



Experiments for improving Nuclear Fuels Models and Performance

Numerical and experimental simulation at the atomic scale

C. Valot

**Commissariat à l'énergie atomique (CEA)
Nuclear Energy Division
Fuel Study Department**

Cadarache, France

Outline



Experiments for improving Nuclear Fuel Models and Performance

Numerical and experimental simulation at the atomic scale

Part 1

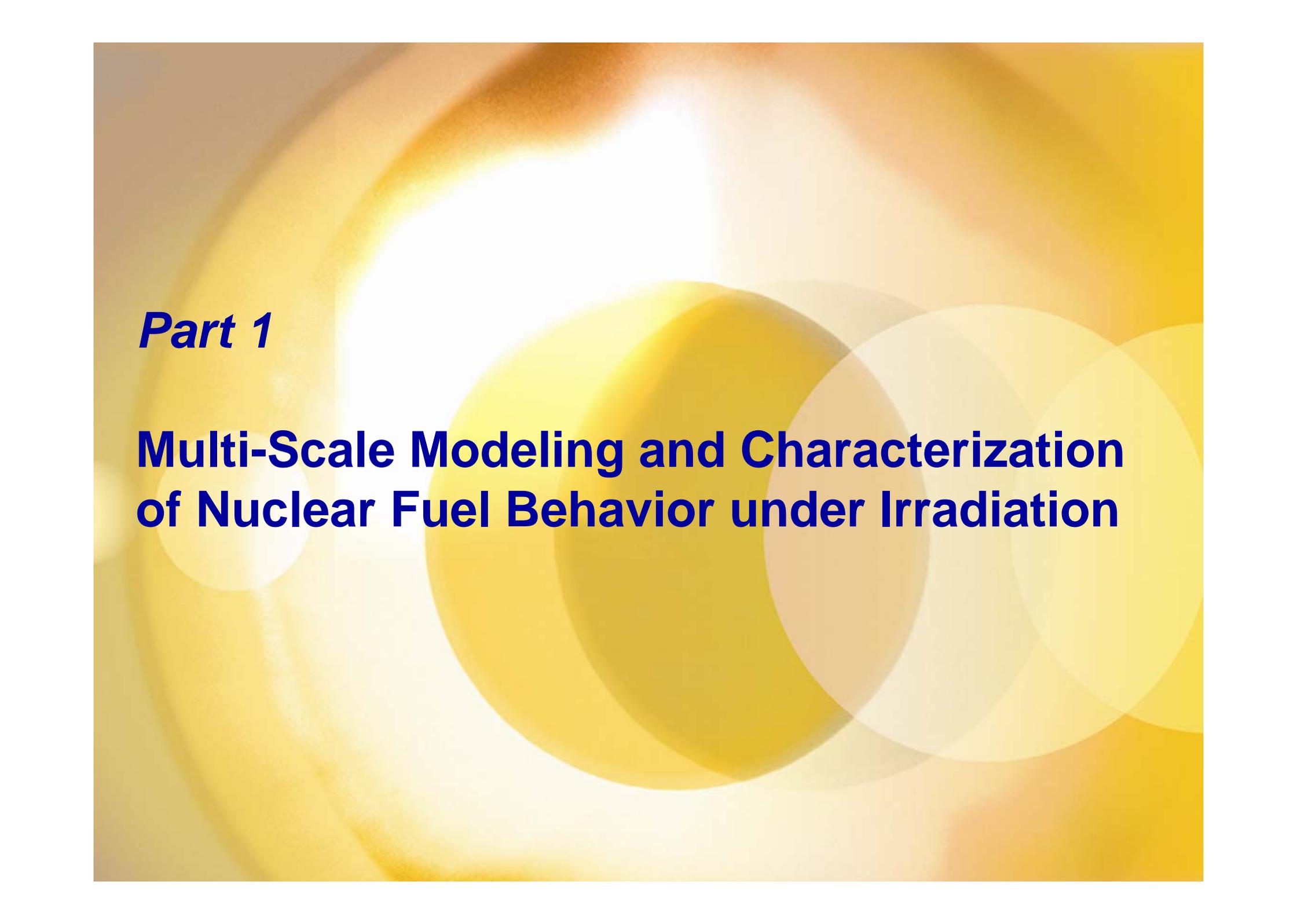
Introduction to multi-scale modeling and characterization of nuclear fuel behavior under irradiation

Part 2

Experimental simulation : separate effect studies approach

Part 3

Numerical simulation : *ab initio* and classical molecular dynamics modeling of nuclear fuels



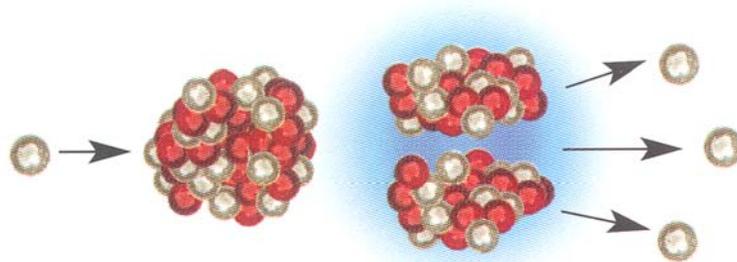
Part 1

**Multi-Scale Modeling and Characterization
of Nuclear Fuel Behavior under Irradiation**

Irradiation damage in nuclear fuels

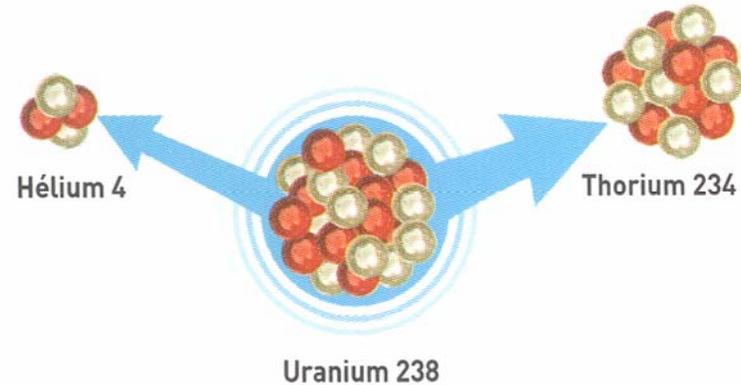


fission



Neutron.

alpha decay



Fission products **Helium**
Volatile elements (Kr, Xe, I...)

Recoil nuclei
→ Collision cascades
Point defects

Dilution ?
Bubble precipitation ?
Swelling ?

Stability ?
Structural changes ?

Nuclear fuels : materials



oxide fuels

(Standard nuclear fuels in PWR)



carbide, nitride fuels



MA containing fuels

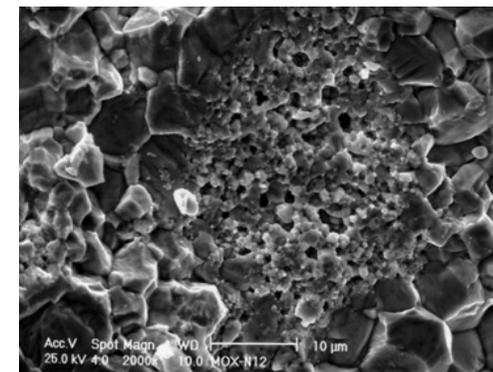
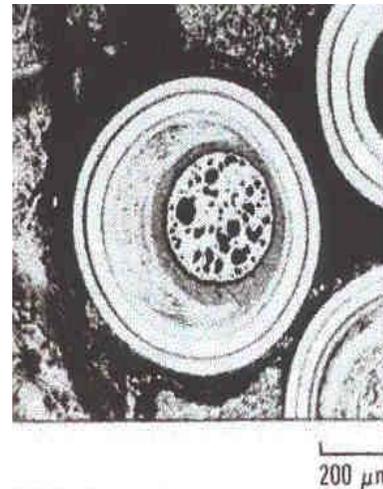
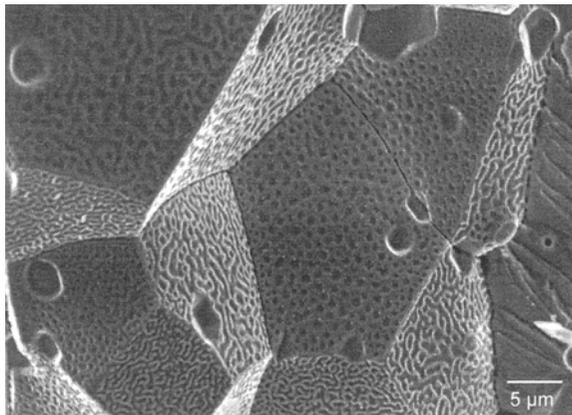
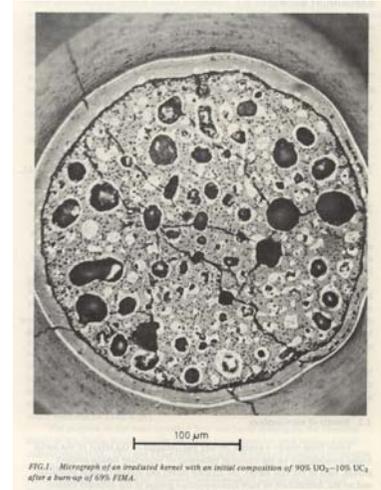
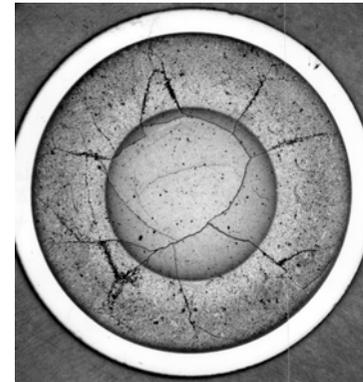
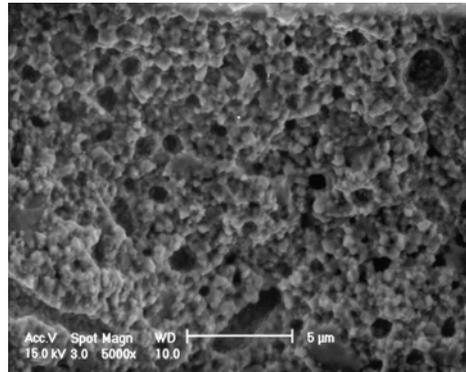


metallic fuels

Fuel under irradiation: a complex behavior

- Fuel under irradiation :

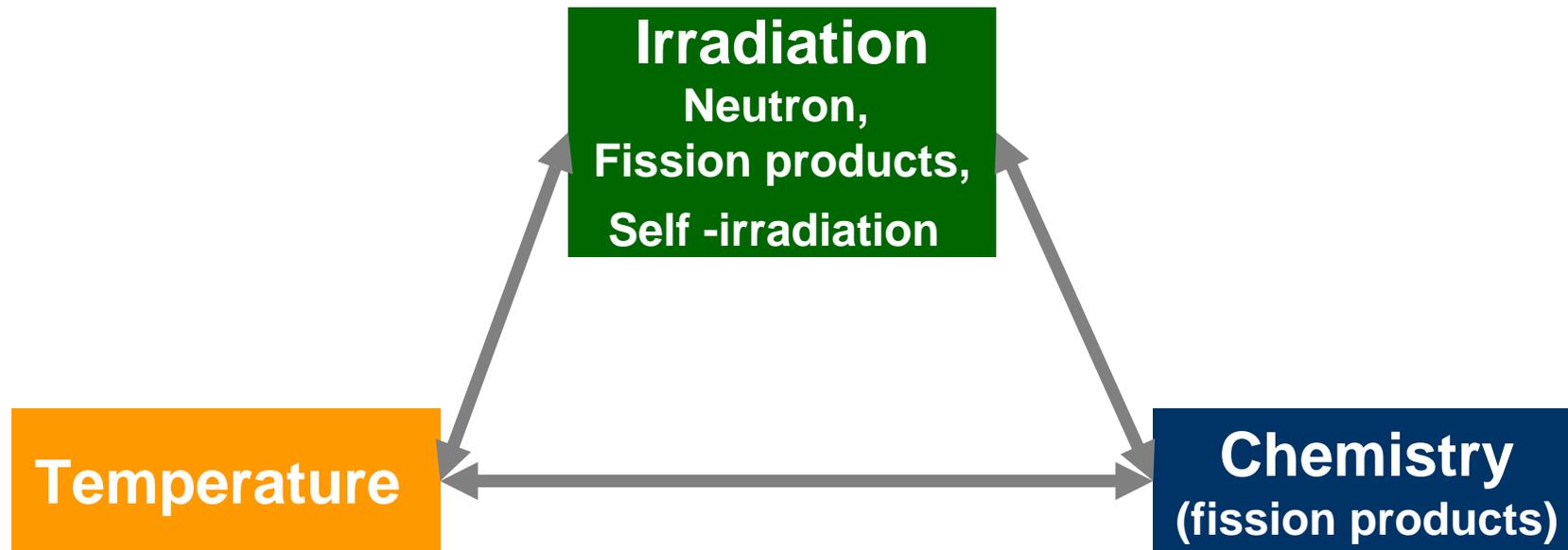
- a very complex behavior, a changing material
- few transformations as illustration !



Fuel under irradiation: a complex behavior



Complex **phenomena** involved
Strong coupling between various effects

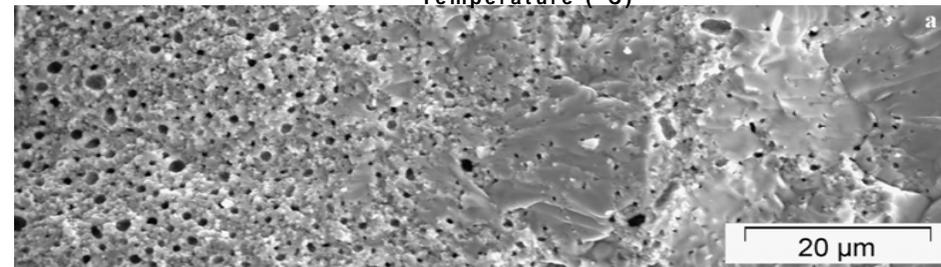
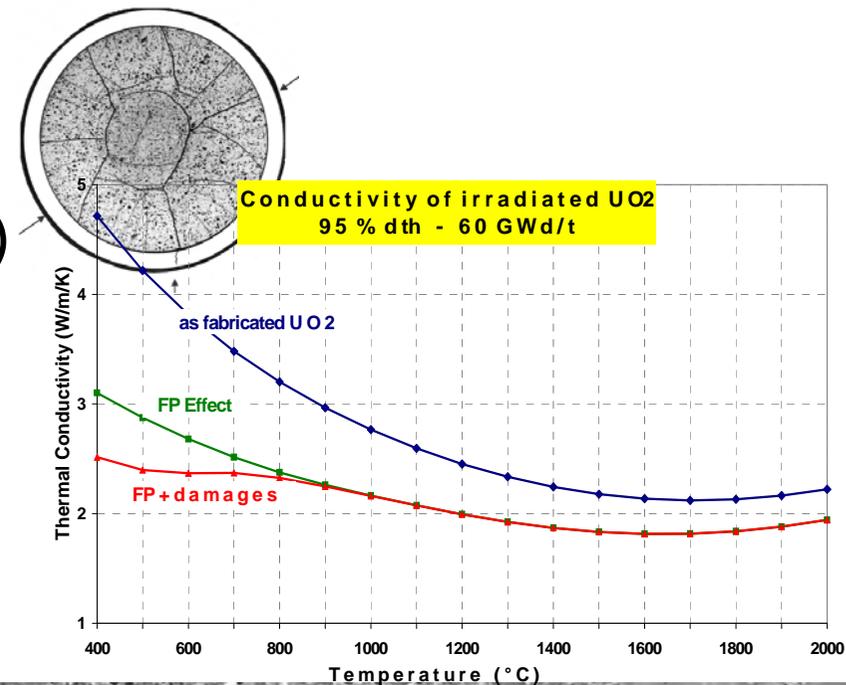


Fuel under irradiation: a complex behavior

- Physical and chemical transformations



- Mechanical changes (cracking)
- Thermal changes (thermal conductivity)
- Structural changes (phase stability)
- Micro-structural changes (defects, HBS structure)
- Species migration
- Formation of fission product compounds...



SEM Fractograph at periphery of a UO₂ pellet (73 GWd/t) J. Noirod 07

Fuel under irradiation: a complex behavior



- Goal : improve our **understanding and our capability to predict** the fuel behavior
 - Need to **de-correlate** the complex **phenomena** involved
 - deeper description of phenomena : **towards the atomistic level**

Coupling between :

- Post irradiation examinations (PIE) after power plant irradiations or specific MTR irradiations
- Separated effect studies
- Modeling and characterization at the relevant scale.

Multi-scale modeling and characterization to understand the fuel behavior



Experimental simulation
Separate effect studies

Cartographie en μ -NRA Microscopie optique

Ga10C2CorrHe. 10 μ m / 14.0

Post irradiation examinations

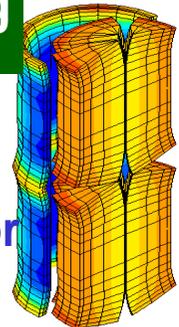
Multi-scale characterization

Multi-scale modeling

Behavior of current and future fuels Materials under irradiation

understanding

Simulation - validation for the prediction of the in-pile fuel behavior



Multi-scale and multi-physics modeling of nuclear fuel behavior

Macroscopic scale

• 1 : Modeling of fuel behavior

Microscopic scale

• 2 : Thermo-mechanical behavior law of nuclear fuels

• 3 : Modeling of fission gas behavior

• 4 : Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

Atomic scale

Dislocations dynamics

DM KMC

ab initio

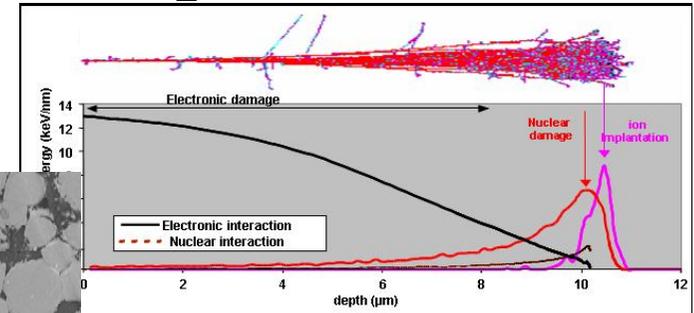
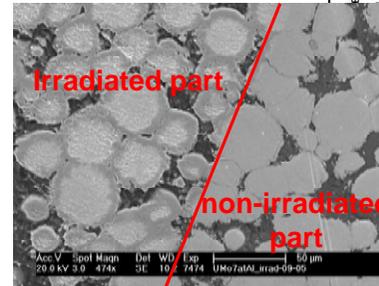
Meeting CEA - DOI March 20 - 21 2007 8

- Improve performance of current fuels
- Design future fuels

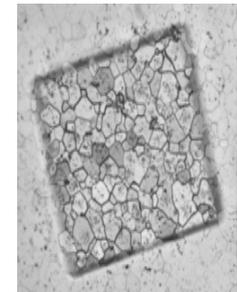
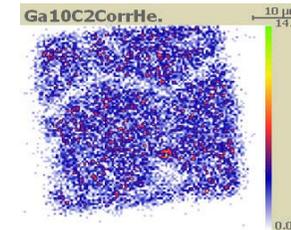
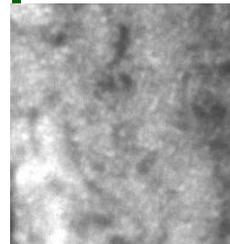
Separated effects studies : the approach



- Non active model materials such as UO_2
- Ion **implantation** to simulate FP
- **Thermal treatment** or heavy ion **irradiation**



- **Characterization with a large panel of dedicated techniques** (SIMS, RBS, NRA, TEM)

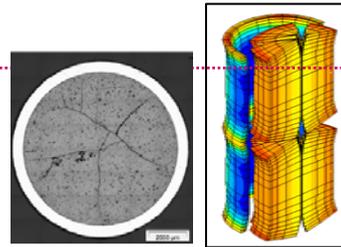


- **Large scientific facilities** (particle accelerators and synchrotron radiation)

Multi-scale modeling of nuclear fuel behavior



Macroscopic scale

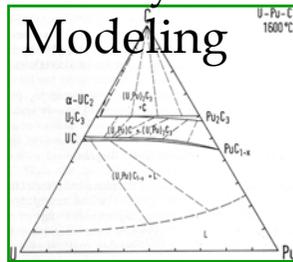


Pellet

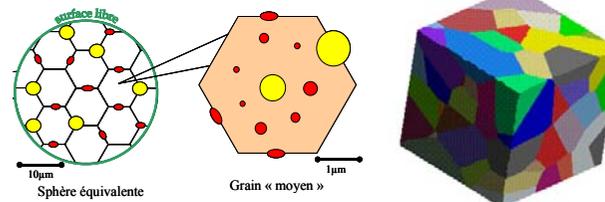
- Modeling of fuel behavior

Microscopic scale

- Thermodynamics



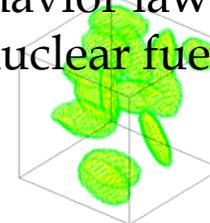
- Modeling of fission gas behavior



10µm
Sphère équivalente

1µm
Grain « moyen »

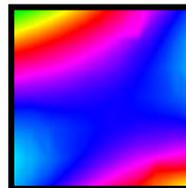
- Thermo-mechanical behavior laws of nuclear fuels



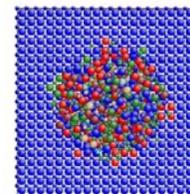
Atomic scale

- Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

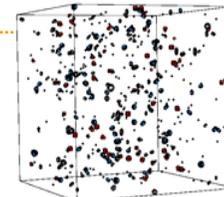
ab initio



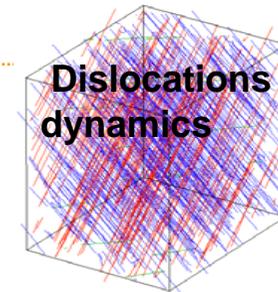
DM



KMC



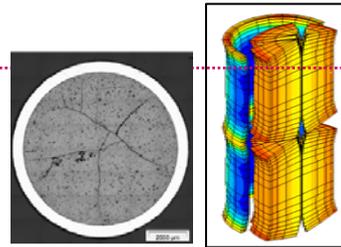
Dislocations dynamics



Multi-scale modeling of nuclear fuel behavior



Macroscopic scale

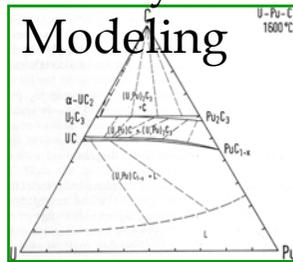


Pellet

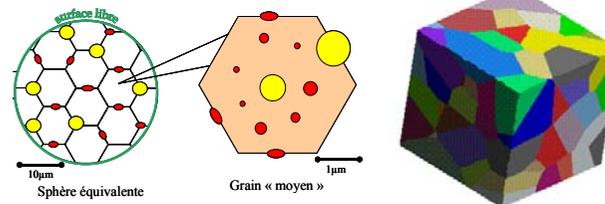
• Modeling of fuel behavior

Microscopic scale

- Thermodynamics



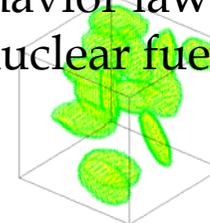
- Modeling of fission gas behavior



10µm
Sphère équivalente

1µm
Grain « moyen »

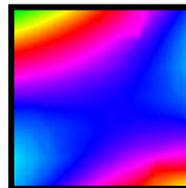
- Thermo-mechanical behavior laws of nuclear fuels



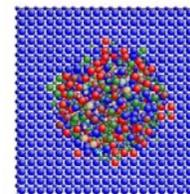
Atomic scale

- Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

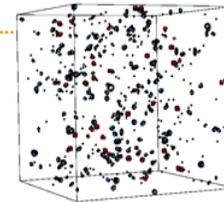
ab initio



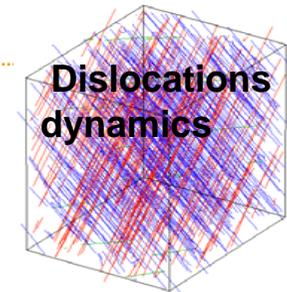
DM



KMC



Dislocations dynamics

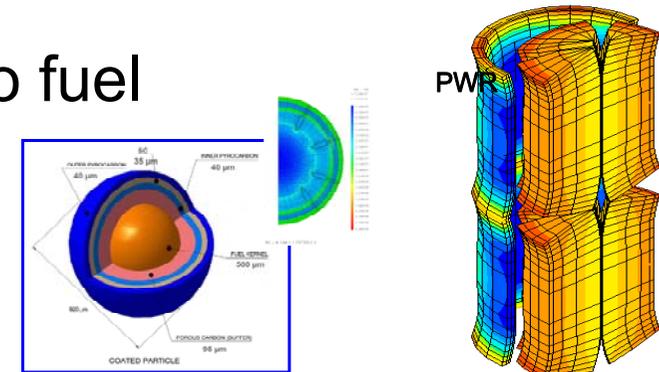


PLEIADES: An Advanced Fuel Performance Code

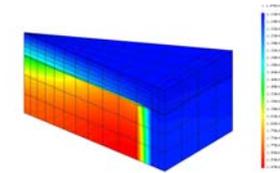
• Multi Reactor Simulation Platform for
Fuel Performance Modeling at CEA



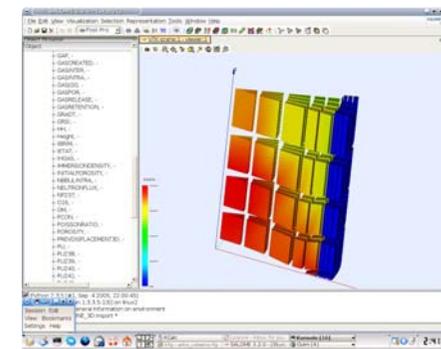
• software environment dedicated to fuel behavior modeling including all fuel types and reactor concepts



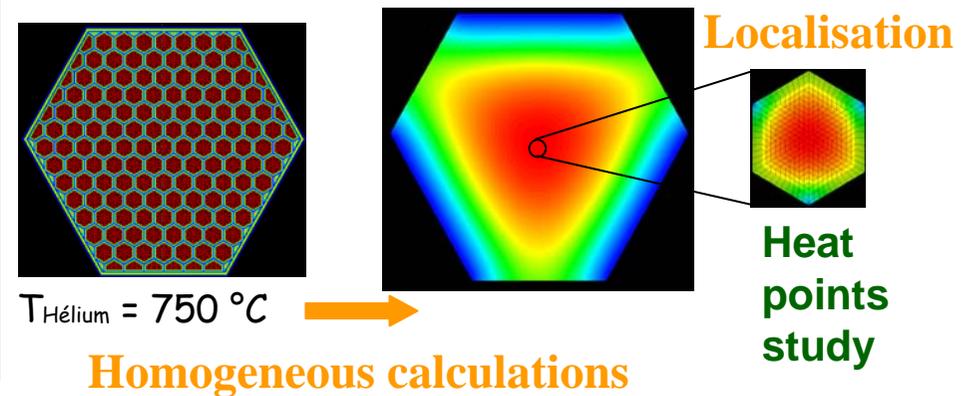
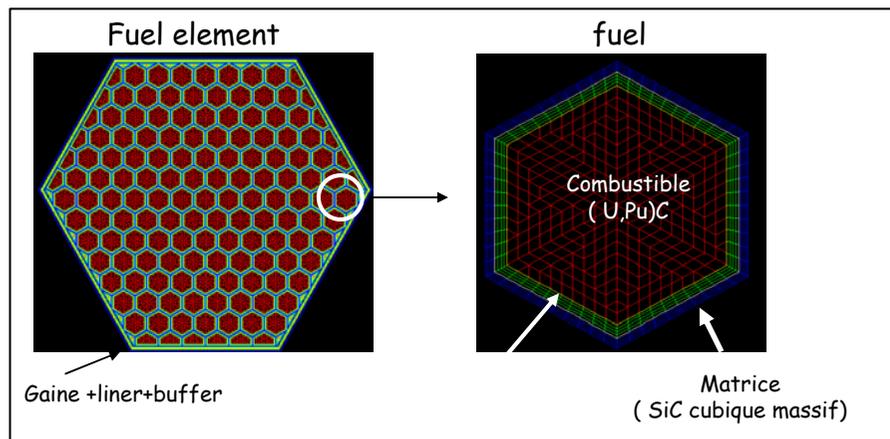
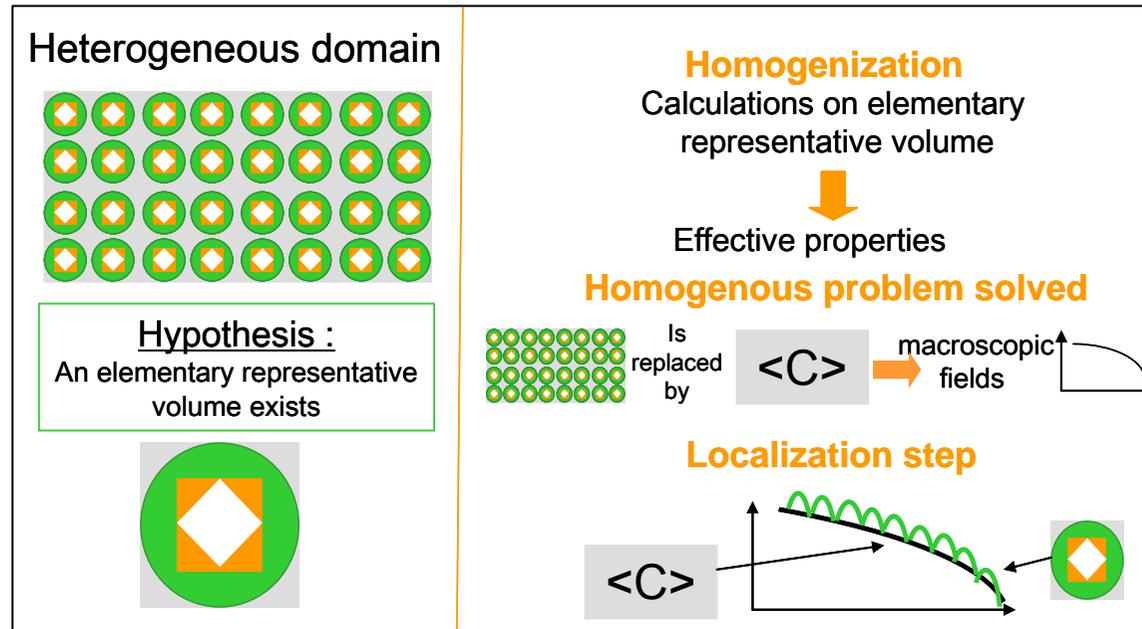
• set of applications for each reactor concept (**SFR, HTR, GFR, MTR**) adapted to the needs of “user” projects and integrating their modeling (industrial as well as research applications)



• capitalization within the same software environment



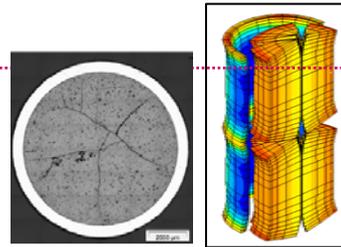
Thermo-mechanical laws : Homogenization/localization techniques



Multi-scale modeling of nuclear fuel behavior



Macroscopic scale

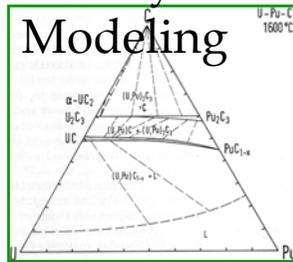


Pellet

- Modeling of fuel behavior

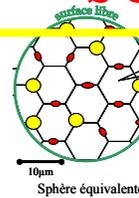
Microscopic scale

- Thermodynamics

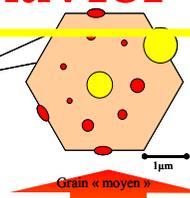


Modeling of fission gas behavior

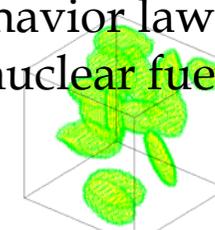
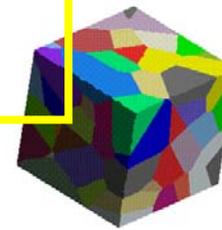
- Thermo-mechanical behavior laws of nuclear fuels



10µm
Sphère équivalente



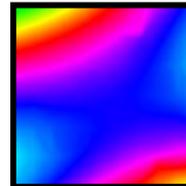
1µm
Grain « moyen »



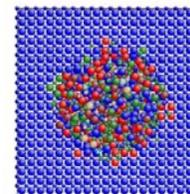
Atomic scale

- Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

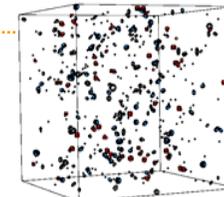
ab initio



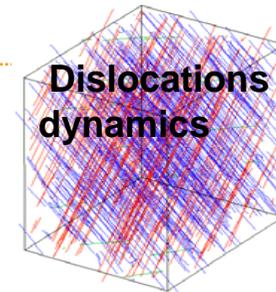
DM



KMC



Dislocations dynamics



Fission gas behavior in PWR fuel: diffusion models

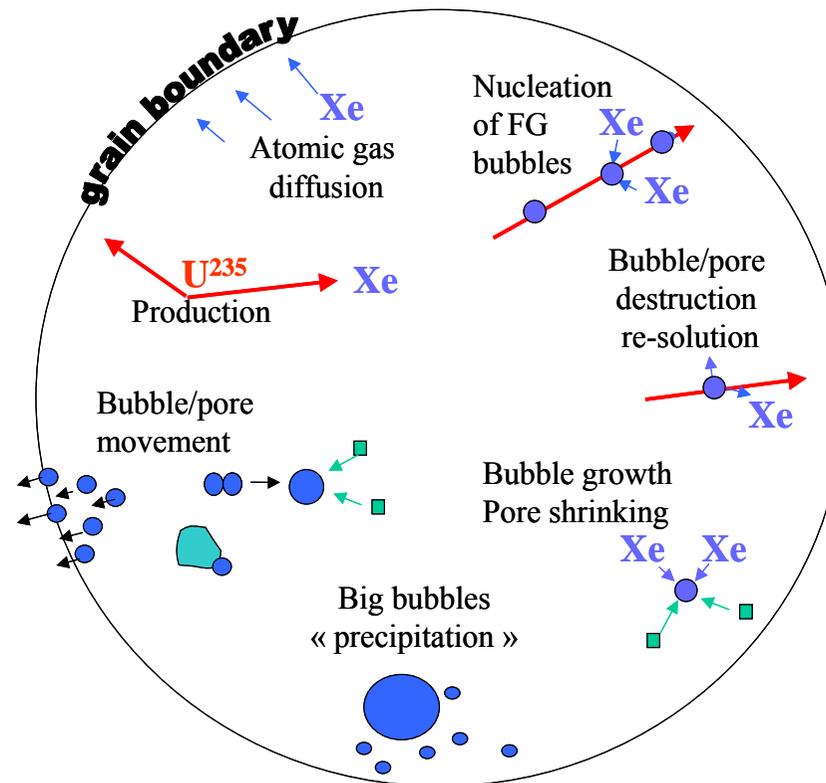


- **Intragranular phenomena**

Modeling of an average grain

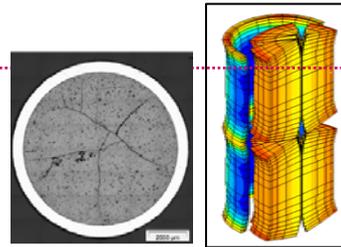
- **Intergranular phenomena**

- Use of an equivalent sphere defined by a free surface / crack



Multi-scale modeling of nuclear fuel behavior

Macroscopic scale

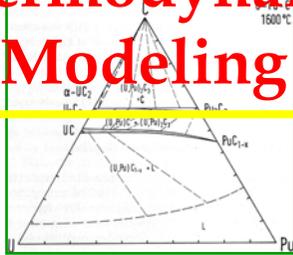


Pellet

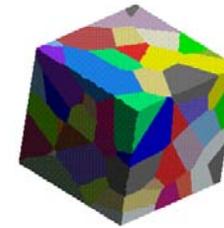
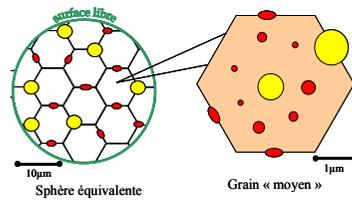
- Modeling of fuel behavior

Microscopic scale

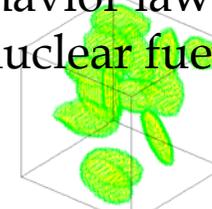
• **Thermodynamics Modeling**



- Modeling of fission gas behavior



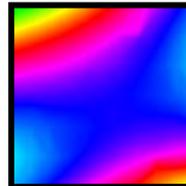
- Thermo-mechanical behavior laws of nuclear fuels



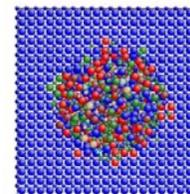
Atomic scale

- Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

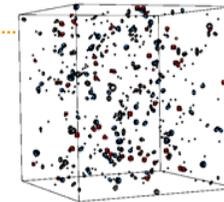
ab initio



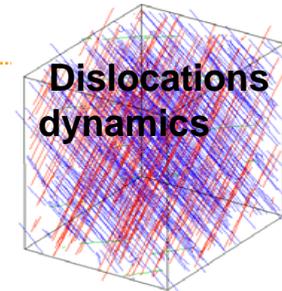
DM



KMC



Dislocations dynamics



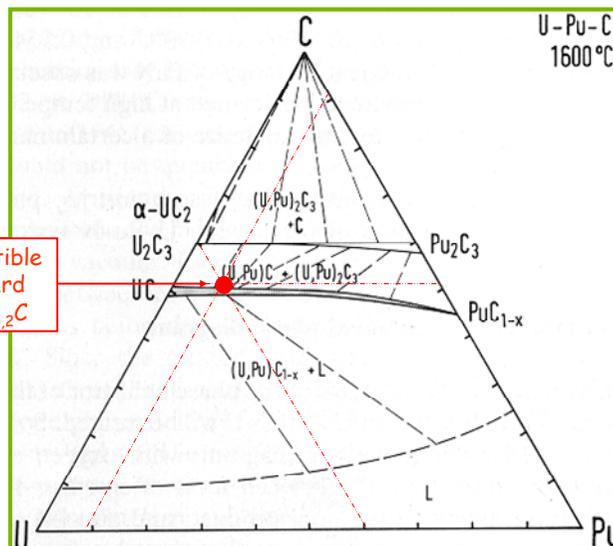
Thermodynamics fuel modeling

• Thermal and chemical stability of fuels

- Phase diagrams of future fuel systems (U, Pu, O, C, N)
- Impact of minor actinides

• Chemical interaction of fuel with environment

- Cladding, coolant, air, water



• Thermodynamics on irradiated fuels

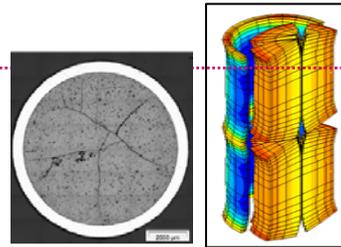
- Impact of FP, FP compounds

• Construction of a “Fuel data base” for future fuels

Multi-scale modeling of nuclear fuel behavior



Macroscopic scale

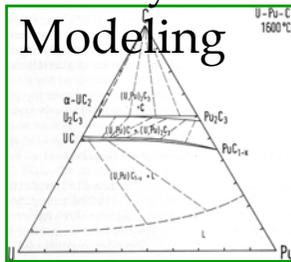


Pellet

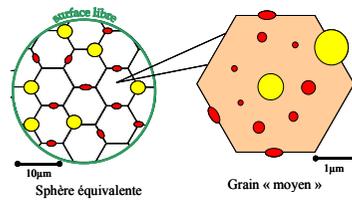
- Modeling of fuel behavior

Microscopic scale

- Thermodynamics

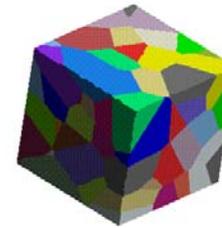


- Modeling of fission gas behavior

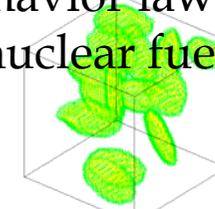


Sphère équivalente

Grain « moyen »



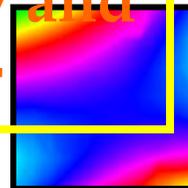
- Thermo-mechanical behavior laws of nuclear fuels



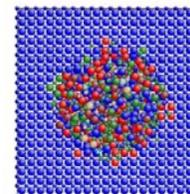
Atomic scale

- Atomistic modeling of nuclear fuels: structure, defect stability and fission gas behavior

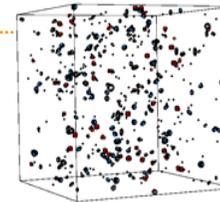
ab initio



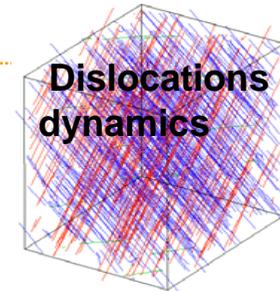
DM



KMC



Dislocations dynamics



Ab initio modeling of nuclear fuel



Determine and understand physical and chemical properties of fuels at the atomic scale

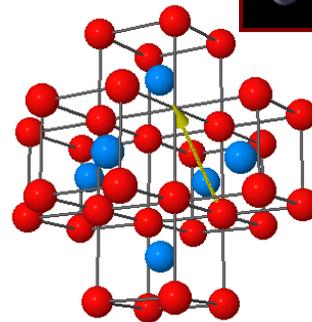
Decouple basic processes

- Stability of a given type of point defect
- Localization of a given fission product
- Migration mechanism of a chemical element

Understanding of the mechanisms involved

Quantify phenomena

- Formation energy of defects
- Incorporation energy of a chemical element
- Structural modification (*swelling*)
- Solubility (*solution energy*)
- Migration (*migration energy*)



Jmol

Provide basic data
→ Models at microscopic scale

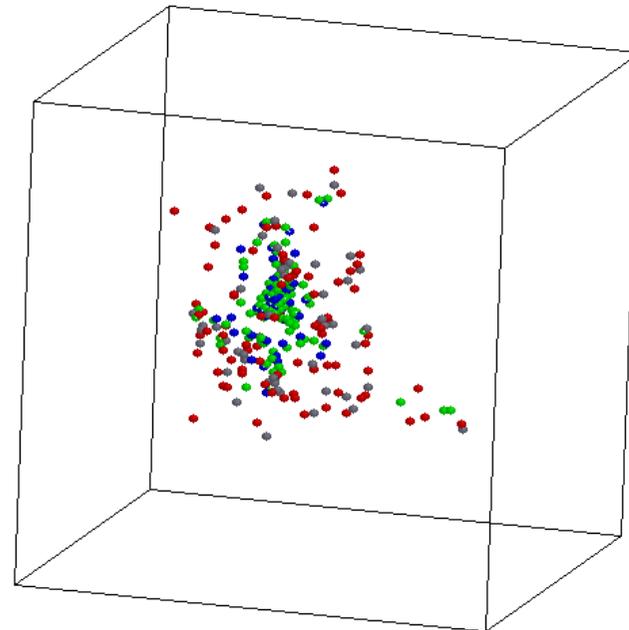
Modeling of irradiation effects using classical Molecular Dynamics



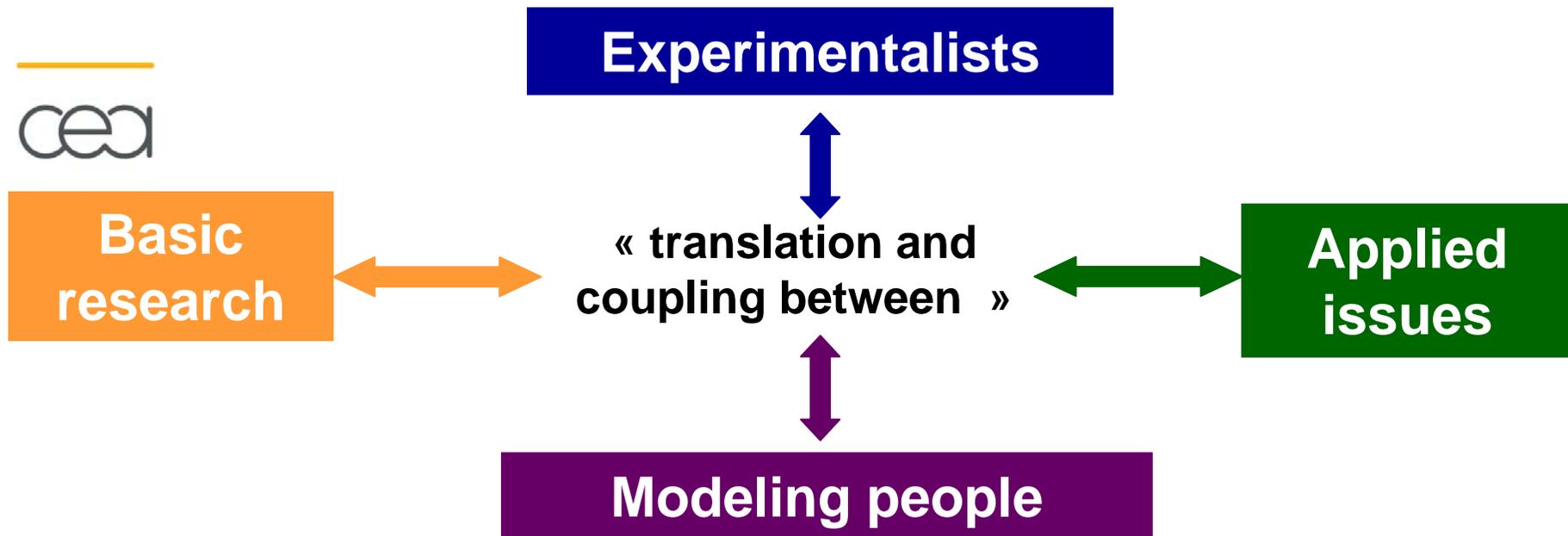
Irradiation effects : Displacement cascades in UO₂ :

- Concentration of free point defects produced
- Recombining/Clustering of defects: nature, size, number
- Fission product: segregation

- Uranium interstitial
- Oxygen interstitial
- Oxygen vacancy
- Uranium vacancy



Translation language to connect various communities

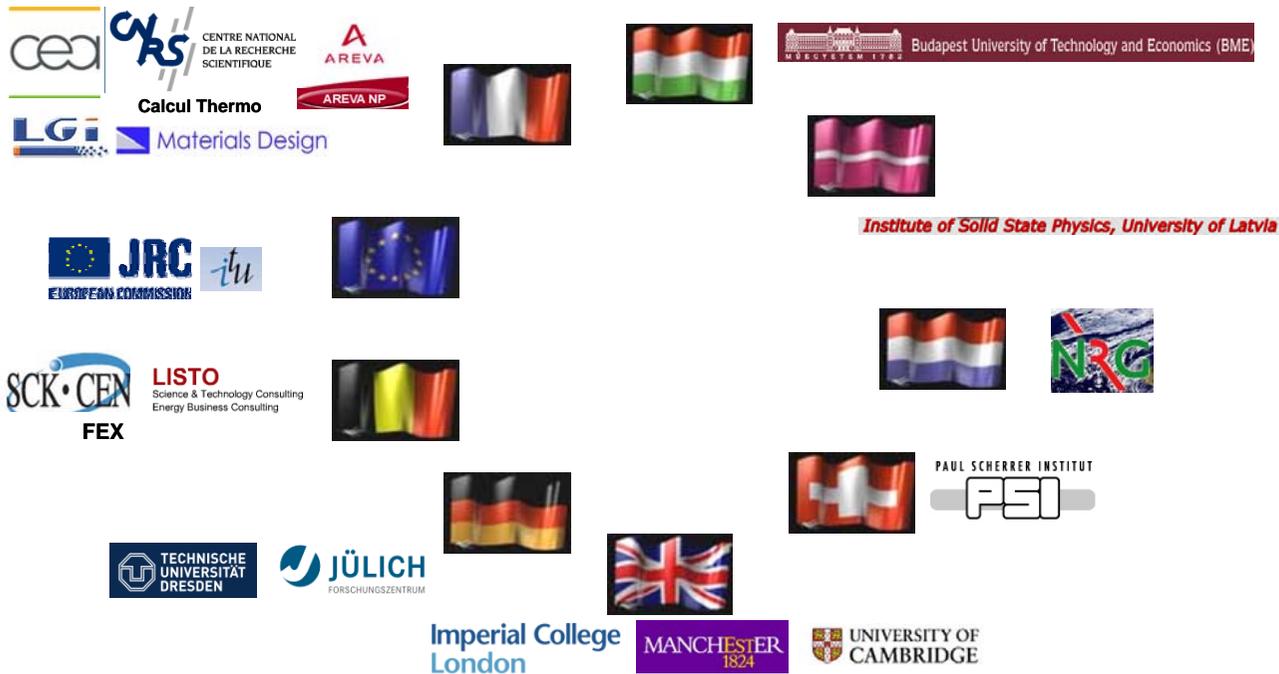


- Look out of your box: Back, Front, up, down and around! (S. De Groot)
- Instead of asking you what your theoretician can do for you, ask what you can do for your theoretician...(B. Schimmelpfennig from the Actinet Theoretical Userlab)!
- Instead of asking you what your experimentalist can do for you, ask what you can do for your experimentalist!

A European initiative : the F-BRIDGE project



Basic Research in support of Innovative Fuels Design for the GEn IV systems



F-BRIDGE European project



Framework



- Framework of the **Euratom Work programme (FP7)**

- **Area: Advanced Nuclear Systems**
 - improve **efficiency of present systems and fuels**
 - investigate **advanced systems and fuel** in collaboration with efforts of GEN IV, **especially upstream research** (material science, study of fuel cycle and innovative fuels)

- **Topic: Fission -2007-2.2.1: Innovative fuels and claddings for generation IV systems**
 - Development and qualification of innovative fuels and claddings
 - Impact: increase efficiency of EU research support to GIF
 - Focusing on cross-cutting and generic issues

F-BRIDGE European project



The needs



- International effort to **increase efficiency in designing innovative fuels** to improve present fuel-cladding systems, to design those for tomorrow
- Up to now fuel development and qualification: successful but long and expensive process essentially based on an **empirical approach**
- Innovative fuel systems: empirical approach **has reached its limit** / difficult to extrapolate to new materials, new environments, or new operating conditions
- **Basic underlying mechanisms** governing manufacturing, behaviour and performance remain poorly understood
- **Challenge** for the next years: complement the empirical approach by a **physically based description** of ceramic fuel and cladding materials

F-BRIDGE European project



Objective : to build a bridge



Integration and Transfer

Basic Research
Activities
on fuel systems

Technological
Issues of the Gen IV
Ceramic Fuel Systems

Improvement of a
promising Composite
Ceramics Concept:
the *Sphere-pac Fuel*

Direct impact and feedback
on generation IV ceramic fuel
systems:

- Fuel design
- Fuel manufacturing
- Irradiation experiments design
- Prediction of the in-pile behavior

F-BRIDGE European project



Beyond the state of the art



■ **Novel approach:** brings together numerous significant actors of the nuclear fuel field: scientists, engineers and end-users

■ **A special team:** shall ensure a direct translation of technological issues into basic research investigations, as well as a facilitated transfer of the knowledge acquired to fuel performance codes, design and manufacturing.

■ **First integrated project on non-metallic nuclear fuels and cladding**

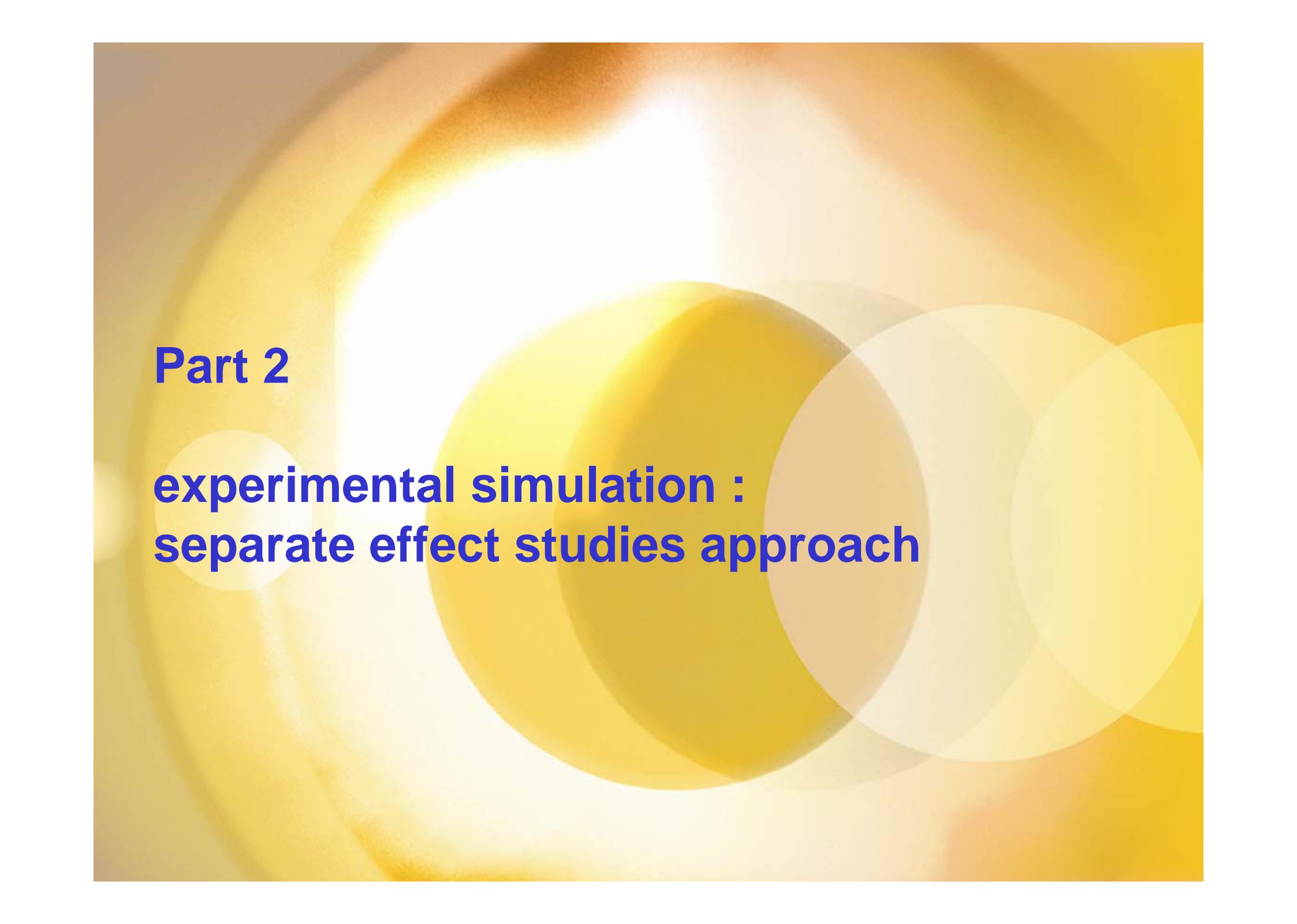
- All relevant length and time scales from the atomic description to macroscopic systems
- Investigation of important properties of fuel and ceramic cladding materials using a combination of modelling and experiments

■ **Main contribution :** to capitalise on recent advances in both theoretical approaches and experimental techniques to develop fuel behaviour descriptions that have a much sounder physical basis

Part 1 conclusions



- A real need to effectively connect experiment and modelling to improve the knowledge on fuel behaviour under irradiation and design the fuels of tomorrow
- Fuel studies are ongoing to achieve a much deeper understanding description using finer characterization as well as modelling down to the atomic level
- Experiment and modeling have to be coupled and to feed each other
- Experiments need modeling and vice versa



Part 2

**experimental simulation :
separate effect studies approach**

Objectives of the separate effect studies



- **To model and to understand nuclear fuel behavior under irradiation** as well as under long term storage conditions

- Volatile fission products I/Xe/Kr/Cs + He
- Transport properties
- Irradiation effects

- **Direct support to modeling**

- Guide: mechanism understanding
- Basic data to be used in the models

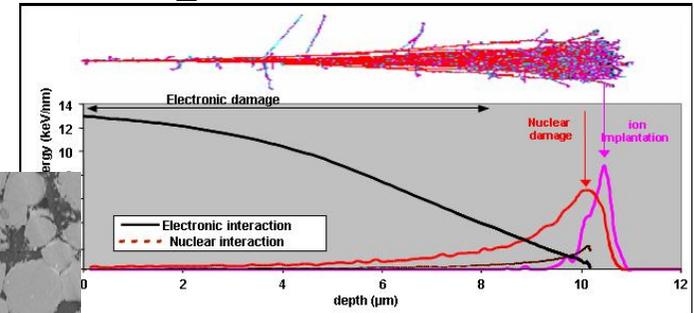
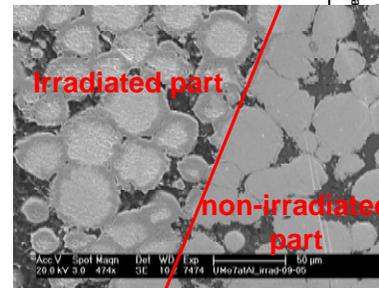
- **Experimental and theoretical methodologies developed for application to a large panel of materials**

- Oxides (UO₂ and MOX)
- Carbide (UC-UPuC...)

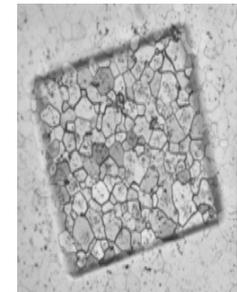
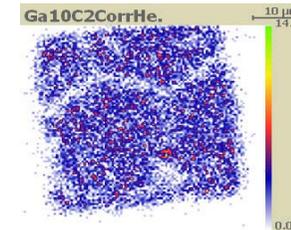
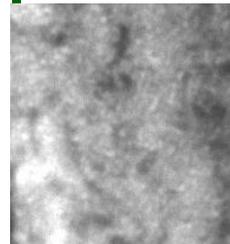
Separated effects studies : the approach



- Non active model materials such as UO_2
- Ion **implantation** to simulate FP
- **Thermal treatment** or heavy ion **irradiation**



- **Characterization with a large panel of dedicated techniques** (SIMS, RBS, NRA, TEM)



- **Large scientific facilities** (particles accelerators and synchrotron radiation)

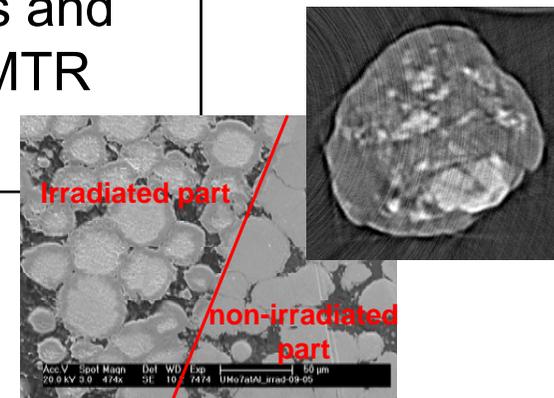
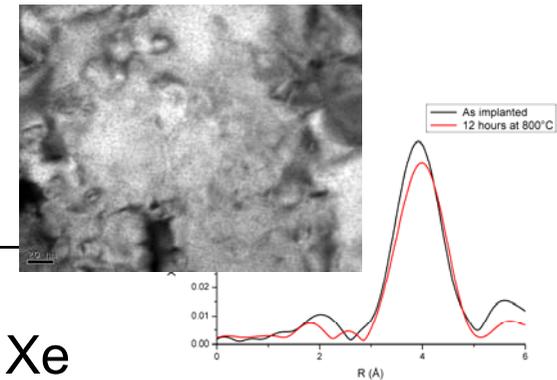
Separated effects studies : illustrations



Objective

Studies

1	Understand and model fission gas diffusion/precipitation/release in nuclear oxide fuels	XAS and TEM characterization of Xe bubbles in uranium dioxide
2	Support UMo fuel development beside in reactor irradiation testing	Synchrotron studies and ion irradiations of MTR UMo fuel



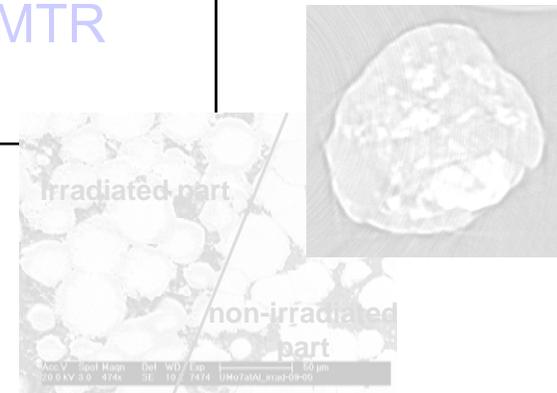
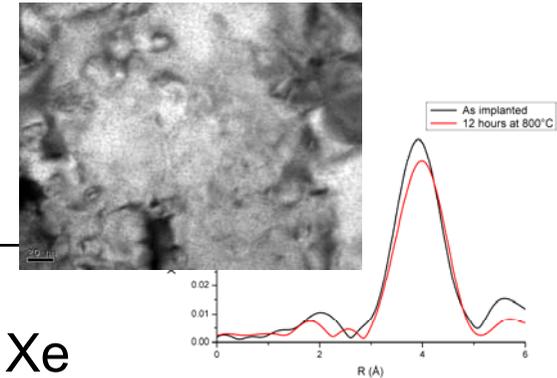
Separated effects studies : illustrations



Objective

Studies

1	Understand and model fission gas diffusion/precipitation/release in nuclear oxide fuels	XAS and TEM characterization of Xe bubbles in uranium dioxide
2	Support UMo fuel development beside in reactor irradiation testing	Synchrotron studies and ion irradiations of MTR UMo fuel



XAS and TEM characterization of Xe bubbles in UO₂



Issue : Understand and model Xe release in nuclear oxide fuels

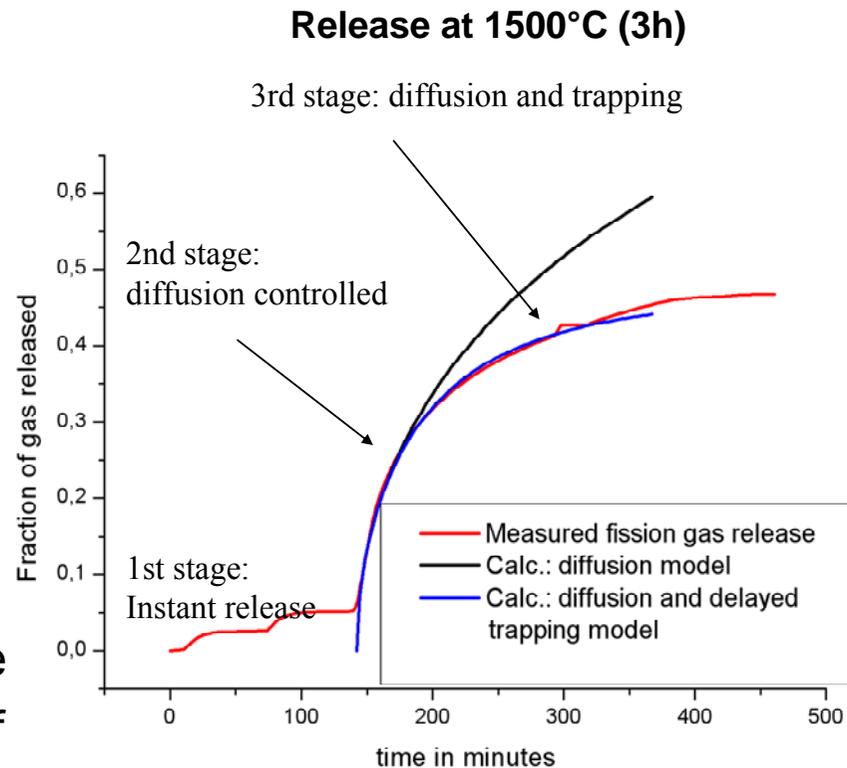
- Rare gases are highly insoluble in most materials
- Therefore predicting rare gas transport requires:
 - * understanding precipitation mechanisms
 - * rare gas bubble characteristics
 - * diffusion of gas atom in presence of bubbles
- Two analytical tools are very powerful when coupled :
Transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS)

XAS and TEM characterization of Xe bubbles in UO₂



Understanding of thermally activated phenomena : post-irradiation annealing on irradiated fuel

- High temperature (>~1300°C) anneals of irradiated material
- At a given temperature, three stages generally identified (*Valin, Portier, PhD theses 1999-2005*)
 - (1) instantaneous release: gas accumulated at grain boundaries
 - (2) diffusion controlled release
 - (3) fractional release levels off



**Trapping efficiency?
Characteristic of bubbles?**

XAS and TEM characterization of Xe bubbles in UO₂



What information can we get from in situ transmission electron microscopy (TEM)?

- Defect accumulation/annealing
- Threshold temperature for bubble precipitation
- Bubble size distribution
- Electronic excitation effects: bubble nucleation and fission gas re-solution

Methodology

- *In situ* TEM experiments carried out in Orsay: IRMA (now JANNUS beam line)
- 390keV Xe implanted UO₂ thin foils (Rp~60nm)
- Samples are observed at increasing doses and annealed for approx. 20min. at various temperatures

XAS and TEM characterization of Xe bubbles in UO₂

Xe bubble precipitation: main results of TEM study



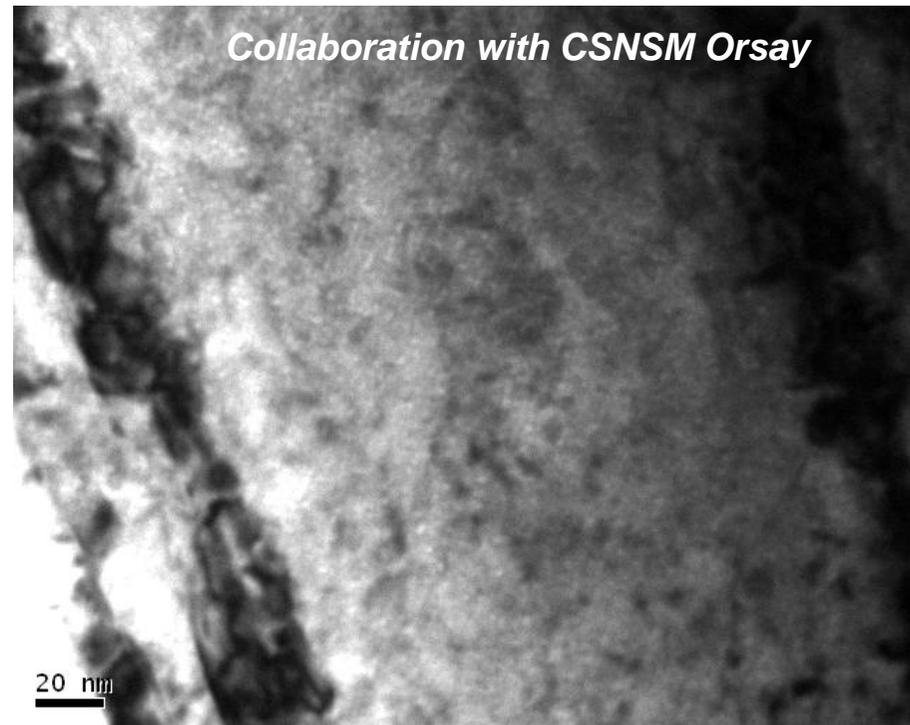
[Xe]	2.10 ¹⁵ Xe/cm ² (0.4 at.%)	10 ¹⁶ Xe/cm ² (2 at.%)
T _{thresh.}	600°C	400°C
Size (nm)	~ 1	2

$$T_{\text{thres.}} = f(C_{\text{Xe}})$$

⇒ defect concentrations

Annealing conditions	400°C ~ 20 min	600°C ~ 20 min
Bubble density (b/m ³)	3.0 10 ²³ ±10 ²³	4.0 10 ²³ ±10 ²³
Bubble size (nm)	2 ± 0.3 nm	2 ± 0.3

TEM observations on 2 at.% sample annealed at 600°C for 20 minutes



Same results obtained on irradiated UO₂ fuel, 49 GWd/Mt (0.5 at%), T~600°C [Nogita et al] : 4.3 10²³ b/m³

C. Sabathier et al NIMB Vol 266, Issues 12-13 (2008)

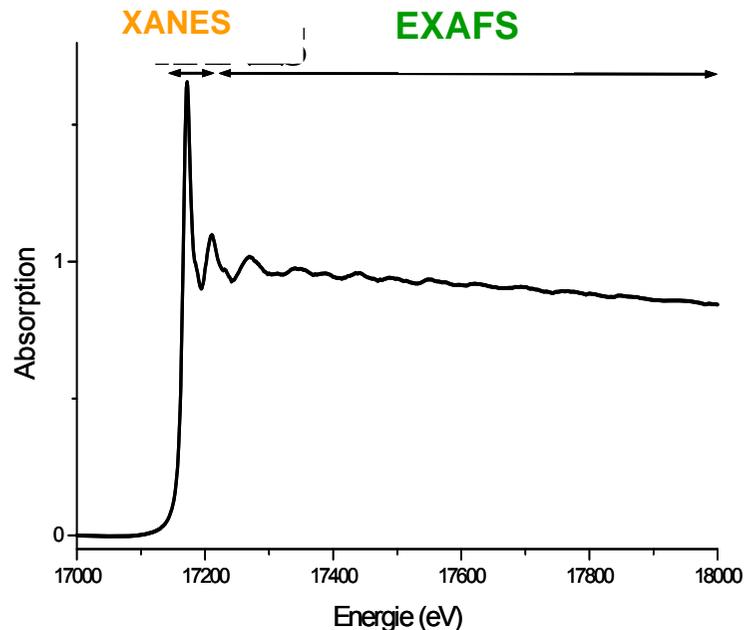
XAS and TEM characterization of Xe bubbles in UO₂



What information can we get from X-ray absorption spectroscopy (XAS)?

Determination of element local environment

EXAFS & XANES



*Extended X-ray Absorption
Fine Structure*

- Inter-atomic distances
- Number of nearest neighbours
- Thermal agitation

**Complete description of
local environment**

*X-ray Absorption
Near Edge Structure*

- Oxidation state
- Local symmetry

1° RG-RG distance

XAS and TEM characterization of Xe bubbles in UO₂



XAS sample preparation

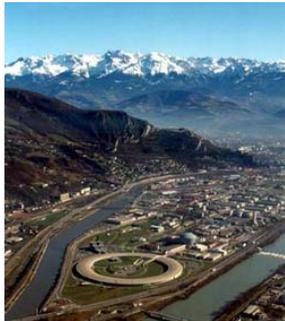
- Polycrystalline UO₂ pellets
- **Ion Xe implantation** Influence of concentration on bubble precipitation
 - Multi-energy ion implantation 2 at.% ($E \leq 800$ keV)
 - Single-energy implantation ~8 at.% max (10^{17} Xe.cm⁻³, $E=800$ keV, ~140 nm)
- **Annealing** for precipitation/stability study of xenon bubbles
 - Annealing between 600°C and 800°C under reducing atmosphere

XAS and TEM characterization of Xe bubbles in UO₂

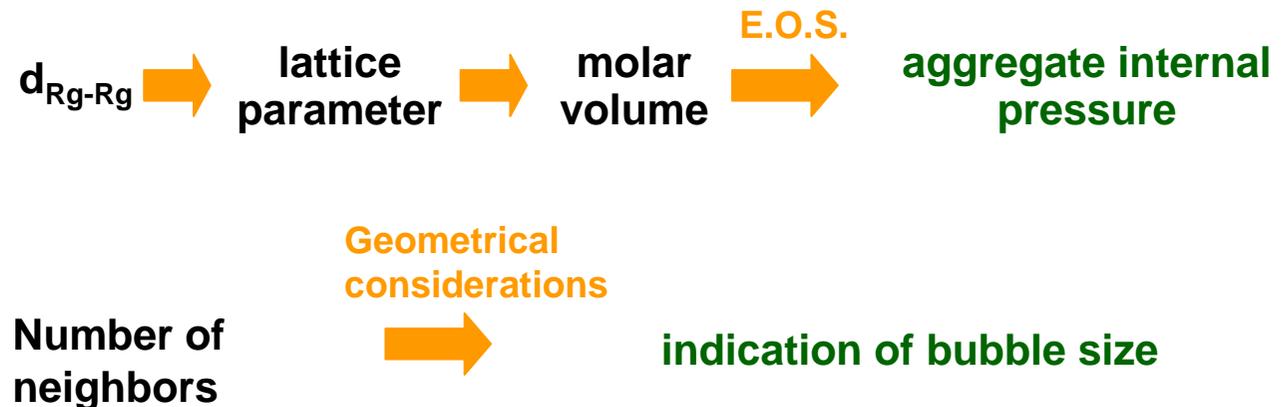


XAS experiment performed and data interpretation methodology

- Probe at the atomic scale, work performed mainly at low T(4-11K)
- Experiments performed on ESRF/FAME (BM30B), at Xe (34,5 keV) & Kr (14,3 keV) K-edges



Information relative to rare gas aggregates



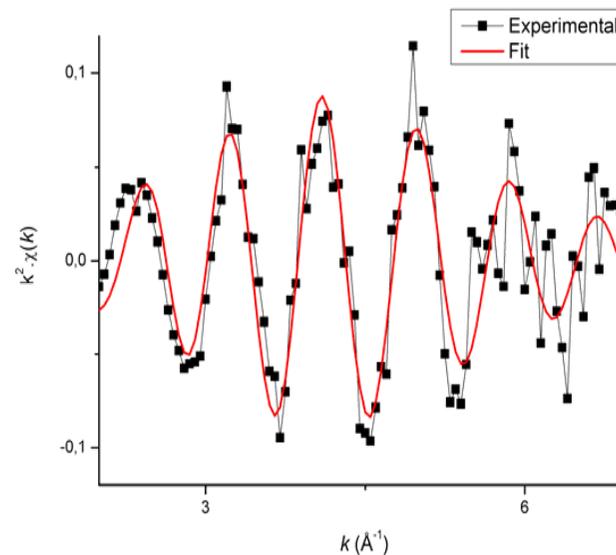
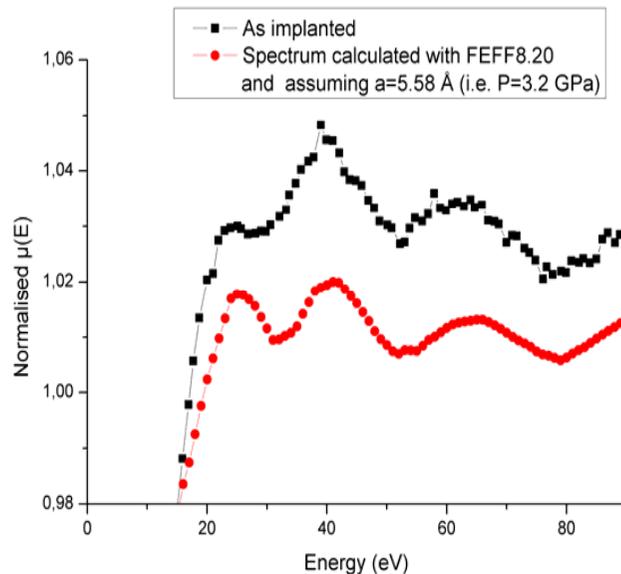
XAS and TEM characterization of Xe bubbles in UO₂

XAS bubble characterization



As implanted samples

- 2 at. % sample : no Xe-Xe bonds, no bubble nucleation / same conclusion using TEM
- 8 at. % sample : bubble nucleation occurs



Only one
Coordination
shell

Xe-Xe distance estimated at $3.97 \pm 0.02 \text{ \AA}$ against 4.39 \AA for un-pressurised crystal

Then using an E.O.S., $P=f(V,T)$ (K. Asaumi, Phys Rev. B 29(1984))

P. Garcia *et al.*, J. Nucl. Mater. **352**, 136 (2006)

P. Martin *et al*/ Nucl. Instrum. and Meth. B 266, 2887-2891(2008)

$P \sim 2,8 \pm 0,3 \text{ GPa}$

Bubble size $\sim 1\text{-}2 \text{ nm}$

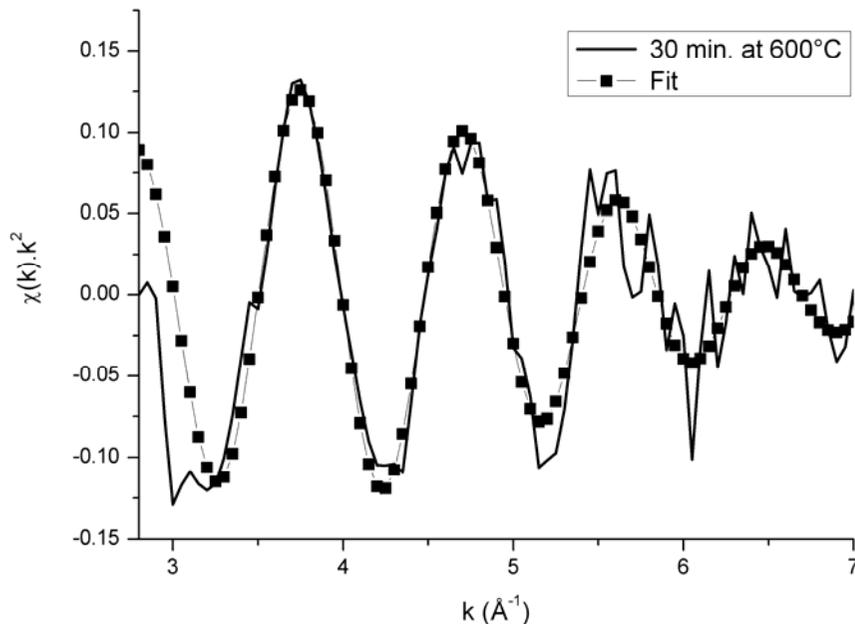
XAS and TEM characterization of Xe bubbles in UO₂

XAS bubble characterization



■ After annealing

■ 2 at.% Xe sample / annealing 600°C 30 minutes



Xe-Xe bonds
bubble nucleation occurs

Same Xe local environment
observed for the 8 at.% as
implanted sample

P ~ 2,8 ± 0,3 GPa,
Bubble size ~ 1-2 nm

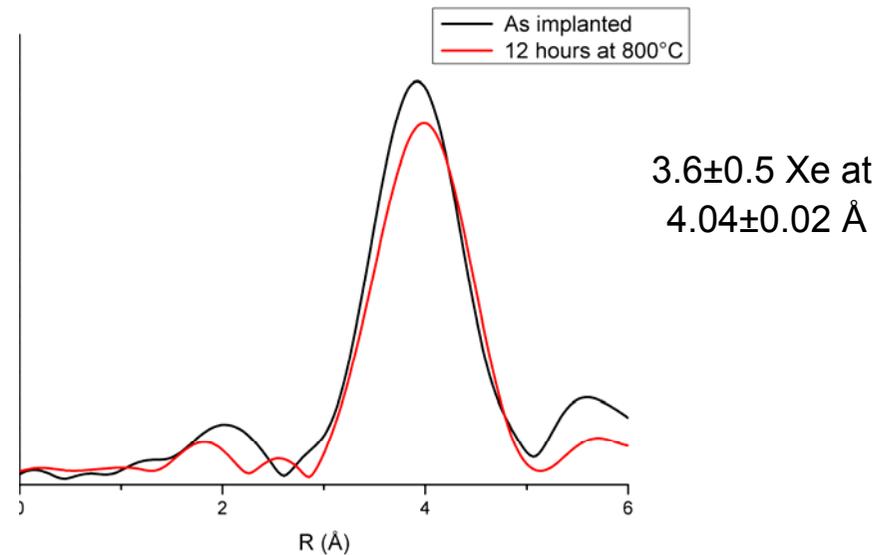
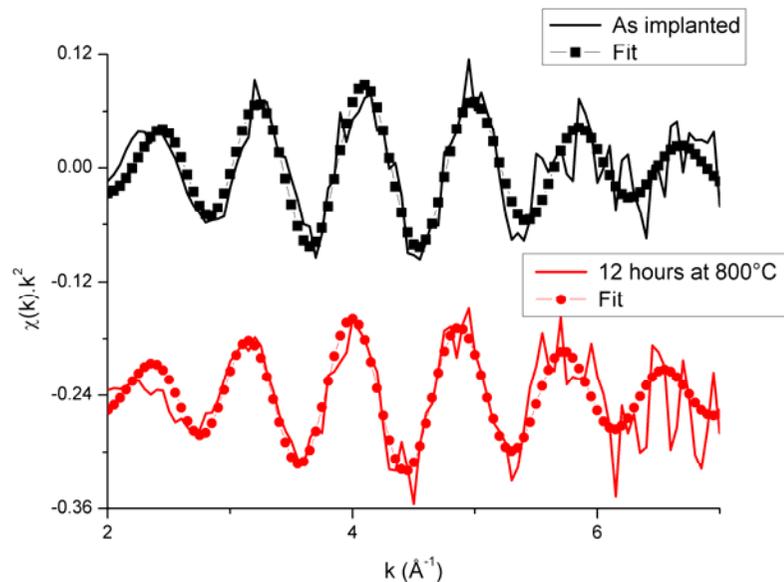
XAS and TEM characterization of Xe bubbles in UO₂

XAS bubble characterization



After annealing

8 at .% Xe sample / annealing 12 hours at 600°C and 800°C



Small increase of Xe-Xe distance : Decrease of aggregate internal pressure **$P \sim 2,0 \pm 0,3 \text{ GPa}$** ,

No variation of N : Xenon bubbles remain small **Bubble size $\sim 1\text{-}2 \text{ nm}$**

With annealing temperature up to 800°C:
xenon aggregates remain small and highly pressurized ($P \sim 2.0 \text{ GPa}$)

XAS and TEM characterization of Xe bubbles in UO₂

Coupling XAS and TEM : very useful to characterize rare gas bubbles

- XAS and TEM are efficient tools for characterising nanometer size bubble distributions
- Temperature and irradiation (in an inelastic or elastic energy loss regime, not presented) induce rare gas nucleation
- Irradiation induced rare gas re-resolution was not observed
- Pressures within nanometer size rare gas aggregates are extremely high
- Provide very important data to be used in the modeling of nuclear fuel behaviour in pile

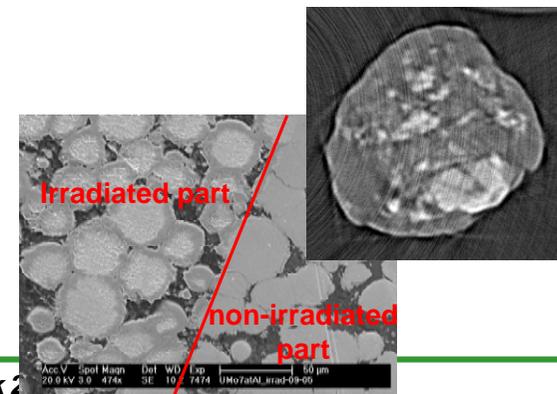
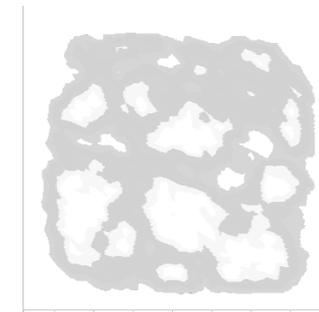
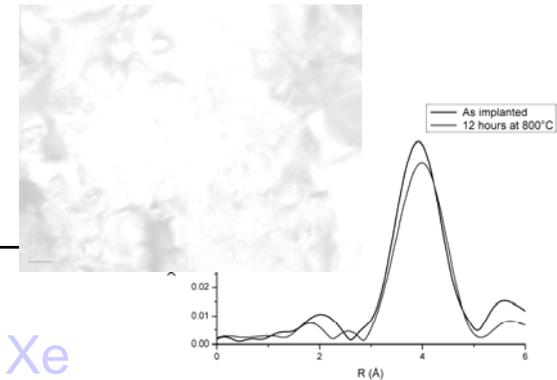
Separated effects studies : illustrations



Objective

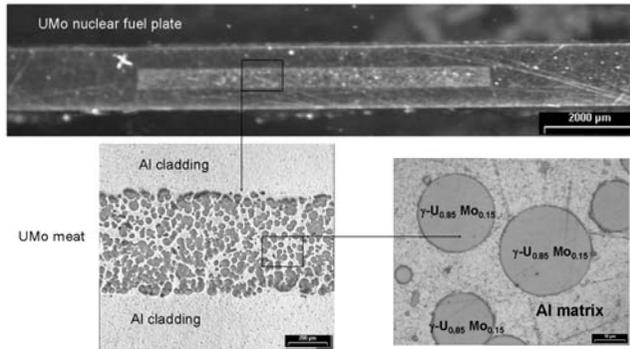
Studies

1	Understand and model fission gas diffusion/precipitation/release in nuclear oxide fuels	XAS and TEM characterization of Xe bubbles in uranium dioxide
2	Support UMo fuel development beside in reactor irradiation testing	Synchrotron studies and ion irradiations of UMo MTR fuel



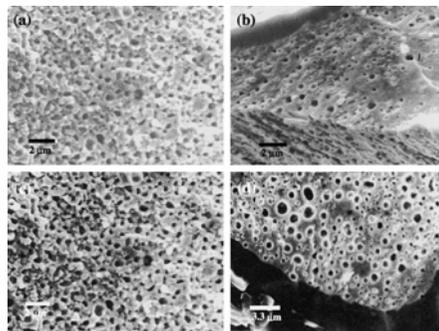
Synchrotron studies and ion irradiations of UMo MTR fuel

Issue : limit UMo/Al interaction



In-pile behaviour

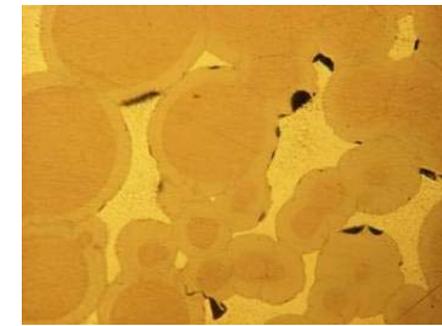
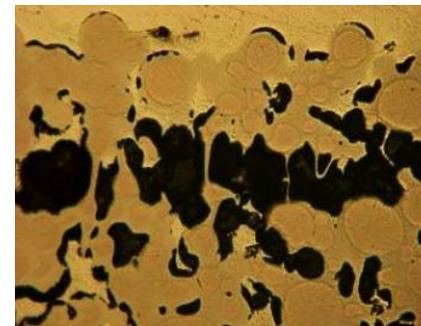
- Very promising for the fissile phase :



Meyer et al., *J. of Nucl. Mat.*, 304, 2002, 221-236.

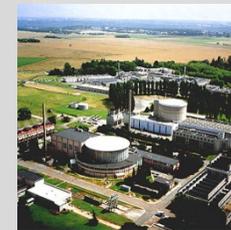
- Problematic at the UMo/Al interface:

An interaction layer has poor gas fission retention properties and is the cause of an unacceptable fuel swelling

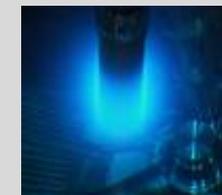


Examples of research reactors

- Material Testing Reactors



- Neutron sources



Synchrotron studies and ion irradiations of UMo MTR fuel



UMo/Al interaction layer grown in-pile under low irradiation temperatures ($T < 200^\circ\text{C}$) and high linear power : **amorphous** (TEM experiment SCK-CEN)

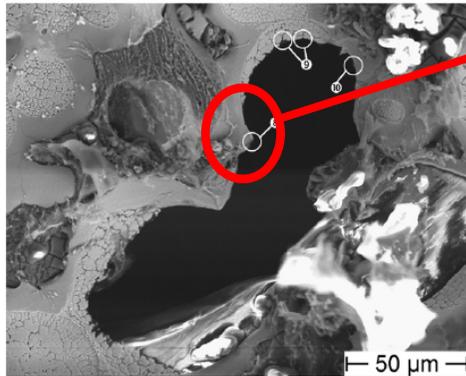


Fig. 1. Scanning electron micrographs of the holes in the irradiated sample produced by the twin jet electrochemical polishing. The numbered areas indicate the regions in which the TEM analyses were performed and are referenced in the text and figure captions.

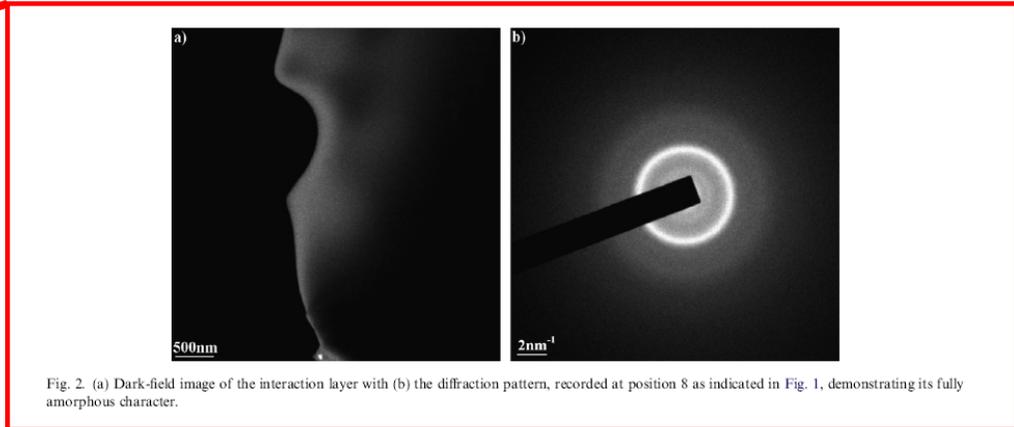


Fig. 2. (a) Dark-field image of the interaction layer with (b) the diffraction pattern, recorded at position 8 as indicated in Fig. 1, demonstrating its fully amorphous character.

Van den Berghe et al., *J. of Nucl. Mater.*, 375, 2008, 340-346

UMo/Al interaction layer grown in-pile at higher temperatures: **crystalline**

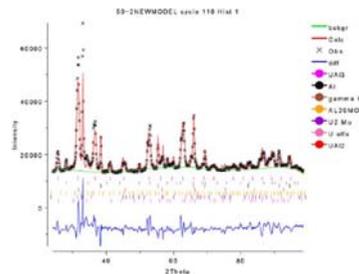
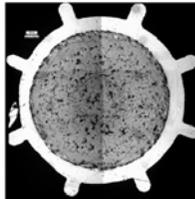


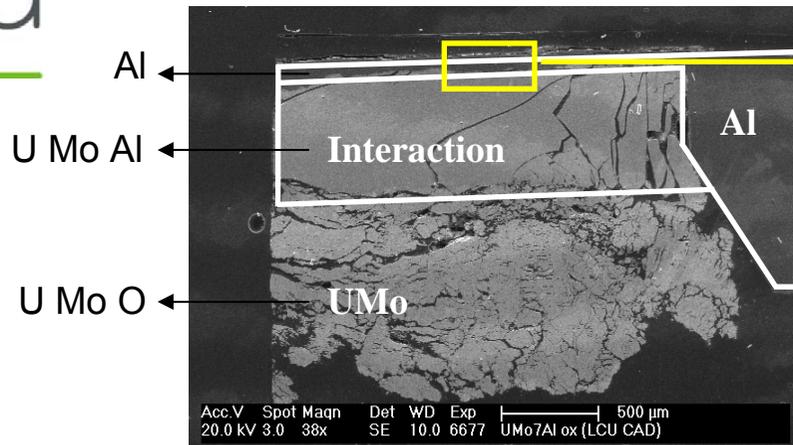
Figure 3: Neutron Diffraction Bragg peaks from specimen 59-2, low resolution scan ($\lambda = 0.133 \text{ nm}$).

Neutron diffraction shows the presence of binary UAl_x and ternary compounds $\text{U}_x\text{Mo}_y\text{Al}_z$

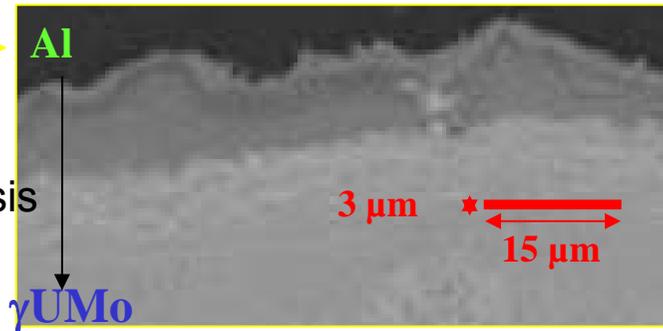
Colon and Sears, *RRFM2007*, 2007, 140-144.

Synchrotron studies and ion irradiations of UMo MTR fuel

μ -XRD to study the UMo/Al interaction on diffusion couple
 UMo/Al annealed 4h at 600°C

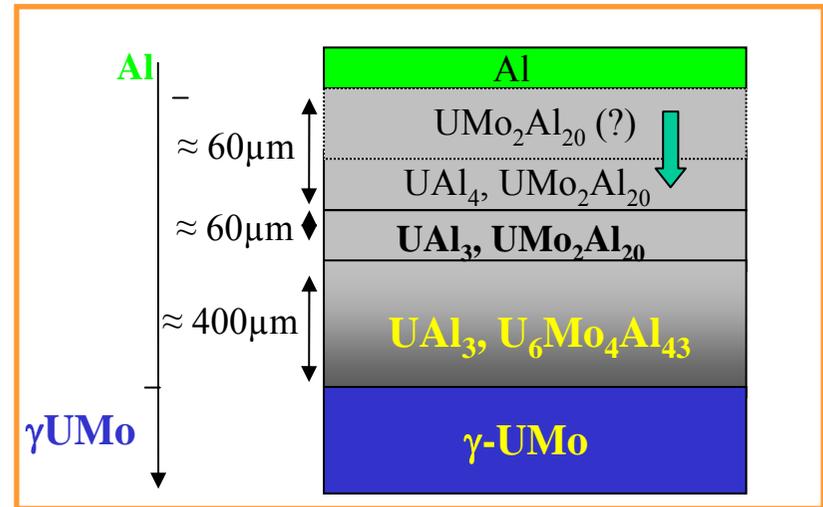
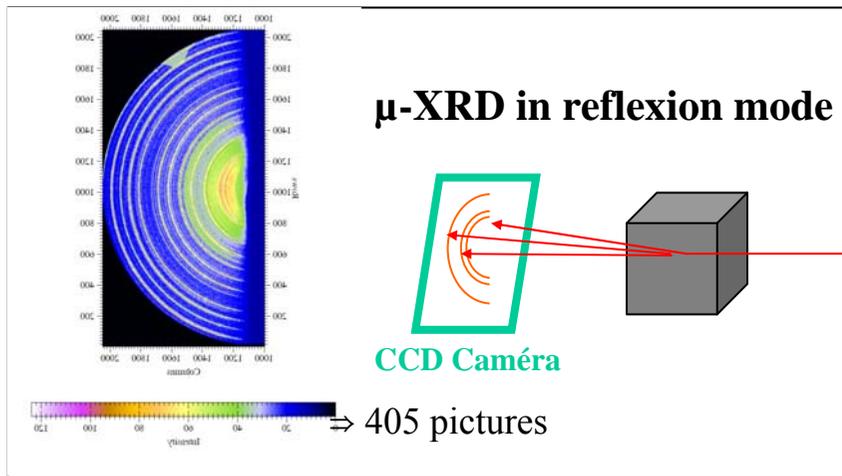


SEM analysis



Three apparent layers with various chemical compositions

Complete structural description of the interaction



Synchrotron studies and ion irradiations of UMo MTR fuel

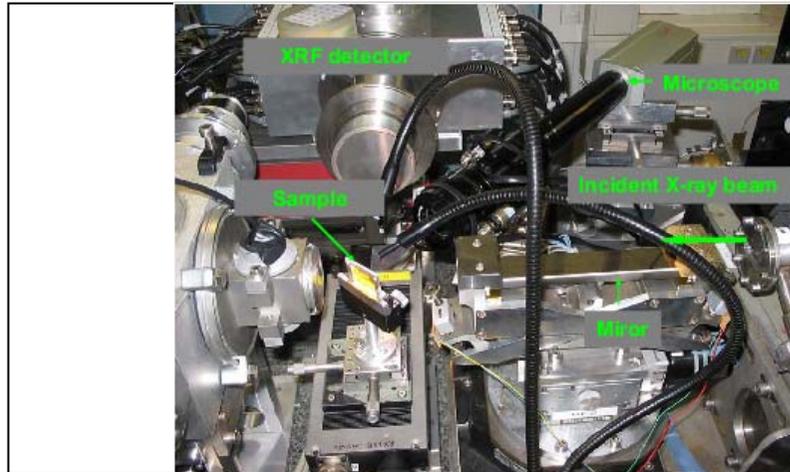
μ -XAS to study the UMo/Al interaction



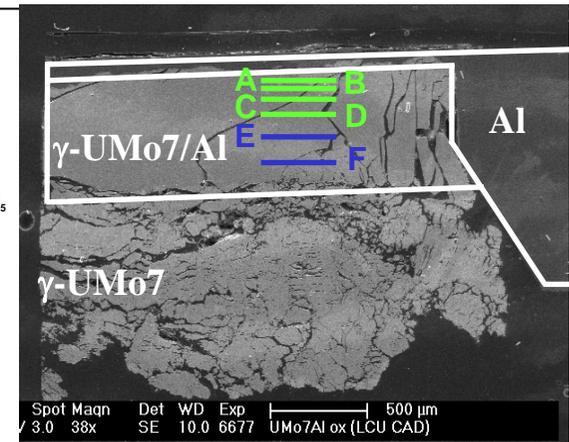
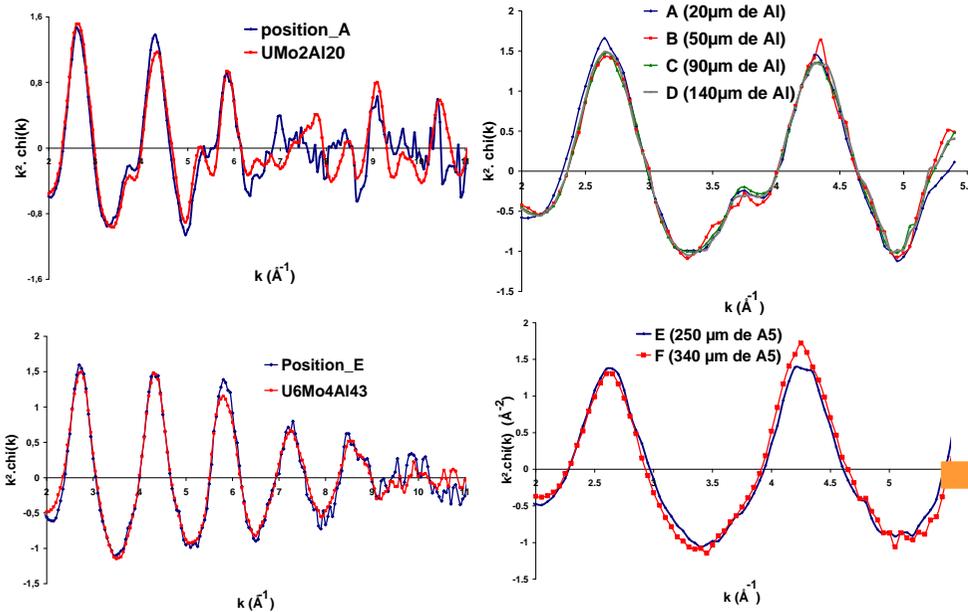
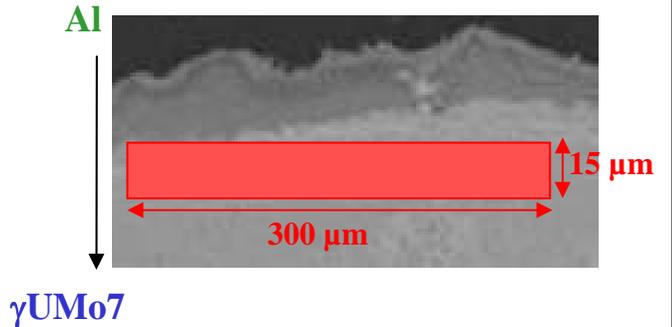
ESRF (Grenoble)

Mo in $\text{UMo}_2\text{Al}_{20}$

Mo in $\text{U}_6\text{Mo}_4\text{Al}_{43}$



Data collection in fluorescence mode



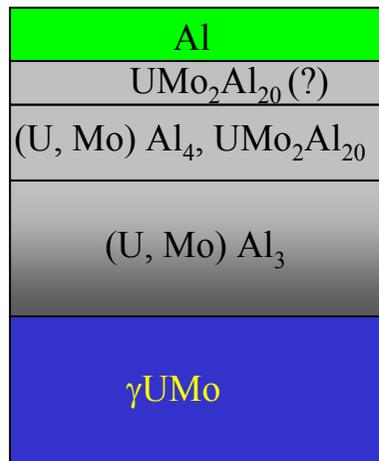
Mo systematically located in ternary phases

Synchrotron studies and ion irradiations of UMo MTR fuel

Coupling μ -DRX and μ -XAS allow to characterize the interaction layer at atomic level



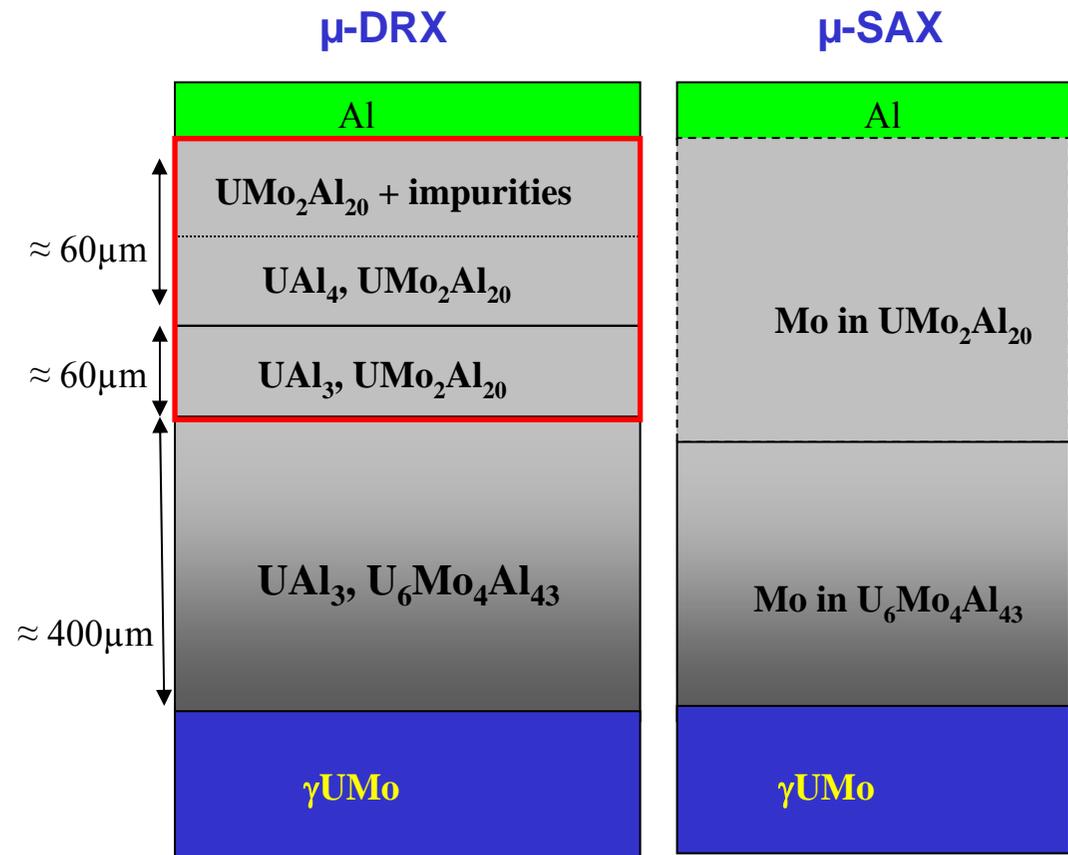
Bibliography



Mirandou *et al.*, JNM, 323 (2003) 29-35.

Results:

- ➔ Quantitative measurements of layer thickness and concentrations
- ➔ $U_6Mo_4Al_{43}$ phase has been identified
- ➔ Mo is not soluble in UAl_3 and UAl_4 (or solubility limit is very limited)



Complementary techniques and results in agreement

H. Palancher (2007) *J. Appl. Crystallogr.*, **40**, 1064-1075

Synchrotron studies and ion irradiations of UMo MTR fuel

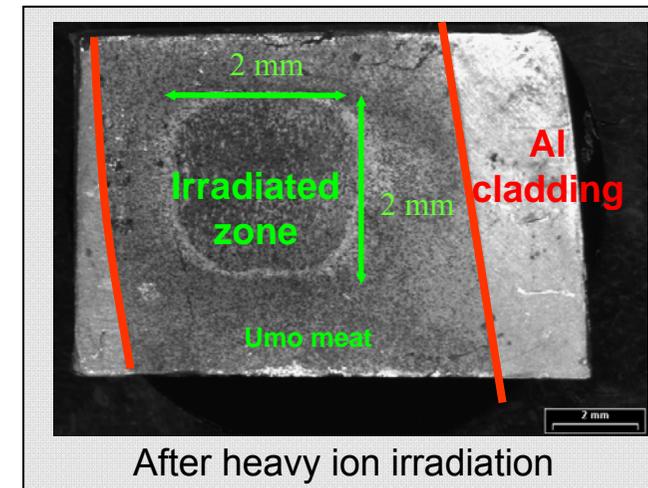
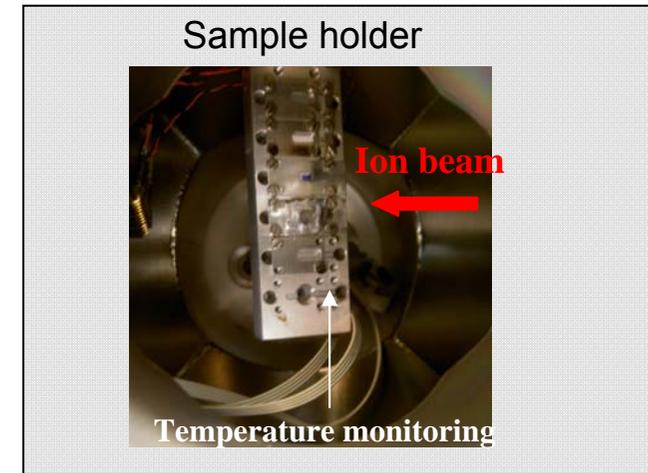
Heavy ion irradiation: some experimental aspects



Technical University of Munich



AREVA-CERCA

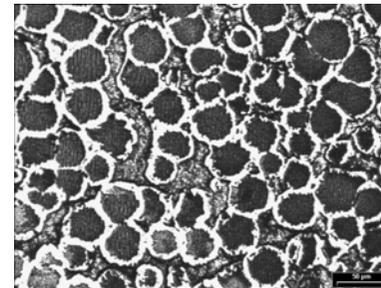
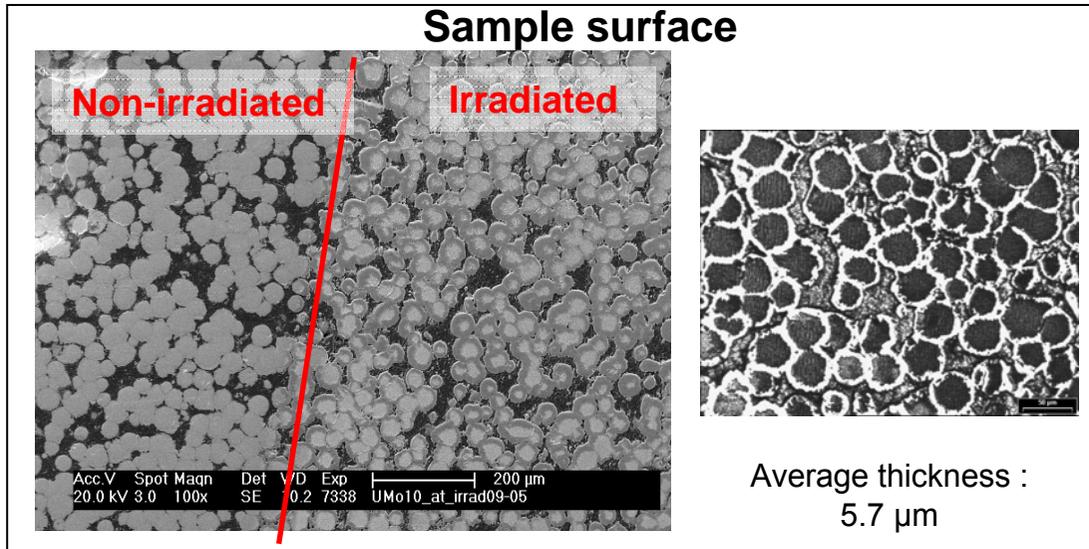


Synchrotron studies and ion irradiations of UMo MTR fuel

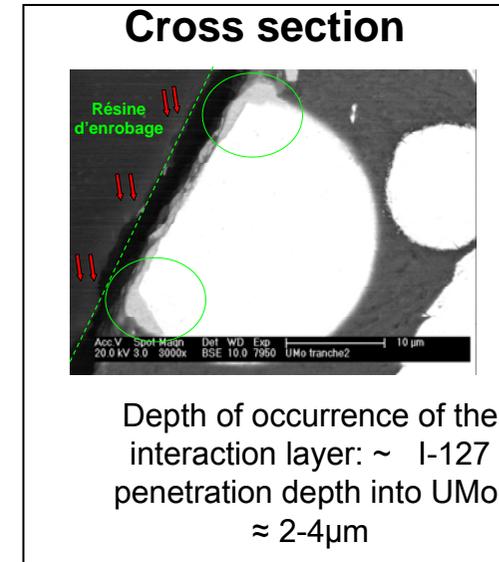
Validation of the methodology on UMo10/Al fuel plates : SEM characterisation after heavy ion irradiation



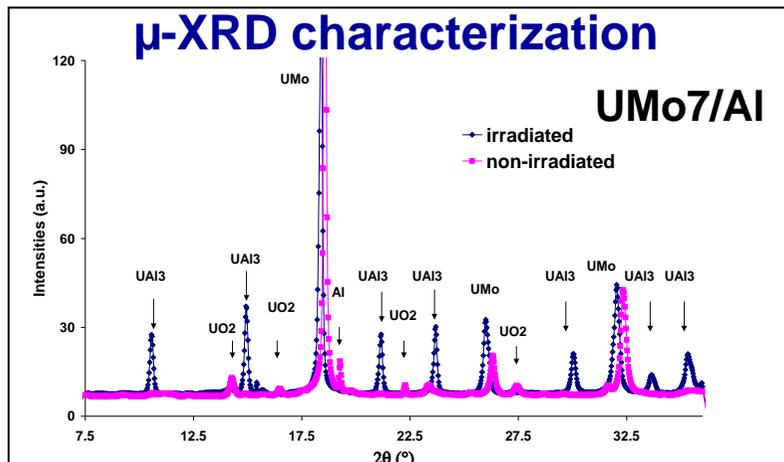
AREVA-CERCA



Average thickness : 5.7 µm



Depth of occurrence of the interaction layer: ~ 1-127 penetration depth into UMo: ≈ 2-4µm



H.Palancher (2008) J.N.M, submitted

- ➔ UAl₃ : main component of the interaction layer
- ➔ Results in agreement with those obtained on in-pile irradiated UMo10/Al fuel rods at low burn-up: ≈ 20% (Sears et al., RRFM 2006)
- ➔ Presence of an amorphous phase to be confirmed?

Synchrotron studies and ion irradiations of UMo MTR fuel

Application of this methodology to select remedies



2wt% silicon addition:

- Very interesting to reduce the size of the interaction layer

2wt% silicon addition + oxide coating:

- The Si addition associated to the oxide improves the behavior

Dispersed fuel	Interaction layer characteristics	
	Presence	Thickness
UMo7 at / Al	YES	≈ 7 μm
UMo7 at / Al, Si	YES	heterogeneous
UMo10 at / Al	YES	≈ 5,7 μm
UMo10 at / Al, Si	NO	
UMo7 ox (μm)/Al	NO	
UMo7 ox (μm)/Al, Si	NO	
UMo7 ox (nm)/Al	Very limited interaction	
UMo7 ox (nm)/Al, Si	NO	
UMo7 /Al, Ti	Limited interaction	

 Methodology : reference samples

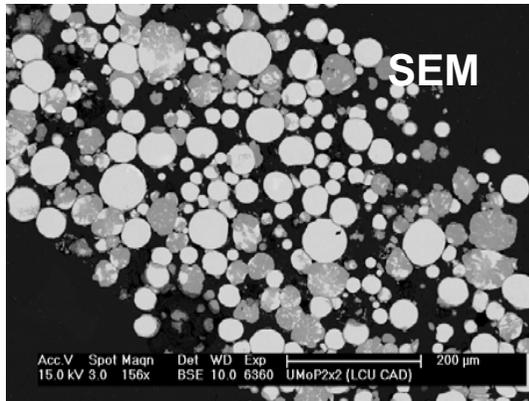
 Oxide solution

 Doped Al Matrices

Provide information to select best candidates for the IRIS4 irradiation test

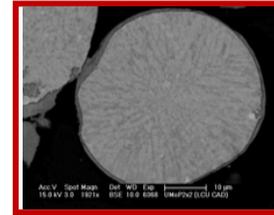
Synchrotron studies and ion irradiations of UMo MTR fuel

X-ray tomography : Recent advances on the characterisation of particular UMo7/Al

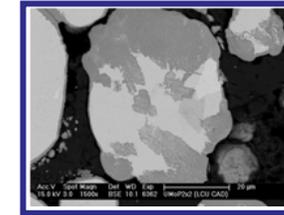


UMo7/Al annealed 500°C 4h

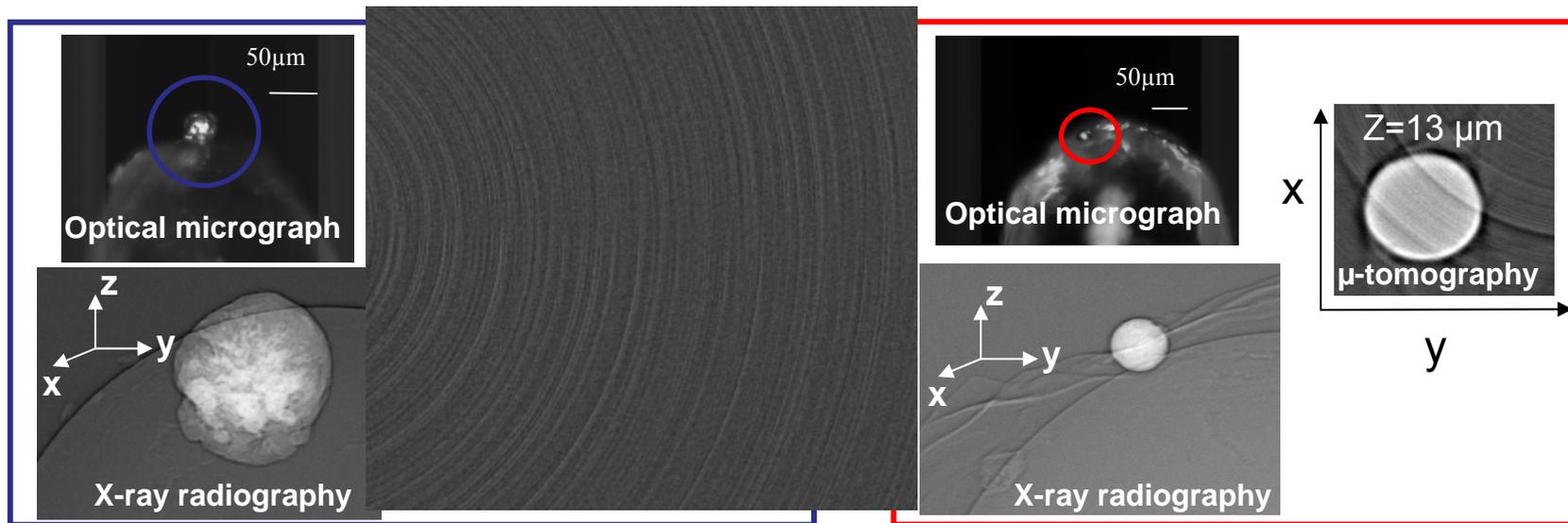
Two kinds of UMo/Al interactions



Interaction surrounding UMo7 particle

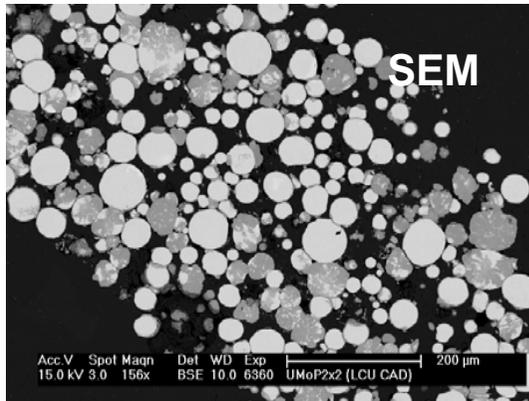


In depth interaction



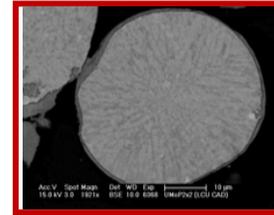
Synchrotron studies and ion irradiations of UMo MTR fuel

X-ray tomography : Recent advances on the characterisation of particular UMo7/Al

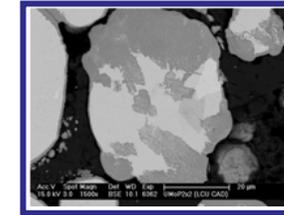


UMo7/Al annealed 500°C 4h

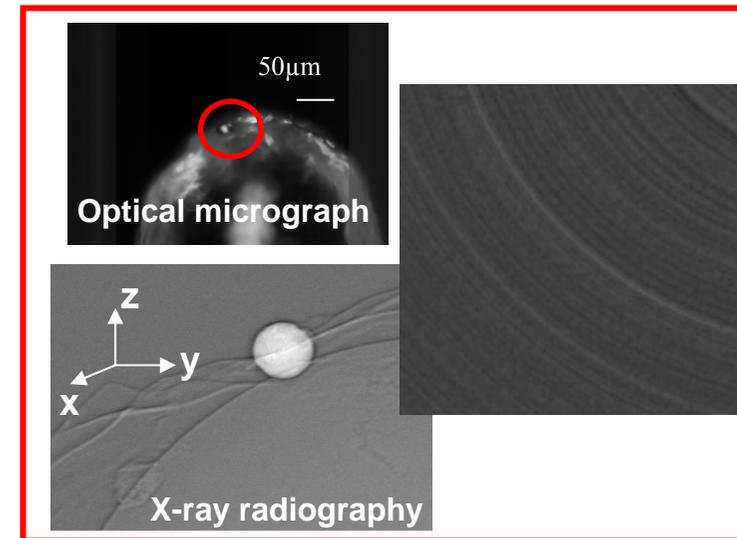
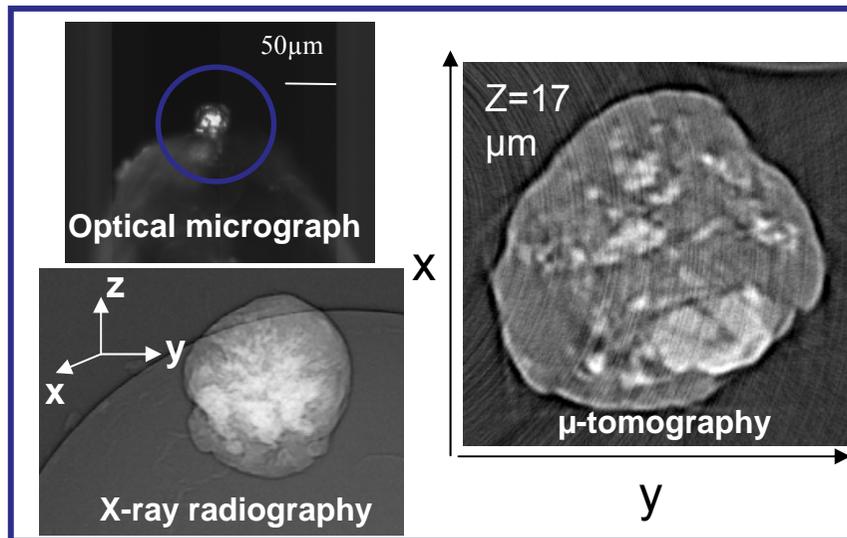
Two kinds of UMo/Al interactions



Interaction surrounding UMo7 particle

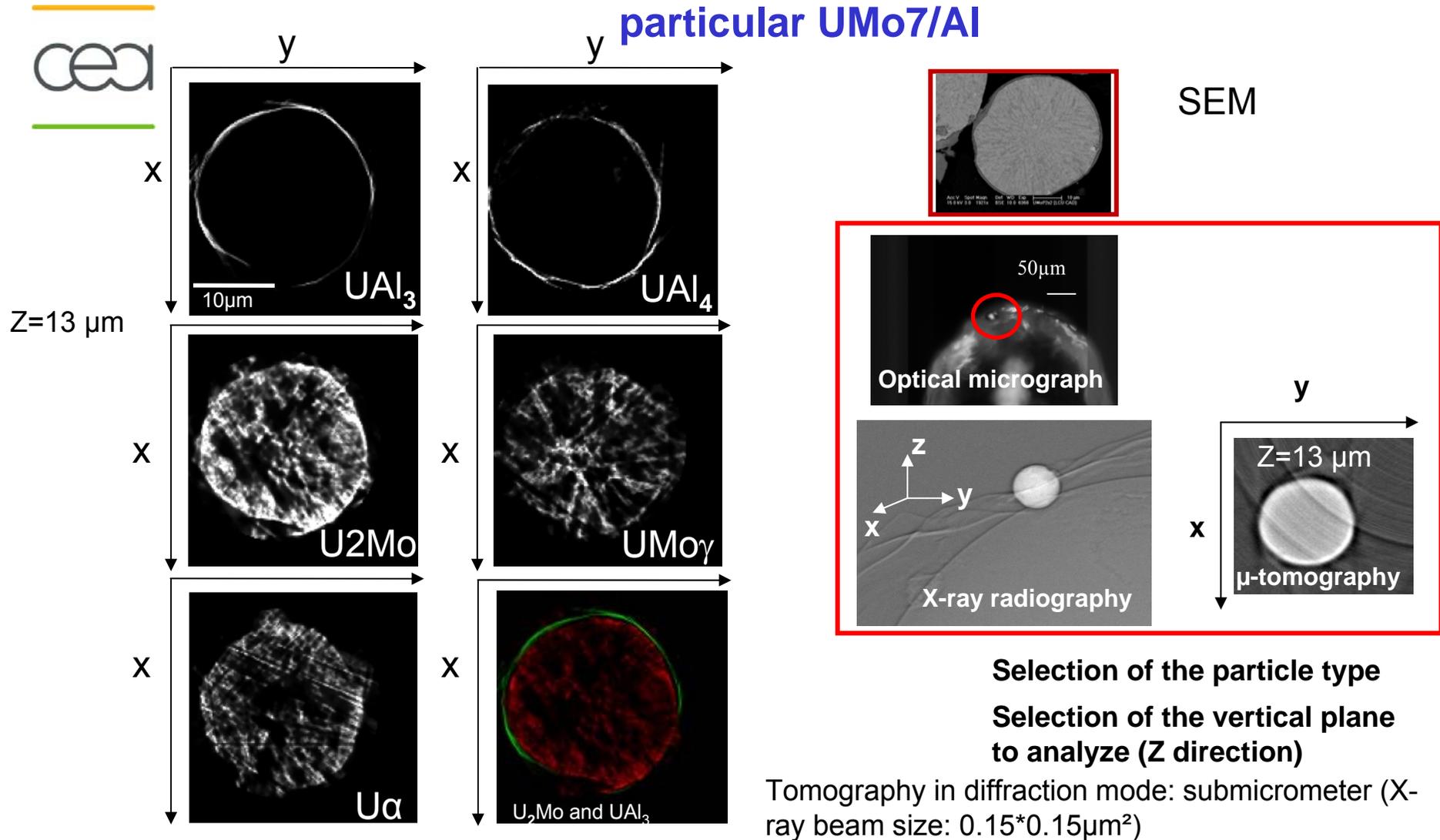


In depth interaction



Synchrotron studies and ion irradiations of UMo MTR fuel

X-ray tomography : Recent advances on the characterisation of particular UMo7/AI



Synchrotron studies and ion irradiations of UMo MTR fuel



Coupling ion irradiations with relevant characterization techniques such as μ -XAS, μ XRD is a powerful tool

- Providing a fine description of the UMo/Al interaction layer at the atomic level
- Providing a methodology to select best remedies to the UMo/Al interaction
- Helping to make a pre-selection and optimize in reactor irradiation testing

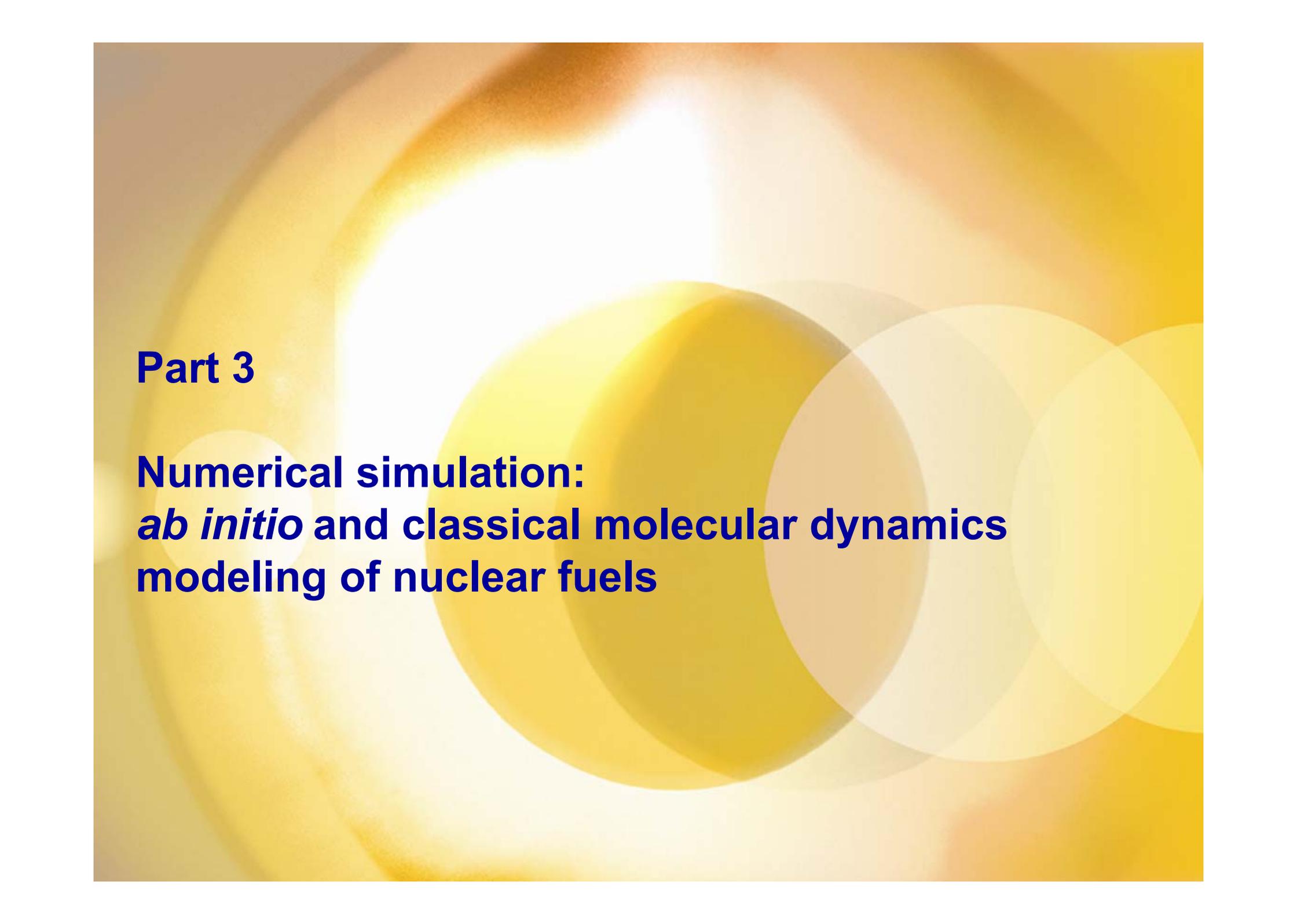
Part 2 conclusion



Necessary coupling between separated effects studies, PIE and fuel modeling

- **The separate effect studies** are complementary to the post irradiation examinations
- **The separate effect studies** enable us
 - to decorrelate and improve understanding of the relevant phenomena (thermal, irradiation, chemical effects)
 - Identification of mechanisms at lower scale
 - Determination of basic data to be used in the fuel behavior codes

➔ **Essential to in-pile fuel behavior modeling**



Part 3

**Numerical simulation:
ab initio and classical molecular dynamics
modeling of nuclear fuels**

Part 3 Outline



Context

Ab initio modeling of actinide compounds

Introduction

Illustrations of *ab initio* studies of nuclear fuels

- Ab initio modeling of defect migration in UO₂
- Behavior of Xe in UO₂ et UC

Classical Molecular Dynamics (CMD) modeling of fuel

Introduction

Illustrations of CMD studies of nuclear fuels in UO₂

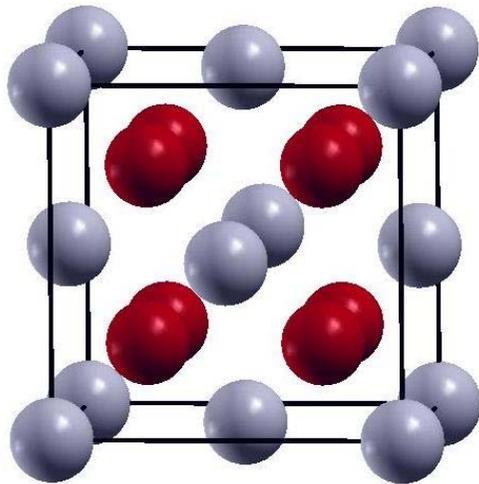
- Formation of defects during displacement cascades
- Influence of grain boundaries on cascades and defects
- Radiation enhanced helium re-solution

Conclusion

Nuclear materials of interest



actinide dioxides



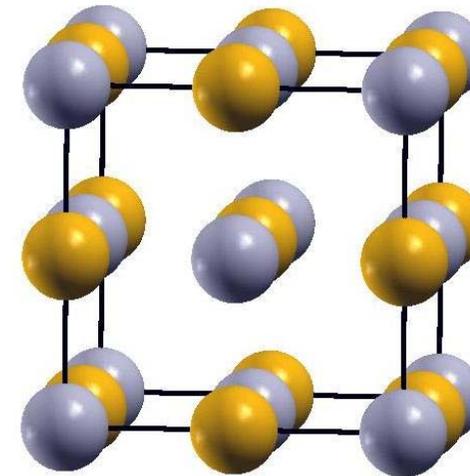
Fluorite structure

Insulators

Mainly ionic bonding (U^{4+} , O^{2-})

$$UO_2: a = 5.47 \text{ \AA}$$
$$d_{U-U} = 3.87 \text{ \AA}$$

actinide carbides and nitrides



Sodium-chloride structure

Metallic bonding

$$UC: a = 4.96 \text{ \AA}$$
$$d_{U-U} = 3.51 \text{ \AA}$$

$$UN: a = 4.89 \text{ \AA}$$
$$d_{U-U} = 3.46 \text{ \AA}$$

Atomistic modeling of nuclear fuel

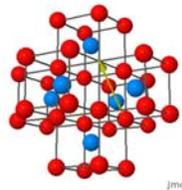
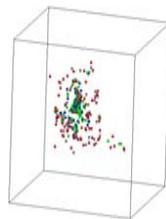
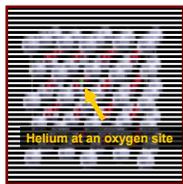


Determine and understand at the atomic scale

- Physical and chemical properties of fuels
- Irradiation effects in fuels

Decouple basic processes

- Stability of a given type of point defect
- Localization of a given fission product
- Migration mechanism of a chemical element
- the damage created by ballistic collisions
- Fission product segregation



Quantify phenomena

- Formation energy of defects
- Incorporation energy of a chemical element
- Structural modification (*swelling*)
- Solubility (*solution energy*)
- Migration (*migration energy*)
- Concentration of free point defects produced
- Recombining/Clustering of defects: nature, size, number

Understanding of the mechanisms involved

Provide basic data
→ Models at higher scale



Ab initio modeling of actinide compounds Density Functional theory method

Ab initio modeling: Density Functional Theory method



Description of interaction between nuclei and electrons

Schrödinger equation

$$H \Psi(\vec{r}) = E \Psi(\vec{r})$$

Impossible to solve for systems with more than 1 electron !

Method to solve it: transform it into a single electron problem

Wave function Ψ for N electrons \rightarrow Wave functions for 1 electron φ_i

But retain description of the electronic interaction: important in bonding

$$E[n] = T_o[n] + V_H[n] + V_{ext}[n] + V_{xc}[n]$$

kinetic energy electrons-electrons electrons-nuclei **exchange-correlation**

Ab initio methods expensive in time and computational resources

Ab initio modeling: Density Functional Theory method



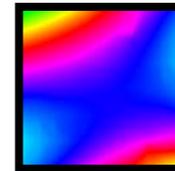
Approximation required for V_{xc} :

⇒ **LDA:** analytical expression for a uniform electron gas

⇒ **GGA:** takes into account the gradient of the electron density

⇒ **GGA + U:** addition of parameters to improve the description of strong correlation between 5f electrons

⇒ **Hybrid functionals:** GGA + exact exchange



Choice imposed by materials properties

Iterative self-consistent process

1. Start with guess wave functions φ_i
2. Calculate density
3. Calculate corresponding V_{ext}
4. Solve the approximate equations new φ_i
5. From these calculate a new density
6. Start again

Procedure repeated until convergence reached

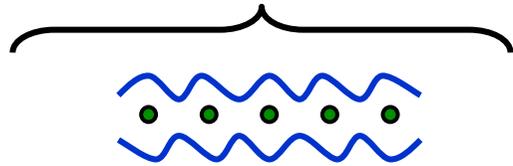
Calculation at 0 K

5f electrons localization



Localization of the **5f orbitals** in the actinide series

delocalized



localized



90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

UO₂: insulator, **localized** 5f electrons, strong electrostatic interaction
underestimated by the DFT ⇒ **GGA + U**

UC, UN: metals, **delocalized** 5f electrons ⇒ **GGA**

Ab initio modeling of UO₂ – GGA / GGA + U

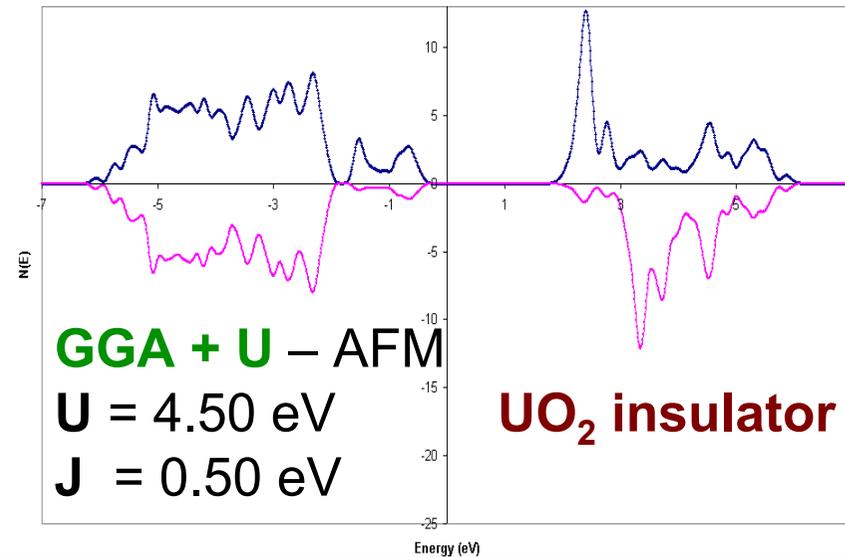
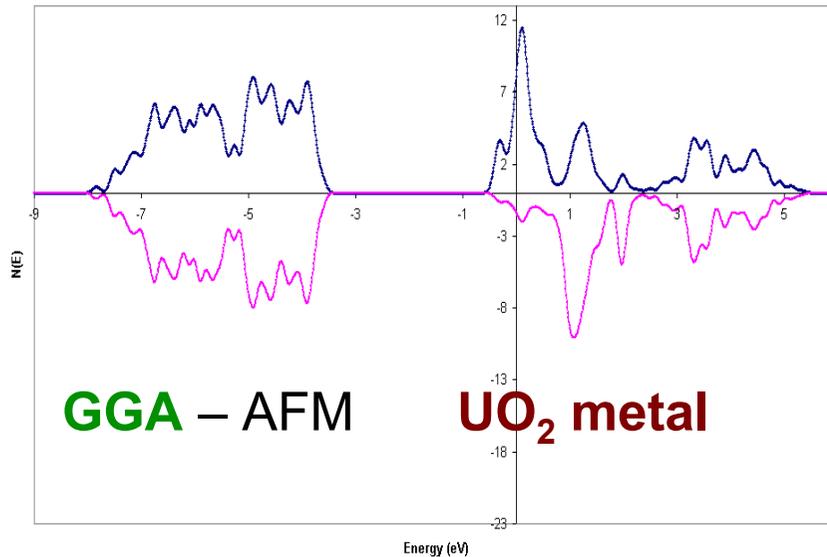


	a (Å)	B (GPa)	m (μ_B/U)
GGA+U	5.52	189	2.0
GGA	5.38	184	1.4
Exp.	5.47	207	1.7

Lattice parameter **a**
Bulk modulus **B**
Magnetic moment **m**

Computational details:

- **PAW** (Projector Augmented Wave) based on **DFT**
- Plane-Wave basis
- **VASP** and **ABINIT** codes
- **Scalar relativistic** approximation



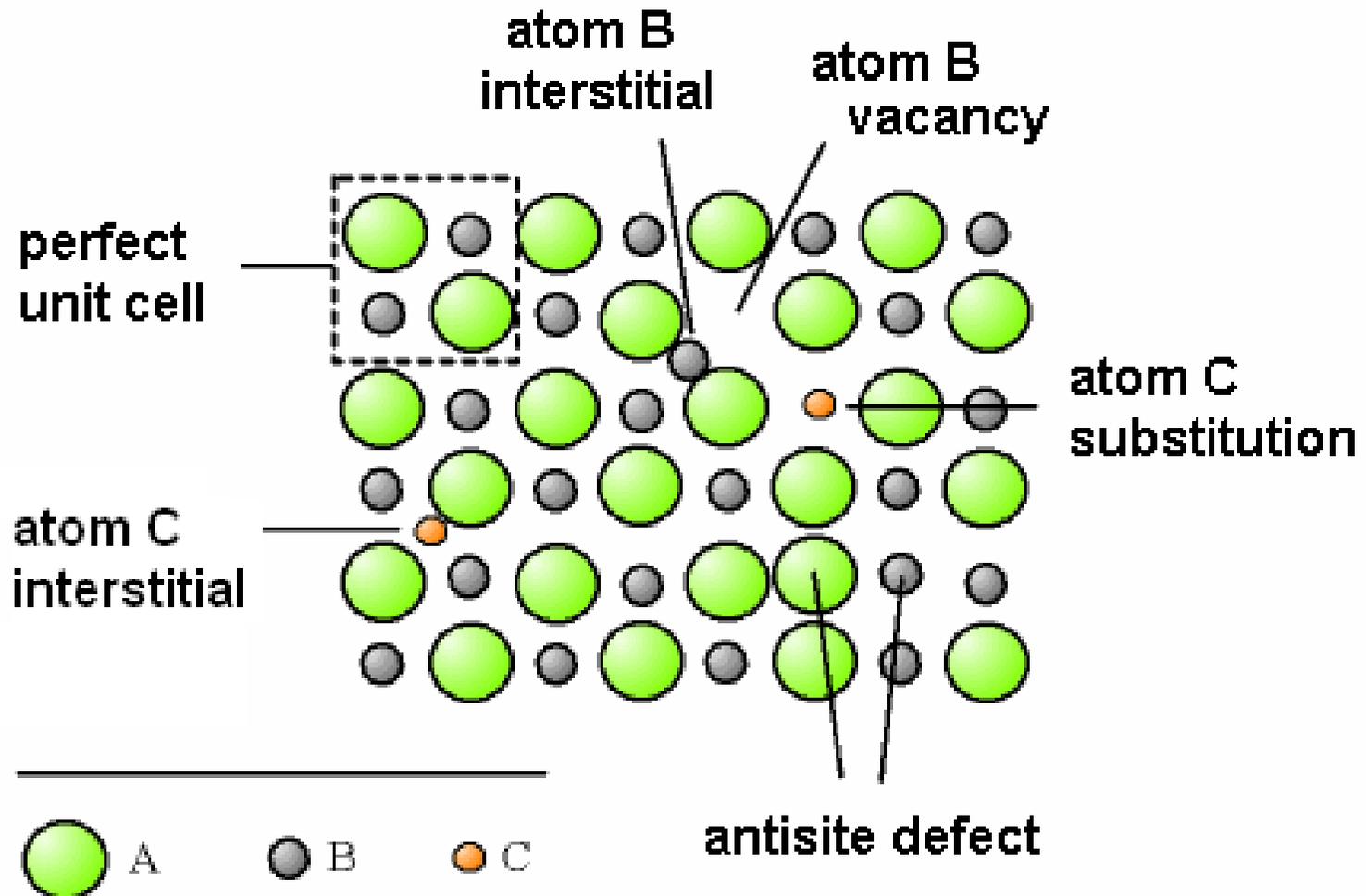
Values of **U** et **J** adjusted to reproduce the 2.1 eV band gap

Illustrations of *ab initio* studies of nuclear fuels



Illustration 1: *Ab initio* modeling of defect migration in UO_2

Point defects

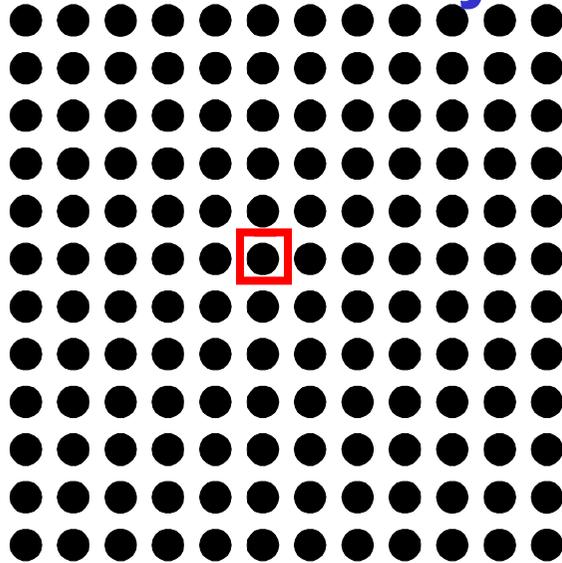


or more complex defects (tri-vacancies, dumbbells, clusters...)

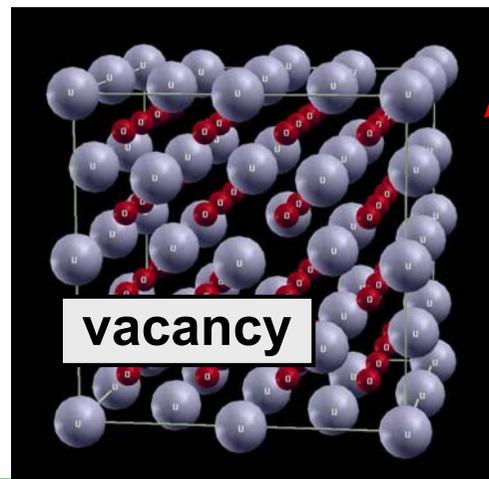
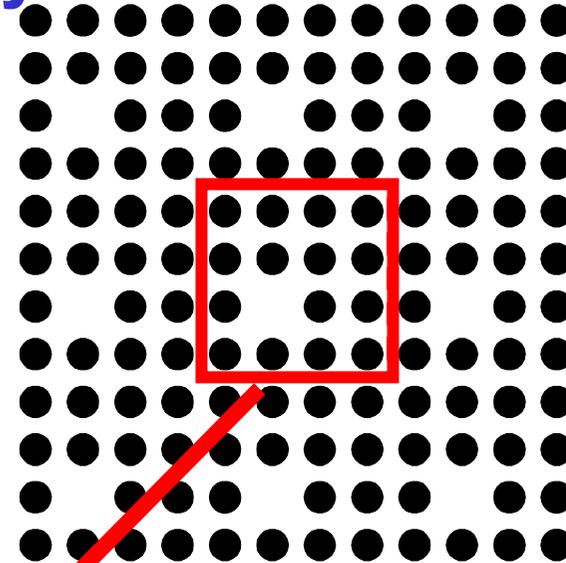
Periodicity: supercell technique



perfect bulk crystal



crystal with vacancies



supercell

~ 100 atom supercell
Possible nowadays for actinide
compounds

Formation energy of point defects

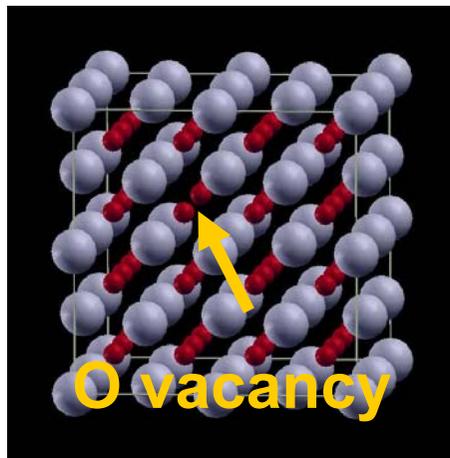


For instance :

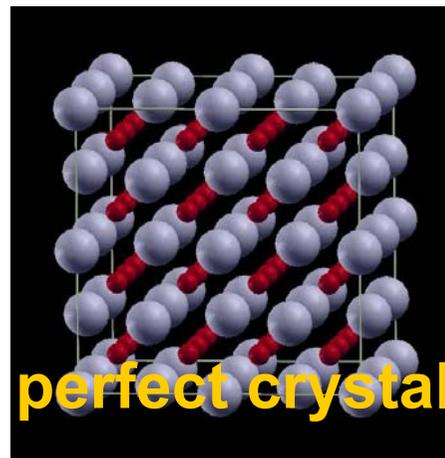
Formation energy of a oxygen **vacancy** in UO_2

$$E^F = E_{\text{UO}_2}^{N-1} - (E_{\text{UO}_2}^N + E_X)$$

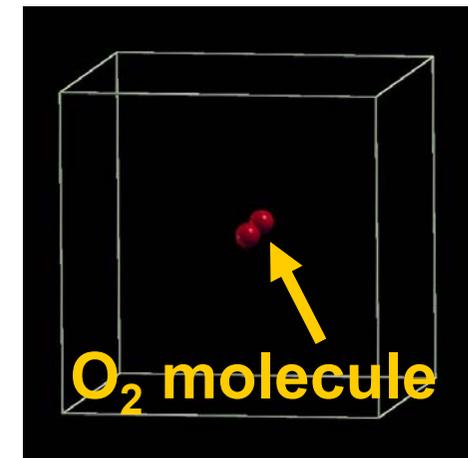
Supercell with
the defect



perfect
crystal



O atom in a
reference state:
O in O_2 molecule

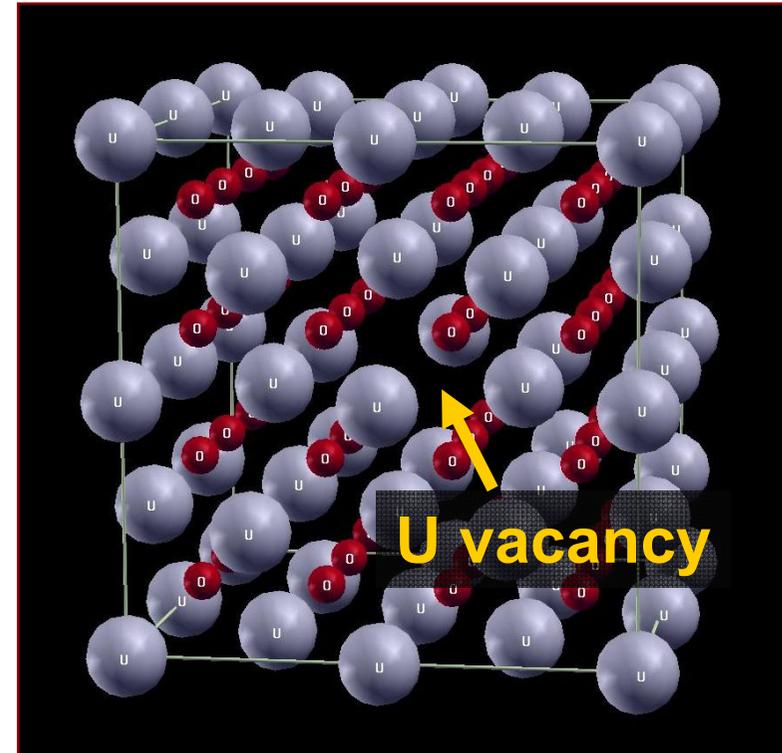


Point defects in uranium dioxide



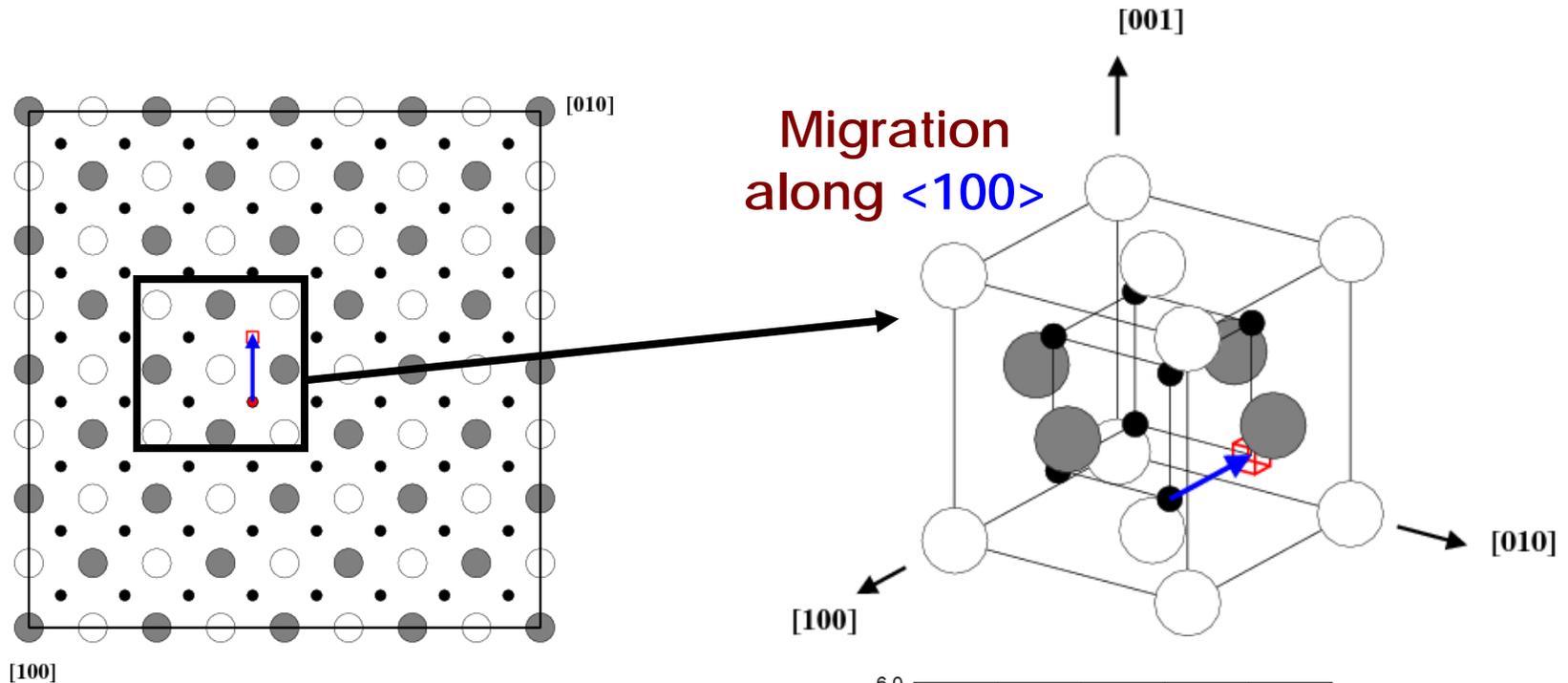
- **Vacancies**
- **Interstitials**
at octahedral site
- **Frenkel pairs**
1 vacancy + 1 interstitial
- **Schottky defects**
1 uranium vacancy
+ 2 oxygen vacancies

→ **Formation energies**



GGA and GGA+U calculations
PAW / VASP & ABINIT
Supercell containing 96 atoms

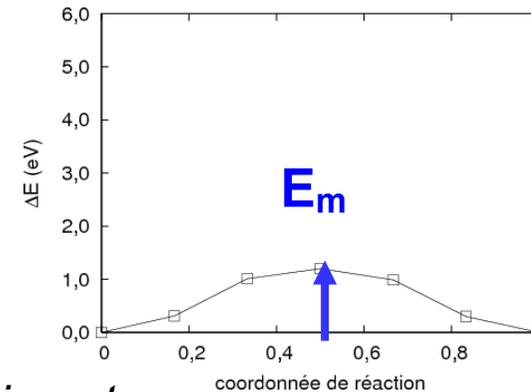
Migration energies of point defects in UO_2



Different migration mechanisms

What is the **lowest migration barrier** ?

Coupling to experimental measurements of diffusion coefficients while monitoring the stoichiometry



Migration energies: calculation method

cea

Diffusion coefficient $D = D_0 \exp\left(-\frac{E_a}{kT}\right) = D_0 \exp\left(-\frac{E_{app}^F + E_m}{kT}\right)$

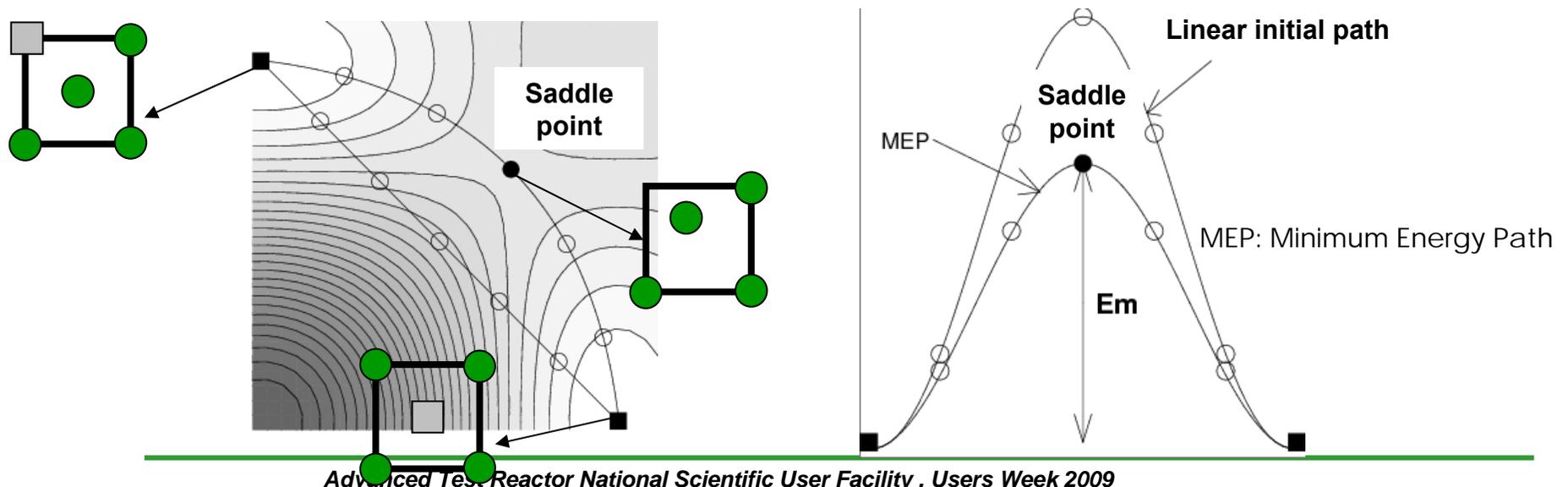
Nudged Elastic Band (NEB)

Determine Minimum Energy Paths for atom migration

→ Choice of a start migration path and images along it

→ Atomic relaxation perpendicular to the path

→ Allows us to get a physical path (path continuity is ensured)

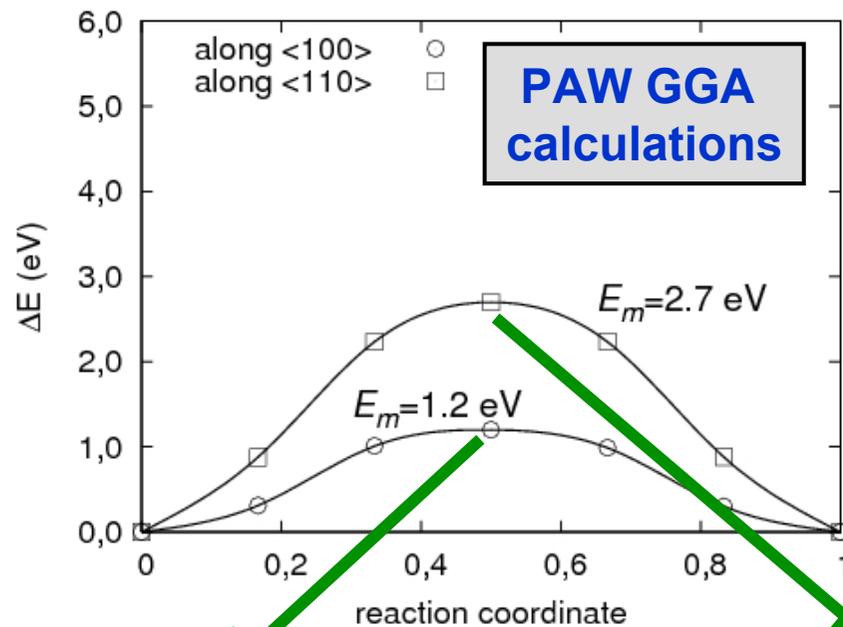


Advanced Test Reactor National Scientific User Facility, Users Week 2009
Experiments for improving nuclear fuels models and performance
Numerical and experimental simulation at the atomic scale, Carole VALOT

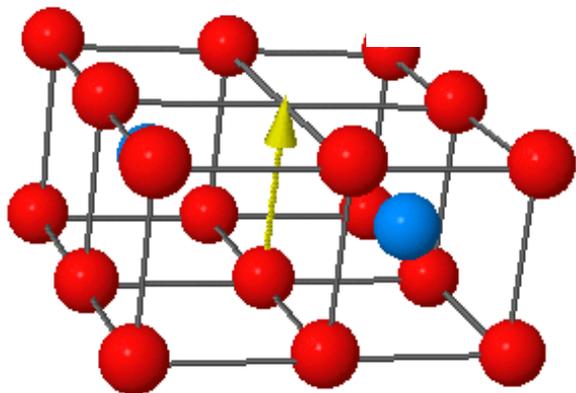
Migration energies: oxygen vacancy



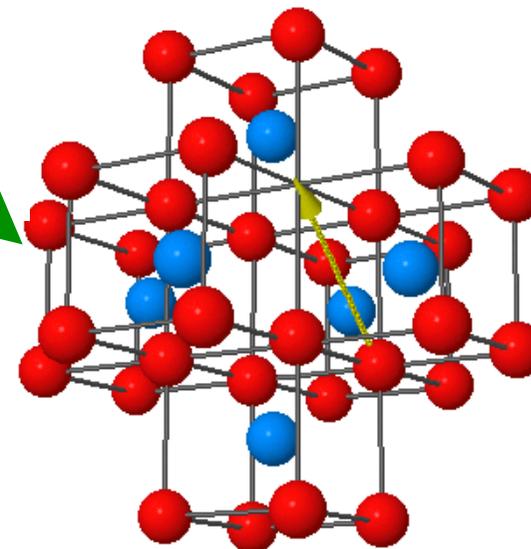
Value of $E_m = 1.2$ eV confirmed by preliminary **GGA+U** calculations [J. Durinck 2007]



along $\langle 100 \rangle$



along $\langle 110 \rangle$



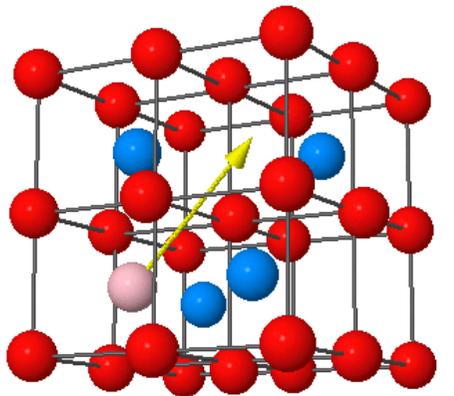
O vacancies are more mobile along the $\langle 100 \rangle$ direction than along the $\langle 110 \rangle$ direction

Jmol

Migration energies: oxygen interstitial

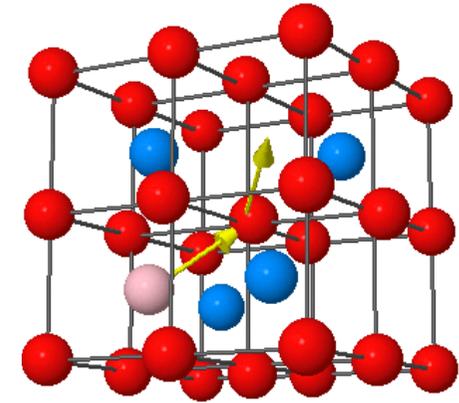


Direct
mechanism

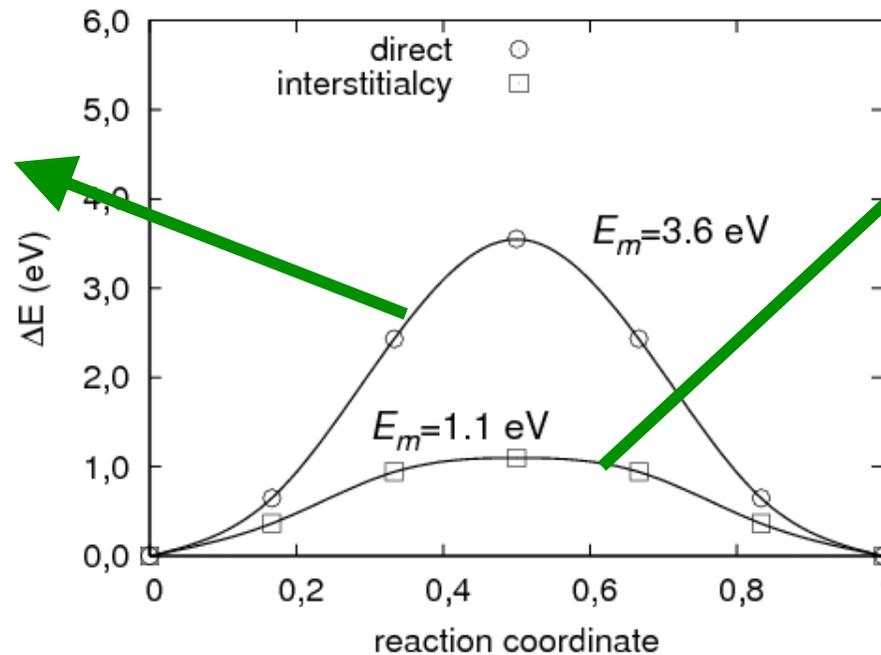


Jmc

Indirect
mechanism



Jmol



The indirect mechanism is the most favorable mechanism for the migration of O interstitials

Illustrations of ab *initio* studies of nuclear fuels

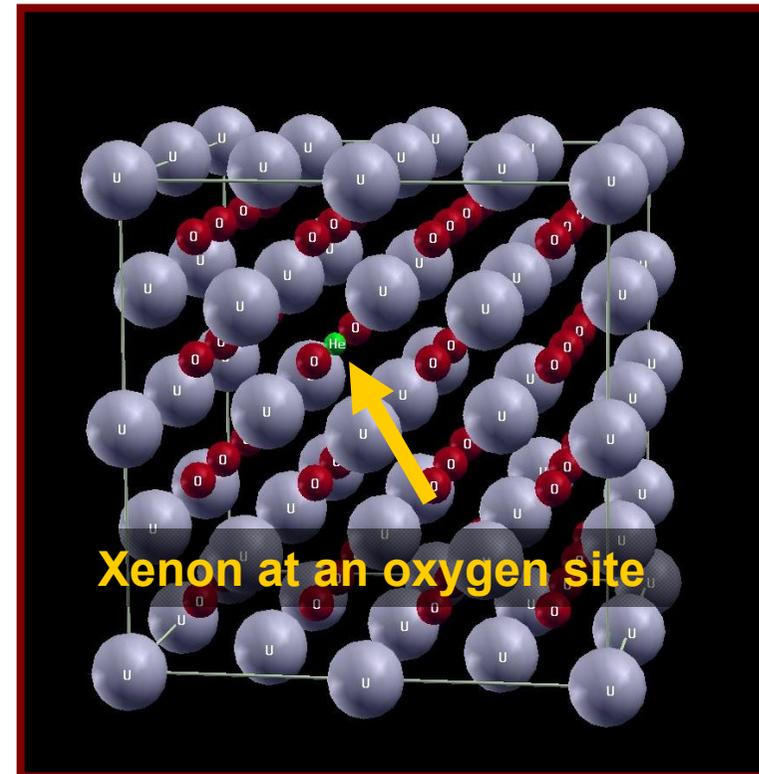


Illustration 2: *Ab initio* modeling of the stability of fission products in UO₂ and UC

Volatile elements in UO_2 : the case of Xe



- **Stability** in the lattice
 - interstitial site
 - substitution site
- **Incorporation energy**
- **Solubility**
- Structure modifications
swelling



GGA or GGA+U calculations
Method: **PAW / VASP**
Supercell with **96 atoms**

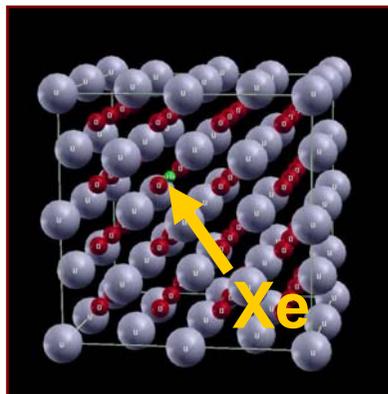
Incorporation Energy



Energy required to incorporate Xe in a pre-existing vacancy or at an interstitial site:

$$E_{inc} = E_{Xe}^N - (E^{N-1} + E_{Xe})$$

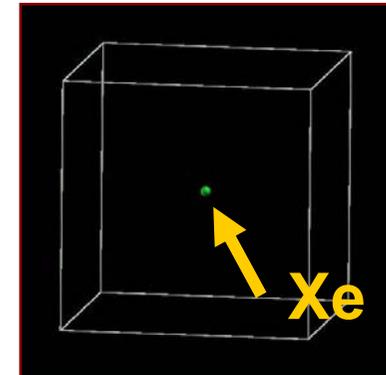
Xe incorporated in the fluorite structure



crystal with a vacant host site



isolated Xe atom



Xenon incorporation in UO_2 and UC



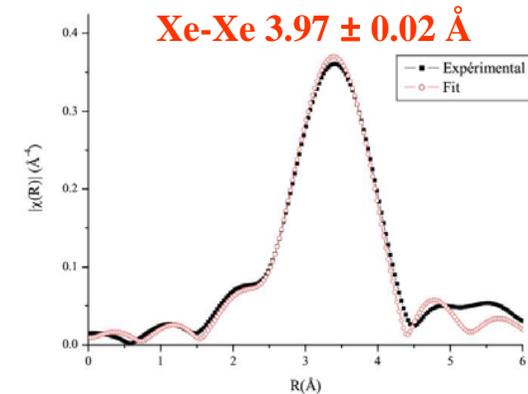
E_{inc} (eV)	site U	site C, O	interst.
UC GGA	4.3	8.6	12.8
UO_2 GGA	6.0	9.7	12.7

Large incorporation energies (> 4 eV) whatever the site: **instability** of diluted xenon atoms in both UC and UO_2

Experimentally characterized in UO_2 by EXAFS and TEM

→ Xe implantation, annealing, EXAFS analysis

→ Formation of pressurized Xe clusters



P. Garcia, P. Martin, G. Carlot, M. Ripert, C. Sabathier *et al.*, J. Nucl. Mater. **352**, 136 (2006)



Classical Molecular Dynamics Simulations of displacement cascades in UO_2

Molecular Dynamics Simulation



Principle

⇒ Computer simulation using Newtonian mechanics

$$F_A = \sum_i F_{i \rightarrow A} \text{ et } F_A = m_A \ddot{x}_A$$

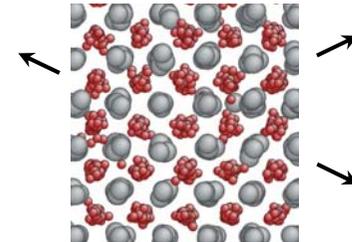
⇒ Simulates evolution of systems in time

⇒ Enables to find the properties of complex systems numerically

⇒ Based on statistical mechanics

⇒ Calculation in a statistical ensemble (example:
N, V, T constant)

⇒ Calculations at finite temperature



Different types depending on the description of atomic interaction

⇒ Empirical potentials: classical molecular dynamics

⇒ *Ab initio* description: *Ab initio* molecular dynamics

Empirical potentials



Principle

- Interatomic interactions described by analytical potential giving the energy as a function of separation distance
- Parametrized on experimental or *ab initio* data
- Potential form different for each system type
- Parameters different for each system

Advantages / Disadvantages

- Quick \Rightarrow Investigation of large systems / long times
- Existing data necessary for parametrization
- Non transferable: potentials only valid in situation close to those used for parametrization
- No description of electronic structure

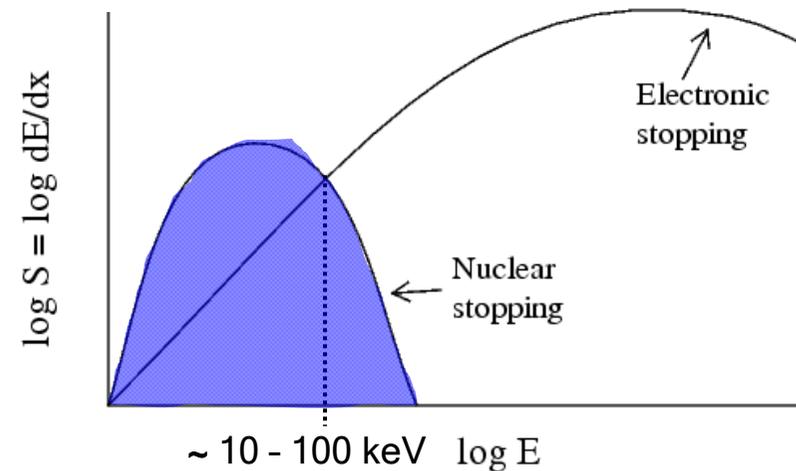
CMD simulation of cascades in UO_2



Slowing down of fission products

⇒ Simulation of displacement cascades generated by U atom

Description of elastic collisions



Empirical potential for UO_2 [1]

- relatively simple: rigid ion potential $\text{U}^{3,2+}$ et $\text{O}^{1,6-}$
- without charge transfer: no description of electronic changes
- satisfactory for UO_2 defect migration/formation properties

[1] N. D. Morelon, *et al.*, *Phil. Mag.* 83, 1533 (2003)

Illustrations of CMD studies of nuclear fuels



Illustration 1 : formation of defects during displacement cascades

Formation of defects during displacement cascades in UO₂

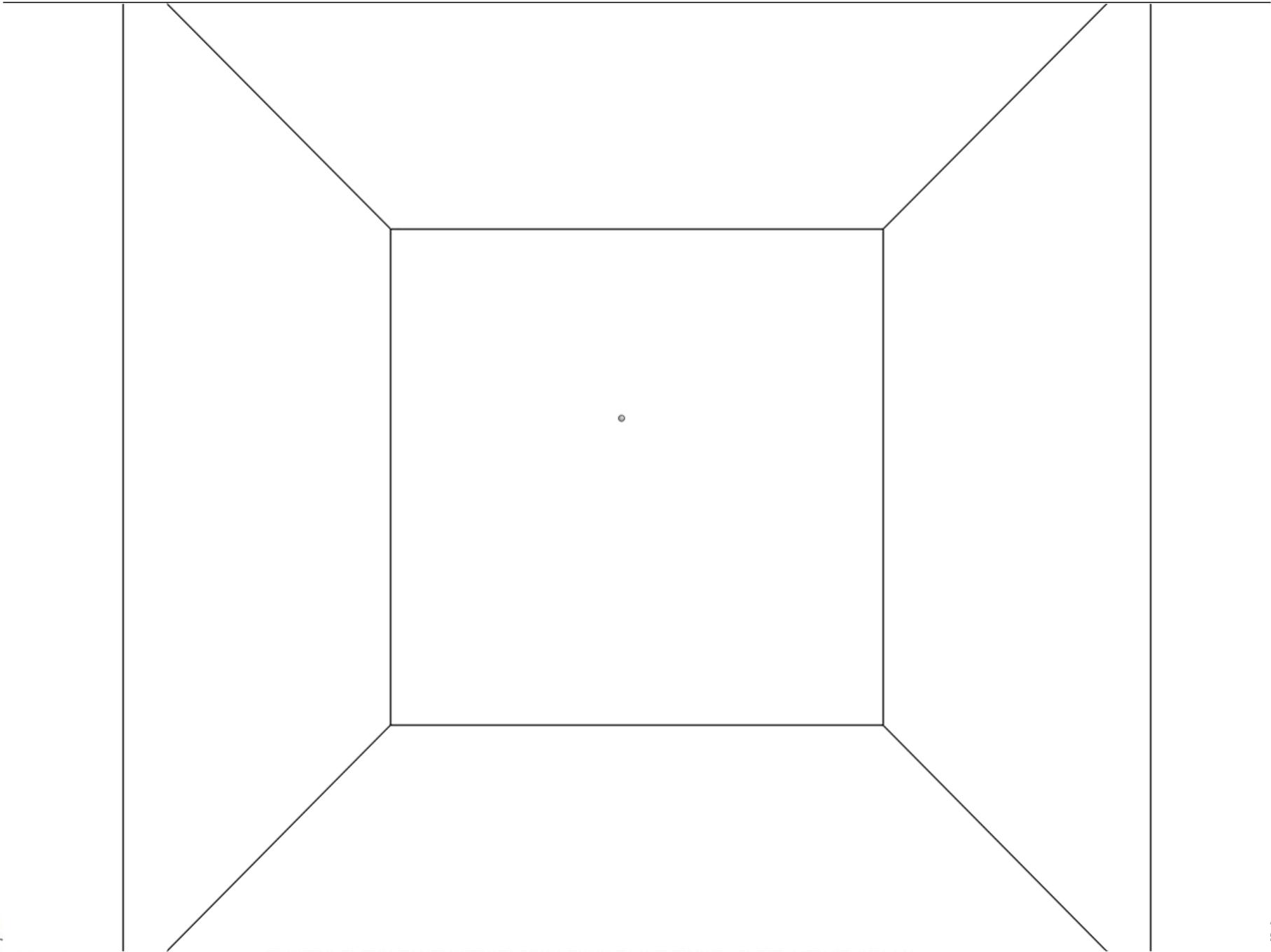


(L. van Brutzel)

- Fluorite structure UO₂
68×68×68 unit cells
Stabilized 20 ps at 300K & 0 GPa
- **Energy pulse given to an atom (PKA) → 80 keV**
- Constant N, V, ~E
- Temperature control at the boundaries (3 Å)
- Periodic boundary conditions
- Variable time steps

● Uranium

● Oxygen



formation of defects during displacement cascades in UO₂

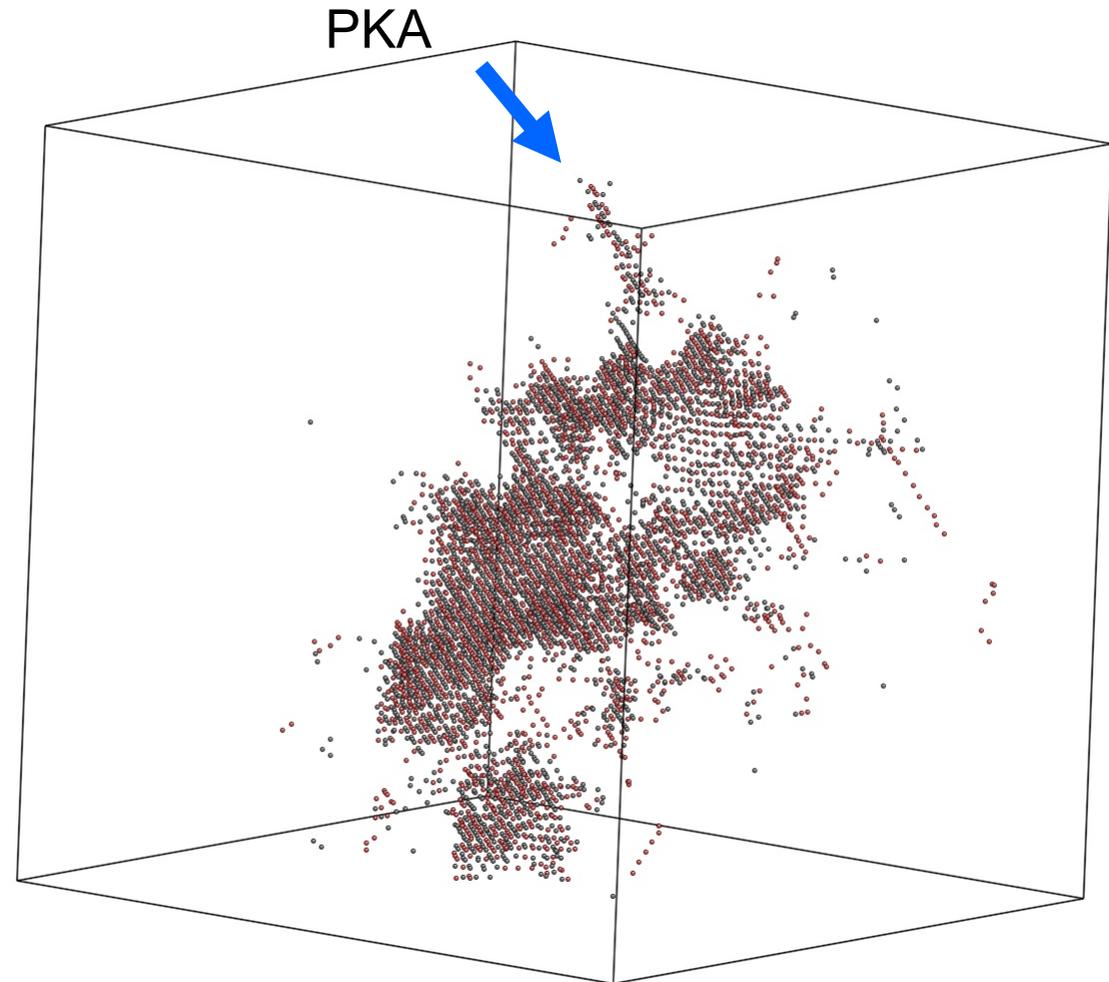


(L. van Brutzel)

Localization of the defects

Vacancies → core of the cascade

Interstitials → periphery in the sub-cascade branches



Illustrations of CMD studies of nuclear fuels



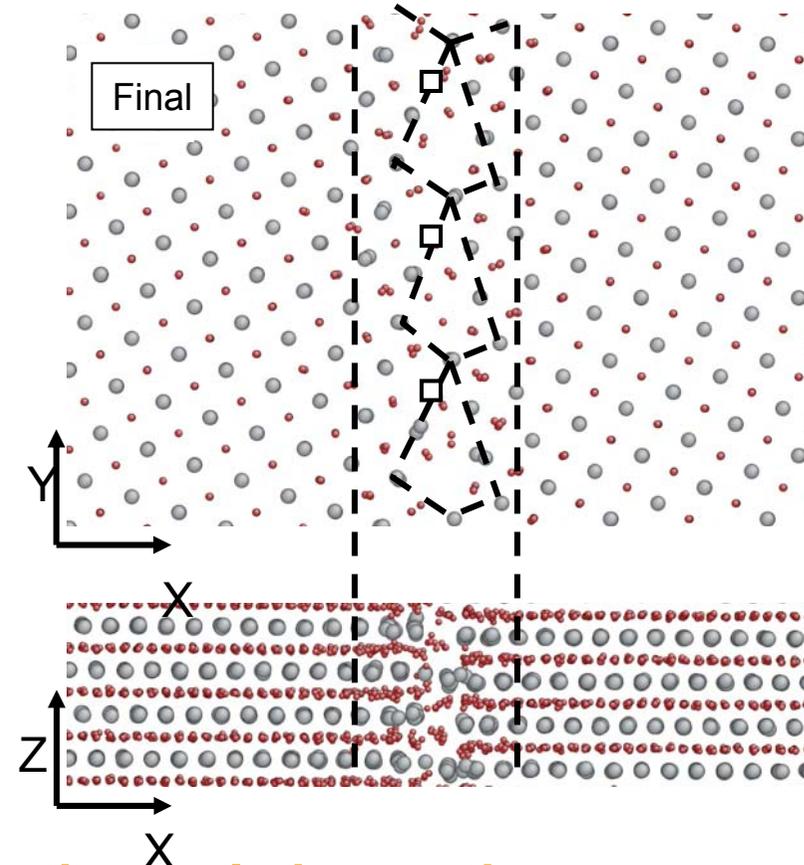
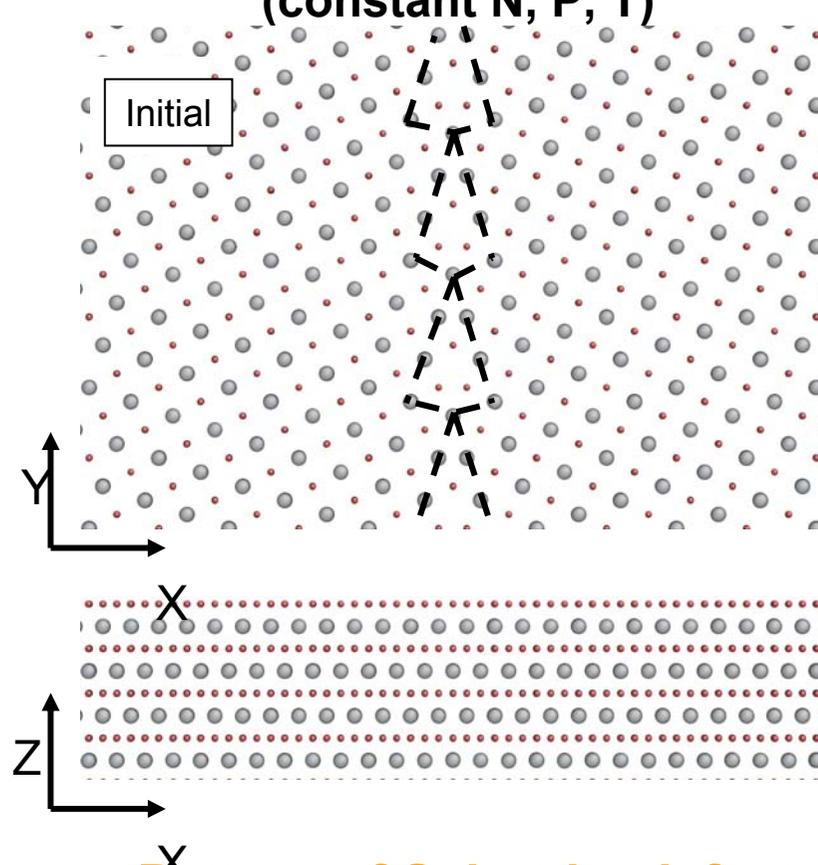
Illustration 2 : Grain boundaries influence in UO_2

Grain boundaries influence in UO_2

(L. van Brutzel)



Evolution of the grain boundary S5 at 300K during relaxation
(constant N, P, T)



Pattern of Schottky defects = experimental observations

Grain boundaries influence in UO_2 (L. van Brutzel)

Displacement Cascade -
10 keV
with a grain boundary

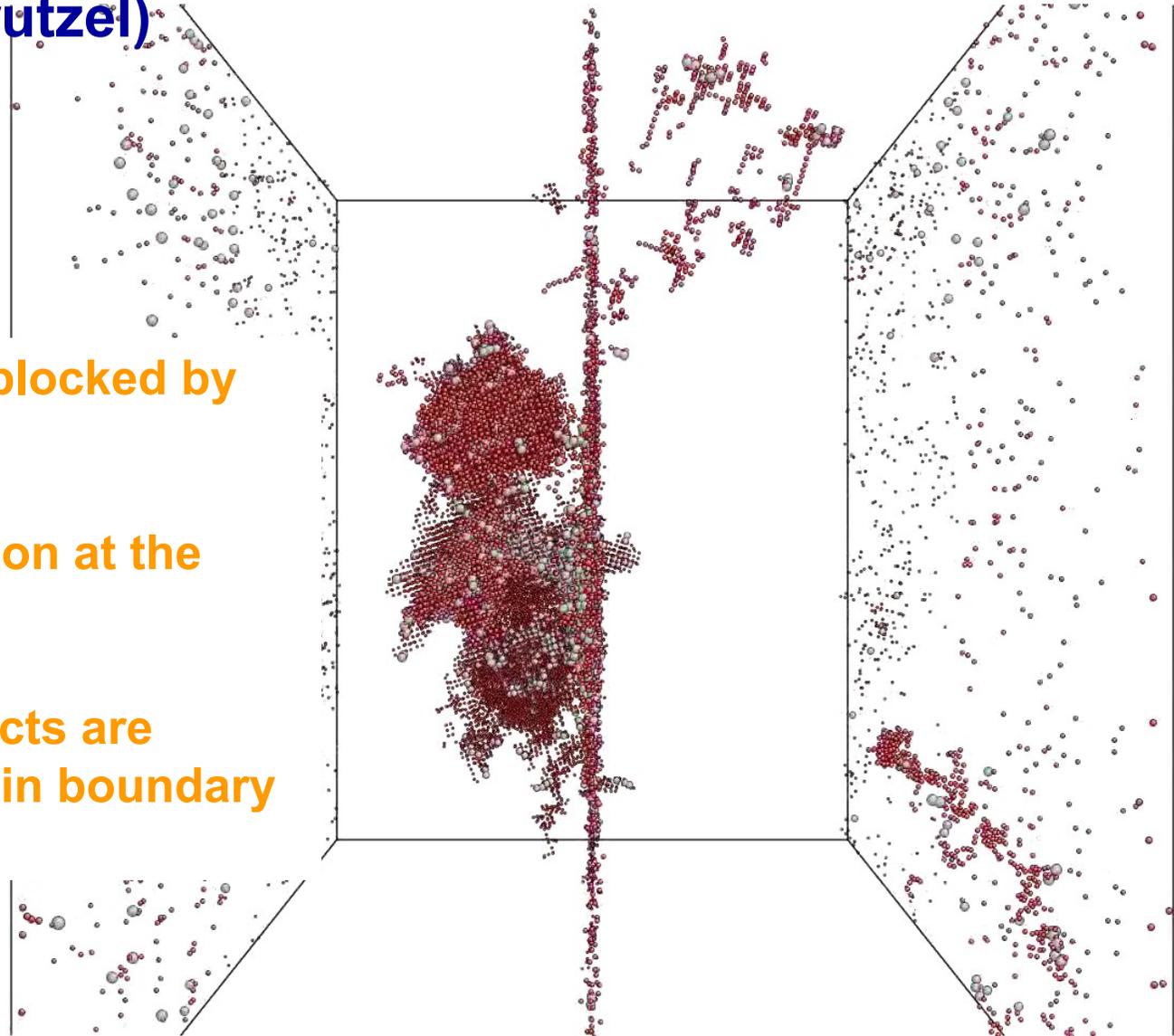


Displaced atoms
> 1Å

Grain boundaries influence in UO_2 (L. van Brutzel)



- The cascade is blocked by the interface
- Energy dissipation at the grain boundary
- Most of the defects are created at the grain boundary



Illustrations of CMD studies of nuclear fuels



Illustration 3 : Radiation enhanced helium re-solution in UO₂

Radiation enhanced helium re-resolution in UO₂

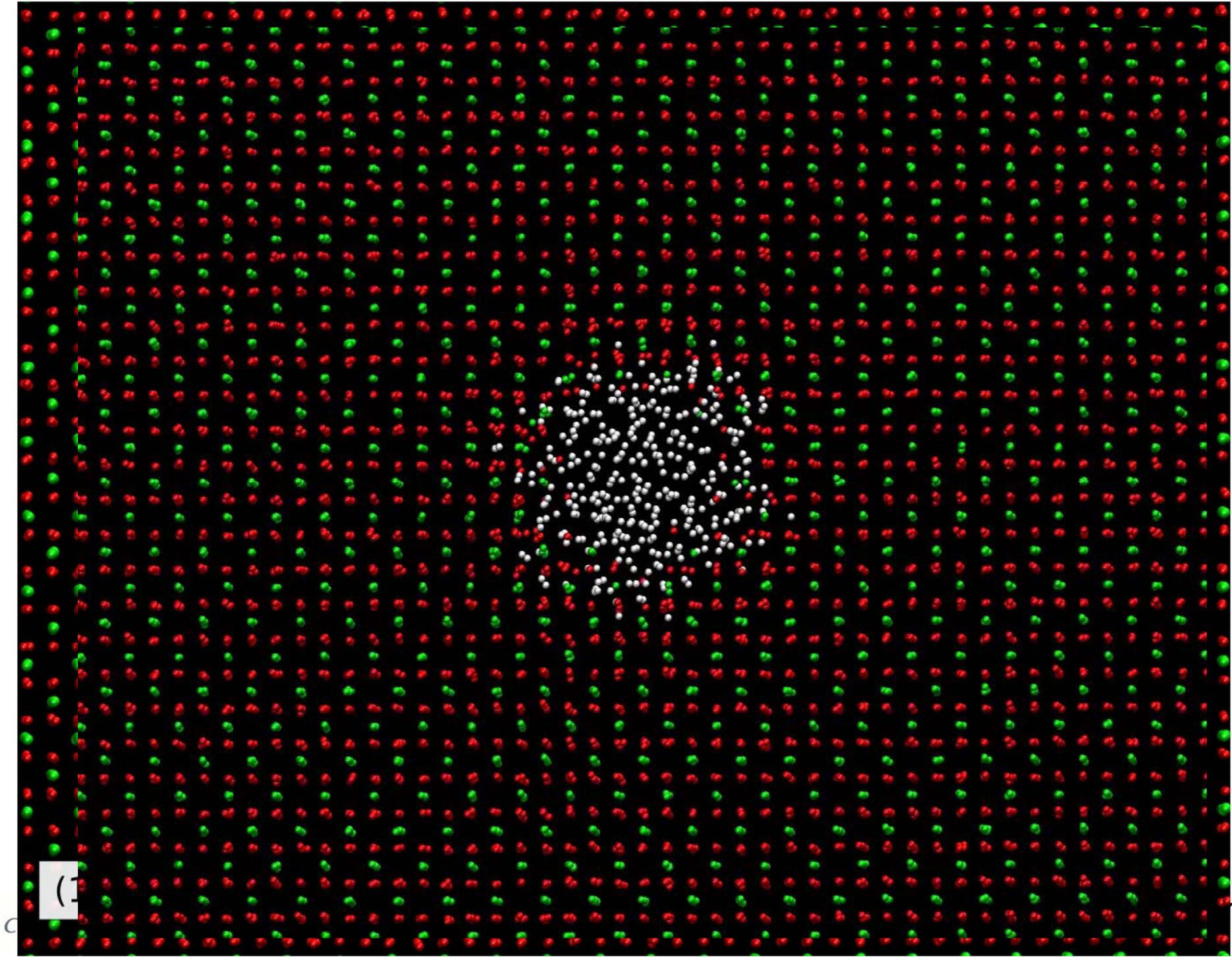
(R. Grimes)



Helium in bubbles can return to the crystal lattice via radiation-enhanced re-resolution rather than thermal resolution

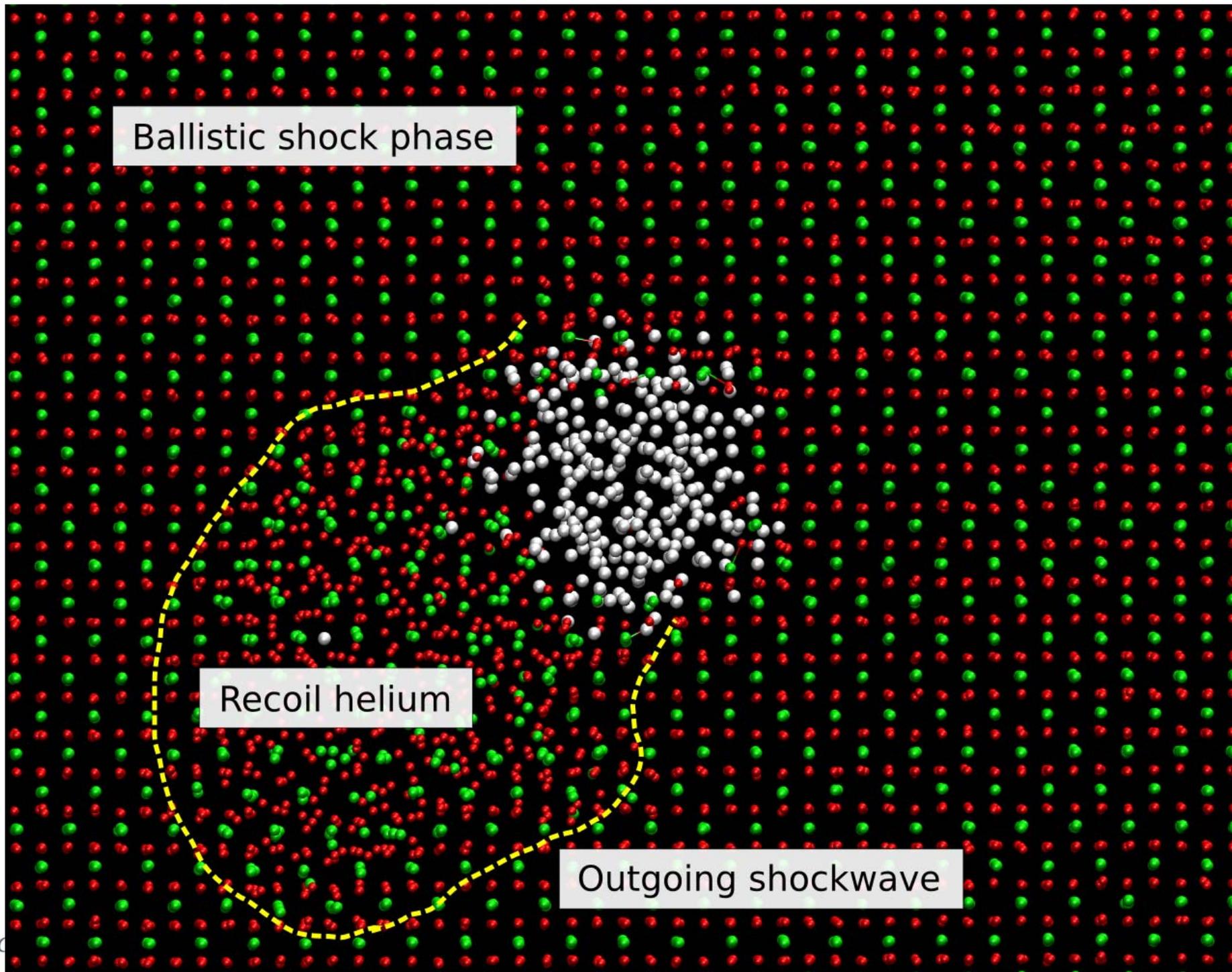
...But how does this happen precisely?

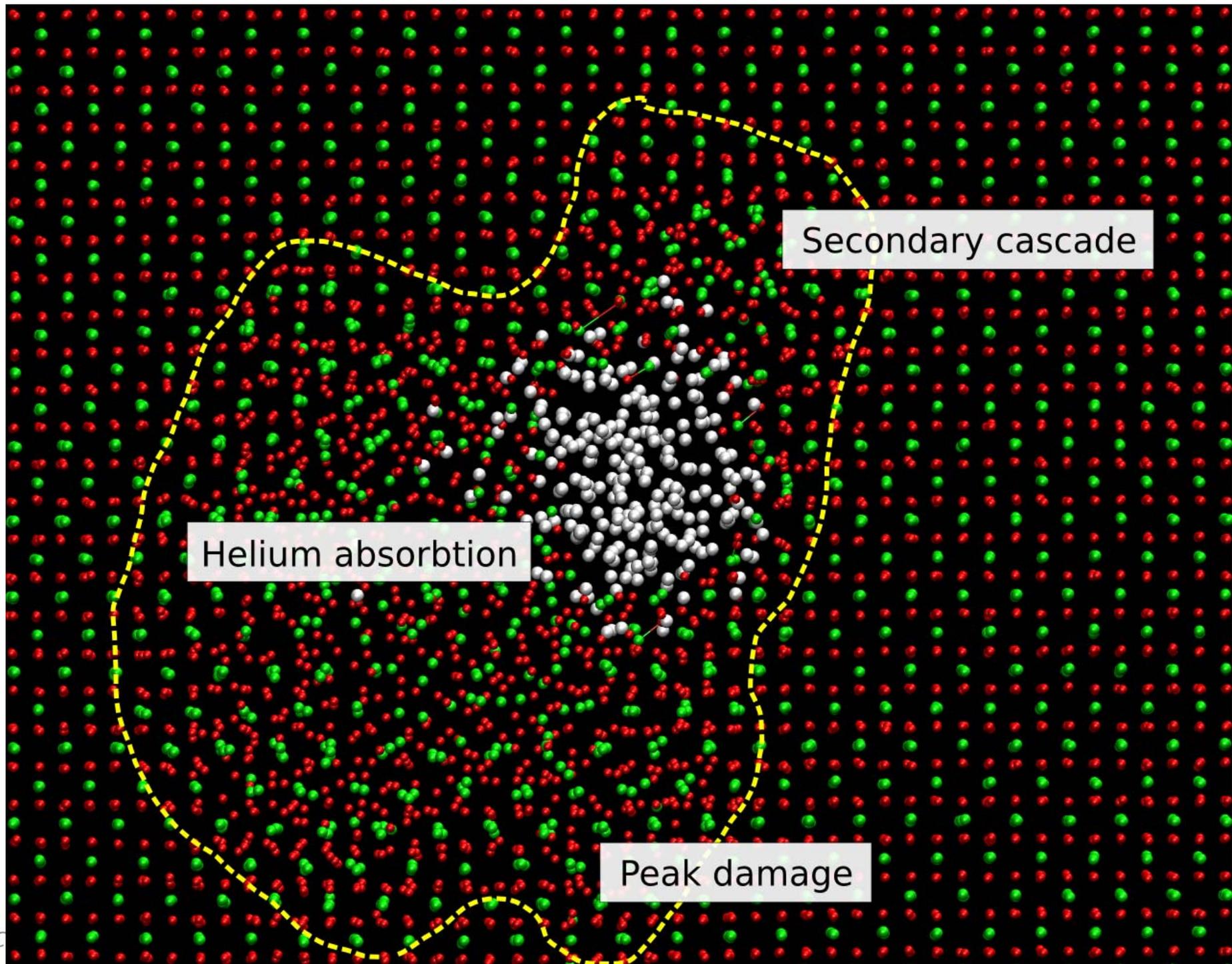
Hypothesis: high-energy fission fragments 'knock out' helium atoms from bubbles leading to resolution.



(1)

c

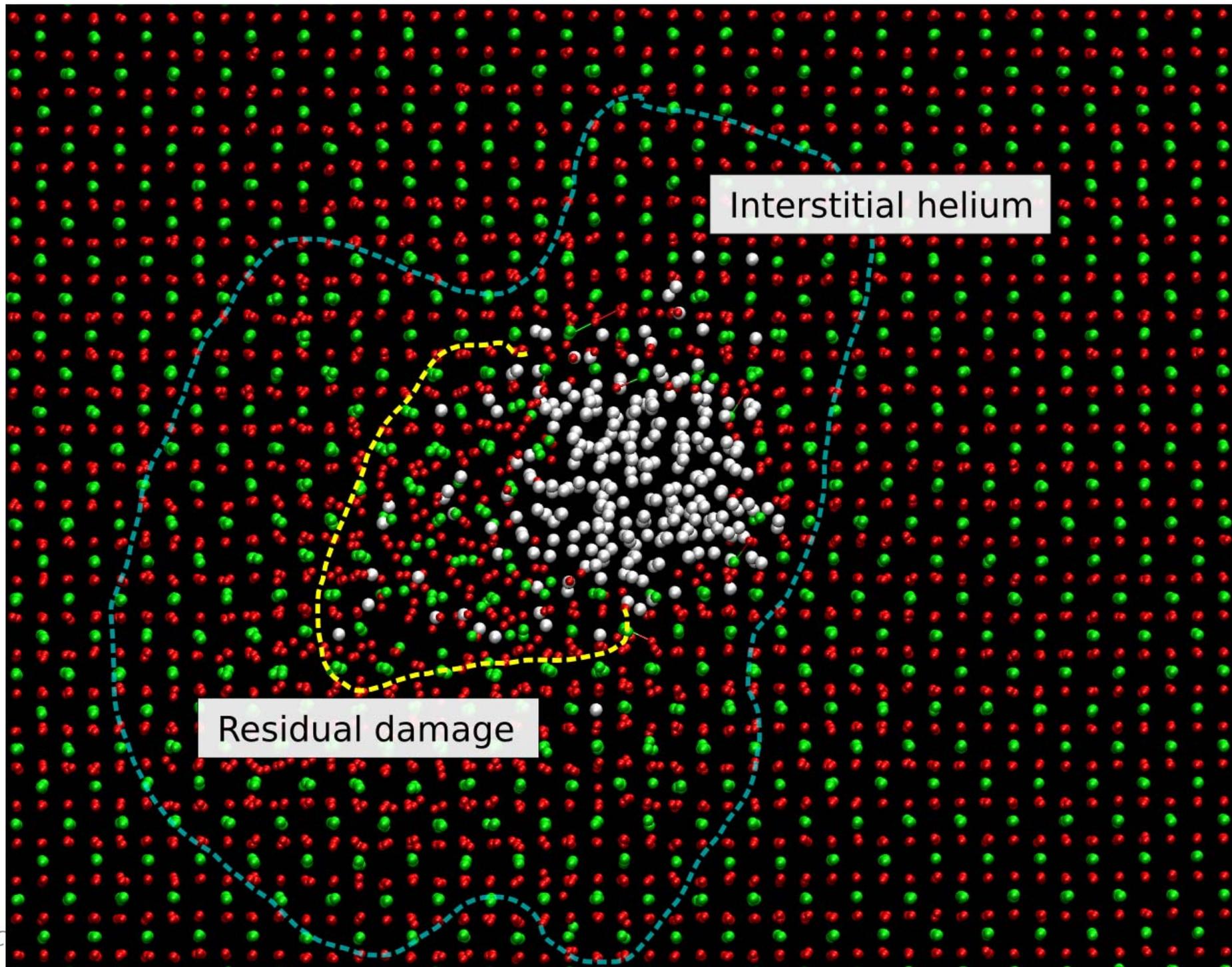




Helium absorbtion

Secondary cascade

Peak damage



Interstitial helium

Residual damage

Part 3 Conclusion

Application of atomistic calculations to nuclear fuels



- Ab initio calculations and CMD simulations are powerful tools
 - to identify atomic scale mechanisms
 - to generate quantitative data
- Studies of phenomena difficult to access experimentally
- Support experiments and microscopic modeling techniques

Challenges for the future

- Better *ab initio* approximation of strong correlation in UO_2
- Better *ab initio* description of Van der Waals interactions to model rare gases in the material
- Development of empirical potentials for rare gases & fission products
- Better integration of *atomistic* calculations in the **multiscale** modeling of nuclear fuels

General conclusion



- **Studying irradiated fuel is like trying to construct a 1000 piece puzzle**
...when you've only been given 10 pieces (P. Garcia)
- **Numerical and experimental simulations at the atomic scale of the fuel behavior under irradiation provide data, mechanisms to be used in fuel performance codes**
- **Various communities have to work together:**
 - **modelling and experiment**
 - **applied physics and basic research**

Acknowledgements



CEA Cadarache / Fuel Study Department

From my team M. Freyss, M. Bertolus, P. Garcia, P. Martin, H. Palancher, G. Carlot, C. Sabathier, C. Martial, JC Dumas, J.P. Piron, B. Dorado, G. Martin, E. Welcomme, J. Durinck, M. Fraczekiewicz

From the group : D. Plancq, B. Michel, A. Bouloré, L. Noirot, P. Obry, Y. Guerin, L. Brunel, E. Touron (previous and actual head of group)

CEA Saclay H. Khodja, C. Rapsaet, L. Van brutzel, A. Chartier, JP Crocombette, C. Gueneau

CEA DAM F. Jollet, F. Bottin, G. Jomard, M. Torrent

Imperial College : R. Grimes, D. Parfitt

CNRS : MF Barthe, T. Sauvage, P. Desgardin, E. Gilabert, F. Garrido

ITU : R. Konings, J. Somers, E. Kotomin, D. Gryaznov, P. van Uffelen

NRG: S. De Groot

ESRF FAME BL : O. Proux, J.-L. Hazemann, V. Nassif

TUM : N. Wieschalla, W. Petry, R. Jungwirth

AREVA-CERCA : C. Jarousse

ACTINET network of excellence



F-BRIDGE European project

