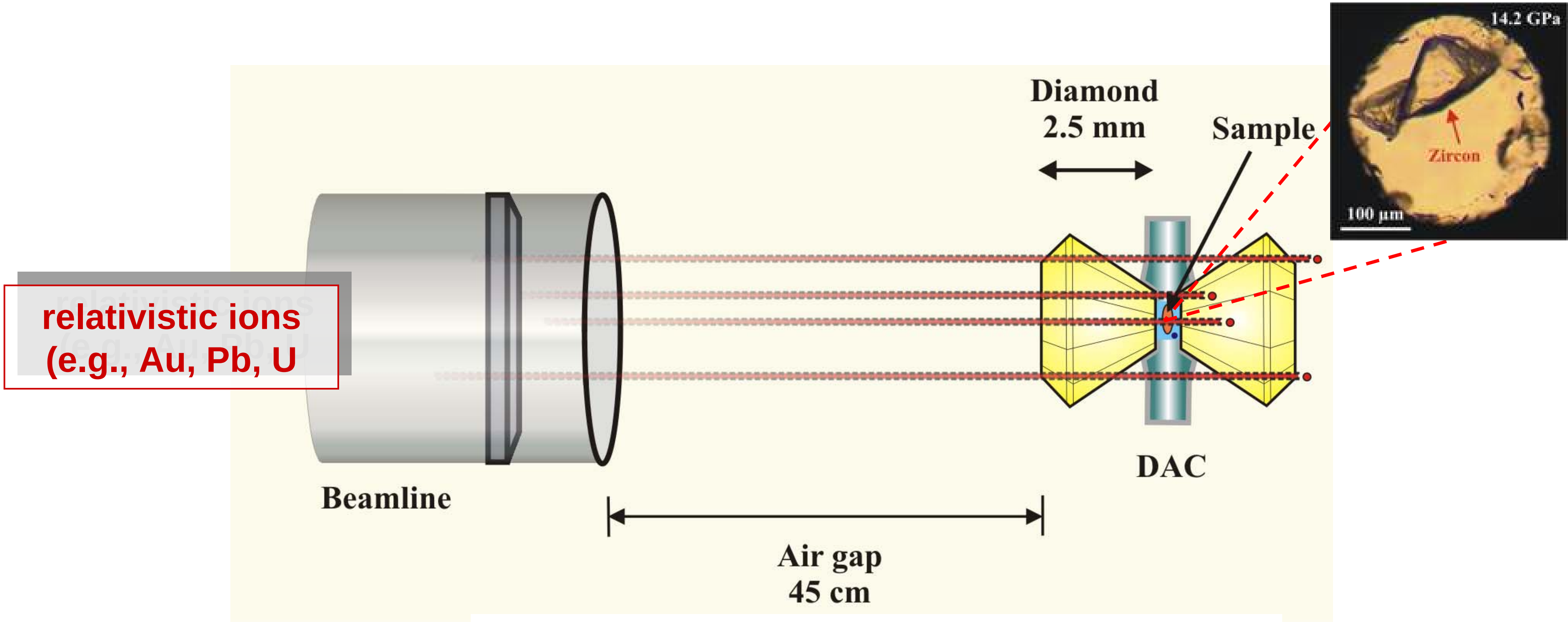
diamond anvil cell (DAC)

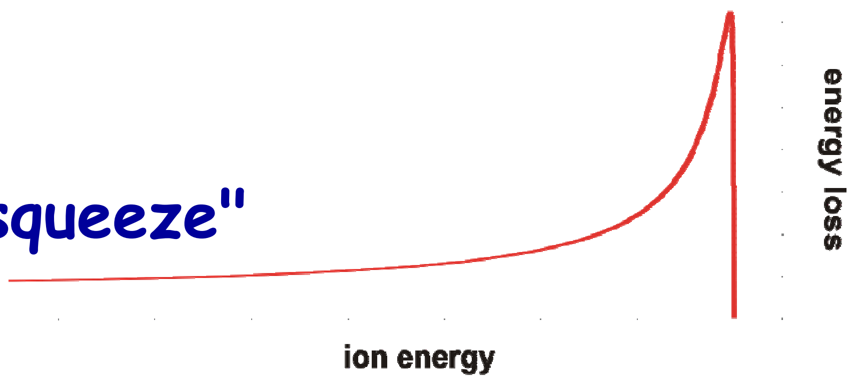
Bassett et al.,
Rev. Sci. Instrum. 64 (1993)





Irradiation experiments with pressurized samples





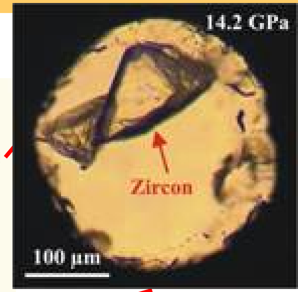
"Heavy ions feel the squeeze"

PhysicsWeb 5/2006
Phys. Rev. Lett. 96 (2006)

Irradiation experiments with samples pressurized in diamond anvil cells (DAC)

Diamond 2.5 mm

Sample



relativistic ions
(e.g., Au, Pb, U

- intense photoluminescence
- pressure remained constant in cell
  (up to > 50 GPa and 5×10^{12} ions/cm^2)
- no instantaneous diamond failure

!!! but after several beamtimes:

- coloration
- risk of diamond fragmentation (stress??)

ion energy