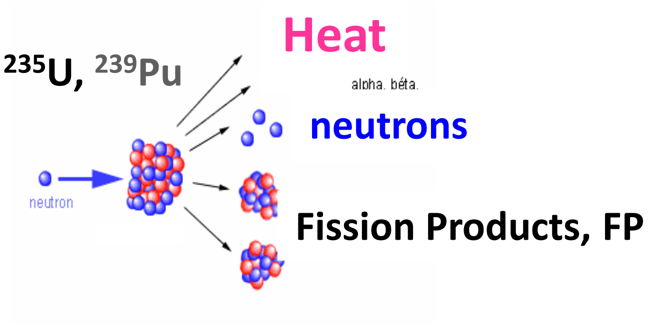
Separate effect studies

Marie-France BARTHE
CEMHTI/CNRS, Orléans France
marie-france.barthe@cnrs-orleans.fr

Fission Reactors

Fission

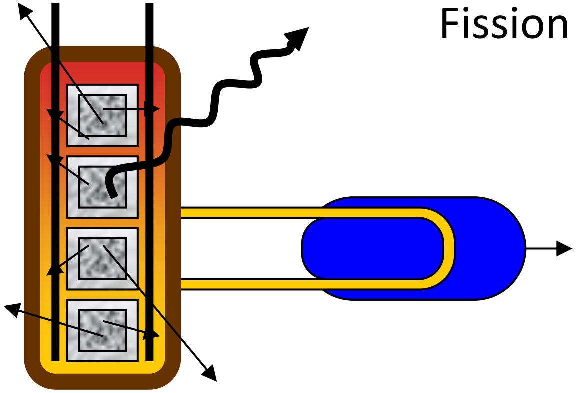


^{235}U, ^{239}Pu

Heat

neutrons

Fission Products, FP



neutrons + Radiations α, β, γ
Fission Products

Hydrogen?
Electricity

🟧 Coolant: water, ***He***

▨ Fuel : with U (UO_2, ***UC***)

▭ Cladding : metals , ***ceramics***

🟫 Structure, Vessels : Metals, ***ceramics***

Extreme Conditions for materials: irradiation, temperatures…

Evolution of the ***chemical*** composition and of the ***microstructure*** (defects ..)

⇩

Evolution of macroscopic properties ?
Thermal, mechanical …..

Fission Reactors

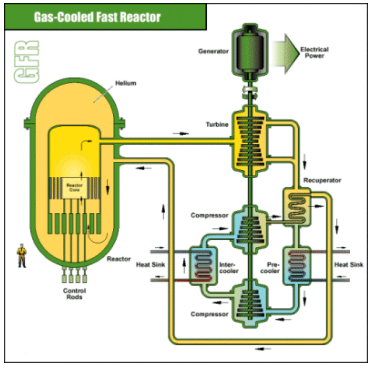
- Improvement of current reactors :

  increase lifetime, safety and fuel efficiency

- Development of **new generation**

  Burn MA (wastes), safety,

Génération IV
VHTR, **GFR** (RNR-G.), **SFR**
(RNR-Na), MSR (RSF)



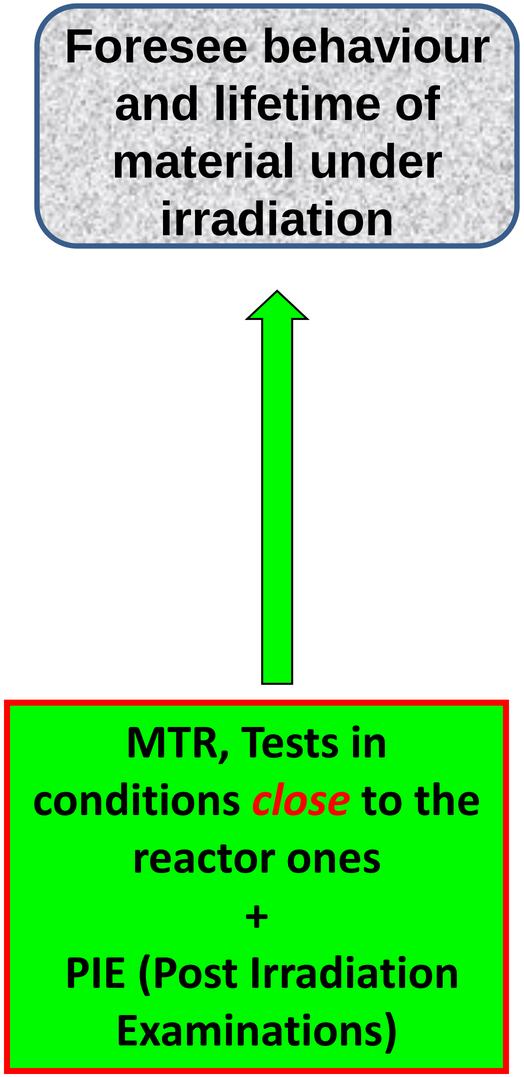
T°C :500-800°C, fast neutrons

New conditions : irradiation and temperature ….

Find or develop new materials or optimisation of the used ones

Knowledge of the behaviour of materials under irradiation to foresee their evolution and lifetime in new conditions

General approach

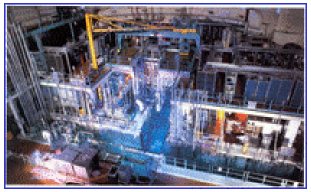


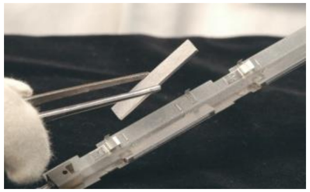
Foresee behaviour and lifetime of material under irradiation

MTR, Tests in conditions *close* to the reactor ones

+

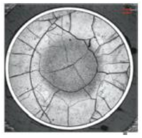
PIE (Post Irradiation Examinations)





HFR , BR2, OSIRIS…

CEA, ITU, NRG, PSI…

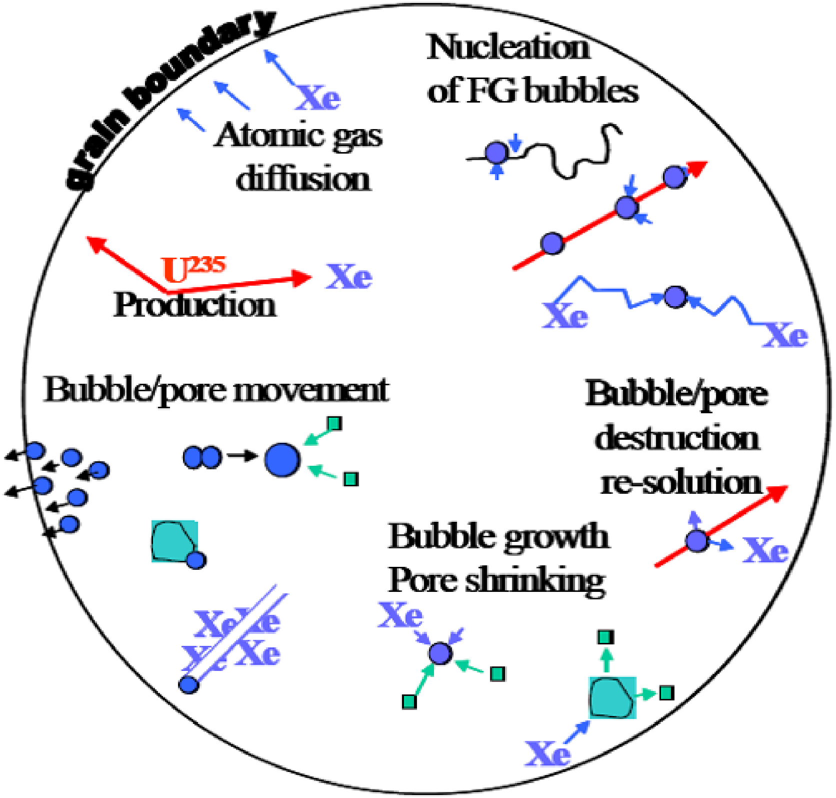


- **Facilities** *Not always* exist
- **Long term experiments** (preparation, irradiation, decay ..)
- **Hot cells for PIE**
- Difficult to investigate Mixed effects

[1] BARC, India

Gas behaviour in fuel

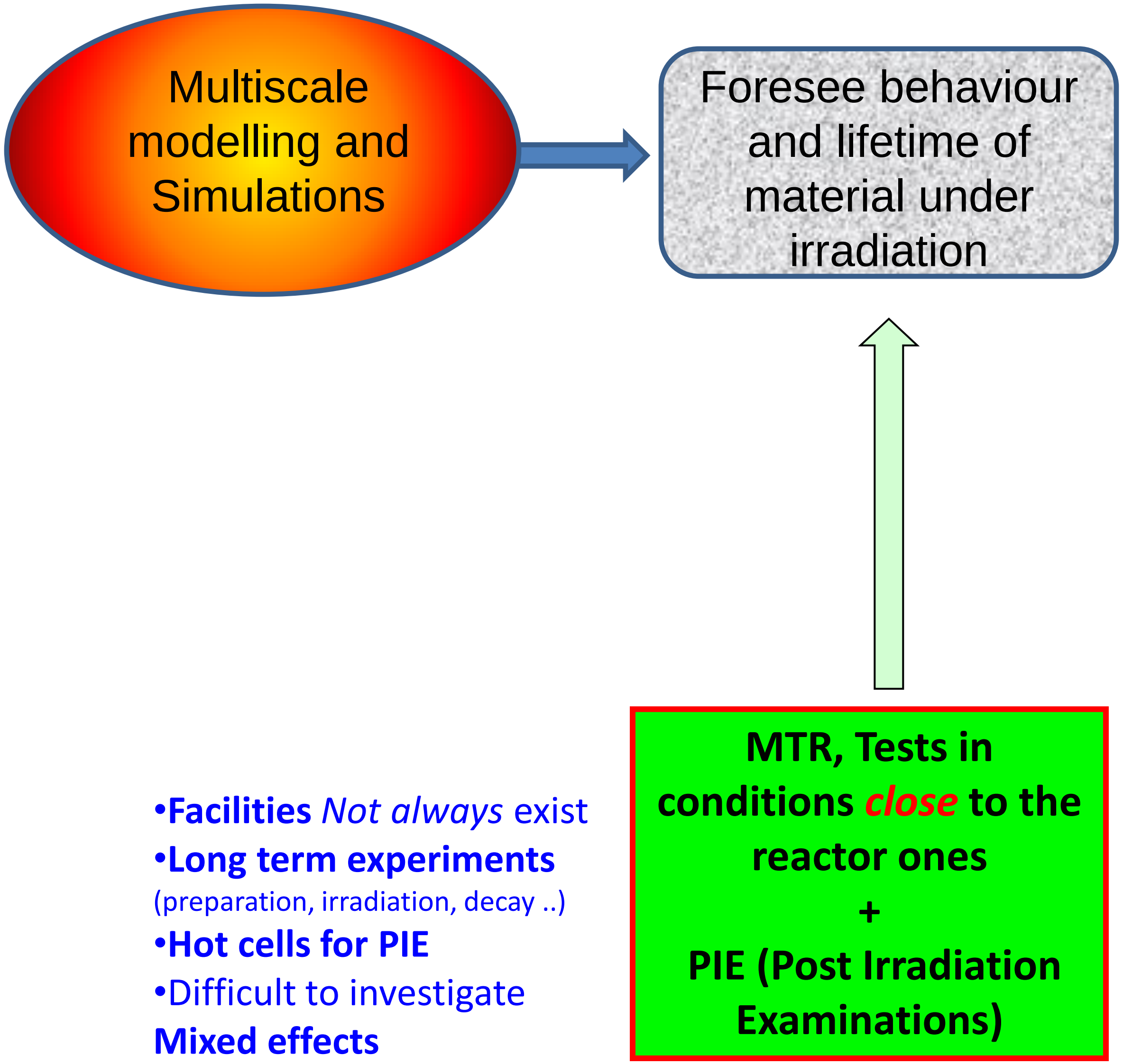
Knowledge of the behaviour of materials under irradiation to foresee their evolution and lifetime



- ✓Gas
  - ✓Solubility
  - ✓Diffusion :intrinsic and defect induced..
  - ✓Trapping, and precipitation, formation of bubbles : role of defects induced by irradiation
  - ✓Migration of bubbles
  - ✓Grain Boundaries effect
  - ✓Re-solution: role of irradiation
  - ✓Thermodynamics and mechanical ………
- ✓Defects
  - ✓Introduction of defects (E_d, E_f, E_m, binding, recombination, ….
  - ✓Evolution with temperature and dose

Multi parameters phenomena

General approach



Multiscale modelling and Simulations

Foresee behaviour and lifetime of material under irradiation

MTR, Tests in conditions *close* to the reactor ones

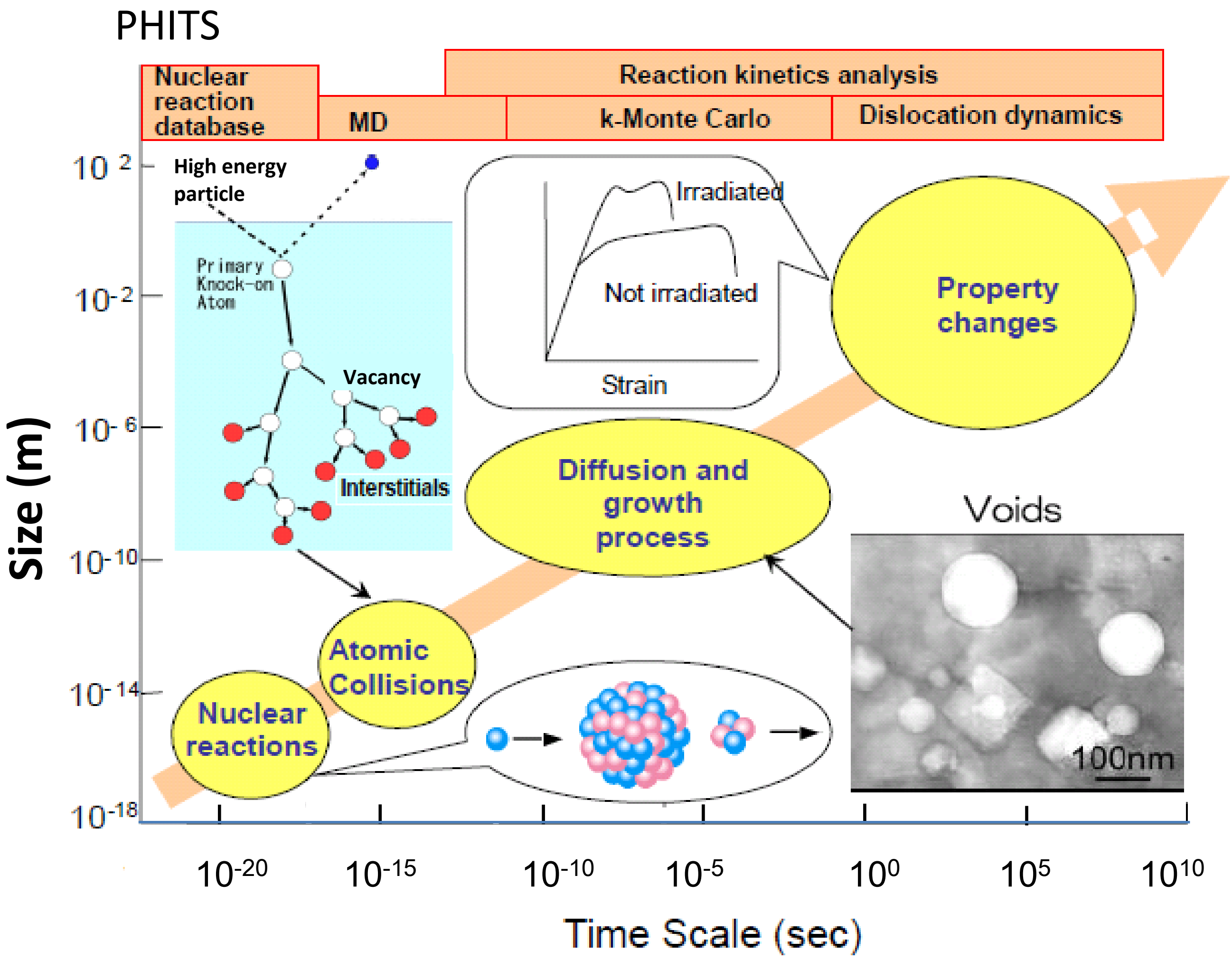
+

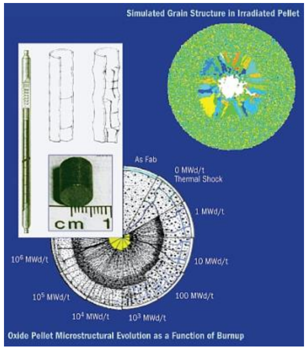
PIE (Post Irradiation Examinations)

- **Facilities** *Not always* exist
- **Long term experiments** (preparation, irradiation, decay ..)
- **Hot cells for PIE**
- Difficult to investigate

Mixed effects

Multiscale modelling



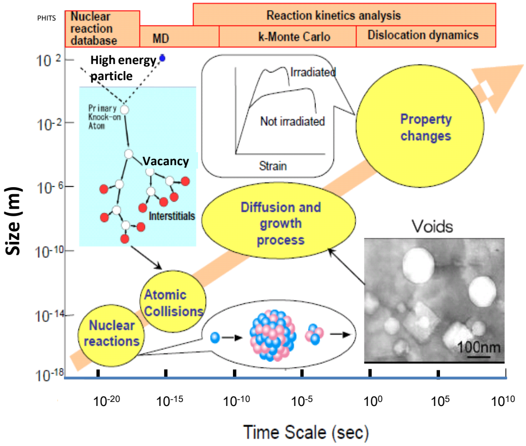


DOE, EXASCALE Initiative

European Processor Initiative

From Toshimasa Yoshiie, Research Reactor Institute, Kyoto University

General approach



Multiscale modelling and Simulations

Foresee behaviour and lifetime of material under irradiation

Input, validation

Fundamental data

Mechanisms understanding

Species Transport properties , defects properties

Observations as a function of **well controled conditions: nature, concentration, localization**

Experimental data

Separate effect studies

- **Model Materials** (composition, structure…)
- **External irradiations** (Electron, ions)

allowing a large panel of **Specific and Fine Characterizations :** TEM, PAS, NRA, SIMS, TDS, XR, APT, ………….

MTR, Tests in conditions *close* to the reactor ones

+ PIE (Post Irradiation Examinations)

Outlines

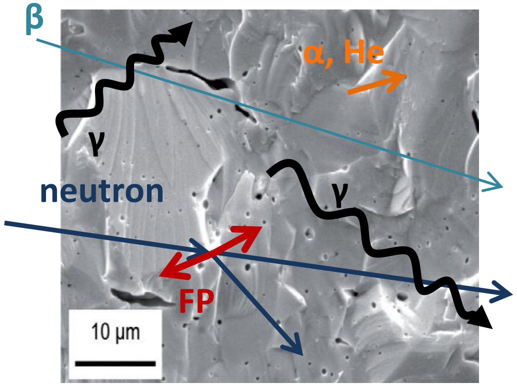
1. MTR and PIE (R. Hania-NRJ and J. Noirot-CEA)
2. Separate effect studies
   a. Experimental approach
   b. External irradiations
      a. How to choose the irradiation conditions
      b. The facilities
   c. Fine characterizations
   d. Illustrations in fuel and other materials

Fuel under irradiation

Irradiations in reactors :

Different radiations : neutrons, α, β, γ, FP (gas and …..)

FP: 70% solids (Ru, Mo, Zr, Nd…)
30% gases (**Xe**, Kr) or volatiles (Cs, I…)
with energy 70 – 90 MeV

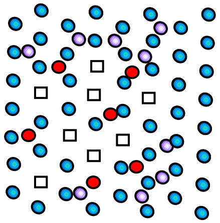


damage :

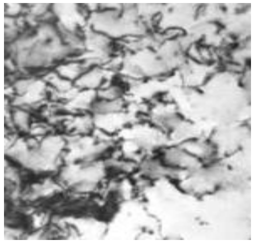
- **point defects : vacancies, interstitiels**
- **extended defects : dislocations, cavities, bubbles …..**
- **Tracks, polygonisation**

Impurities :

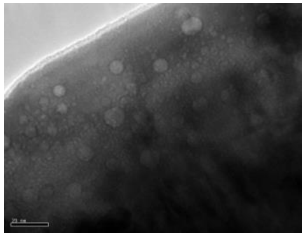
…. Nd, Sr, Zr, Mo
… He, Xe, Kr, Cs, I : Gas bubbles



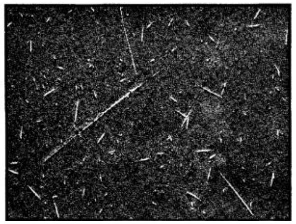
Point defects



Dislocations100 dpa [1]



Xe Bubbles [2]

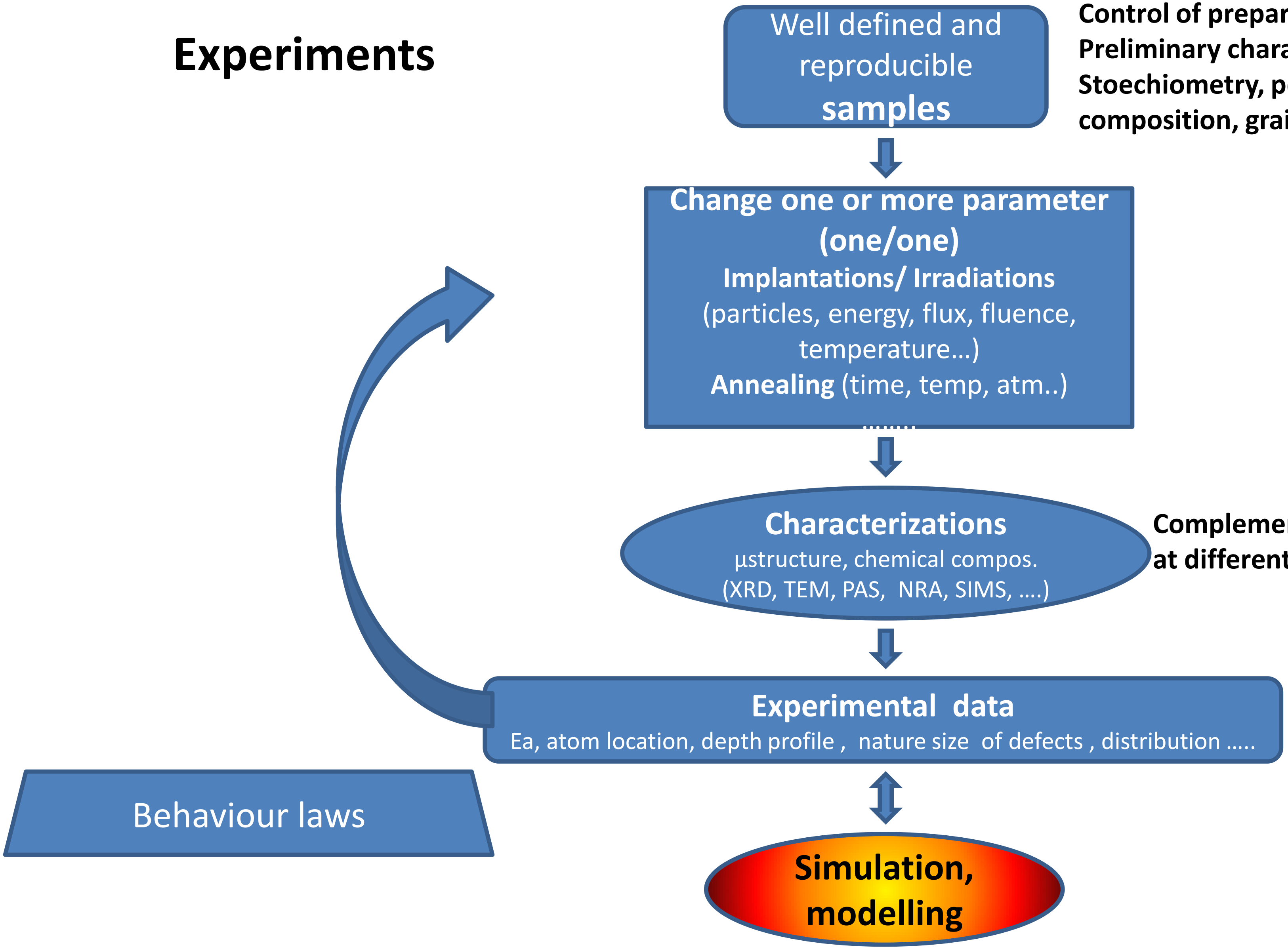


Tracks [3]

[1] T. Wiss et al, [2] A Michel et al, [3] T. S. Noggle, and J. O. Stiegler, JAP **31**, 2199 (1960); **[4]** Hj. Matzke et al. / NIM B 166±167 (2000) 920±92

Separate effects approach

Experiments



Well defined and reproducible **samples**

Control of preparation
Preliminary characterizations
Stoechiometry, porosity, chemical composition, grain size…….

Change one or more parameter (one/one)
Implantations/ Irradiations (particles, energy, flux, fluence, temperature…)
Annealing (time, temp, atm..)
……..

Characterizations
µstructure, chemical compos.
(XRD, TEM, PAS, NRA, SIMS, ….)

Complementary techniques at different scale…….

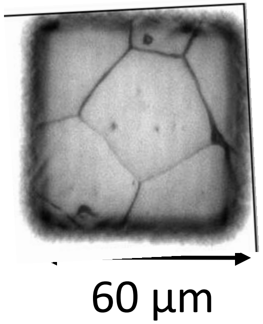
Experimental data
Ea, atom location, depth profile , nature size of defects , distribution …..

Behaviour laws

Simulation, modelling

Sample Preparation

- Material : Model
- UO_2 polycristalline or single crystals
- Grain size, porosity (or density)
- Stoechiometry, Impurity level,
- Preparation : polishing, post annealing (ArH_2)



Impurity and / or defect introduction

For He

- Separately
  - Only impurities
    - Infusion : For He
      - at high pressure (50-200MPa), high temperature(1473-1743 K), low concentration (≈320ppm), (Heidi [1], JRC)
  - Only defects
    - Stoechiometry
    - Irradiations
      - electrons (0.5 – 3 MeV)
      - high energy ions (10 MeV – 1GeV
- Together
  - Implantations (impurity = low energy ions 10 keV-MeV)
  - Alpha Doping : ^{233}U, **^{238}Pu** (decay $\longrightarrow$ 5 MeV alpha particles) (Mox, Pu, stoechiometry effects ?)
  - Neutrons (more complex, radioactivity..) MTR (not separate effects)

[1] E. Maugeri, T. Wiss, J.P. Hiernaut, K. Desai, C. Thiriet, V.V. Rondinella, *et al.* J Nucl Mater, 385 (2009), pp. 461-466

Impurity and / or defect introduction

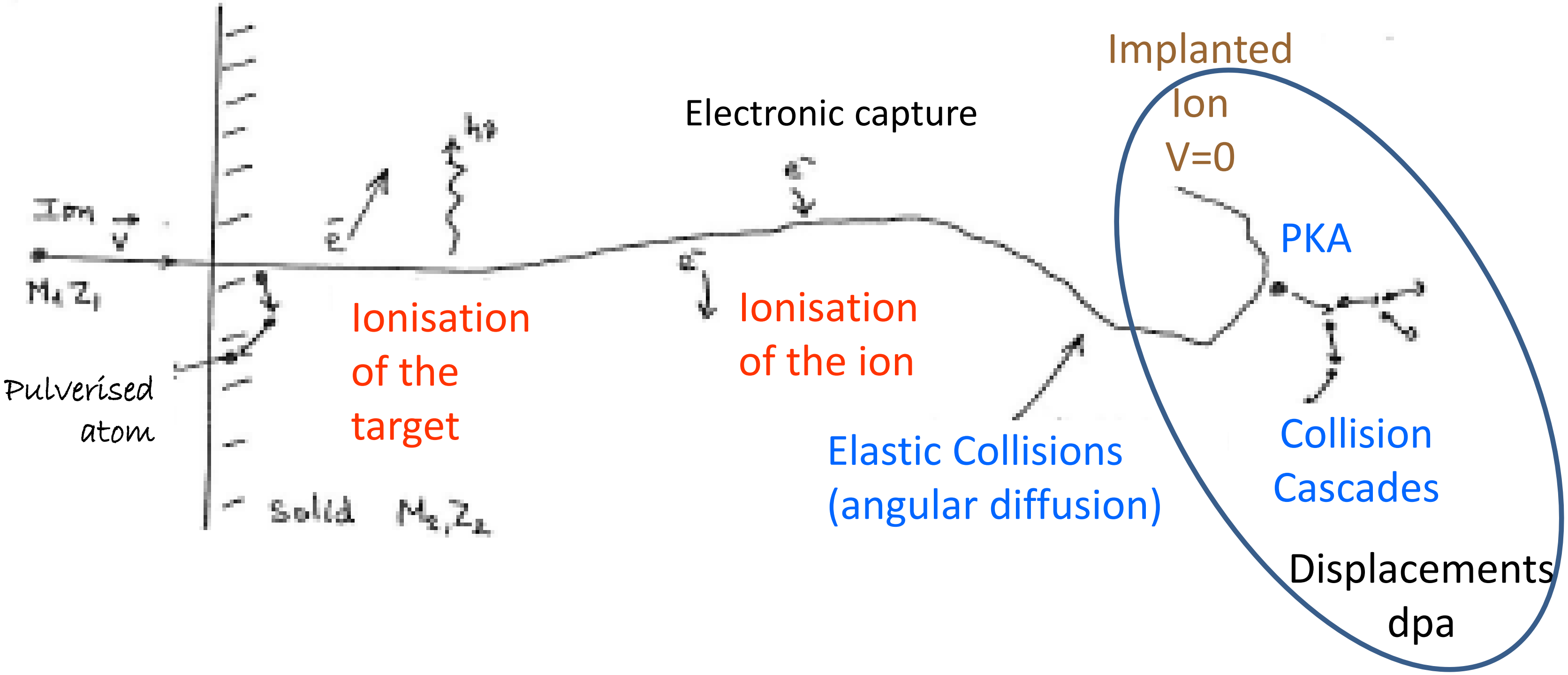
- Separately
  - Only impurities
    - Infusion : For He
      - at high pressure (50-200MPa) , high temperature(1473-1743 K) , low concentration (≈320ppm), (Heidi [1], JRC)
  - Only defects
    - Stoechiometry
    - Irradiations
      - electrons (0.5 – 3 MeV)– Van de Graaff
      - high energy ions (10 MeV – 1GeV) –Cyclotron, Tandem
- Together
  - Implantations (impurity = low energy ions 10 keV-MeV) implantors, Van de Graaff
  - Alpha Doping : ^{233}U, **^{238}Pu** (decay $\longrightarrow$ 5 MeV alpha particles) (Mox)
  - Neutrons (more complex, radioactivity..) MTR (not separate effects)

Take into account the temperature (recombinations, binding….)

Outlines

1. MTR and PIE (R. Hania-NRJ and J. Noirot-CEA)
2. Separate effects studies
    a. Experimental approach
    b. External irradiations
        a. How to choose the irradiation conditions
        b. The facilities
    c. Fine characterizations
    d. Illustrations in fuel and other materials

Ion – material Interactions



Pulverised atom

Ionisation of the target

Electronic capture

Ionisation of the ion

Elastic Collisions (angular diffusion)

Implanted Ion V=0

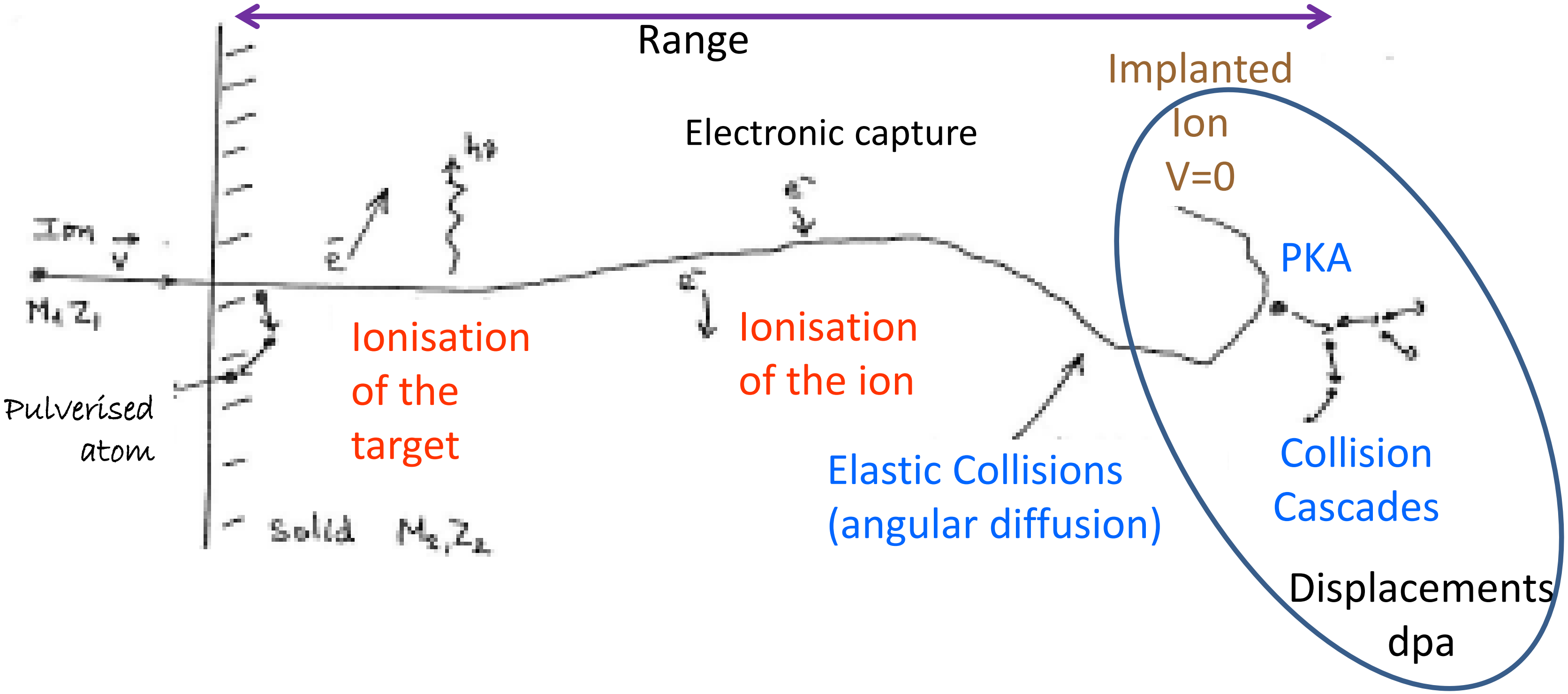
PKA

Collision Cascades

Displacements dpa

-PKA : Primary Knocked atom

Ion – material Interactions



Range

Electronic capture

Implanted
Ion
V=0

PKA

Pulverised
atom

Ionisation
of the
target

Ionisation
of the ion

Elastic Collisions
(angular diffusion)

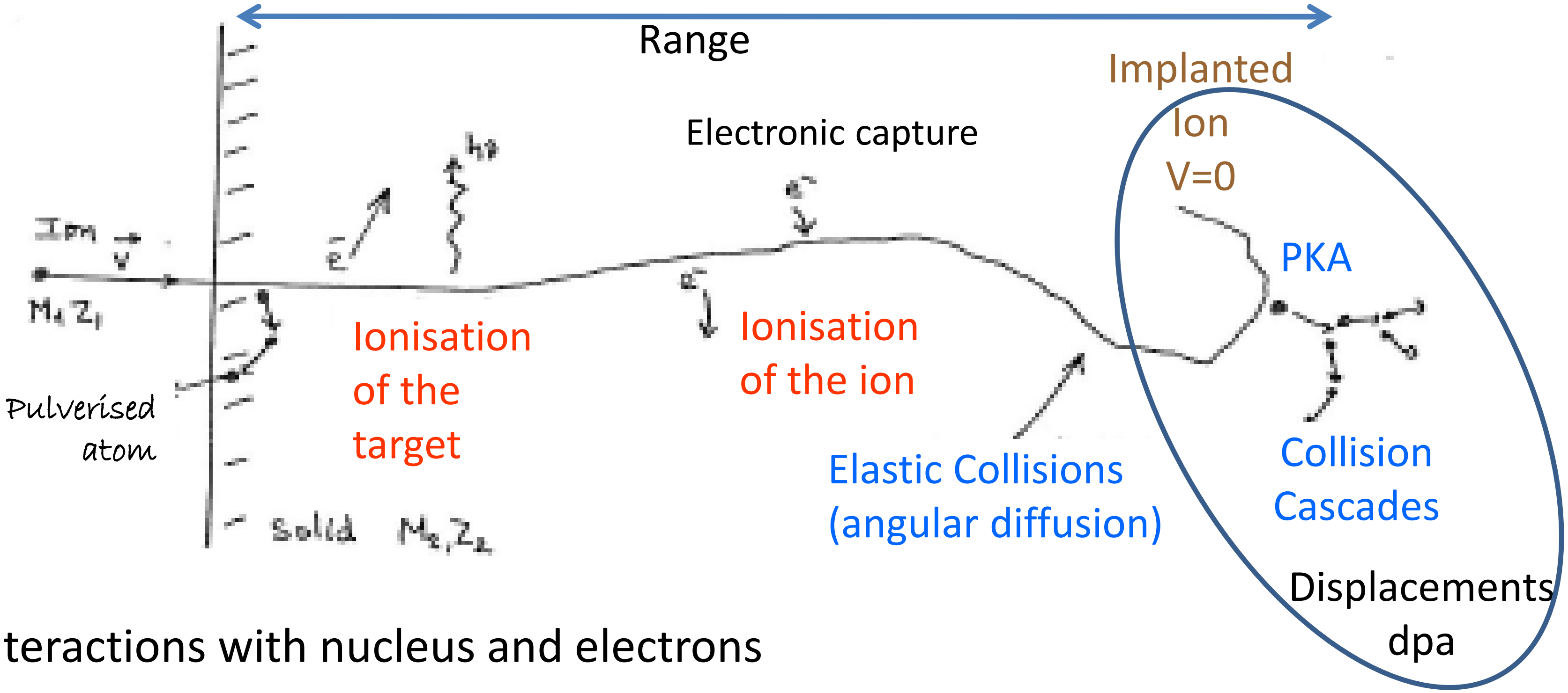
Collision
Cascades

Displacements
dpa

-Range : depth at which ions stop

-PKA : Primary Knocked atom

Ion – material Interactions



Range

Electronic capture

Implanted Ion V=0

PKA

Ionisation of the target

Ionisation of the ion

Elastic Collisions (angular diffusion)

Collision Cascades

Displacements dpa

Interactions with nucleus and electrons

Elastic Collision (E<10 keV/uma) $S_n=-(dE/dx)_n$ n : nuclear

Inelastic Collision (E>1MeV/uma) $S_e=-(dE/dx)_e$ e : electronic

Stopping Power $-dE/dx=(-dE/dx)_n+(-dE/dx)_e$

-Range : depth at which ions stop

-PKA : Primary Knocked atom

Ion – material Interactions

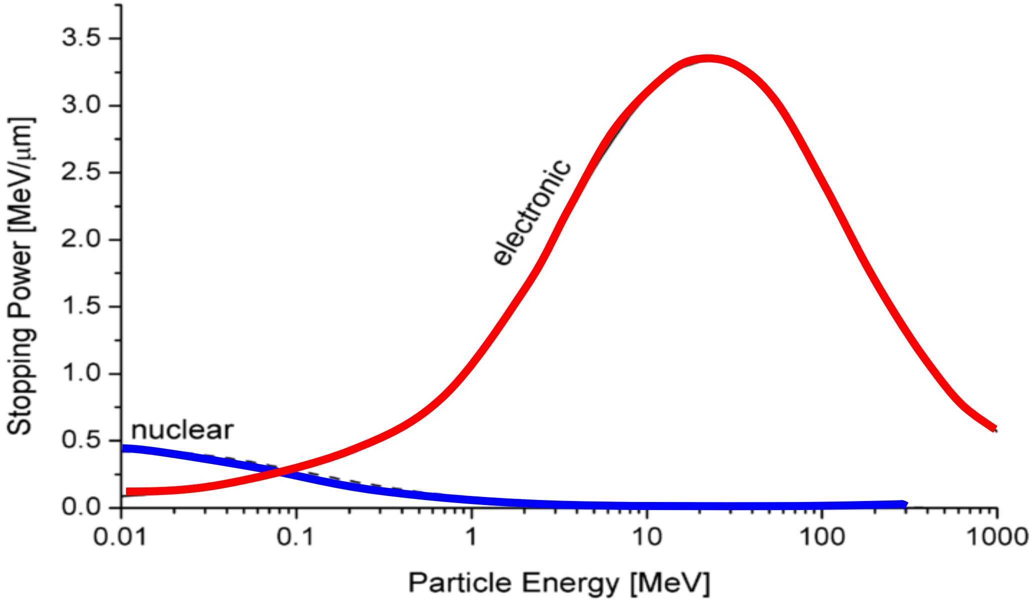
Stopping Power

- electronic (ionisation)

Energy released to electrons

- nuclear (collisions)

Energy released to nucleus



SRIM

SRIM: ***The Stopping and range of ions in Matter***, by J. F. Ziegler, J. P. Biersack and M. D. Ziegler, available from *www.SRIM.org* (2013)

Monte-Carlo : the path and interaction of ion through a matrix made of independant atoms without considering their cristallographic arrangement, where each collision is processed as individual .

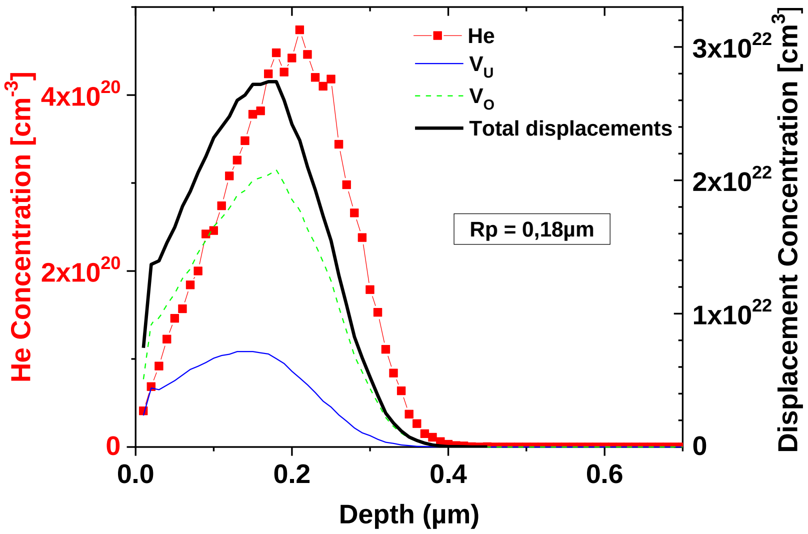
He in UO_2

Fluence :$1x10^{16}$ cm^{-2}

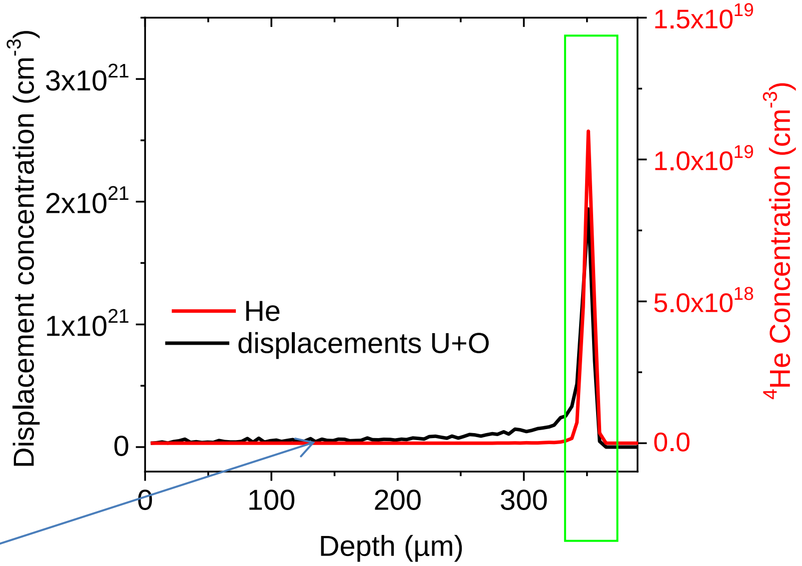
^{3}He 50 keV

Alpha 45 MeV

At Rp 0.4 dpa



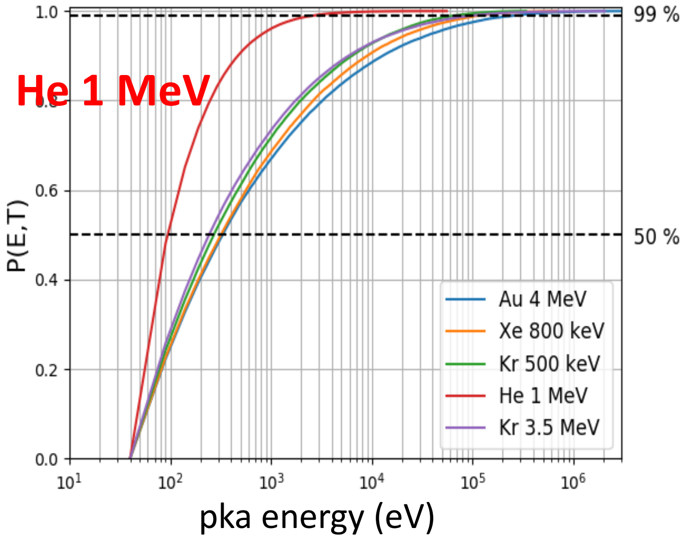
Nuclear collision cascades



Track region 6 x10^{19} cm^{-3} ➔ 9x10^{-4} dpa

SRIM

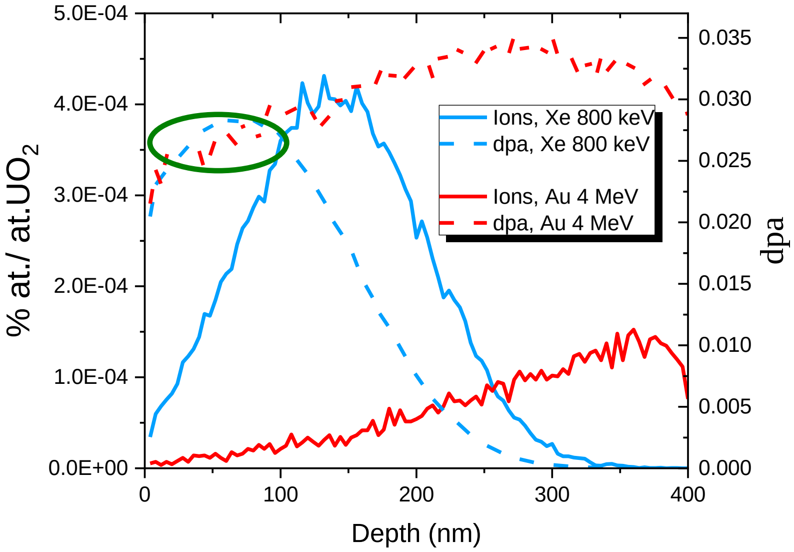
PKA energy distribution



very close energy distribution of pka for Xe 800 keV and Au 4 MeV

In the **first 100 nm**

- ➢ same dpa level, and very close distribution of pka energy
- ➢ but no Xe in Au irradiated UO_2



Study the evolution of defects in Xe implanted

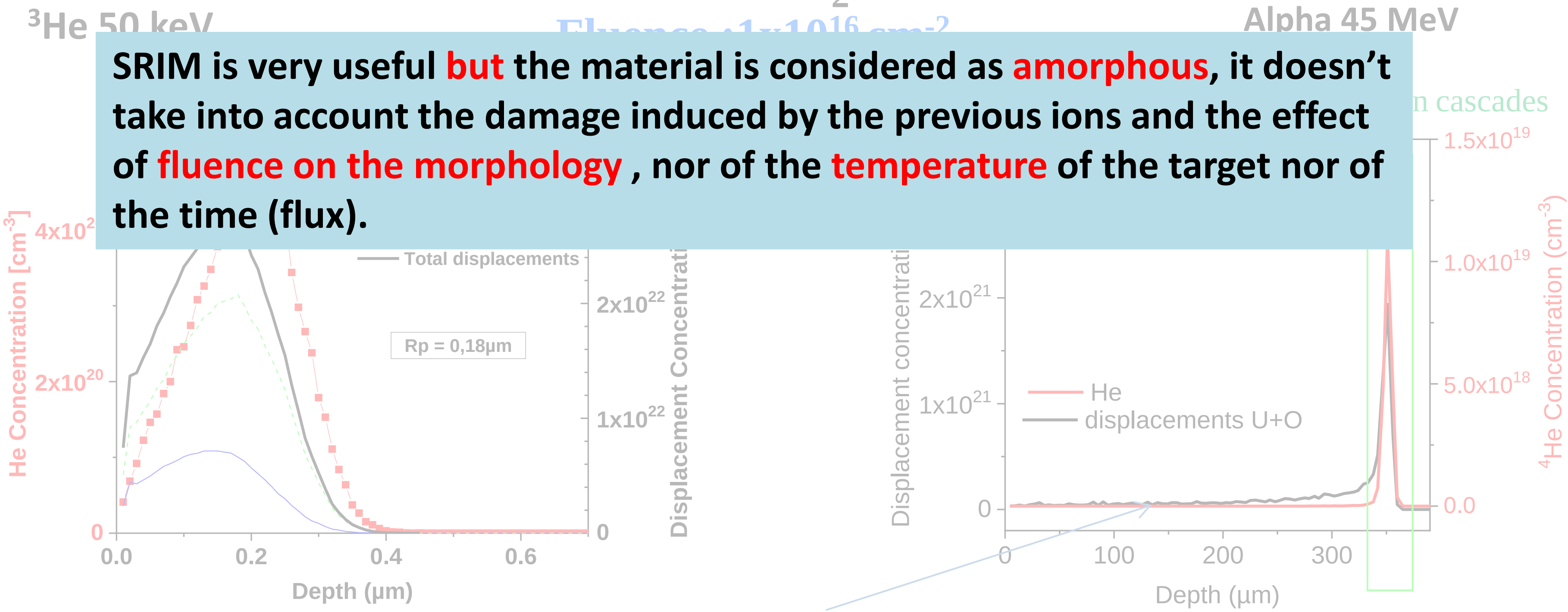
- ➢ ***With Xe → Xe 800 keV implantation***
- ➢ ***Without Xe → Au 4 MeV irradiation***

SRIM

- SRIM: ***The Stopping and range of ions in Matter***, by J. F. Ziegler, J. P. Biersack and M. D. Ziegler, available from *www.SRIM.org* (2013)

Monte-Carlo : the path and interaction of ion through a matrix made of independant atoms without considering their cristallographic arrangement, where each collision is processed as individual .

He in UO_2

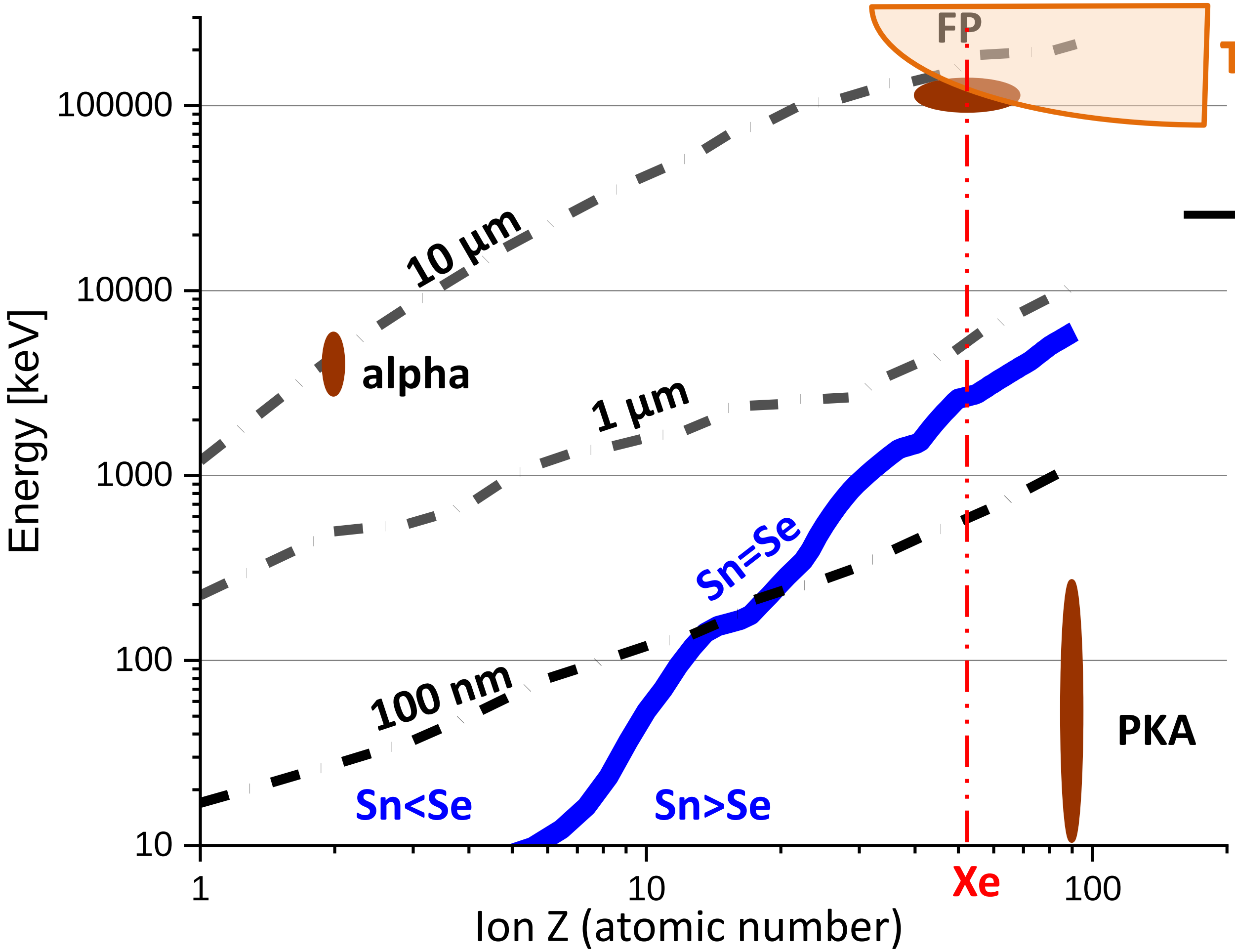


SRIM is very useful but the material is considered as amorphous, it doesn't take into account the damage induced by the previous ions and the effect of fluence on the morphology , nor of the temperature of the target nor of the time (flux).

Track region 6 x10^{19} cm^{-3} → 9x10^{-4} dpa

Ion – material Interactions

In UO_2



Tracks S_e>22±29 keV/nm [4]

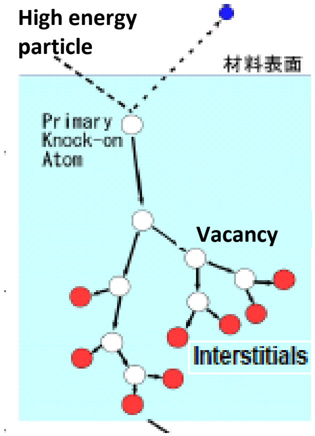
Mean projected range
0.1, 1 and 10 µm
(SRIM [1])

[1] **SRIM - The Stopping and Range of Ions in Matter,** freeware, http://www.srim.org/

Implantations/ irradiations:

Main parameters to choose irradiation conditions

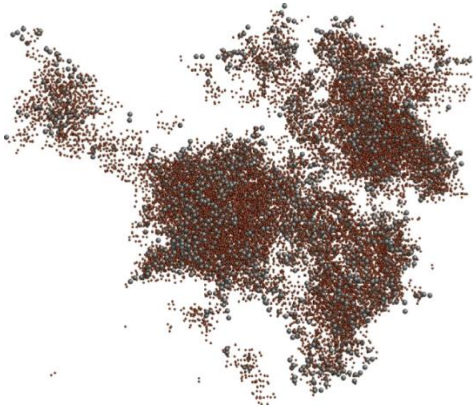
- Stopping power Se, Sn
- PKA (Primary Knocked Atom) energy : Mainly from FP with about 100 MeV PKA several hundred keV
- Range (related to energy for a type of ion, to be chosen in regard with the Characterization technique (sensitivity, probed depth …)
- Fluence (concentration, dpa, cascade overlapping)
- Flux
- Impurity /dpa (dual or triple beam)
- Nuclear colisions/electronic
- Controled temperature ???



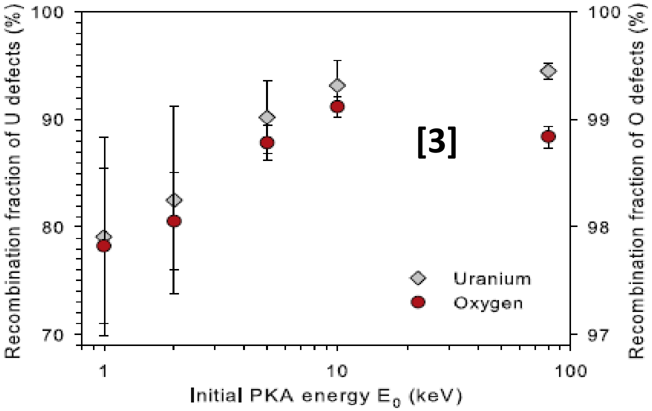
[1] J.Soullard, J.Nucl. Mater **135** (1985) 190-196.; [2] C. Meis, J. .Nucl. Mater **341** (2005) 25-30.

MD simulations in UO_2

- PKA (Primary Knocked Atom) energy : Mainly from FP with about 100 MeV PKA several hundred keV



MD simulations of a displacement cascade initiated at 100 keV at 700 K.[3]



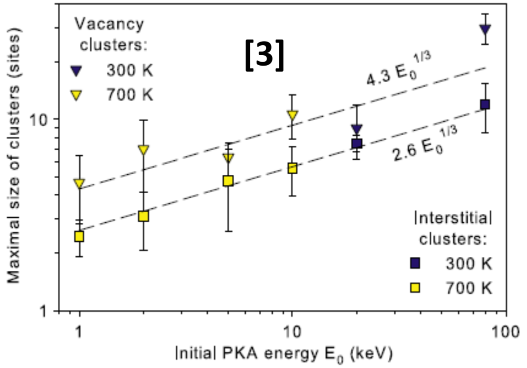


Fig. 3. Size of the biggest vacancy clusters and interstitial clusters formed after the simulation of a displacement cascade in UO_2.

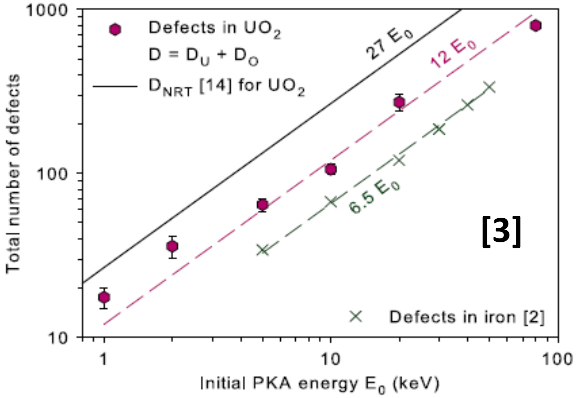


Fig. 5. Total number of defects as a function of the cascade energy from MD simulations in iron [2], and in UO_2 compared with the NRT law [14].

Effect of fluence and cascade overlapping

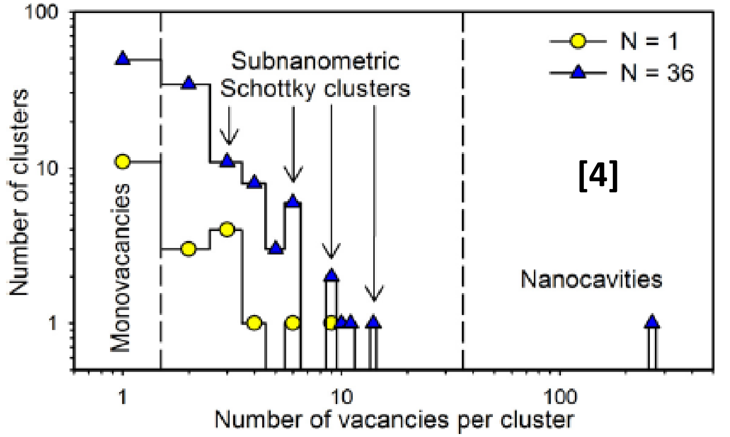
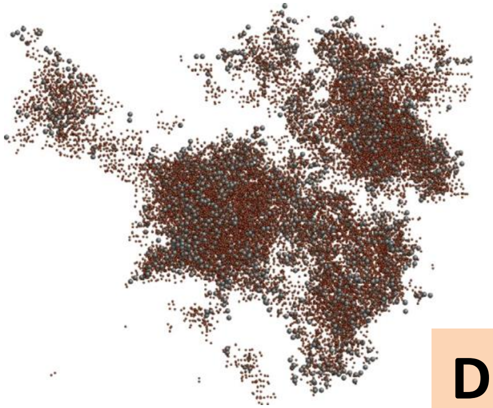


Fig. 2. CMD-simulated size distribution of vacancy clusters after $N = 1$ and $N = 36$ successive cascades of 10 keV (here O and U point defects are considered separately). (Fig. 6 from [21]).

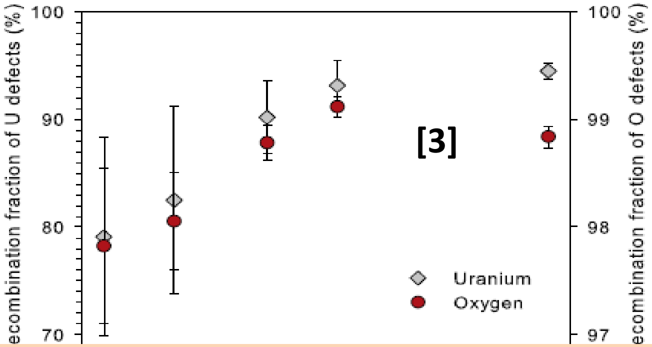
[3] G. Martin et al. /NIMB 269 (2011) 1727–1730; S. Maillard et al. / NIM B 374 (2016) 58–66

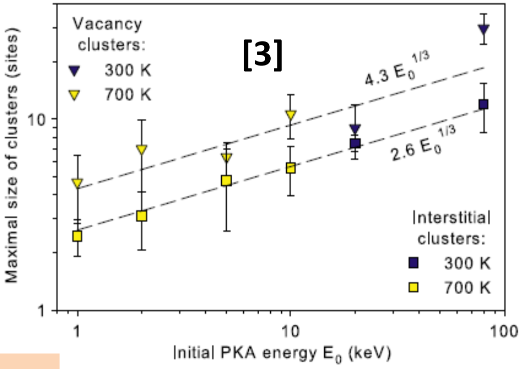
MD simulations in UO_2

- PKA (Primary Knocked Atom) energy : Mainly from FP with about 100 MeV PKA several hundred keV



MD simulations of a displacement
initiated at 100 keV at 700 K.[3]





e of the biggest vacancy clusters and interstitial clusters formed after the
n of a displacement cascade in UO_2.

Defect distribution depends on the PKA energy, the fluence and the irradiation temperature

uence and cascade overlapping

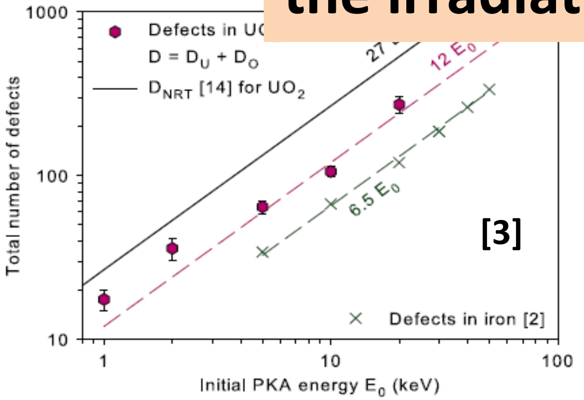


Fig. 5. Total number of defects as a function of the cascade energy from MD simulations in iron [2], and in UO_2 compared with the NRT law [14].

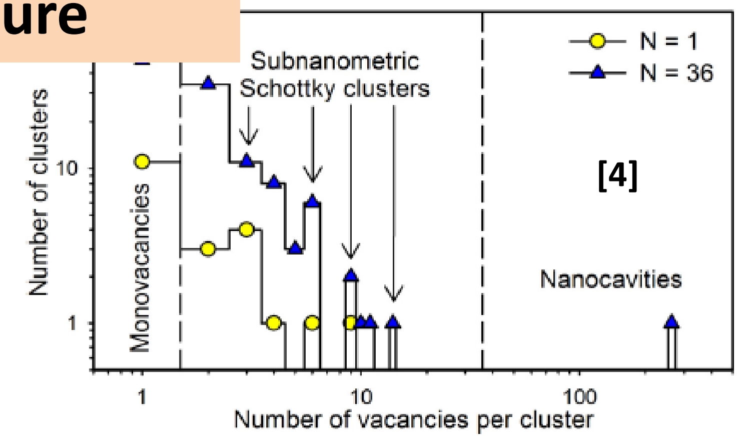


Fig. 2. CMD-simulated size distribution of vacancy clusters after $N = 1$ and $N = 36$ successive cascades of 10 keV (here O and U point defects are considered separately). (Fig. 6 from [21]).

[3] G. Martin et al. /NIMB 269 (2011) 1727–1730; S. Maillard et al. / NIM B 374 (2016) 58–66

Implantation/irradiation

From SRIM Calculations

Fluence: $1x10^{16}$ ^{3}He.cm^{-2}

When E_i increases ,
Rp increases, $[He]_{max}$, dpa_{max}, decrease

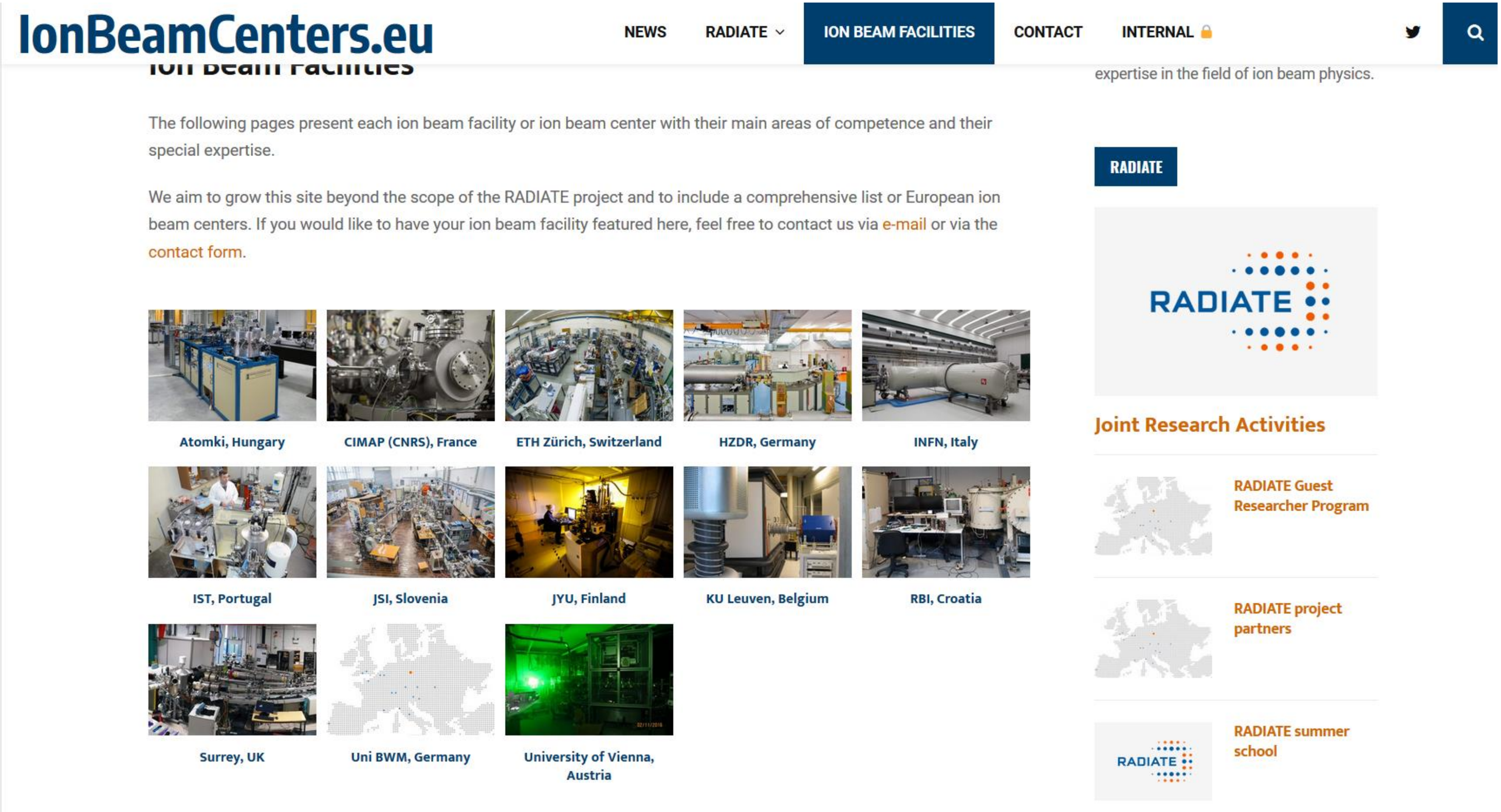
	Rp (µm)	At Rp			Track region			Stopping powers	
		[He] Max (%at)	Dpa max	[He] %at/dpa	[He] Max (%at)	Dpa mean	[He] at/dpa ($x10^{-2}$)	Se (keV/µm)	Sn (keV/µm)
50 keV	0.2	6.25	0.4	1.61				175	7
1 MeV	1.8	0.35	0.2	1.56	0.0014	0.014	0.1	608	0.9
45 MeV	347	0. 015	0.03	0.54	0	0.0009	0	78	$4x10^{-2}$

For 1 MeV 2 zones

- **≈ only Defects**
- **Defects + He introduction**
- **High Se**

To change the ratio He/dpa
Use of double beam (JANNUS)

European irradiation platforms



Ion Beam Facilities

The following pages present each ion beam facility or ion beam center with their main areas of competence and their special expertise.

We aim to grow this site beyond the scope of the RADIATE project and to include a comprehensive list or European ion beam centers. If you would like to have your ion beam facility featured here, feel free to contact us via e-mail or via the contact form.

- Atomki, Hungary
- CIMAP (CNRS), France
- ETH Zürich, Switzerland
- HZDR, Germany
- INFN, Italy
- IST, Portugal
- JSI, Slovenia
- JYU, Finland
- KU Leuven, Belgium
- RBI, Croatia
- Surrey, UK
- Uni BWM, Germany
- University of Vienna, Austria

expertise in the field of ion beam physics.

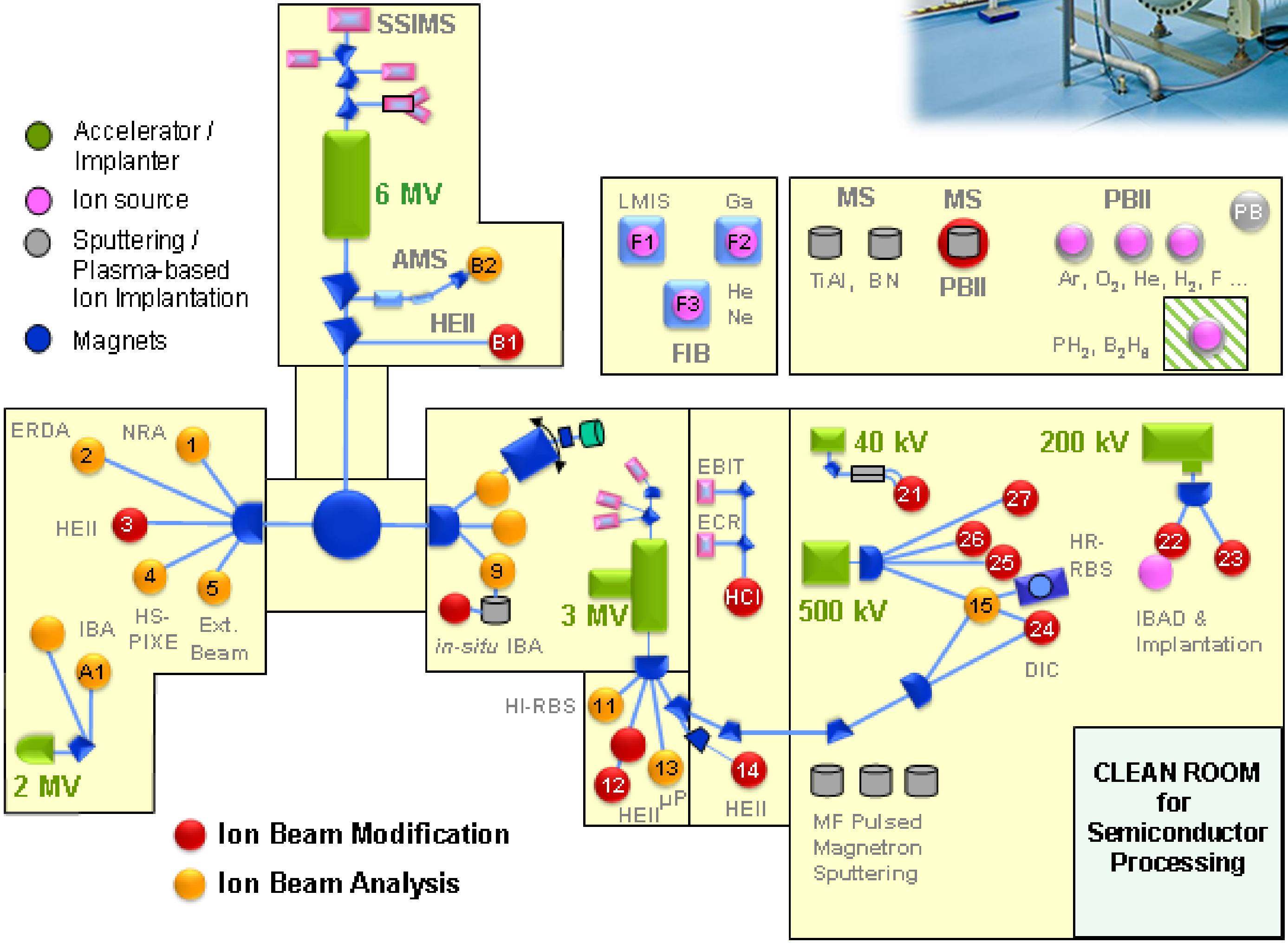
RADIATE

Joint Research Activities

- RADIATE Guest Researcher Program
- RADIATE project partners
- RADIATE summer school

https://www.ionbeamcenters.eu/ion-beam-facilities/

HZDR
HELMHOLTZ
ZENTRUM DRESDEN
ROSSENDORF

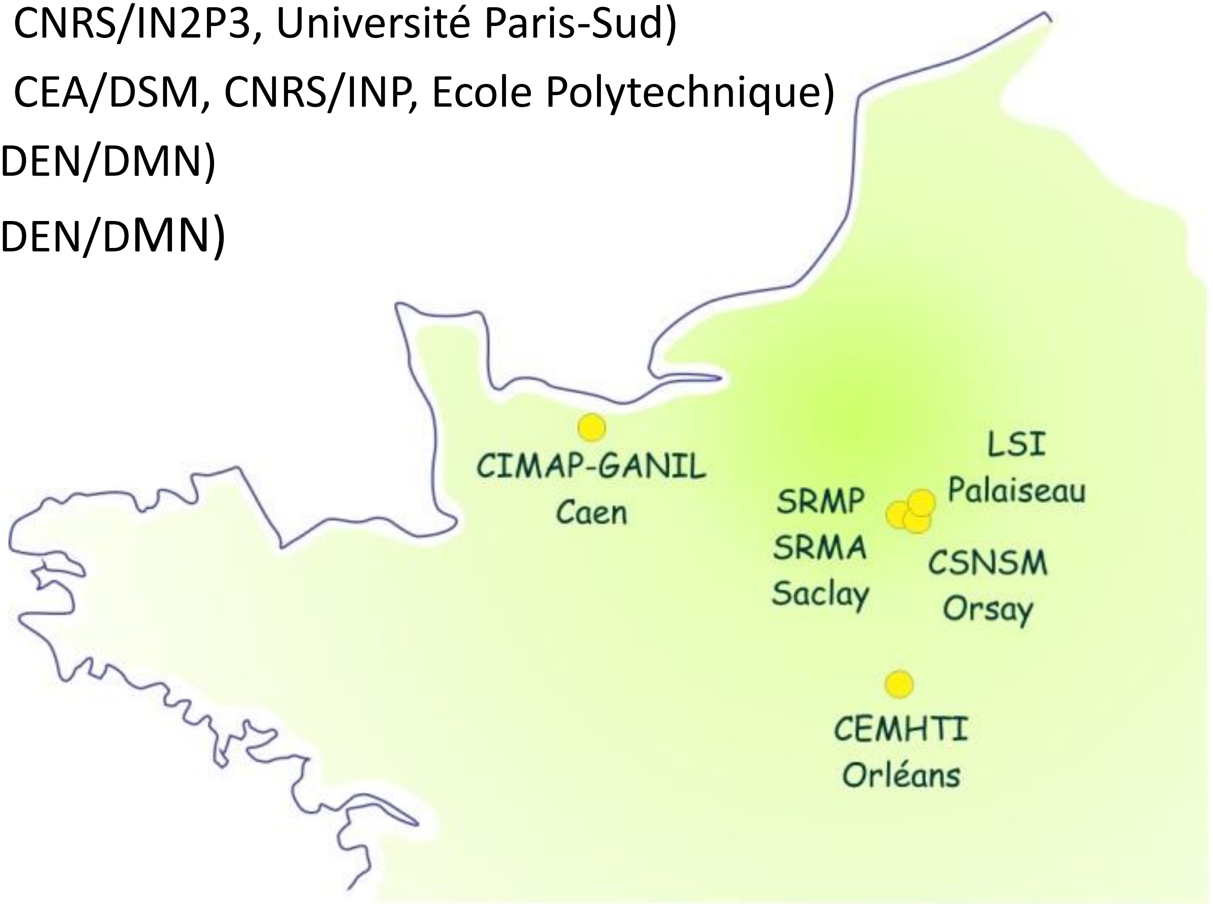


● Accelerator / Implanter
● Ion source
● Sputtering / Plasma-based Ion Implantation
● Magnets

● **Ion Beam Modification**
● **Ion Beam Analysis**

EMIR french national network

- CEMHTI - Orléans (UPR CNRS/INC, Université d'Orléans)
- CIMAP - Caen (UMR CEA/DSM, CNRS/INP, ENSICAEN, Université de Caen)
- CSNSM - Orsay (UMR CNRS/IN2P3, Université Paris-Sud)
- LSI - Palaiseau (UMR CEA/DSM, CNRS/INP, Ecole Polytechnique)
- SRMP - Saclay (CEA/DEN/DMN)
- SRMA - Saclay (CEA/DEN/DMN)

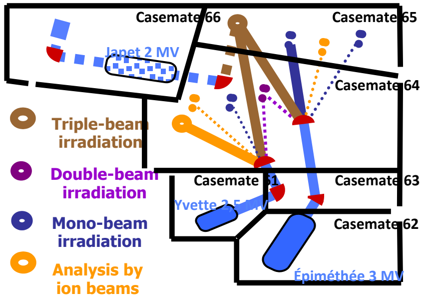


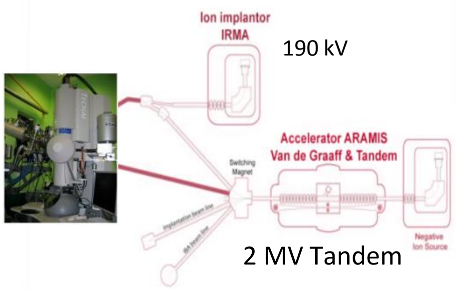
Supported by

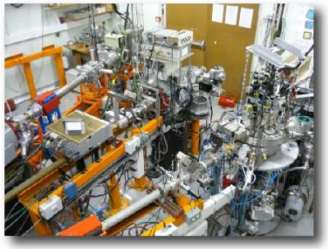
- CNRS
  - INP – INC – IN2P3
- CEA
  - DEN
- Ecole Polytechnique
- Université de Caen

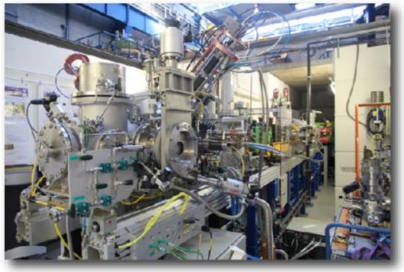
http://emir.in2p3.fr/

EMIR Platforms





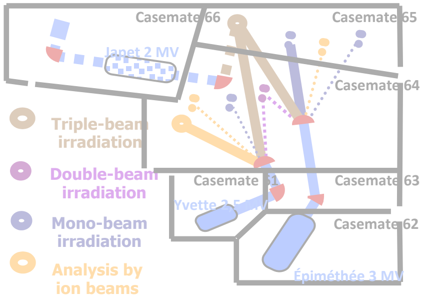


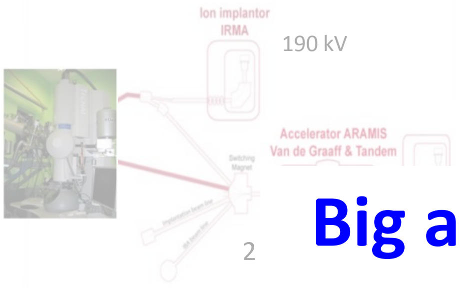


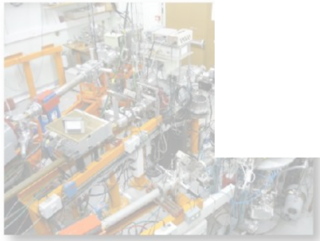
ions
JANNuS – Saclay – SRMP
triple beams
irradiation and implantations simultaneously *in situ* RAMAN and RBS, NRA, ERDA
JANNuS – Orsay – CSNSM
Double beam, energy range
In situ TEM and RBS
CEMHTI
Middle and high-energy light ions
large range
In situ RBS, NRA and variable temperature, *in situ* Raman, *in situ* mechanical stress
CIMAP – GANIL
swift heavy ions (very high energy)
large range, effects dominated by electronic excitations
In situ X-ray diffraction, infrared, UV-visible spectroscopies, gas emission

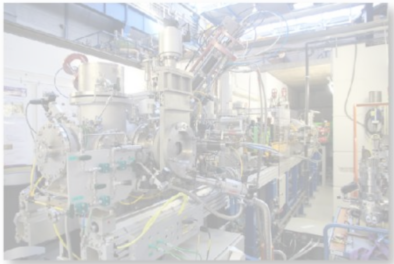
electrons
SIRIUS – LSI
large irradiated area energy range
In situ : electric, magnetic, optic properties
HVEM – SMRA
In situ imaging of structural evolution

EMIR Platforms









ions

JANNuS – Saclay – SRMP

triple beams

irradiation and implantations simultaneously

in situ RAMAN and RBS, NRA, ERDA

JANNuS – Orsay – CSNSM

energy range

In situ TEM and RBS

CIMAP – GANIL

swift heavy ions

large range

effects dominated by electronic excitations

In situ X-ray diffraction, infrared, UV-visible spectroscopies, gas emission

electrons

SIRIUS – LSI

large irradiated area

energy range

In situ : electric, magnetic, optic properties

HVEM – SMRA

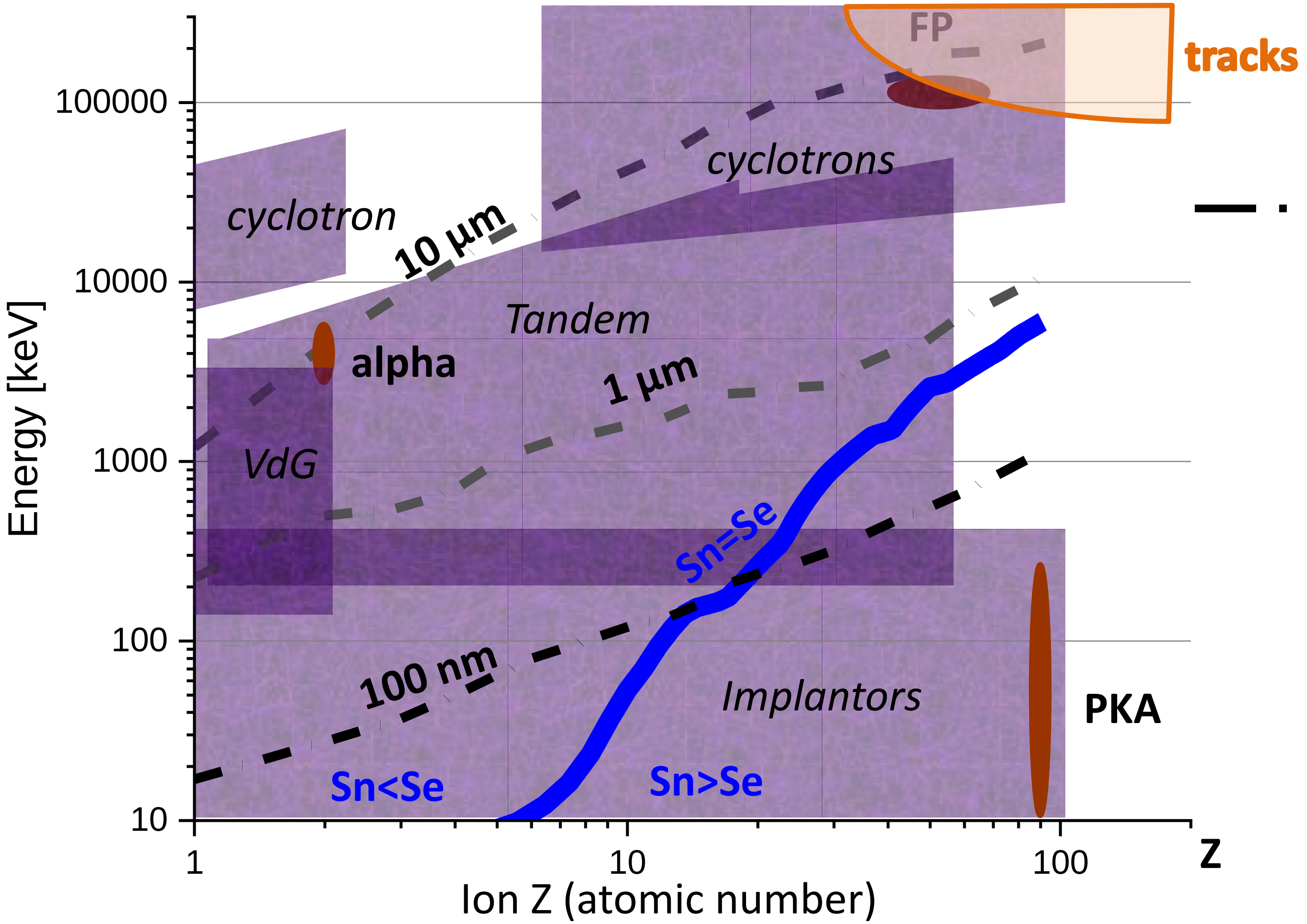
In situ imaging of

evolution

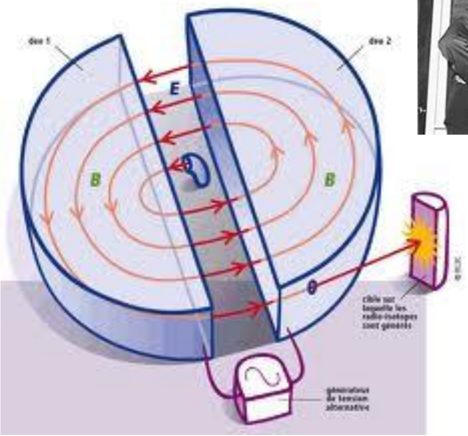
Big advantage : *in situ* characterization with the strong effort on their development

EMIR Platform

In UO_2

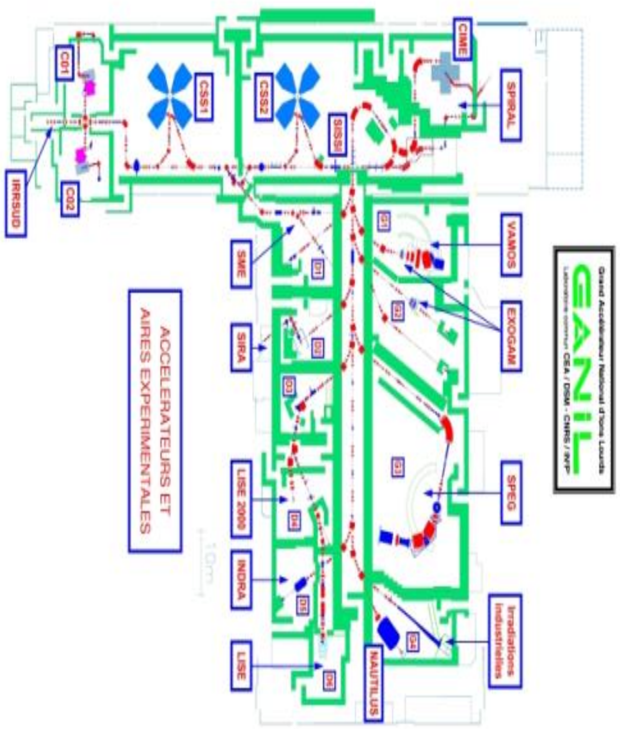


Cyclotron



Ernest Orlando Lawrence
(1901-1958)

<u>GANIL</u>, Caen, France
Heavy ions :C-U
O.3 – 95 MeV/A 0.1 – 20 µA,



<u>CEMHTI-cyclotron</u>, Orléans, France

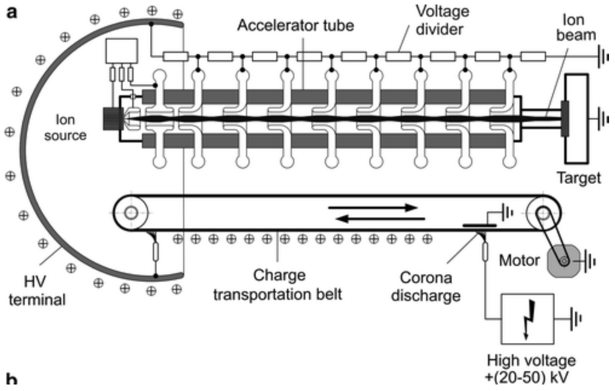
- Light ions : H^+, D^+, ^3He, α
- Energies = 10 - 45 MeV
  - 3×10^6 at.cm^{-2}.s^{-1} < flux < 4×10^{12} at.cm^{-2}.s^{-1}
  - 5×10^8 at.cm^{-2} < fluence < 5×10^{16} at. cm^{-2}
  - Temperatures -120° to 1200°C
  - under stress (in-beam creep with PSI)
- Neutrons flux ⇒ 10^{12} neutron/cm^2/s

In-beam creep device (PSI)

-120-1200°C irradiation in-situ µRaman

Van de Graaff : VDG

Robert J. Van de Graaff
(1901-1967)



– **Van de Graaff** (Pelletron) in CEMHTI

(light ions : H^+, D^+, ^3He, α)

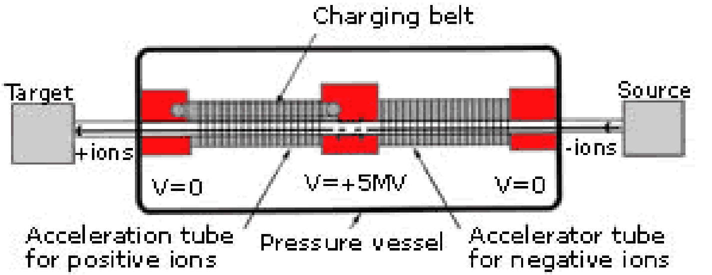
- Energies = 0.5 - 3 MeV

10^9 at.cm^{-2}.s^{-1} < flux < 2×10^{12} at.cm^{-2}.s^{-1}

5×10^{11} at.cm^{-2} <fluence < 2×10^{17} at.cm^{-2}

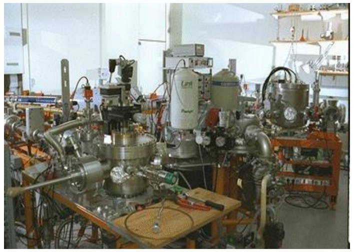
- Temperatures -130°C to 1200°C

TANDEM



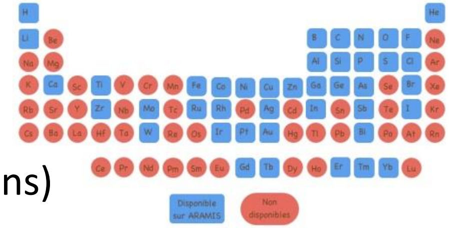
for heavy ions ARAMIS, (CSNSM) JANNUS (CEA Saclay), HZDR…with higher energy depending on charge/mass ratio.

Ion beam Analysis
(NRA, RBS, PIXE ….)



Experimental devices
(DIADDHEM on the front)

ARAMIS
(2MV, ions)



Outlines

1. MTR and PIE (R. Hania-NRJ and J. Noirot-CEA)
2. Separate effect studies
    a. Experimental approach
    b. External irradiations
        a. How to choose the irradiation conditions
        b. The facilities
    c. Fine characterizations
    d. Illustrations in fuel and other materials

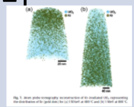
Defects / damage

Characterization techniques		Basic phenomena	Type of defects	Modeling	Probing scale	In fuel
ESR	Electron spin resonance	Transition between two electron spin states (Zeeman)	spin$\neq 0$, Point defects		Atomic/global (mm)	
PL	Photolumines-cence	Light absorption and emission	Point defects		Atomic/global (µm^2-mm^2 x µm)	
PAS	Positron annihilation spectroscopy	Positron trapping and annihilation with electrons	Mainly Vacancy defects (single to clusters)	2comp. DFT [1]	Atomic/global (mm^3 as a function of depth)	[1, 2,3]
TEM	Transmission electron micoscopy	Diffraction of electron	Clusters (cavities/bubbles, loops, dislocation lines)		nm/local (0.05 µm^3)	[5]
Raman	Raman diffusion	Diffused light analysis due to vibrational modes	Phase, specific symetry due to cristal. arrangement		Global (µm^2-mm^2 x µm)	[3]
RBS/C	Channeling Rutherford Bacscattering	In single crystal , ion interaction with matter	Disorder (interstitials)	Mc Chasy []	Depth on µmxmm^2	[6]

………… Non exhaustive list

[1] J. Wiktor et al Phys. Rev. B **90**, 184101 (2014); [2] D. Roudil et al. JNM 420 (2012) 63–68; [3] R. Mohun et al Acta Materialia 164 (2019) 512-519; [4] C. Onofri et al. / JNM 482 (2016) 105-113; [2] JNM 494 (2017) 252-259; [6] F. Garrido et al. NIM B 266 (2008) 2842–2847

Chemical inventory

Characterization techniques		Basic phenomena	advantages	Probing scale	In fuel ?
APT	Atom probe tomography	Mass recording of detached (HV or Laser) ions from pin	Precipitates, segregation	Atomic/local (0.05 µm^3)	[1] 
SIMS	Secondary ion Mass spectrometry	Mass recording of sputtered ions	Depth profiling	global (µm^2-mm^2 x µm, as a function of depth)	[2]
EPMA	Electron probe micro analysis	Electron XR emission Wavelength Dispersive Spectroscopy	µbeam, quantitative and high sensitivity for elt >Li	Mapping (µm scale)	Gas, volatile [3]
TEM/ EELS, EDS	TEM/ energy loss spectroscopy, energy dispersive spect.	Electron energy losses, XR emission with electrons	Precipitates (chem comp. and crist. phase), segregation,	nm/local (0.05 µm^3)	[4,5]
XAS, EXAFS, XANES	XR absorption spectroscopy	XR absorption (synchrotrons)	Local environment of one type of elt	Atomic/Global (mm^3)	[6]
NRA and RBS (/C)	Nuclear reaction analysis and Rutherford Bacscattering (Channeling)	ion interaction with matter (In single crystal)	Depth profile, (localization in the cristal)	Depth on µmxmm^2	[7]

………… Non exhaustive list

[1] L.F. He et al. / JNM 456 (2015) 125–132; [2] L. Desgranges et al, NIM B 215 (2004) 545–551; [3] C. T. Walker et al, JNM 138 (1986) 155-161; [4] L. He et al Microsc. Microanal. 21 (Suppl 3), 2015; [5] A. Espriu-Gascon et al Int. J. Nanotechnol., 13, Nos. 8/9, 2016 627; [6] P.M. Martin et al. JNM 466 (2015) 379; [7] T. Belhabib et al. JNM 467 (2015) 1-8

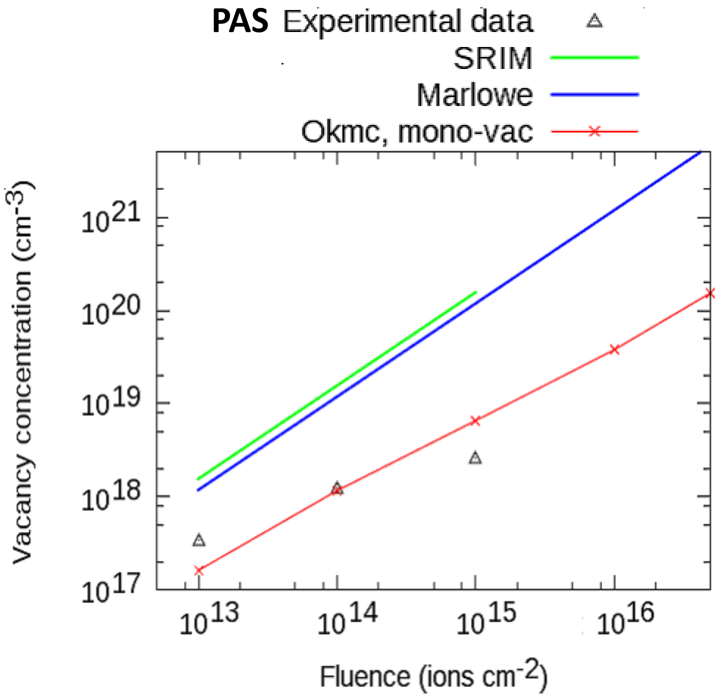
Outlines

1. MTR and PIE (R. Hania-NRJ and J. Noirot-CEA)
2. Separate effect studies
    a. Experimental approach
    b. External irradiations
        a. How to choose the irradiation conditions
        b. The facilities
    c. Fine characterizations
    d. Illustrations in fuel and other materials

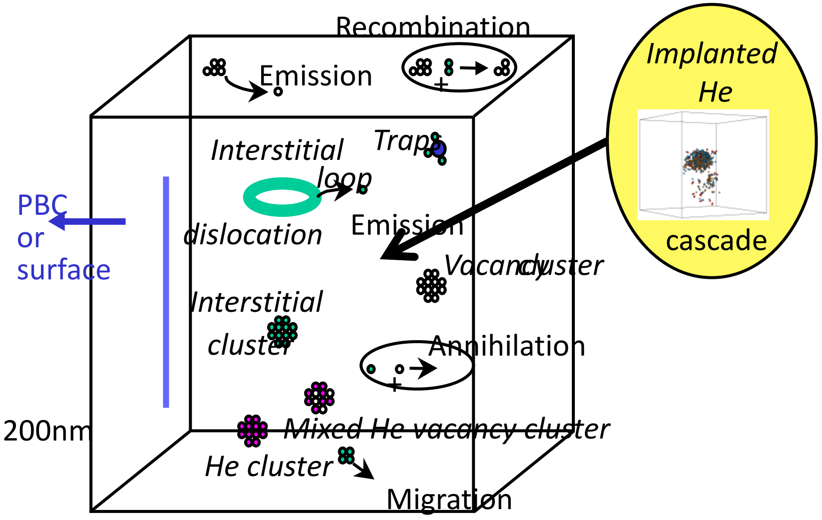
SRIM and other codes/ Experimental data comparison

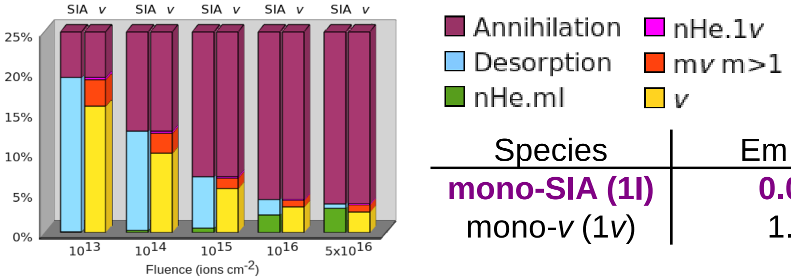
SRIM/experimental

800 keV ^{3}He irradiated W



Object Kinetic Monte Carlo:
LAKIMOCA, C.Domain (EDF)





Species	Em (eV)
mono-SIA (1I)	**0.013**
mono-*v* (1*v*)	1.66

Parameterised with ab initio calculations for E_m and E_b, [3]

- The He and the defects can diffuse or emit (thermally activated events)

→ Arrhenius law, $\Gamma = f_v \times e^{(-E/KT)}$

- Residence time algorithm, $\Delta t = \Sigma_i \Gamma_i$
- Reactions submitted to distance criteria $d_{ij} < R_i + R_j$

[1] PE Lhuillier Thesis CEMHTI 2010, [2] A. De Backer et al. JNM 429 (2012) 78–91; [3] C.Becquart,et al JNM 403, Issues 1-3, 2010, 75-88

Identification of vacancy defects in UO_2

Irradiations with electrons at 1 or 2.5 MeV

- Irradiations with electrons from 1 to 2.5 MeV at different fluences between $5x10^{17}$ and $1x10^{19}$ cm^{-2}

(~ 25°C) VDG at LSI (Palaiseau)

- Calculations : Smott Program [1]
  - electron <1.6 MeV :

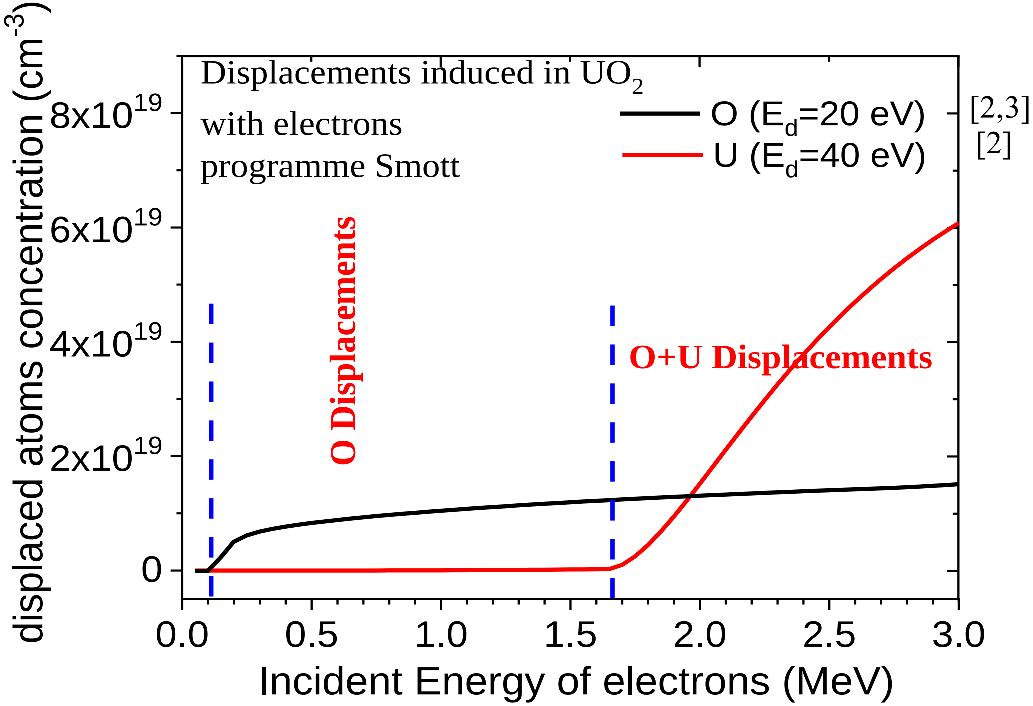
    only O atoms can be displaced

    damaged layer ~400µm

  - electron >1.7 MeV :

    displacement of both O and U atoms

    damaged layer ~260µm (U lattice)

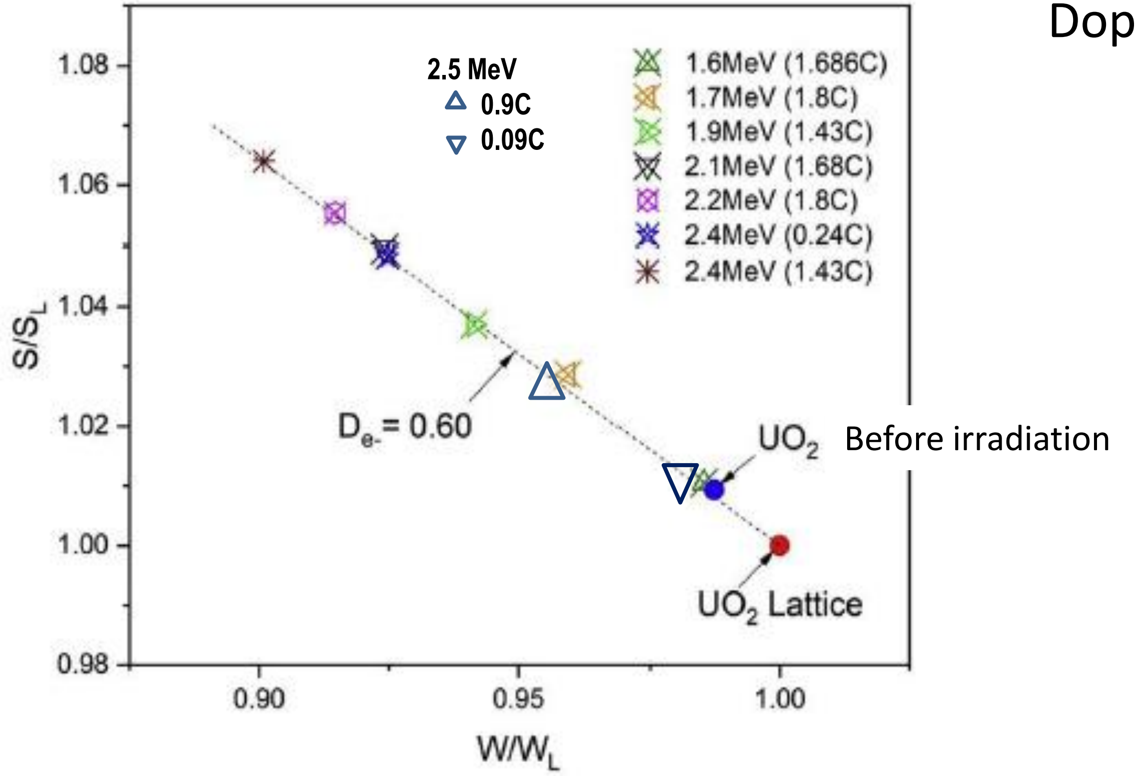


The. E_d(U)=50eV [3]

[1] Dunlop A., Lesueur D., Dural J., NIM-B **42**, 182 (1989); [2] J.Soullard, J.Nucl. Mater **135** (1985) 190-196.; [3] C. Meis, J. .Nucl. Mater **341** (2005) 25-30.

PAS (Doppler) electron irradiated UO_2

Slow positrons : 0.5 – 25 keV
Doppler broadening at 300K

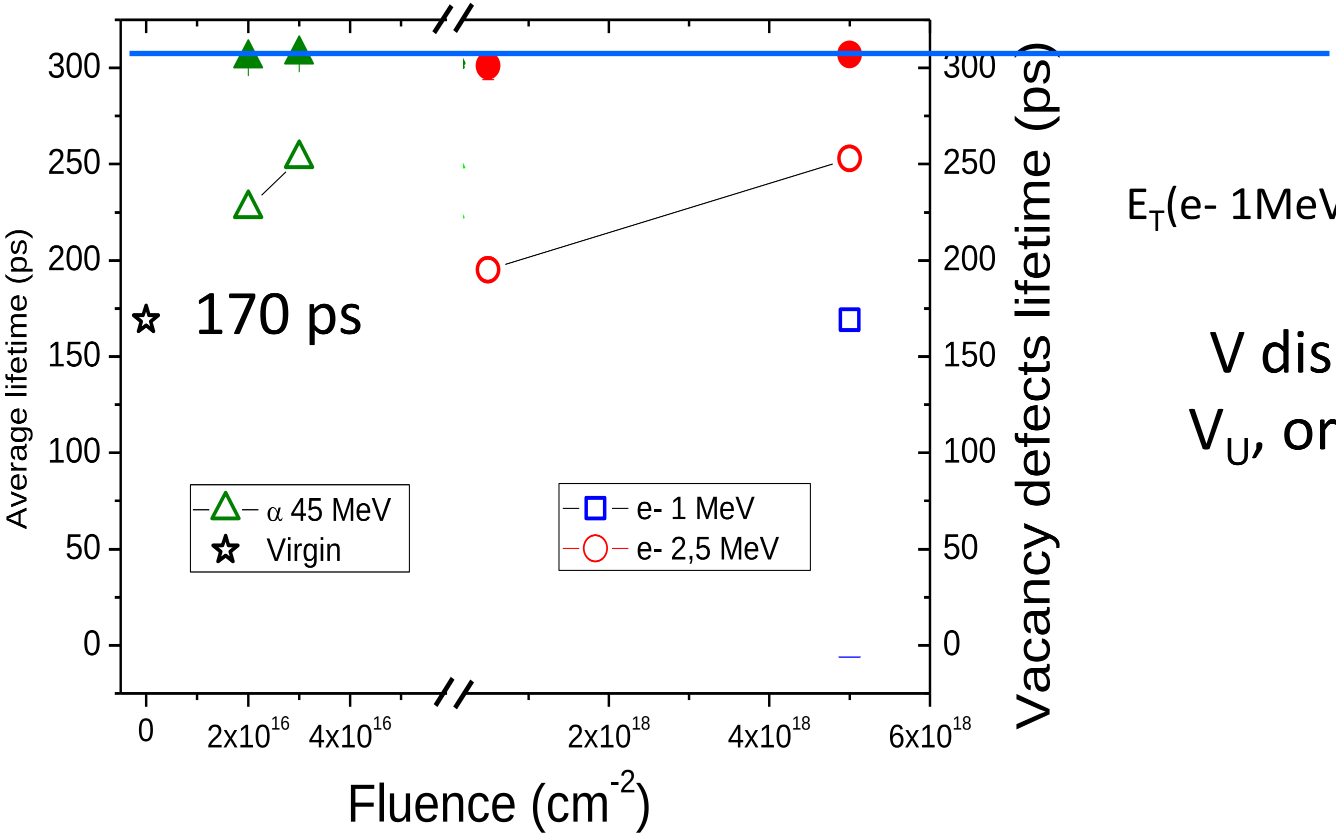


- Lattice SW in UO_2 annealed at 1700°C in Ar/H_2+H_20
- Characteristic line due to annihilation in one type of vacancy defects

[2] Mohun et al. / Acta Materialia 164 (2019) 512-519

Vacancy defects in UO_2

Irradiations α 45 MeV, 1 MeV and 2,5 MeV electrons
Positron Annihilation Spectroscopy (Fast Positrons), 300K Lifetime



$\tau_V = 310 \pm 10$ ps

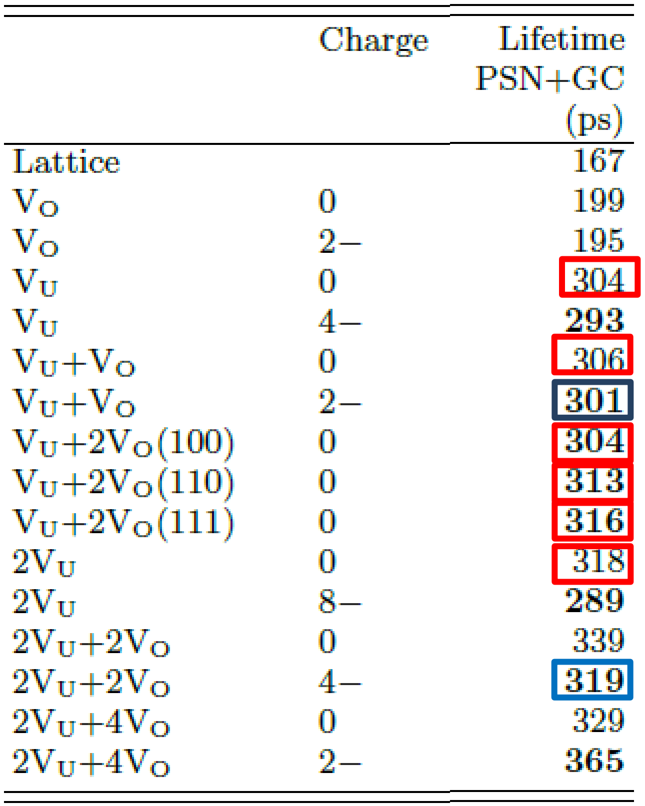
E_T(e- 1MeV) <E_d(U)< E_T(e- 2.5MeV)

V displacement of U
V_U, or complexes V_{UO2}

Identification of vacancy defects in UO_2

Calculations in the **ABINIT code** (Two Components DFT) [1]

Self consistent scheme PSN [2] with gradient correction GC for the enhancement factor g; **DFT**(GGA, PBE)**+*U*** formalism [3] to treat the **5*f*** electrons; Defects were fully relaxed



	Charge	Lifetime PSN+GC (ps)
Lattice		167
V_O	0	199
V_O	2−	195
V_U	0	304
V_U	4−	293
V_U+V_O	0	306
V_U+V_O	2−	301
$V_U+2V_O(100)$	0	304
$V_U+2V_O(110)$	0	313
$V_U+2V_O(111)$	0	316
$2V_U$	0	318
$2V_U$	8−	289
$2V_U+2V_O$	0	339
$2V_U+2V_O$	4−	319
$2V_U+4V_O$	0	329
$2V_U+4V_O$	2−	365

Exp .

Long lifetime ~310±10 ps

Several Vacancy defects

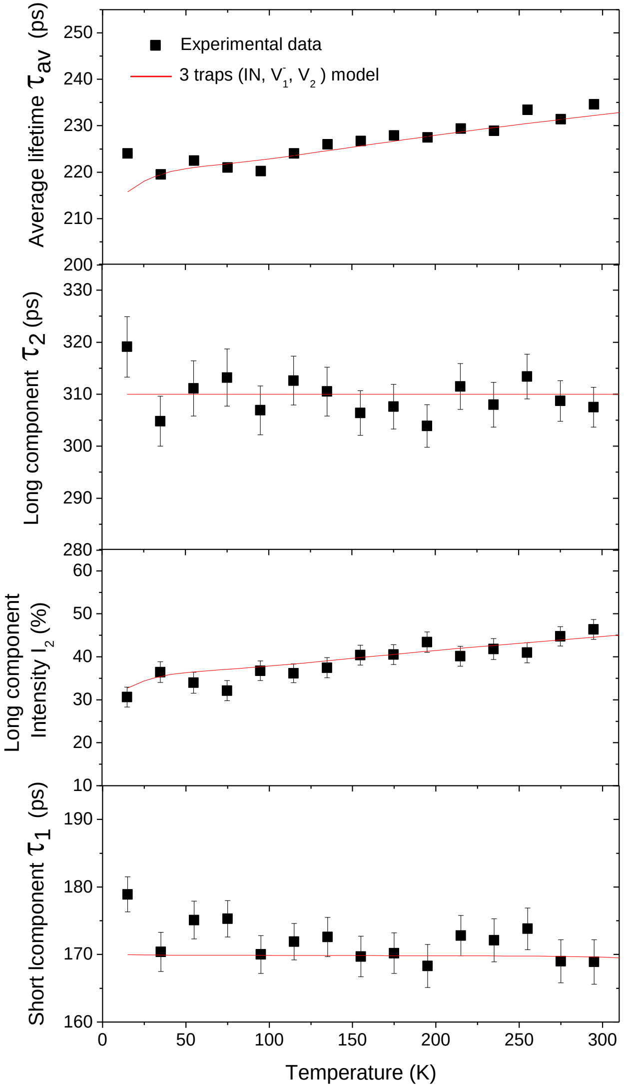
Neutral or **negatively charged**

Measurement of positron lifetime as a function temperature

Is there any negatively charged vacancy ?

[1] J. Wiktor et al Phys. Rev. B **90**, 184101 (2014)

3 traps model



Model with 3 Traps : negative ions NI, V°, V$^-$

τ_{NI}=170 ps and τ_{V^-}= τ_{V° =310 ps

Neutral** vacancy **V°

Cv°(cm^{-3})	µv°
6,50E+19	1,00E+15

>30 times more **neutral** vacancies than negatively charged ones

Negatively charged** vacancy **V$^-$

Cv-(cm^{-3})	μ_0r	μ_0V-	Er(eV)	Vr(s^{-1})
2.0E+18	3,40E+16	4,00E+16	1,00E-02	1,00E+11

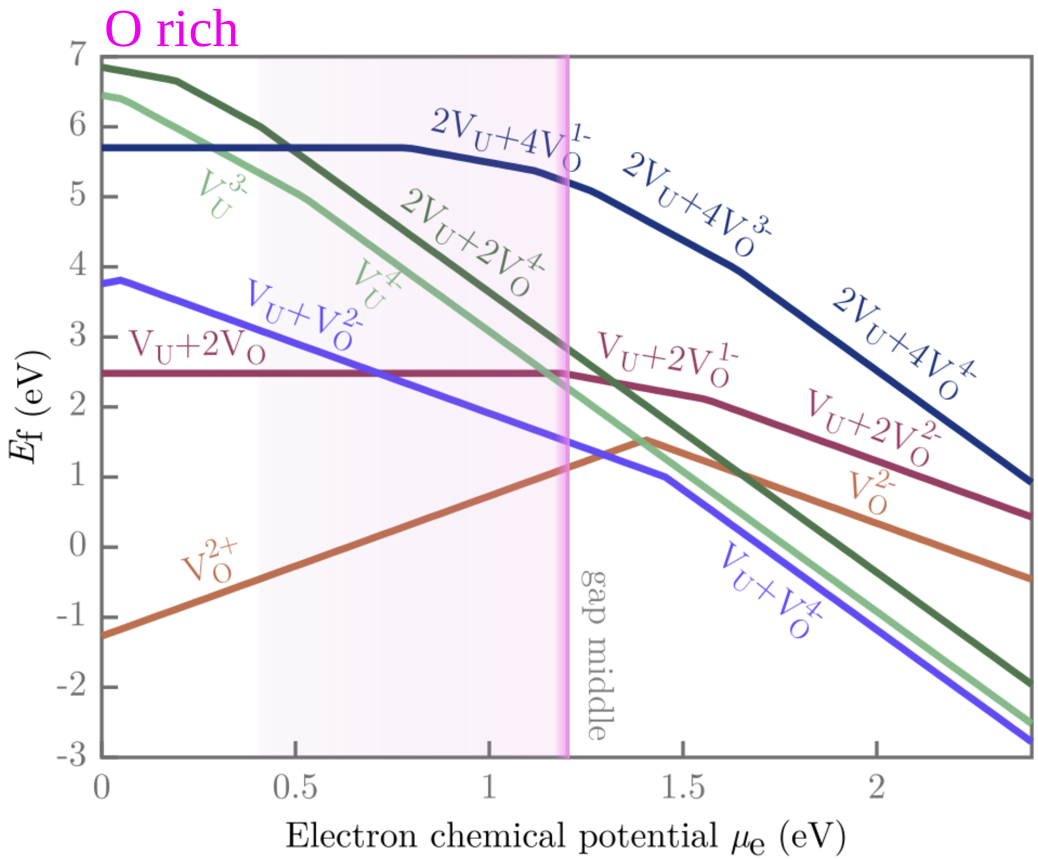
C_{NI}(cm^{-3})	μ_0(NI)	E_{NI}(eV)
1,00E+19	4,20E+16	3,00E-01

High binding energy
at Rydberg state of negative ions

short lifetime is constant
Trapping saturation

Calculated formation energies

Formation energies of defects in close stoichiometric (O/U~ 2.005) UO_2 [1]



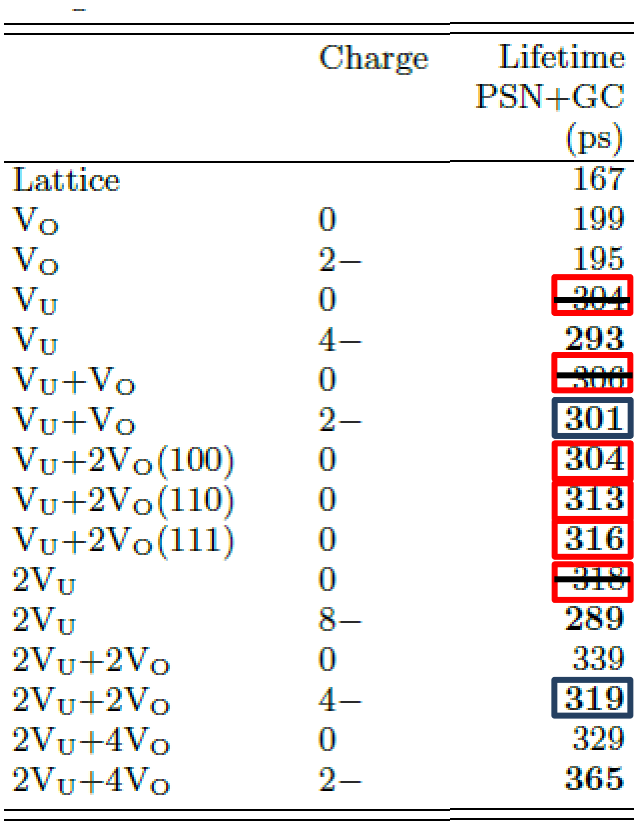
In the undoped UO_2 V_O should be **positive**, hence not detected by PAS

V_U and V_U+V_O defects should be **negative**, while the V_U+$2V_O$ should be **neutral.**

Close to stoechiometry , I_O^{2-},V_O^{2+} , V_U^{4-} DFT LDA+U [2]

[1] 1 J Wiktor, M. Bertolus, G. Jomard, MF Barthe et al, Phys Rev B 90, 184101 (2014), [2] J P Crocombette Phys Rev B **85, 144101 (2012)**

Identification of vacancy defects in UO_2 irr



	Charge	Lifetime PSN+GC (ps)
Lattice		167
V_O	0	199
V_O	2−	195
V_U	0	~~304~~
V_U	4−	293
V_U+V_O	0	~~306~~
V_U+V_O	2−	301
$V_U+2V_O(100)$	0	304
$V_U+2V_O(110)$	0	313
$V_U+2V_O(111)$	0	316
$2V_U$	0	~~318~~
$2V_U$	8−	289
$2V_U+2V_O$	0	339
$2V_U+2V_O$	4−	319
$2V_U+4V_O$	0	329
$2V_U+4V_O$	2−	365

V_U and V_U-V_O are negatively charged close to the middle of the bandgap in close stoechiometric UO_2

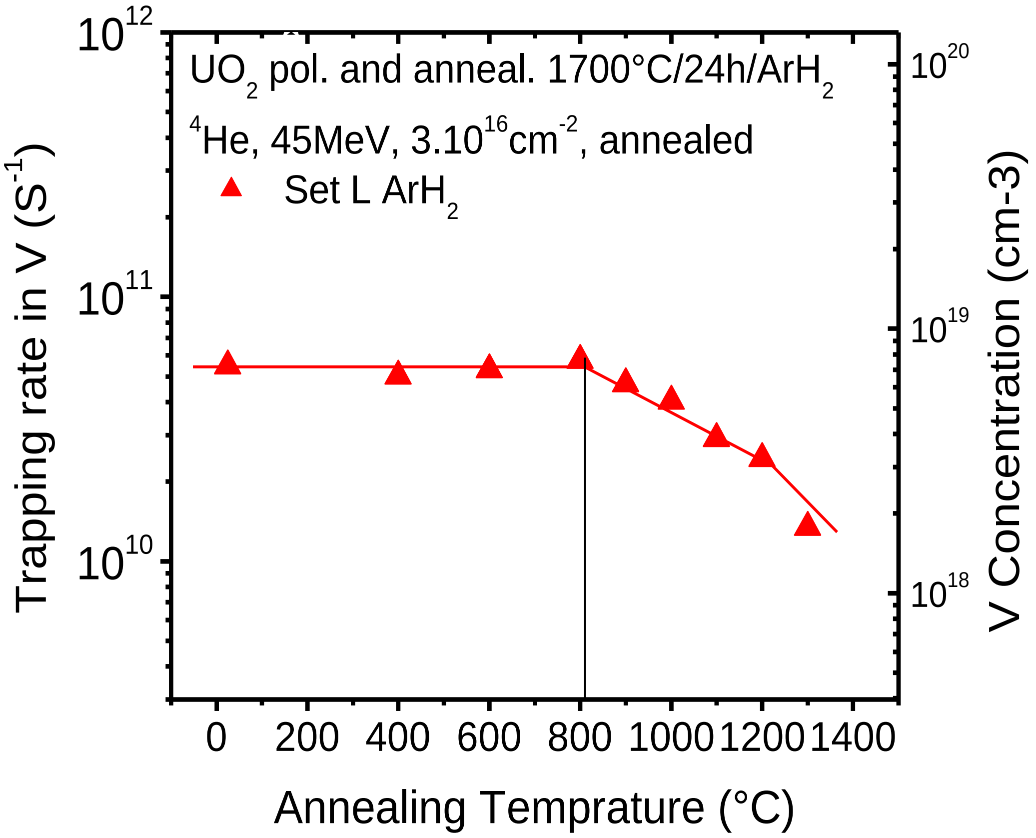
Exp .
Long lifetime ~310±10 ps
Vacancy defects

$2V_U$ is 8- close to the middle of the bandgap in close stoechiometric UO_2

We propose
Neutral vacancy defects which are preponderant = Schottky defects
Negatively charged vacancy defects = a mixing of $(V_U\text{-}V_O)^{2-}$, $(2V_U\text{-}2V_O)^{4-}$

Vacancy defects recombination in UO_2

Vacancy recombinations

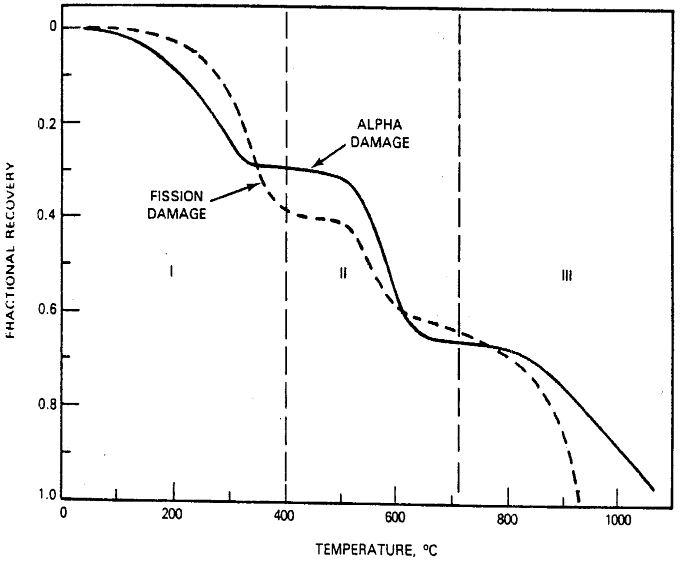


Annealing Stage : T°> 800°C

When T°C ↗, τ_{av} ↘

K_V ↘ ⇒ V Concentration ↘
Migration of interstitials or V ?

U defects recovery 400-800°C [2]

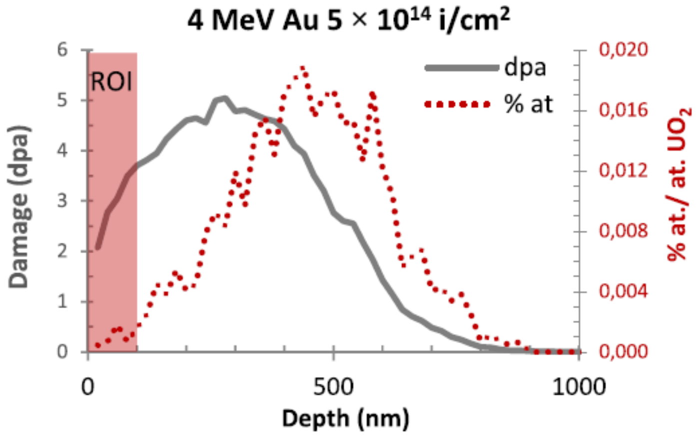


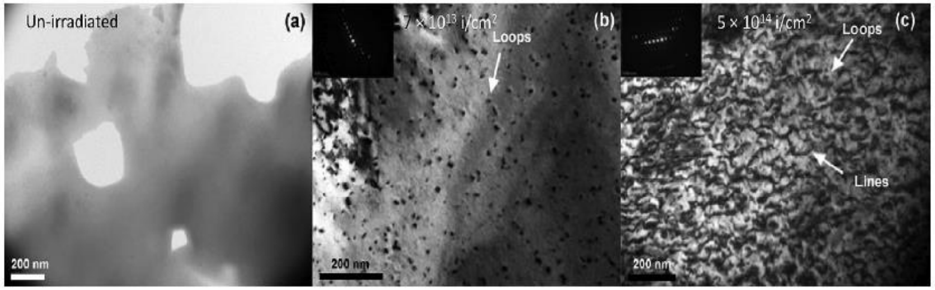
[1] W.J. Weber, Journal Nucl. Mater. **114** (1983) 213 ; [2] Hj. Matzke, Nucl. Instr. Meth. Phys. Res. B**32** (1988) 455 ; [3] A.Turos, H. Matzke, S. Kwiatkowski, Physical Review Letters **65** (1990) 10.

Dislocation formation in UO_2

Dislocation lines formation in UO_2

Au 4 MeV in situ irradiations ARAMIS/TEM, at the JANNuS-Orsay (CSNSM)





At 25°C g=111, a)non irradiated,b) 7x10^{13} cm^{-2}, c) 5x10^{14} cm^{-2}

Size

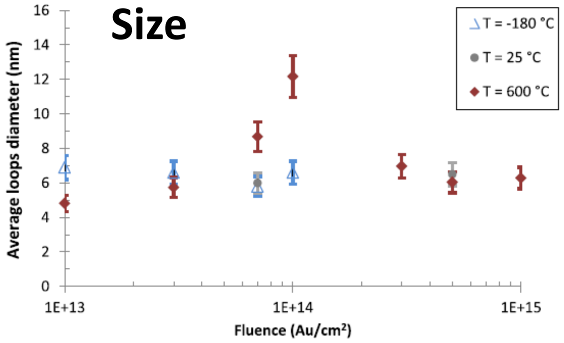
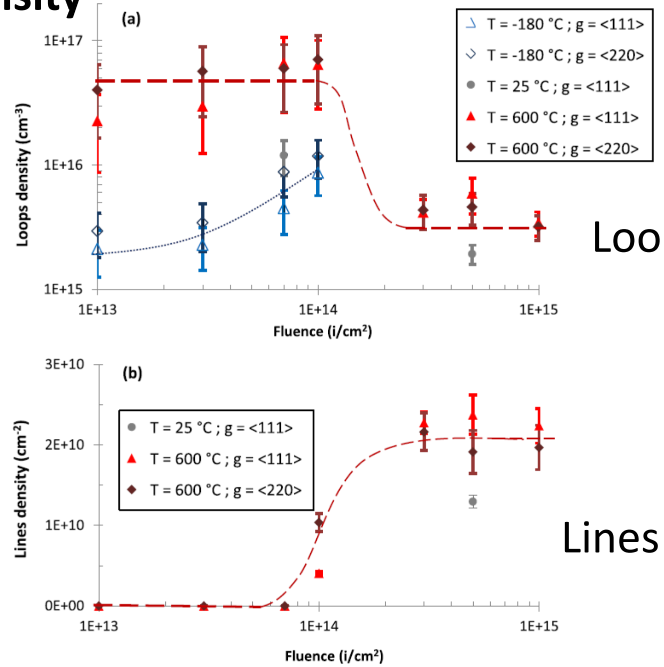


Fig. 10. Average loops diameter as a function of fluence for 4 MeV Au irradiations at −180, 25 and 600 °C.

Density



Loops

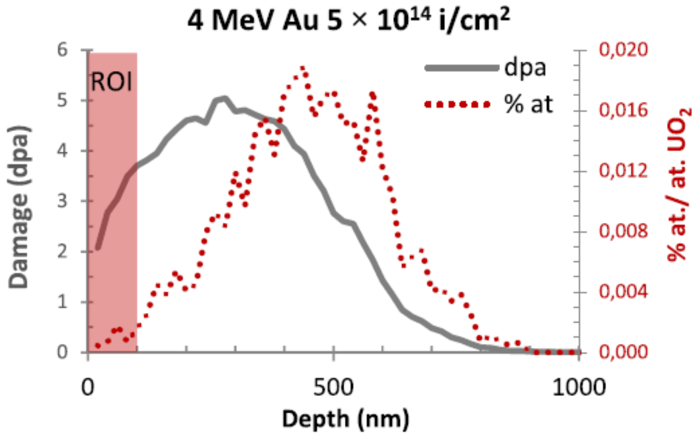
Lines

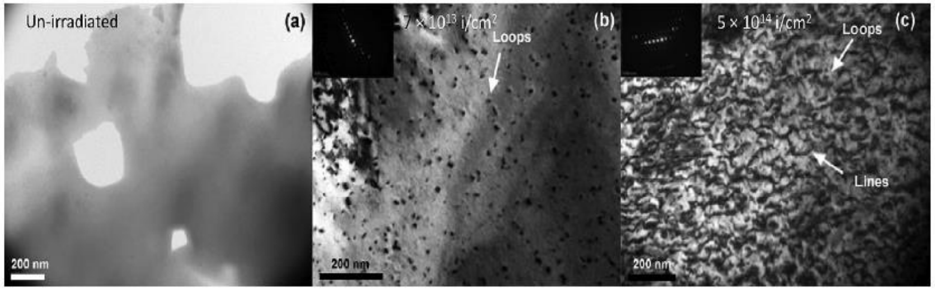
Dislocation lines are formed by loop overlapping with increasing fluence [1]

[1] C. Onofri et al. / JNM 482 (2016) 105-113; [2] JNM 494 (2017) 252-259

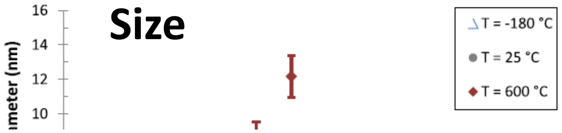
Dislocation lines formation in UO_2

Au 4 MeV in situ irradiations ARAMIS/TEM, at the JANNuS-Orsay (CSNSM)



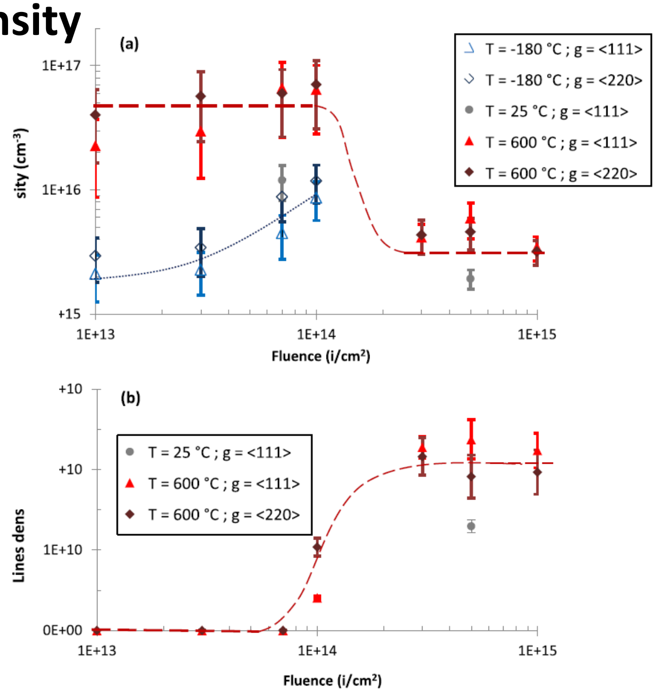


At 25°C g=111, a)non irradiated,b) $7x10^{13}$ cm^{-2}, c) $5x10^{14}$ cm^{-2}



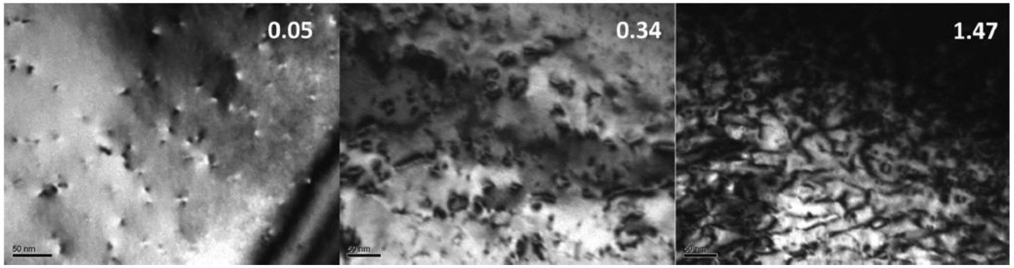
Careful identification of the nature, size and density of loops and dislocations [2].

The dislocation lines, formed by loop overlapping with increasing fluence, are very similar to those induced under mechanical stress.

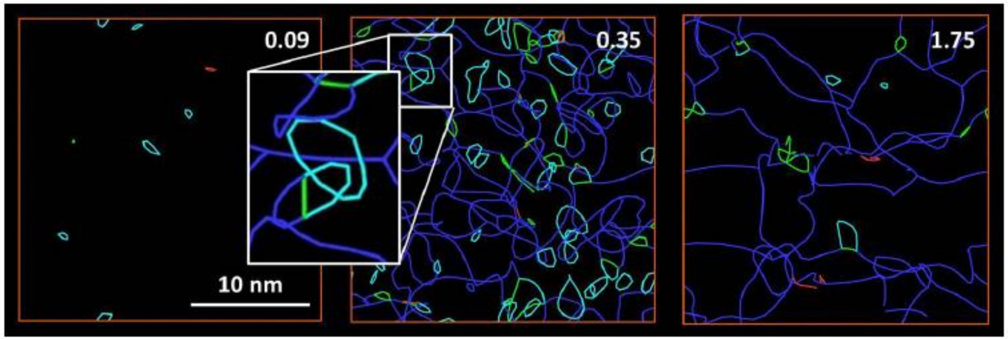


C. Onofri et al. / JNM 482 (2016) 105-113; [2] JNM 494 (2017) 252-259

Dislocation lines formation in UO$_2$



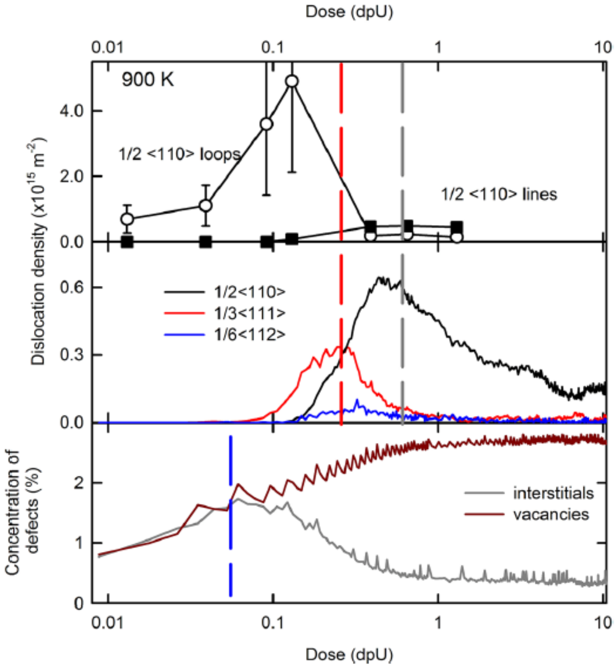
Exp, TEM Au 4 MeV, at 600°C with increasing dpU



Exp: 2 nm min *(TEM resolution)* ½ <110> loops ➞ ½ <110> lines

MD: point defects ➞ ⅓<111> loops ➞ ½ <110> loops ➞ ½ <110> lines

Frank loops perfect loops



5 stages process

1. point defects creation
2. aggregation into clusters
3. nucleation of Frank loops
4. transformation into unfaulted loops via Shockley that in turn grow
5. reorganization into forest dislocations

A. Chartier et al. APL 109, 181902 (2016)

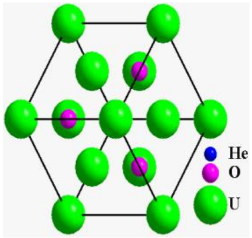
He location in UO_2 lattice
Evolution as a function of temperature

He location in UO_2

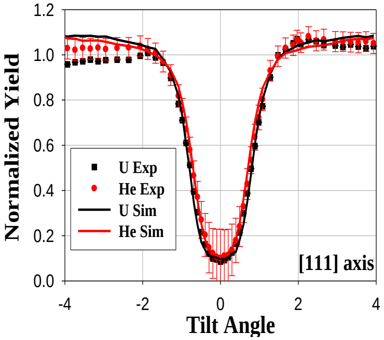
UO_2 Single crystal, ^3He 50 keV (Rp=0.18 µm)

NRA / channeling **^3He (d, p) α**

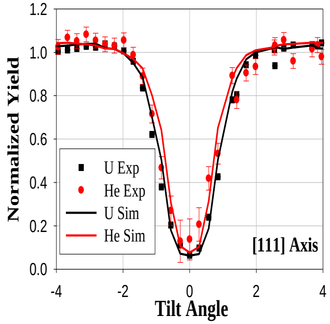
[111] axis



As-implanted

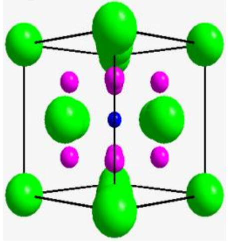


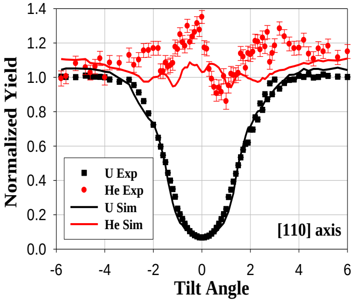
600°C/ 60 min

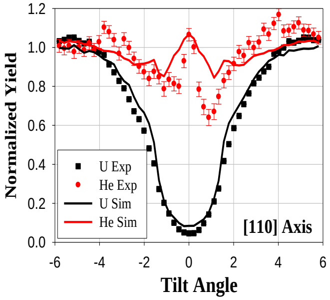


	As implanted	600°C/ 60min
U SIA octahedral	0.03	0.03
U and O random	0.07	0.03
He random	0.03	0.03

[110] axis

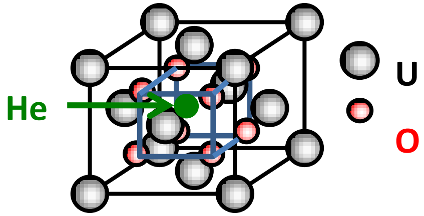






Code McChasy

As-implanted



He position in UO_2 lattice is the octahedral site[1,2]

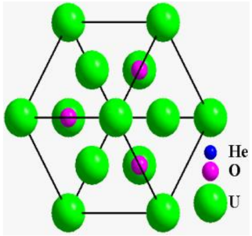
[1]F.Garrido, L.Nowicki, G.Sattonnay, T.Sauvage, L. Thomé, Nuc. Instru. Methods. Phys.Research,196, 2004
[2]T.Petit, M.Freyss, P.Garcia, P.Martin, M.Ripert, J.P.Crocombette, F.Jollet, J. Nucl. Mater. 320 (2003)133
[3] K. Govers, S. Lemehov, M. Hou, M. Verwerft *Journal of Nuclear Materials 395 (2009) 131–139*.

He location in UO_2

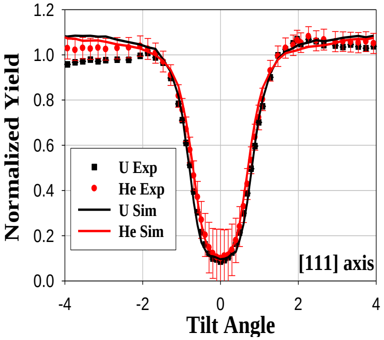
UO_2 Single crystal, ^3He 50 keV

NRA / channeling **^3He (d, p) α**

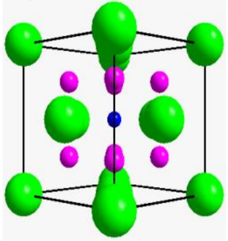
[111] axis

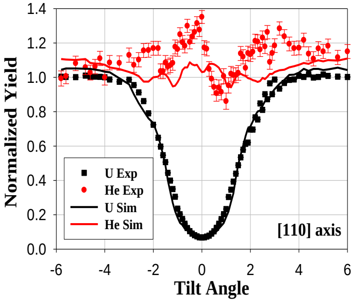


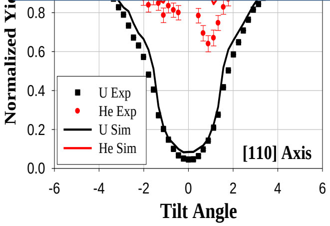
As-implanted

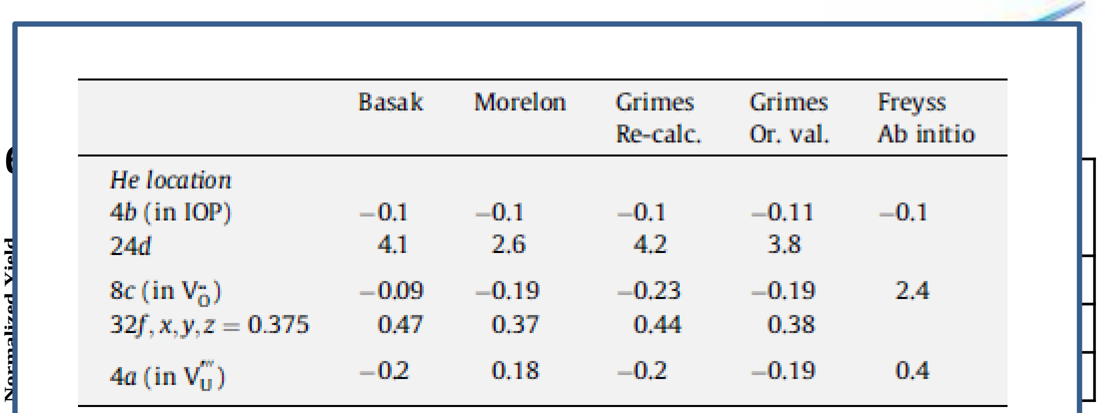


[110] axis







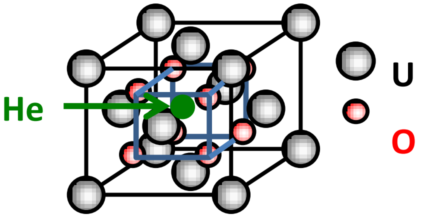


	Basak	Morelon	Grimes Re-calc.	Grimes Or. val.	Freyss Ab initio
He location					
4*b* (in IOP)	−0.1	−0.1	−0.1	−0.11	−0.1
24*d*	4.1	2.6	4.2	3.8	
8*c* (in $V_O^{\bullet\bullet}$)	−0.09	−0.19	−0.23	−0.19	2.4
32*f*, $x, y, z = 0.375$	0.47	0.37	0.44	0.38	
4*a* (in $V_U^{''''}$)	−0.2	0.18	−0.2	−0.19	0.4

Incorporation energy (in eV) of He obtained with the potentials used in different potential and ab initio calculations [2].From [3]

Code McChasy

As-implanted

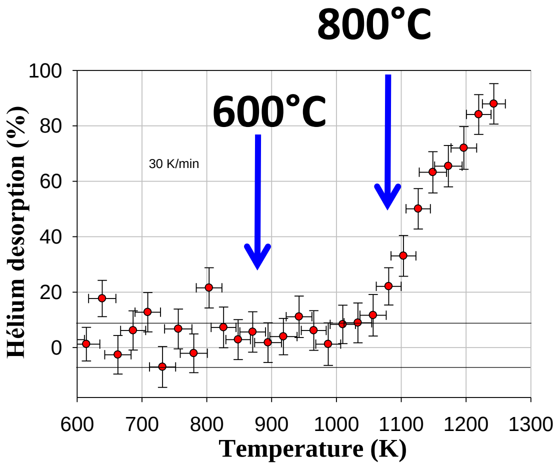


He position in UO_2 lattice is the octahedral site[1,2]

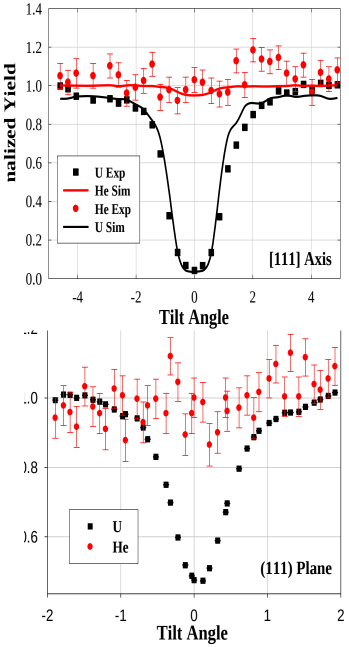
[1]F.Garrido, L.Nowicki, G.Sattonnay, T.Sauvage, L. Thomé, Nuc. Instru. Methods. Phys.Research,196, 2004
[2]T.Petit, M.Freyss, P.Garcia, P.Martin, M.Ripert, J.P.Crocombette, F.Jollet, J. Nucl. Mater. 320 (2003)133
[3] K. Govers, S. Lemehov, M. Hou, M. Verwerft *Journal of Nuclear Materials 395 (2009) 131–139*.

He location in UO_2

UO_2 Single crystal, ^{3}He 50 keV
NRA / channeling



800°C/60min [111]

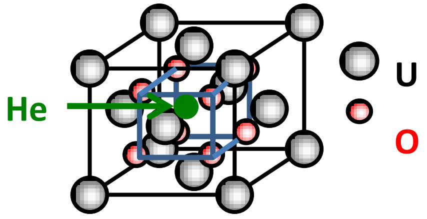


	As implanted	600°C/ 60min	800°C/ 30min
U SIA octahedral	0.03	0.03	0
U and O random	0.07	0.03	0
He random	0.03	0.03	0.95

After 800°C/60 min
He Randomly distributed

He Bubbles ? [3]

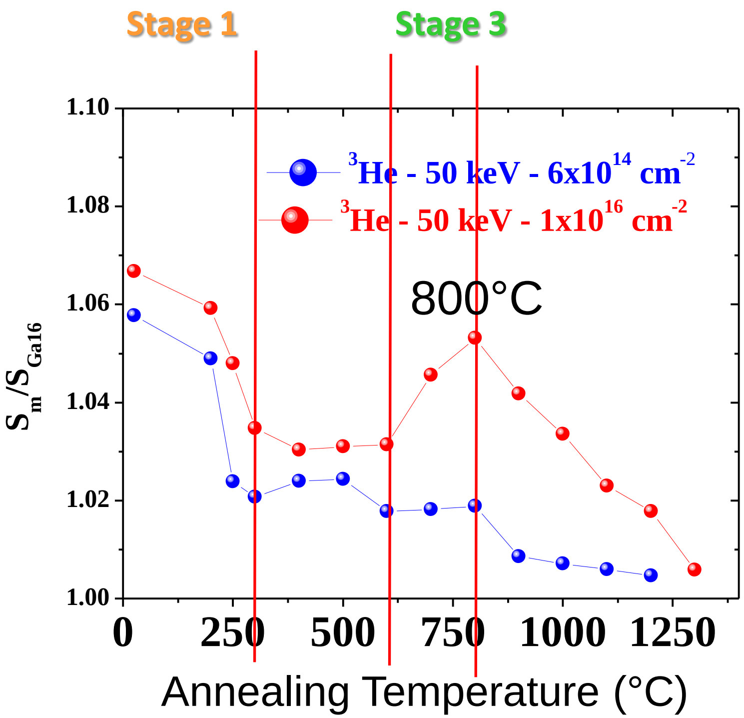
As-implanted



[1]F.Garrido, L.Nowicki, G.Sattonnay, T.Sauvage, L. Thomé, Nuc. Instru. Methods. Phys.Research,196, 2004
[2]T.Petit, M.Freyss, P.Garcia, P.Martin, M.Ripert, J.P.Crocombette, F.Jollet, J. Nucl. Mater. 320 (2003)133
[2] G. Sattonnay, L. Vincent, F. Garrido, L. Thomé J. Nuc. Mat. 131, 2006

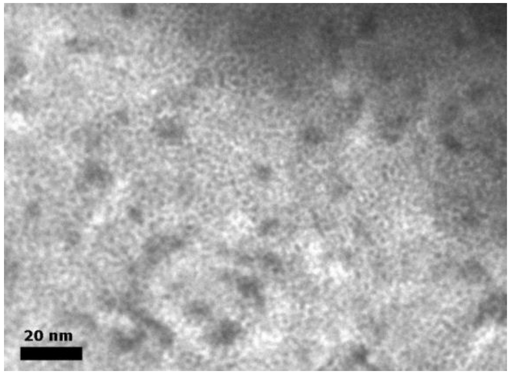
He Precipitation

He 50 keV (0.3 at. %, 0.3 dpa) **in the first 100 nm under the surface**



Stage 3 (700°C) Nature of Vacancy defects evolves due to He precipitation ?[1]

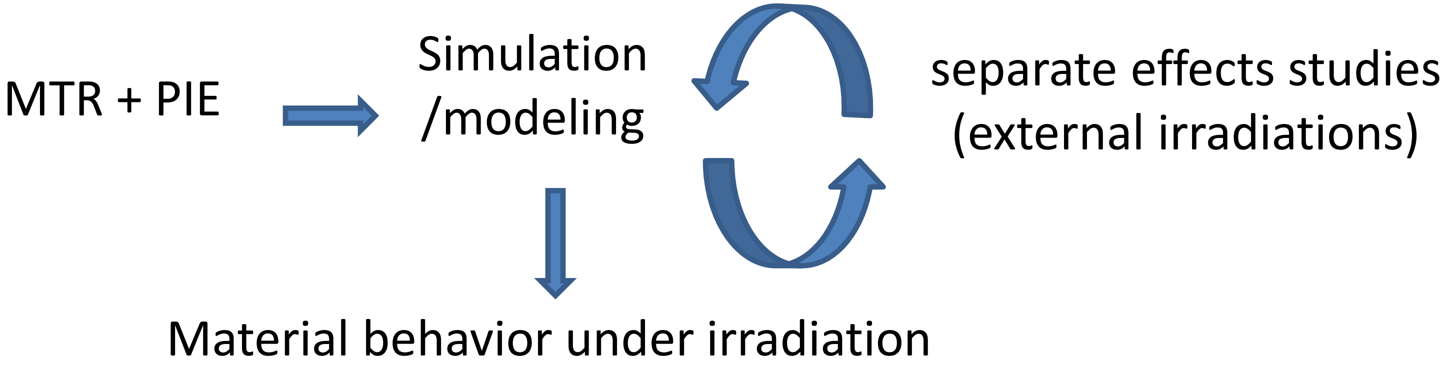
He 500 keV: (0.3 at. %, 0.3 dpa) 1000°C 35 min, **nano-bubbles appear after an annealing stage (10^{24} /m^3, a few nm) [2]**



[1] T Belabib Thesis, [2] C Sabathier, G. Martin, A. Michel, G. Carlot, P. Garcia F-Bridge WP1.1 and 2.2 joint meeting, Orleans, May 2011

Conclusions

Knowledge of the behaviour of materials under irradiation to foresee the evolution and lifetime



MTR + PIE

Simulation /modeling

separate effects studies (external irradiations)

Material behavior under irradiation

- Separate effects studies

Impurity and defect introduction (Irradiations) : **control parameters**

+

Characterizations : microstructure (various scales and techniques), chemical composition (concentration, distribution, profile,…)

Sensitive complementary techniques

Fundamental data on impurity and defects : Em, Eb, nature, size, concentration……

Mechanisms

Thank you for your kind attention