The Abdus Salam
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Educational, Scientific and
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12 - 23 April 2010

Numerical simulation of transport properties in nuclear fuels : from the atomistic scale to the mesoscopic scale (Part 3)

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Part 3

Numerical simulation of transport properties in nuclear fuels: from the atomistic scale to the mesoscopic scale

Part 3 Outline

Ab initio modeling of actinide compounds

Illustrations of *ab initio* studies of nuclear fuels

- Stability of point defects in UO_2
- Atomic transport in UO_2
- Behavior of Xe in UO_2 et UC

Classical Molecular Dynamics (CMD) modeling

Illustrations of CMD studies of nuclear fuels in UO_2

- Formation of defects during displacement cascades
- Influence of grain boundaries on cascades and defects

Conclusion

Illustrations of *ab initio* studies of nuclear fuels

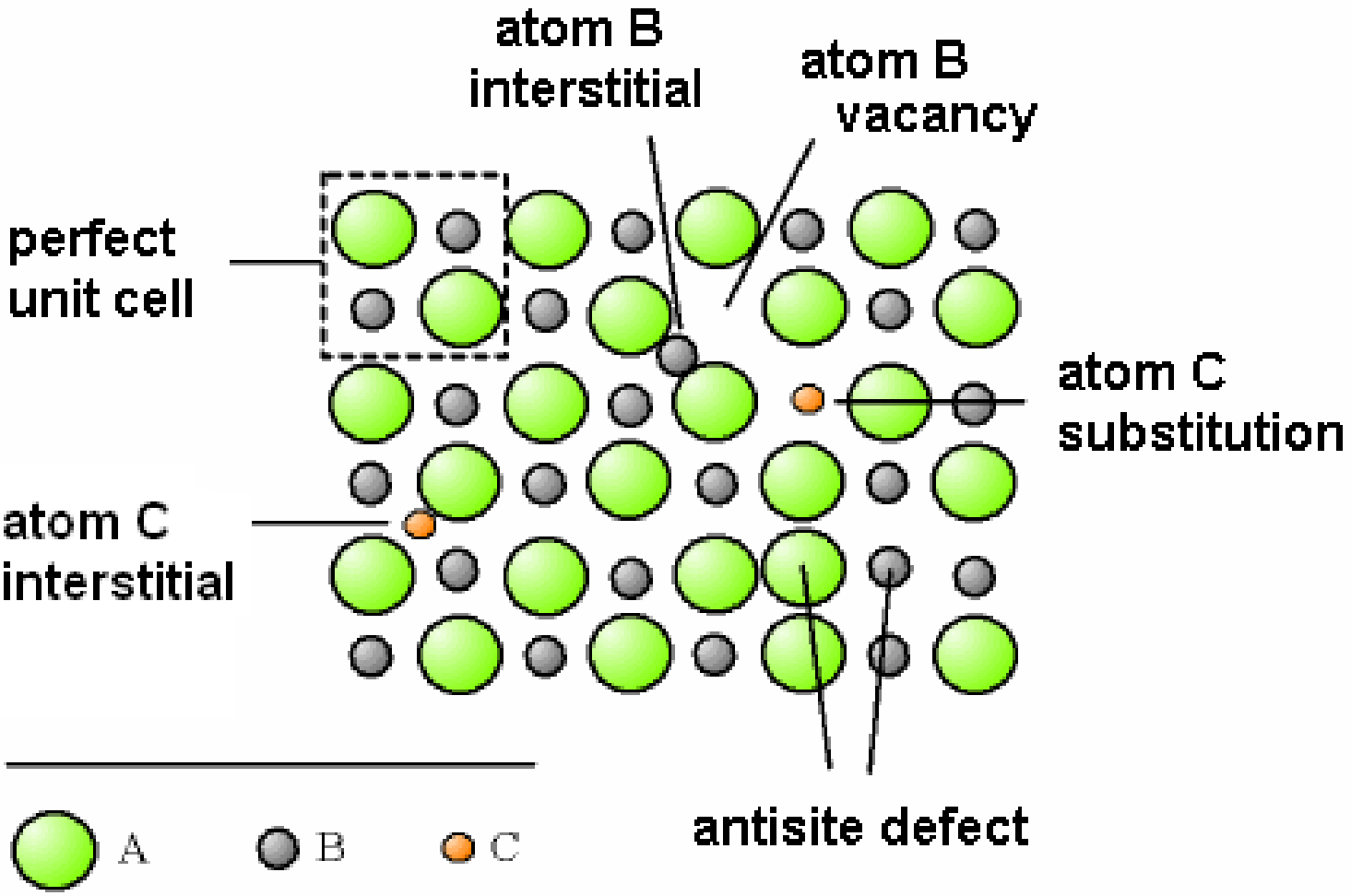
Illustration 1:
Ab initio modeling of the stability of point defects in uranium dioxide UO_2 and uranium carbide UC

Ab initio method for modeling of UO_2 and UC

Projector Augmented Wave method (PAW)

- Based on the Density Functional Theory (**DFT**)
- **Plane-Waves** as basis functions for valence electrons
- **Core electron** density taken into account
- Code **VASP** (http://cms.mpi.univie.ac.at/vasp/)
- Scalar relativistic approximation
- Exchange-correlation functional: **GGA** for **UC**
  GGA+U for **UO_2**
- Low **cut-off energy** of the plane-wave basis:
  350 eV for UC, 450 eV for UO_2
- Defects in UC in a **64 atom supercell**
  in UO_2 in a **96 atom supercell**
- **4x4x4** Monkhorst-Pack *k*-point mesh

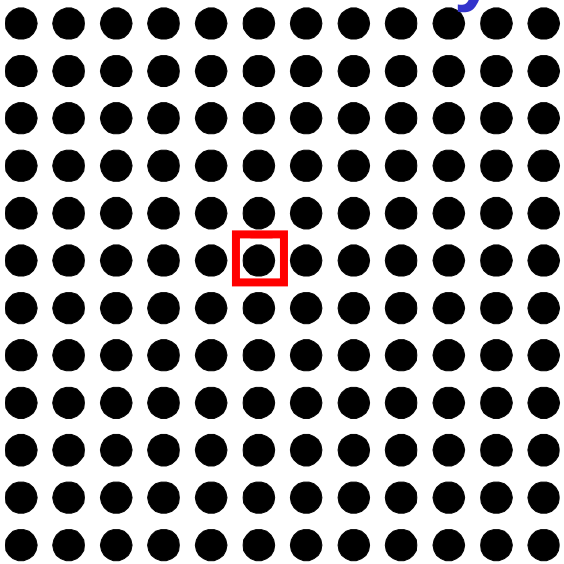
Point defects



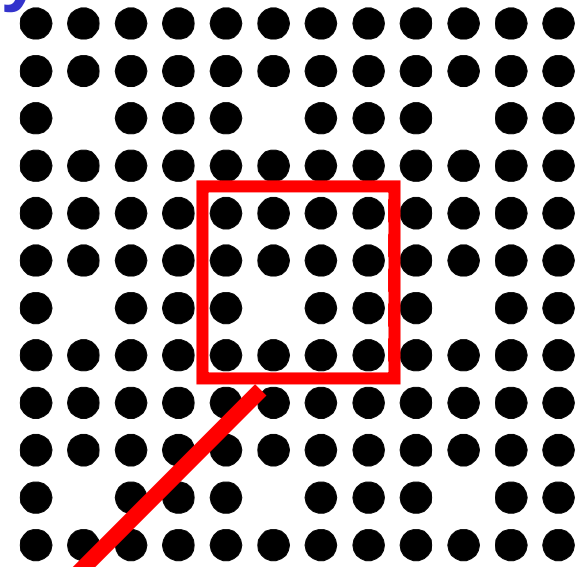
or more complex defects (tri-vacancies, dumbbells, clusters…)

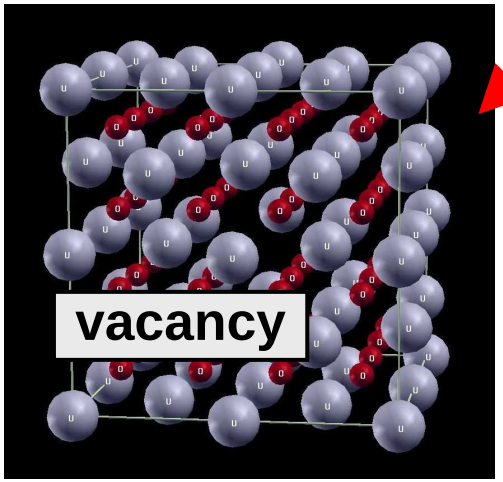
Periodicity: supercell technique

perfect bulk crystal



crystal with vacancies





supercell

~ 100 atom supercells possible nowadays for actinide compounds

Formation energy of point defects

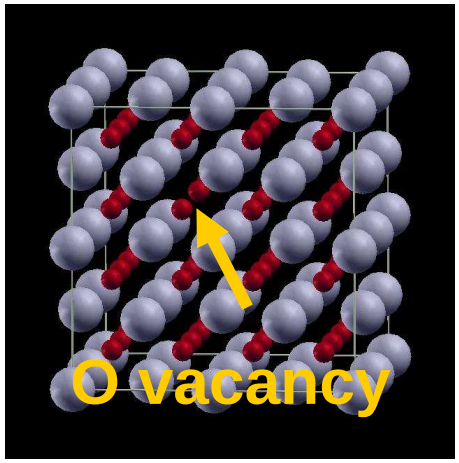
As an example :
Formation energy of a oxygen **vacancy** in UO_2

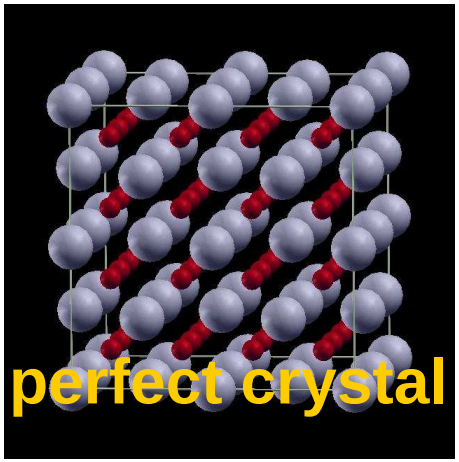
$$E^F = E^{N-1}_{UO_2} - (E^N_{UO_2} + E_X)$$

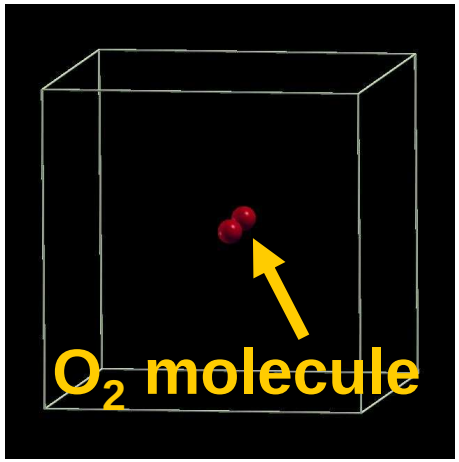
Supercell with the defect

perfect crystal

O atom in a reference state: O in O_2 molecule







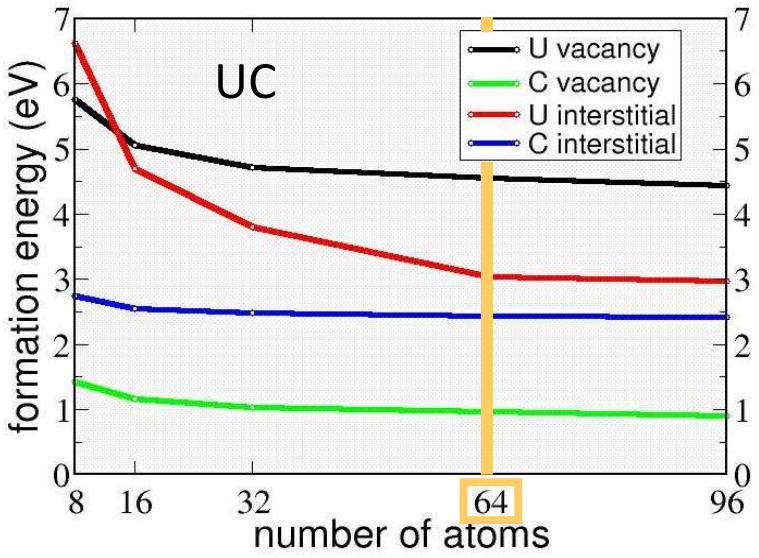
Point defects in uranium dioxide and carbide

- **Vacancies**
- **Interstitials**
- **Frenkel pairs**
  1 vacancy + 1 interstitial
- **Schottky defects**
  1 uranium vacancy
  + 2 oxygen vacancies
- **Small vacancy aggregates**

Relative stability:

➔ **Formation energies**

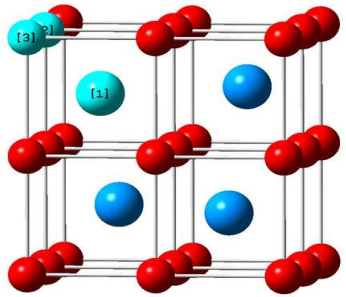
Exchange-correlation:	**GGA (UC) GGA+U (UO_2)**
Supercellule:	**64 atoms (UC), 96 atoms (UO_2)**
Cut-off energy:	**350 eV (UC), 500 eV (UO_2)**
k points:	**4x4x4 grid**
Relaxation of atomic positions and volume	



DFT+U formation energies of defects in UO_2

E^F (eV)	Fluorite	Jahn-Teller
Oxygen interstitial	**0.10**	**0.47**
Oxygen vacancy	**5.67**	**6.01**
Uranium interstitial	5.38	5.05
Uranium vacancy	10.43	9.87
1st bound Schottky defect *	**3.32**	**4.07**
2nd bound Schottky defect **	**2.55**	**3.26**
3rd bound Schottky defect ***	**2.92**	**3.41**
Isolated Schottky defect	10.66	10.62
Uranium Frenkel pair	15.80	14.62
Oxygen Frenkel pair	**5.78**	**6.48**

*



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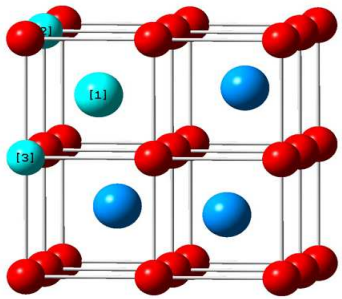

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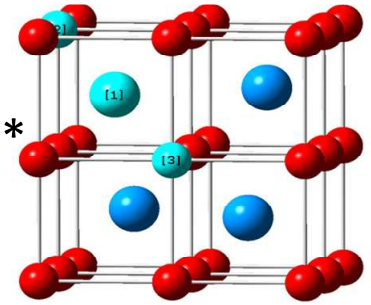

- Crystal field: **moderate effect** on formation energies (except I_O)
- Uranium and oxygen vacancy formation energies > 5 eV.
- Diffusion very likely to occur *via* **Schottky defects**
- Ability of vacancies to trap fission gases?

B. Dorado et a., submitted (2010)

DFT+U formation energies of defects in UO_2

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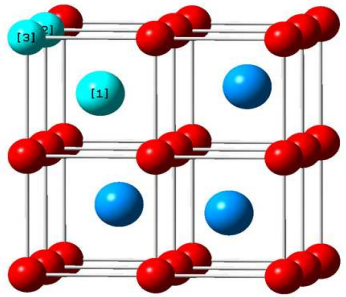

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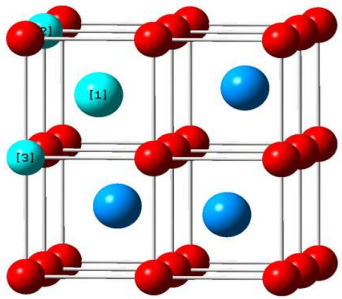

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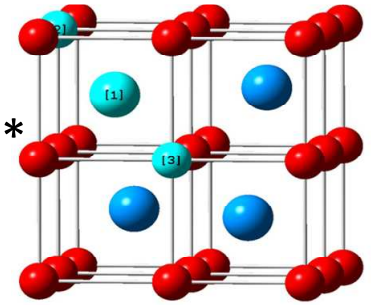


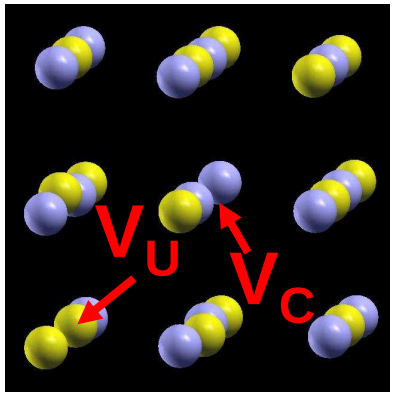
- Experimental data H-j. Matzke, J. Chem. Soc., Faraday Trans. 2, 83, 1121 (1987)

  E^F (O Frenkel pair)= 3.0-4.0 eV, E^F (U Frenkel pair)= 9.5 eV

  E^F (Schottky)= 6.0-7.0 eV
- Relative agreement

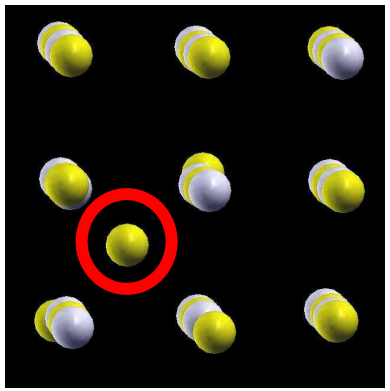
Point defects in UC

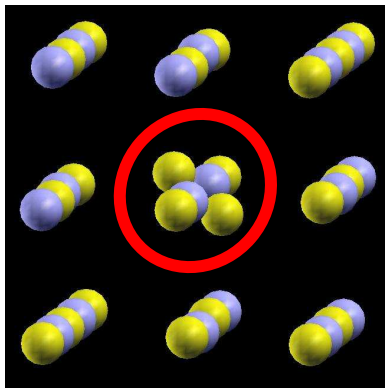
- Irradiation damage in UC better accomodated in the carbon sub-lattice
- Weak perturbation of the crystal structure
- Aggregation of U and C vacancies more favorable than isolated vancancies
- « **Dumbbell »** configuration of interstitials more stable than tetraedral interstitials



Carbon at tetraedral site

E^F=2.5 eV





Carbon in a dumbbell <111>

E^F=2.2 eV

M. Freyss, Phys. Rev. B **81**, 014101 (2010)

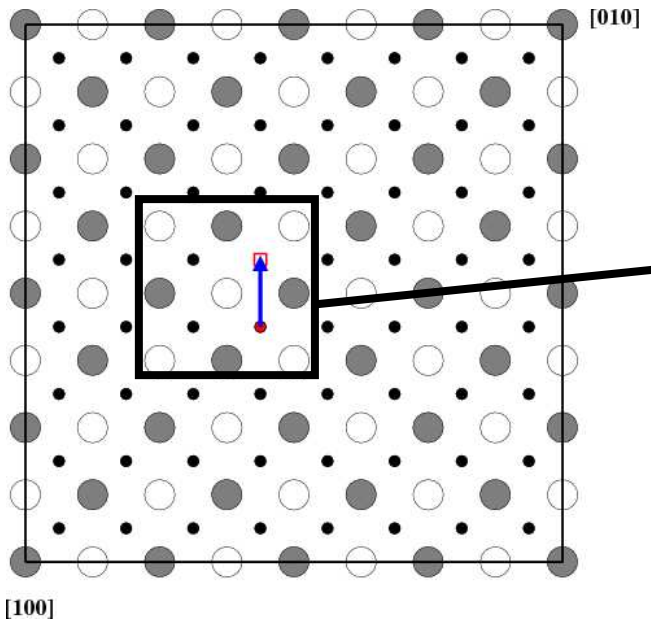
Illustrations of ab *initio* studies of nuclear fuels

Illustration 2:
***Ab initio* modeling of**
migration of defects in UO_2 and UC

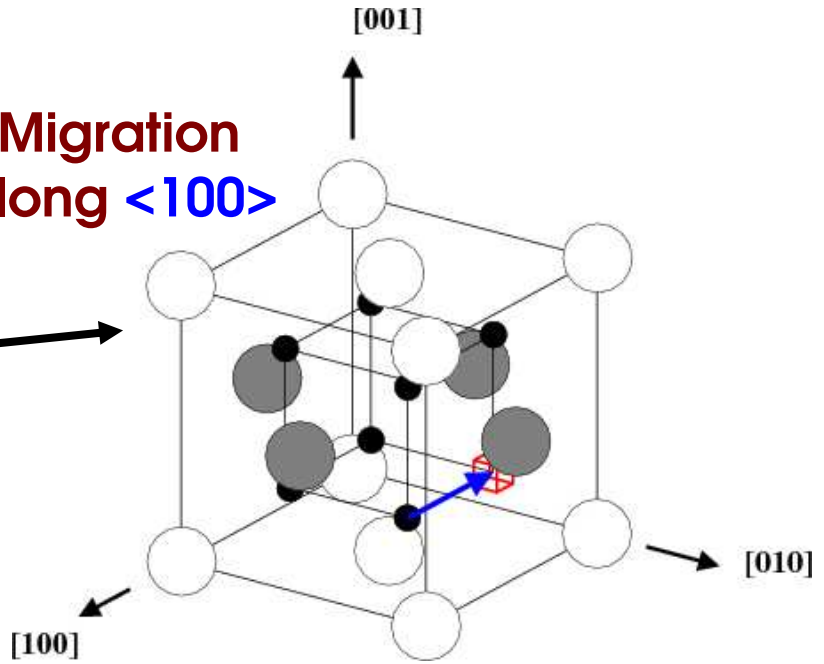
Migration energies of point defects in UO_2

- Experimentally: activation energies measured and reported in the literature (Auskern 1961, Belle 1969, Marin 1969, Contamin 1972).
  - Generally no control of oxygen partial pressure
  - No measurement of impurity content
  - Dominant migration mechanism remains unknown
- **New data for identifying diffusion mechanisms** (Garcia *et al.*, J. Nucl. Mater. (2010) *in press.* Cf presentation 4)
- Theoretically: migration energies calculated with
  - **Empirical potentials** (Catlow 1977): migration mechanisms
  - **Standard DFT** (Dorado 2009) : DFT-GGA description of UO_2
  - **DFT+U** approximation (Gupta 2010) without the NEB method (migration path not optimized)
- Need to use **up-to-date methods** to determine accurate activation energies for oxygen diffusion. **In progress…**

Migration energies of point defects in UO_2

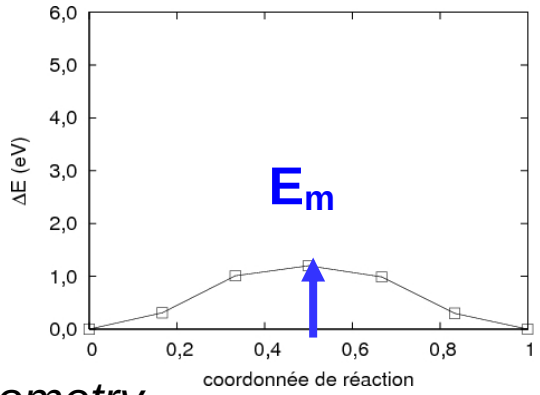


Migration along <100>



Different migration mechanisms

What is the **lowest migration barrier** ?



Coupling to experimental measurements of diffusion coefficients while monitoring the stoichiometry

Migration energies: calculation method

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

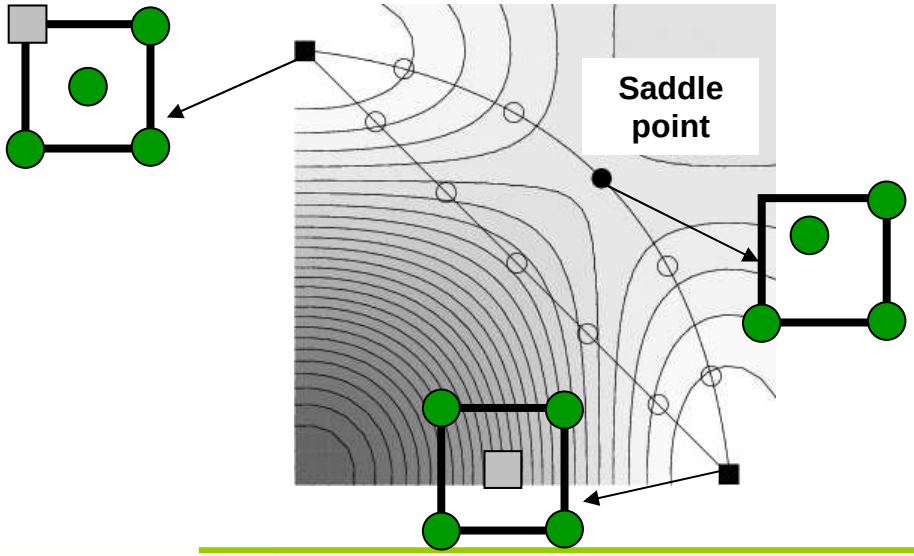
Nudged Elastic Band (NEB)

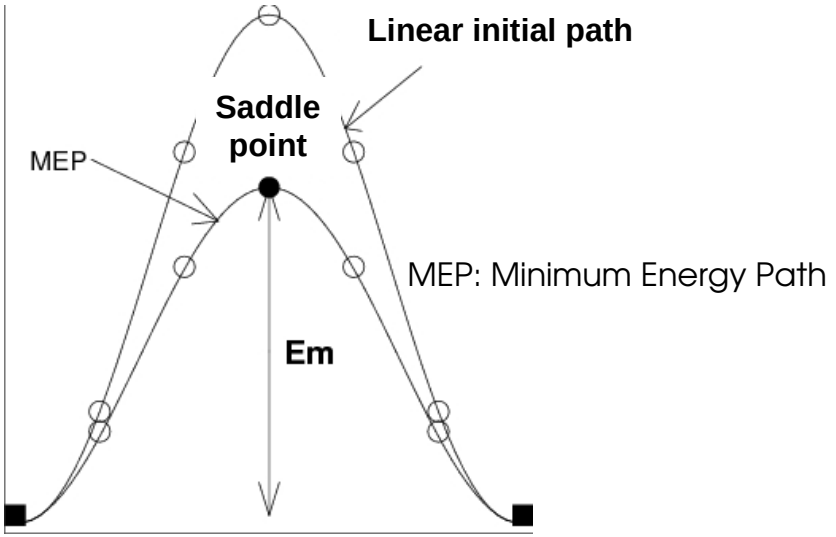
Determine Minimum Energy Paths for atom migration

→Choice of a start migration path and images along it

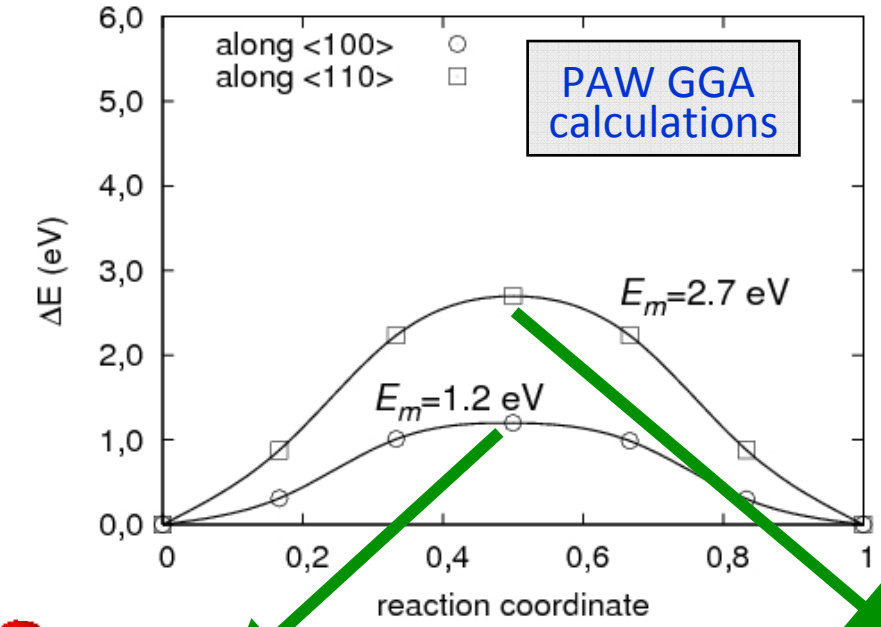
→Atomic relaxation perpendicular to the path

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



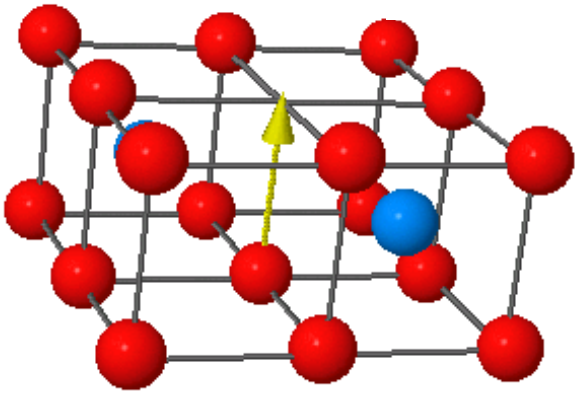


Migration energies: oxygen vacancy

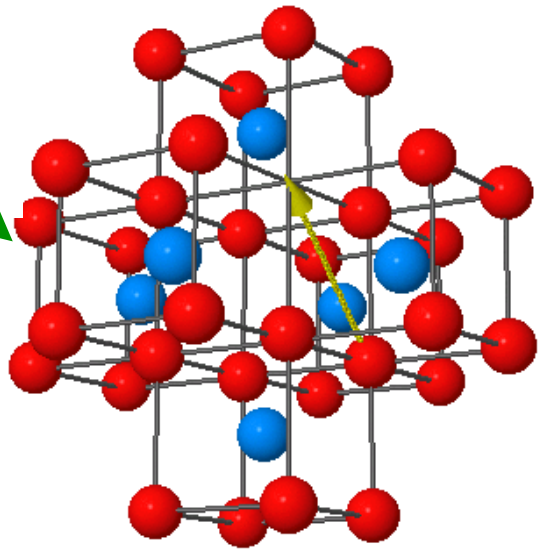


B. Dorado *et al.*, J. Nucl. Mater. (2010) in press

along <100>



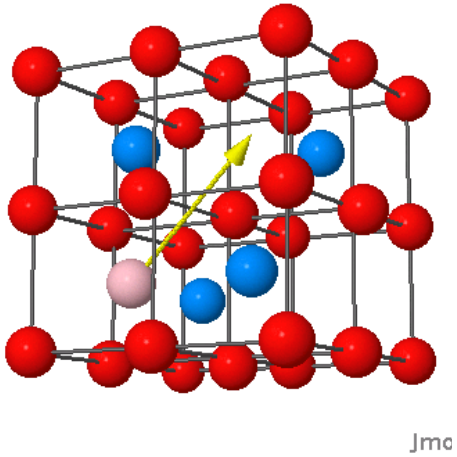
along <110>



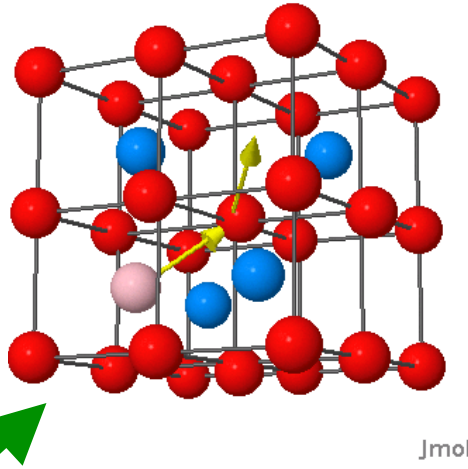
O vacancies are more mobile along the <100> direction than along the <110> direction

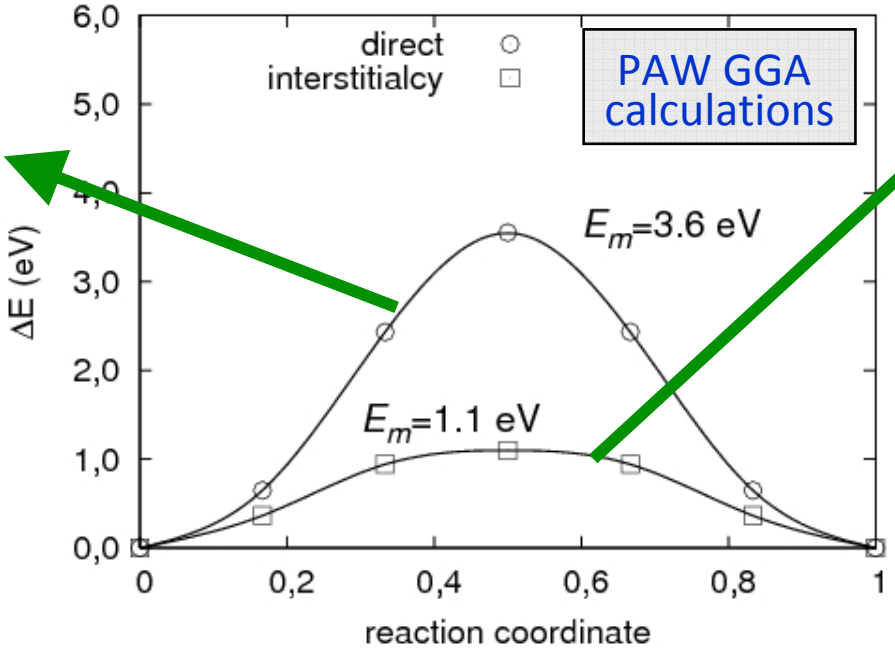
Migration energies: oxygen interstitial

Direct mechanism



Indirect mechanism



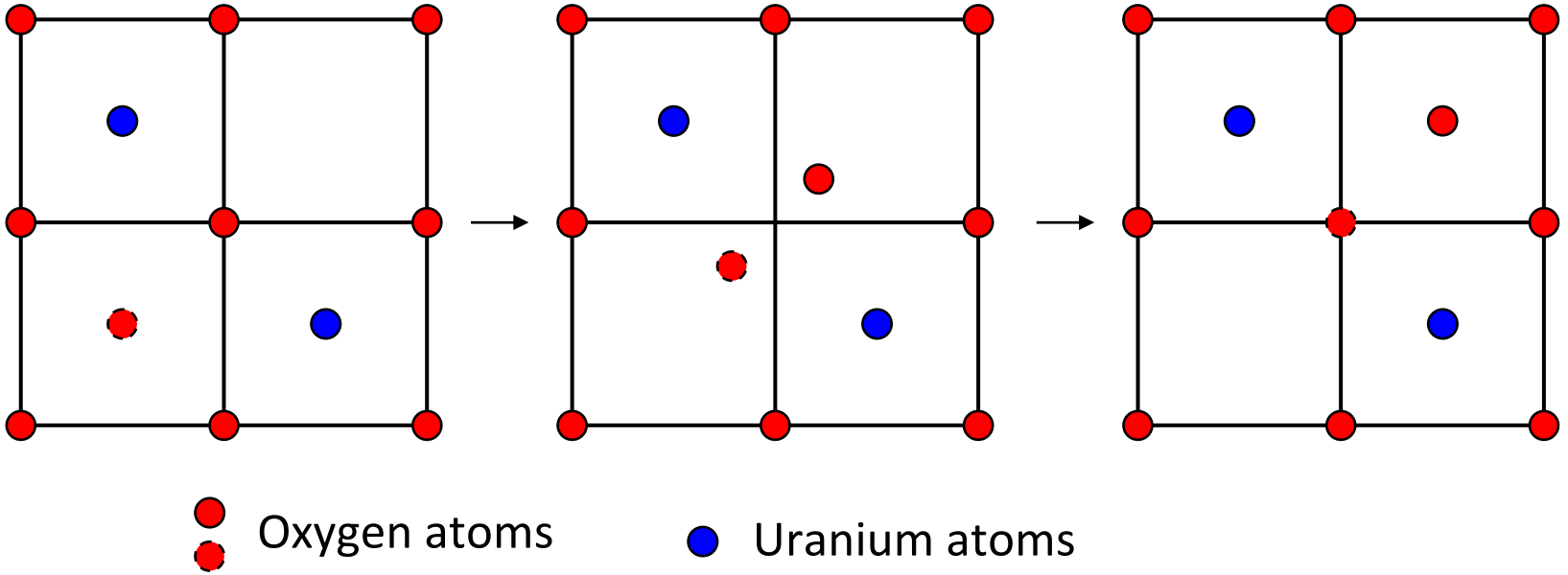


B. Dorado *et al*.,
J. Nucl. Mater. (2010)
in press

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

Migration energies: oxygen interstitial

- Electrical conductivity measurements:
  - Control of parameters that affect the material (oxygen partial pressure and impurity content)
  - Oxygen diffusion occurs *via* interstitial mechanism
  - Measured activation energy = 0.6 eV
- **DFT+U + NEB calculations** of the **interstitialcy mechanism**



Migration energies: oxygen interstitial

- During the NEB calculation, symmetries are switched off.

- Calculated migration barrier : 0.6 eV $\Rightarrow$ Calculated activation energy $E_a = E^F + E_m$ = 0.7 eV (recent measured value: 0.6 eV).

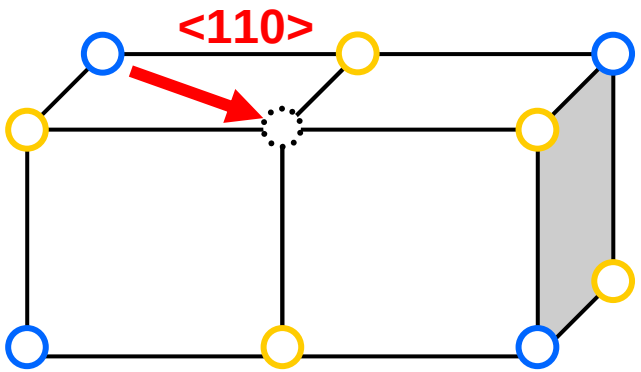
- **Good agreement between the calculated and experimental activation energies.**

- **Oxygen diffusion in UO_2 occurs *via* the interstitialcy mechanism.**

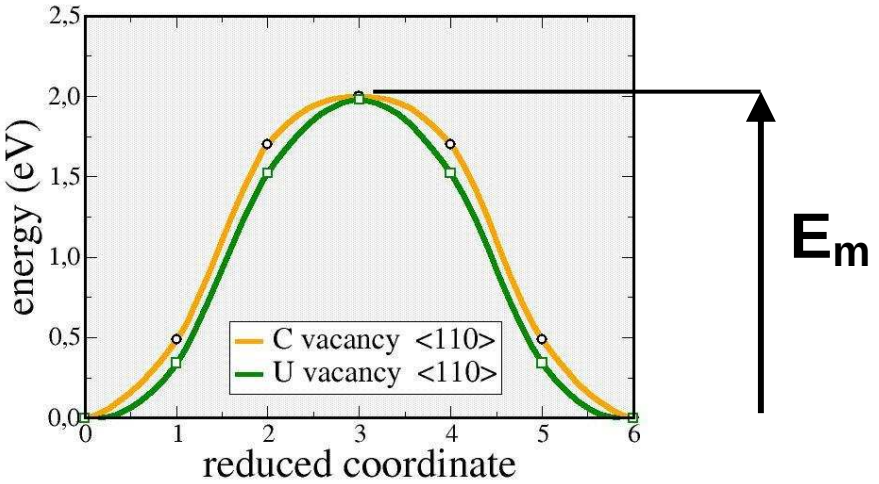
- Other vacancy-assisted mechanisms are currently considered but much higher activation energy (because high formation energy)

Migration in UC: carbon and uranium vacancies

Migration energy



NEB calculations in a 64 atom UC supercell with the relaxed volume for each defect



E_m (eV)	C defects	U defects
vacancy along <110>	**2.0**	**2.0**
experimental data	0.9-1.5 *	2.4 ± 0.4 *

* Hj. Matzke, *Science of Advanced LMFBR fuels* (1986)

Uranium: vacancy mechanism
Carbon: interstitial mechanisms to be investigated

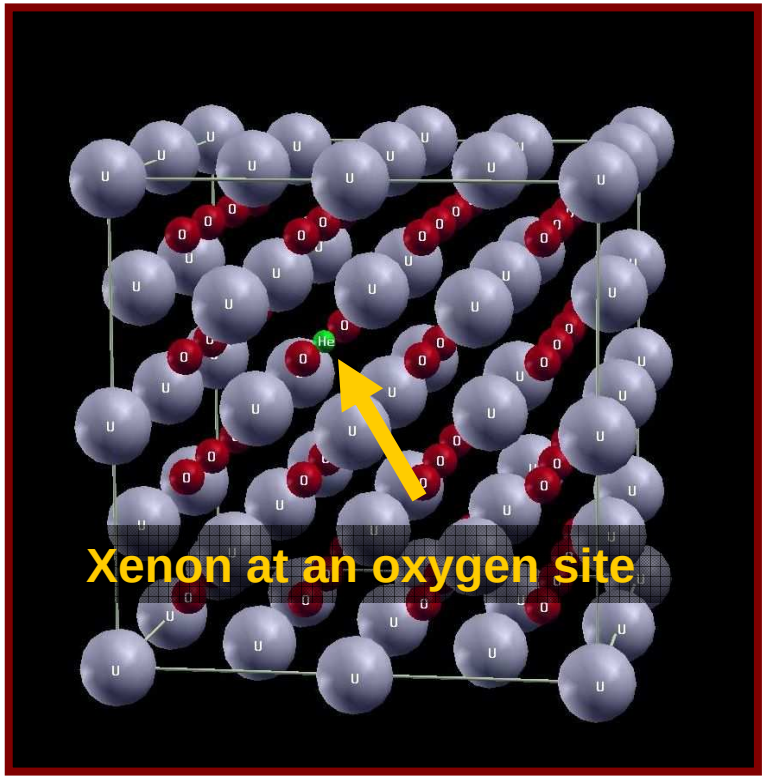
Same trend in **UN**: $E_{mig}(U) = E_{mig}(N) = 3.5eV$ D. Gryaznov *et al.* J. Nucl. Mater (2009)
Not in **UO_2** : $E_{mig}(U) = 4.4eV > E_{mig}(O) = 1.2eV$ B. Dorado *et al.* J. Nucl. Mater (2010)

Illustrations of ab *initio* studies of nuclear fuels

Illustration 3:
Modeling of the stability of fission products in UO_2 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**

Completed by empirical potential calculations A. Chartier et al., submitted (2010)

Incorporation energy

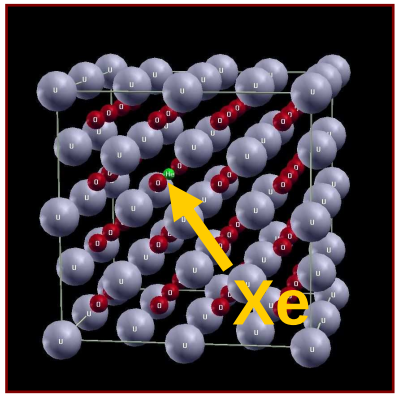
Energy required to incorporate Xe in a pre-existing vacancy or at an interstitial site:

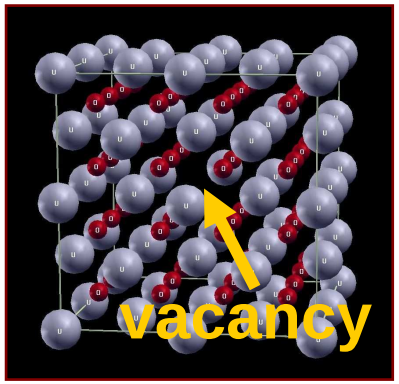
$$E_{inc} = E_{Xe}^{N} - (E^{N-1} + E_{Xe})$$

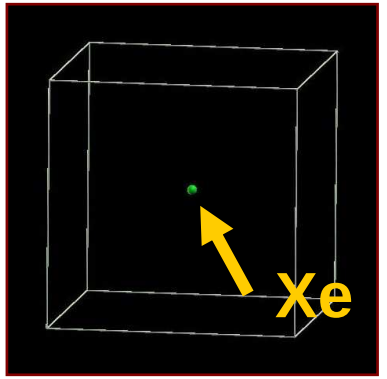
Xe incorporated in the fluorite structure

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	**4.2**	8.2	12.1
UO_2	**5.8**	9.1	**12.0**

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

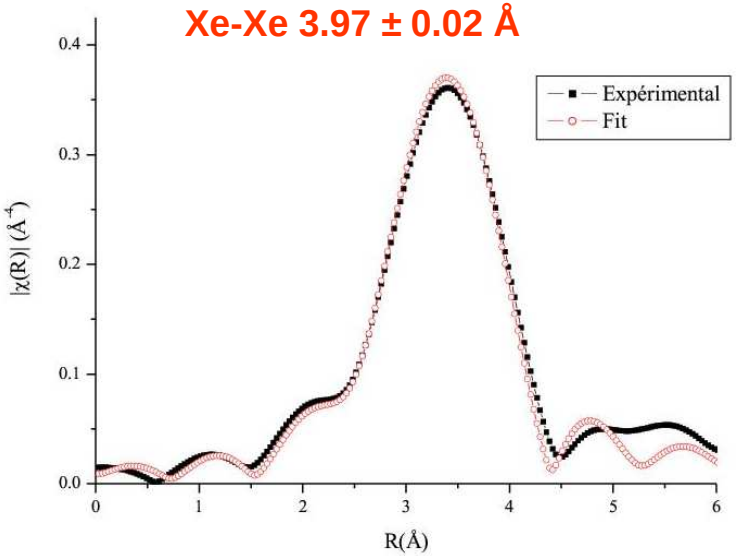
DFT+U studies of Xe in UO_2 :
Nerikar *et al.*, J. Phys.: Condens. Matter 21 (2009) 435602
Yu *et al.*, J. Phys.: Condens. Matter 21 (2009) 435401.
but problems of metastable states not taken into account

Experimentally characterized in UO_2 by EXAFS and TEM

➔ Xe implantation, annealing, EXAFS analysis

➔ **Formation of pressurized Xe clusters**

See presentation 4



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

Xenon incorporation in UO_2

Formation of nano-voids and stability of bubbles of xenon in UO_2

A. Chartier *et al.* submitted (2010)

Study with **empirical potentials** (static calculations) fitted on **DFT calculations**

Buckingham potentials for UO_2 and Xe-U and Xe-O interactions (cf. presentation 2). Tang and Toennies potential for Xe-Xe interactions.

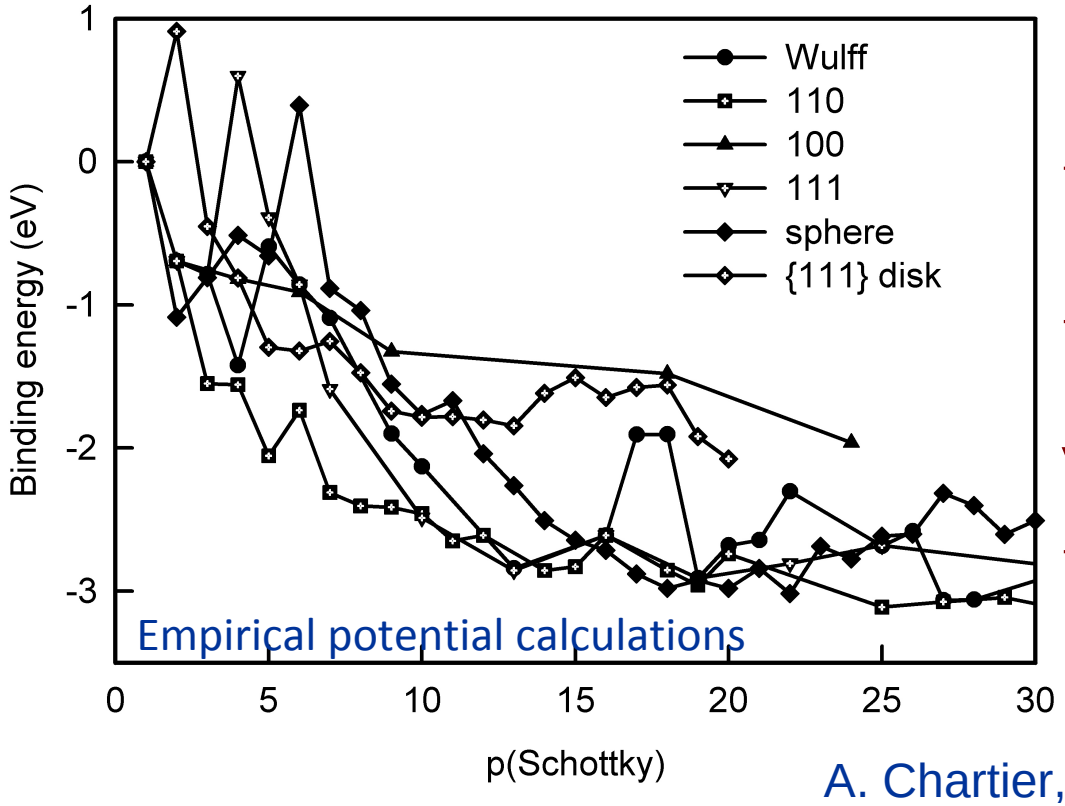
	Incorp. energies E_{inc} (eV)			
Incorp. sites	Xe(**Int**)	Xe(**Vu**)	Xe(**Vo**)	Xe(**S**)
DFT	12.0	**5.8**	9.1	***I***
emp. pot.	11.9	**5.4**	9.3	**4.2**

Higher stability of Xe atoms in Schottky defects (S) compared to substitution or interstitial sites

Xenon in UO_2 : stability of nanovoids

Binding energies of various shapes of voids as a function of the number *p* of Schottky (S) defects.

$$E_{binding}\left(Void_p^S\right) = \left[E\left(Void_p^S\right) - pE(S)\right]/p$$



Binding energy < 0:
→ **Aggregation** of Schottky defects
→ Formation of **nanovoids**

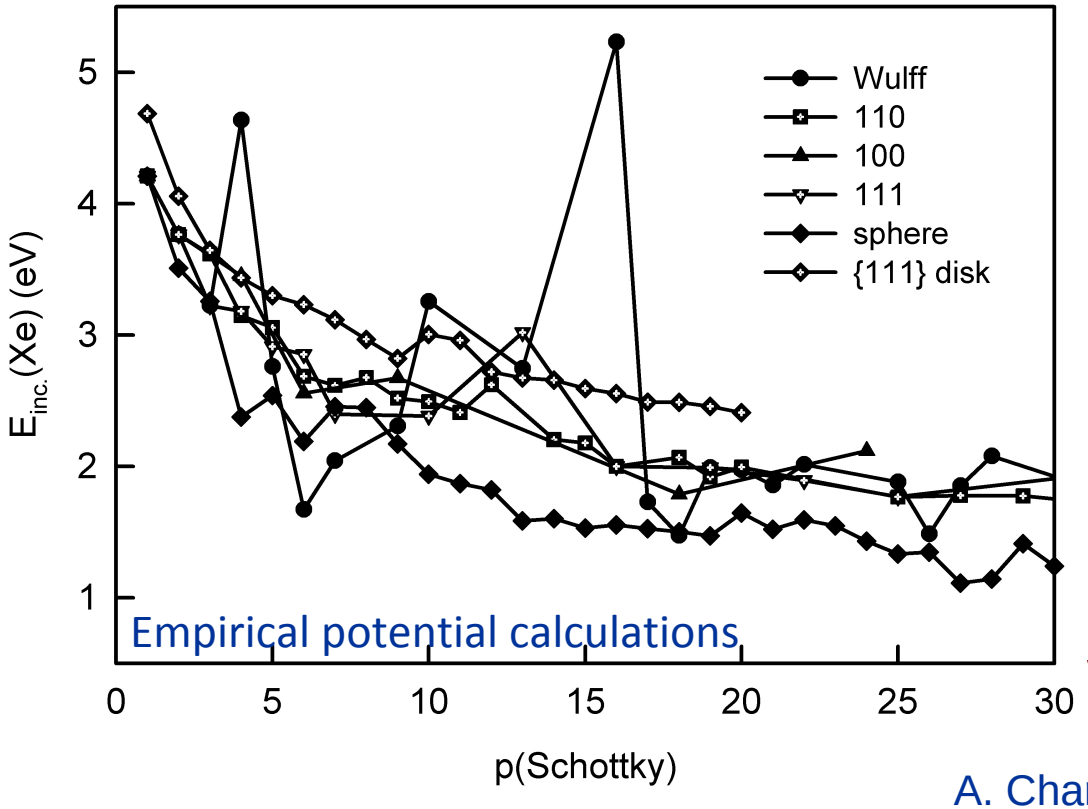
Various shapes of voids:
→ Facetted voids more stable

A. Chartier, L. van Brutzel *et al.* submitted (2010)

Xenon in UO_2 : incorporation in nanovoids

Xenon incorporation energies (in eV/Xe atom) in different void shapes, as a function of the number *p* of Schottky defects, which contain *p* Xe atoms

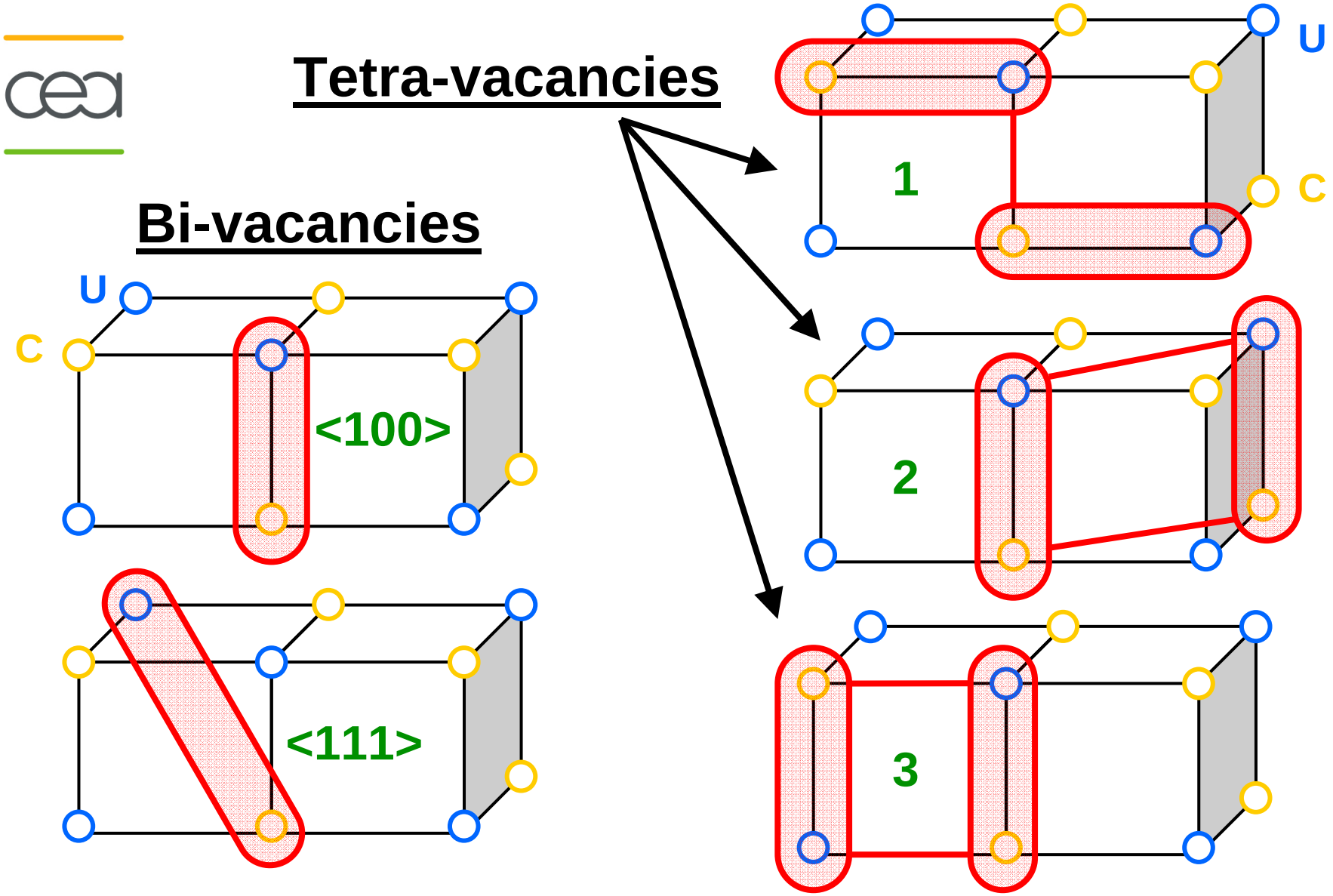
$$E_{inc}\left(Xe(S)_p\right) = \left[E\left(Xe(S)_p\right) - E\left(Void_p^S\right) - pE\left(Xe_g\right)\right] / p$$



- Incorp. energy decreases with *p* → stability of **xenon clusters**
- Various shapes of voids → **spherical** xenon clusters more stable
- Incorp. energy saturates *p*~20 → spherical xenon clusters with **radius of 1.3 nm**. In agreement with TEM analysis (cf presentation 4)

A. Chartier, L. van Brutzel *et al.* submitted (2010)

Stability of U-C vacancy clusters in UC



Stability of U-C vacancies in UC: DFT calculations

vacancies	E_F (eV)	E_b (eV)
monovac U	4.5	/
monovac C	**0.8**	/
bivac U-C <100>	4.6	**- 0.7**
bivac U-C <111>	5.3	~ 0
tetravac 1	7.8	**- 2.8**
tetravac 2	7.3	**- 3.3**
tetravac 3	8.9	**- 1.7**

Binding energy **E_b** :

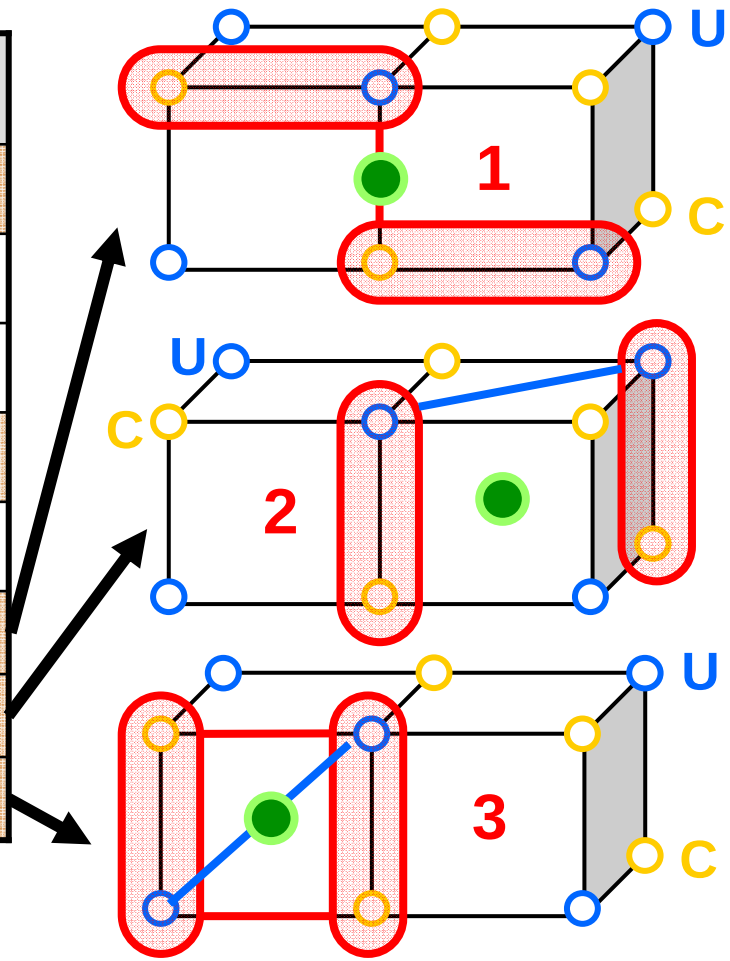
Bound vacancies E^F(Vac U-C) *vs*. isolated vacancies E^F(Vac U) + E^F (Vac C)

E_b < 0: bound vacancies are more stable than isolated vacancies

Possible traps for fission products and helium

Incorporation of volatile fission products in UC

E_{inc} (eV)	Kr	Xe
monovac U	3.6	4.2
monovac C	6.0	8.2
interst. tetra.	10.1	12.1
bivac U-C <100>	**2.6**	**3.2**
bivac U-C <111>	3.7	4.3
tetravac 1	**2.2**	**2.4**
tetravac 2	**1.7**	**2.2**
tetravac 3	**2.7**	**3.4**



E_{inc} < 0 : stability

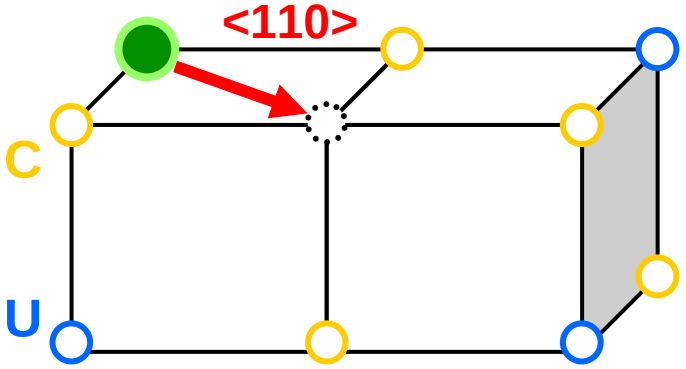
Kr and **Xe** **not favorably incorporated: not soluble in UC**
Most stable at a U substitution site and **extended defects, like in UO_2**
Larger defects out of scope of ab initio calculations: empirical potentials

Migration of volatile fission products in UC

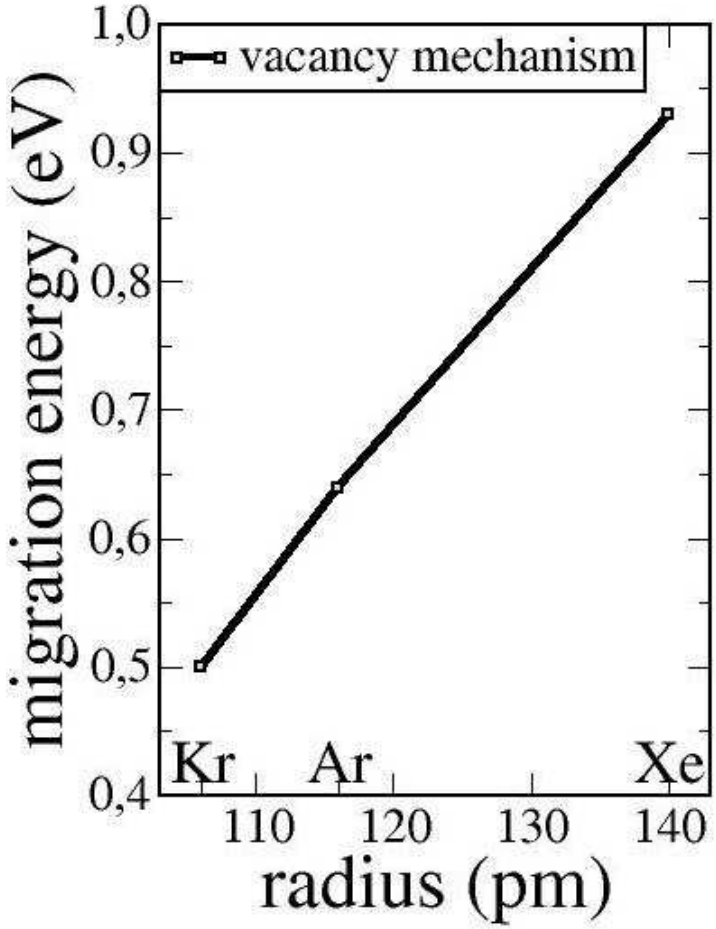
Nudge Elastic Band (NEB) calculations in a 64 atom UC supercell

Only one migration path investigated so far:

U substitution site → U vacancy



	Ar	Kr	Xe
E_{migr} (eV)	0.50	0.64	0.93



Mainly steric effect.
Other migration mechanisms involving more complex defects ?

Classical Molecular Dynamics Simulations of displacement cascades in UO_2

Empirical potentials and molecular dynamics

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

- Simulates evolution of systems in time
- Based on statistical mechanics. Calculation in a statistical ensemble (example: N, V, T constant)
- Calculations at finite temperature

Advantages / Disadvantages

- Quick ⇨ 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

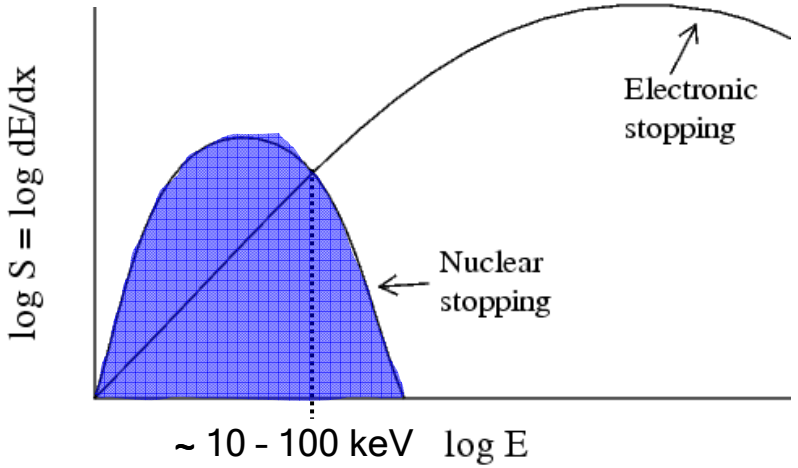
Cf presentation 2

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 pair potential for UO_2 [1]

- relatively simple: rigid ion potential $U^{3,2+}$ et $O^{1,6-}$
- 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 UO_2

Fluorite structure UO_2

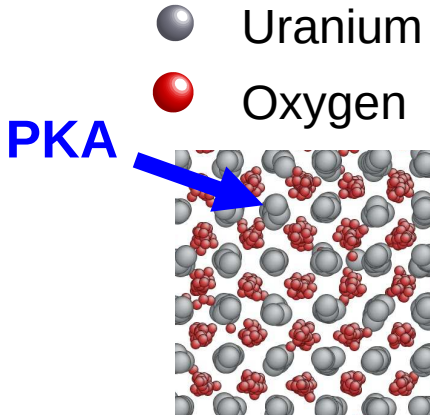
Up to 68×68×68 unit cells (**3 million atoms**), stabilized 20 ps at 300K and 0 GPa

Energy pulse given to an atom (Primary Knock-on Atom PKA) → 1 to 80 keV

- Cascades simulated with constant N,V,~E
- Temperature control at the boundaries of the box (3 Å)
- Periodic boundary conditions
- Variable time steps
- **Statistical approach** to interpret results:

  several cascades performed in the same conditions

  with different locations and directions of the PKA.



- **Single cascade**: successive steps of defect formation and recombination
- **Cascade overlaps**: saturation of defect formation

Displacement cascade in UO_2 with a 80 keV PKA

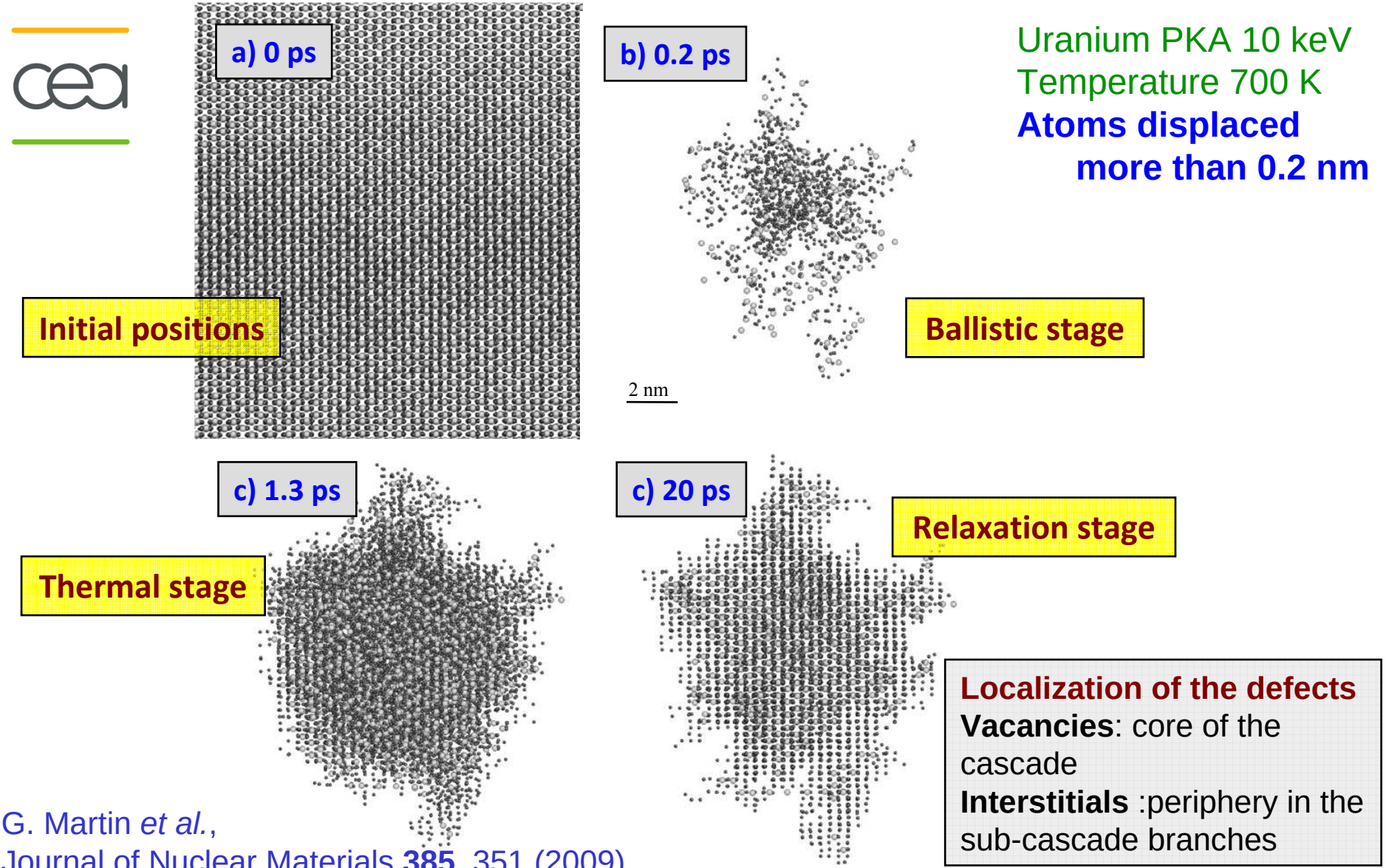
Atoms represented
= displaced atoms

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

film

80 keV U PKA
68x68x68 cell
300 K

Successive steps of a displacement cascade in UO_2



Uranium PKA 10 keV
Temperature 700 K
Atoms displaced more than 0.2 nm

Localization of the defects
Vacancies: core of the cascade
Interstitials :periphery in the sub-cascade branches

G. Martin *et al.*,
Journal of Nuclear Materials **385**, 351 (2009)

Number of defects after a cascade in UO_2

The total number of defects created **increases** with the energy of the PKA

High recombination rate: a displaced atoms finds an equivalent crystal site.

No amorphisation of UO_2 .

The recombination rate for uranium increases rapidly with temperature.

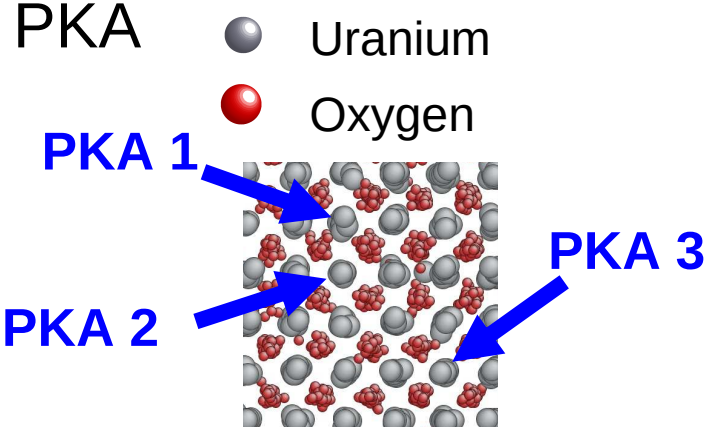
G. Martin *et al.*, J. Nucl. Mater. **385**, 351 (2009)
L. Van Brutzel *et al.*, Phys. Rev. B **78**, 024111 (2008)

Overlap of cascades in UO_2

Study of primary damage produced by a flux of energetic particles

Cascade overlap **within the same simulation box**
→ **response of the material to increasing damage levels**

Sequence of cascades: **new PKA every 25 ps**
Energy of the uranium PKA: **10 keV**
Different directions and locations of the PKA
Total duration of the simulation: 350 ps
Temperature **700 K**



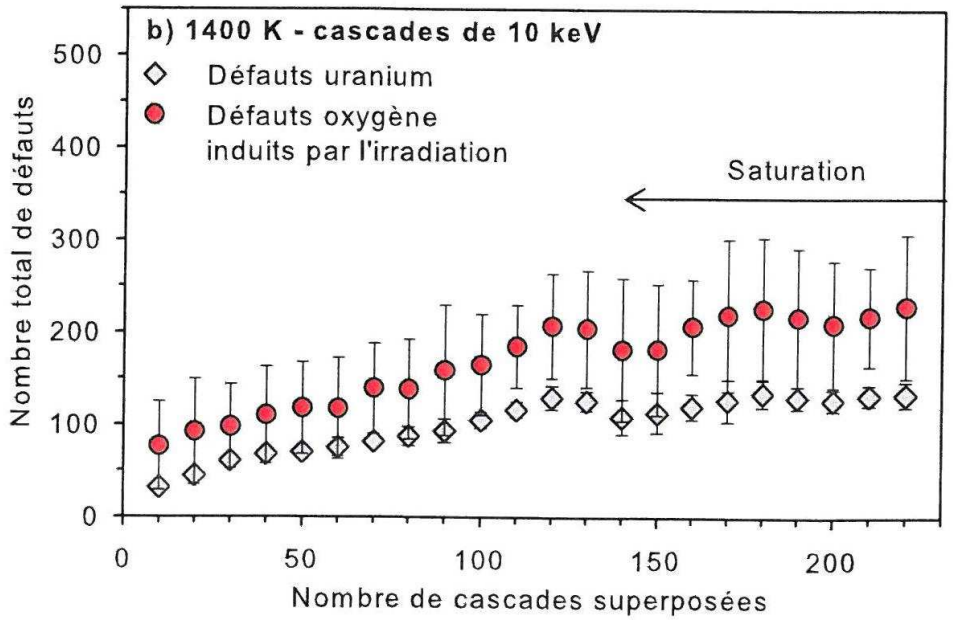
Overlap of cascades in UO_2

film

Damage production after displacement cascades in UO_2

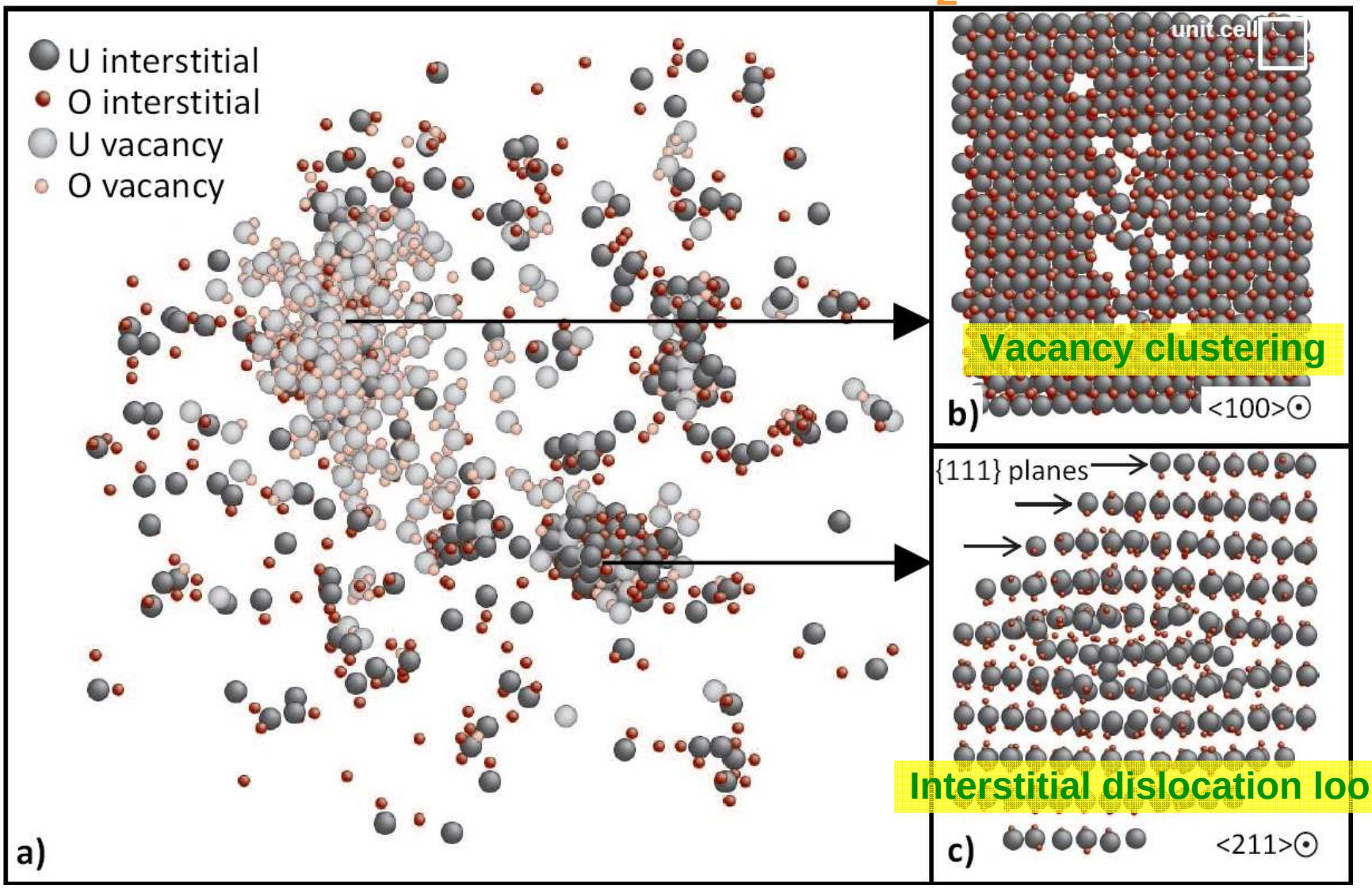
Total number of defects generated first increases (linearly) with the number of cascades, then increases slower to reach **saturation**

G. Martin *et al.*,
to be published (2010)



Saturation is reached for a smaller total number of defects when the temperature is higher

Damage production after displacement cascades in UO_2



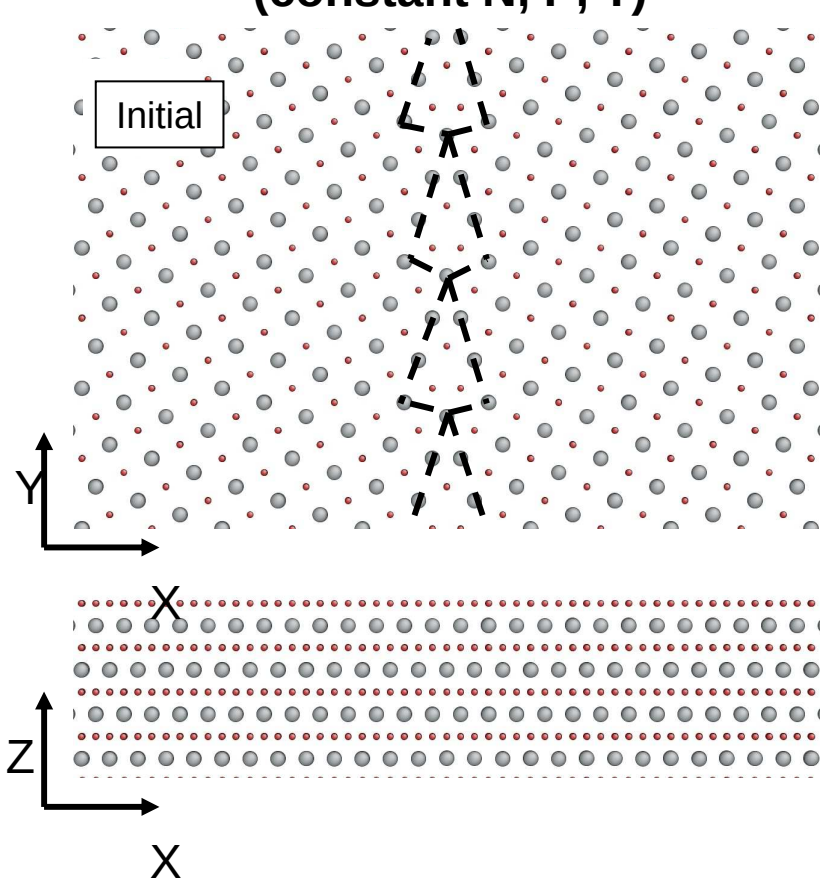
Illustrations of CMD studies of nuclear fuels

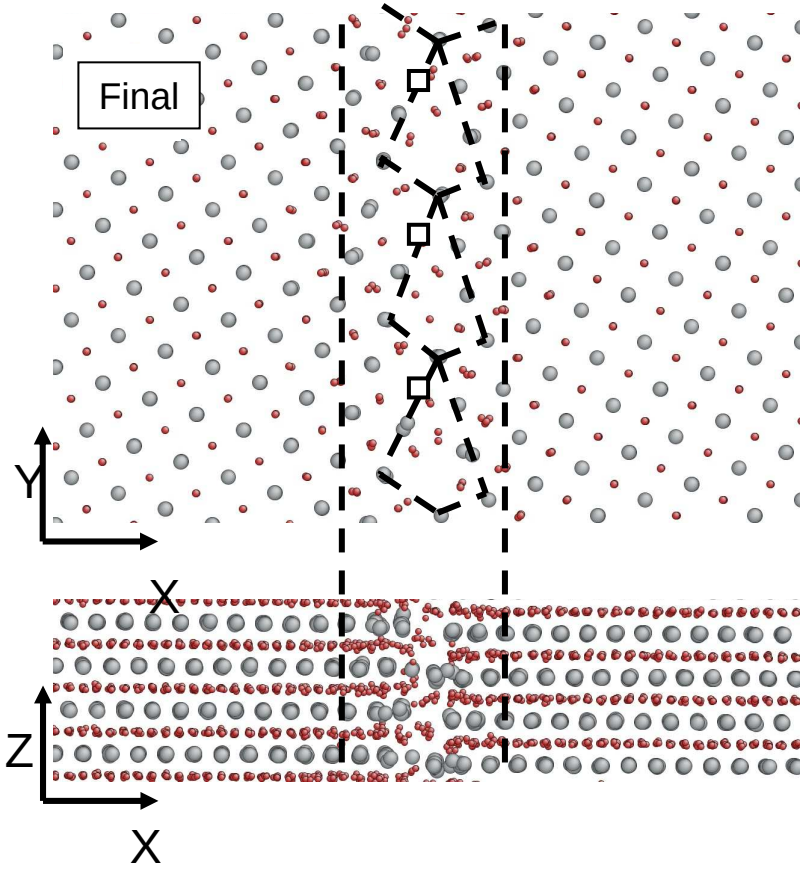
Illustration 2 :
Grain boundaries influence in UO_2

Grain boundaries influence in UO_2

(L. van Brutzel, CEA Saclay)

Evolution of the grain boundary Σ5 at 300K during relaxation (constant N, P, T)

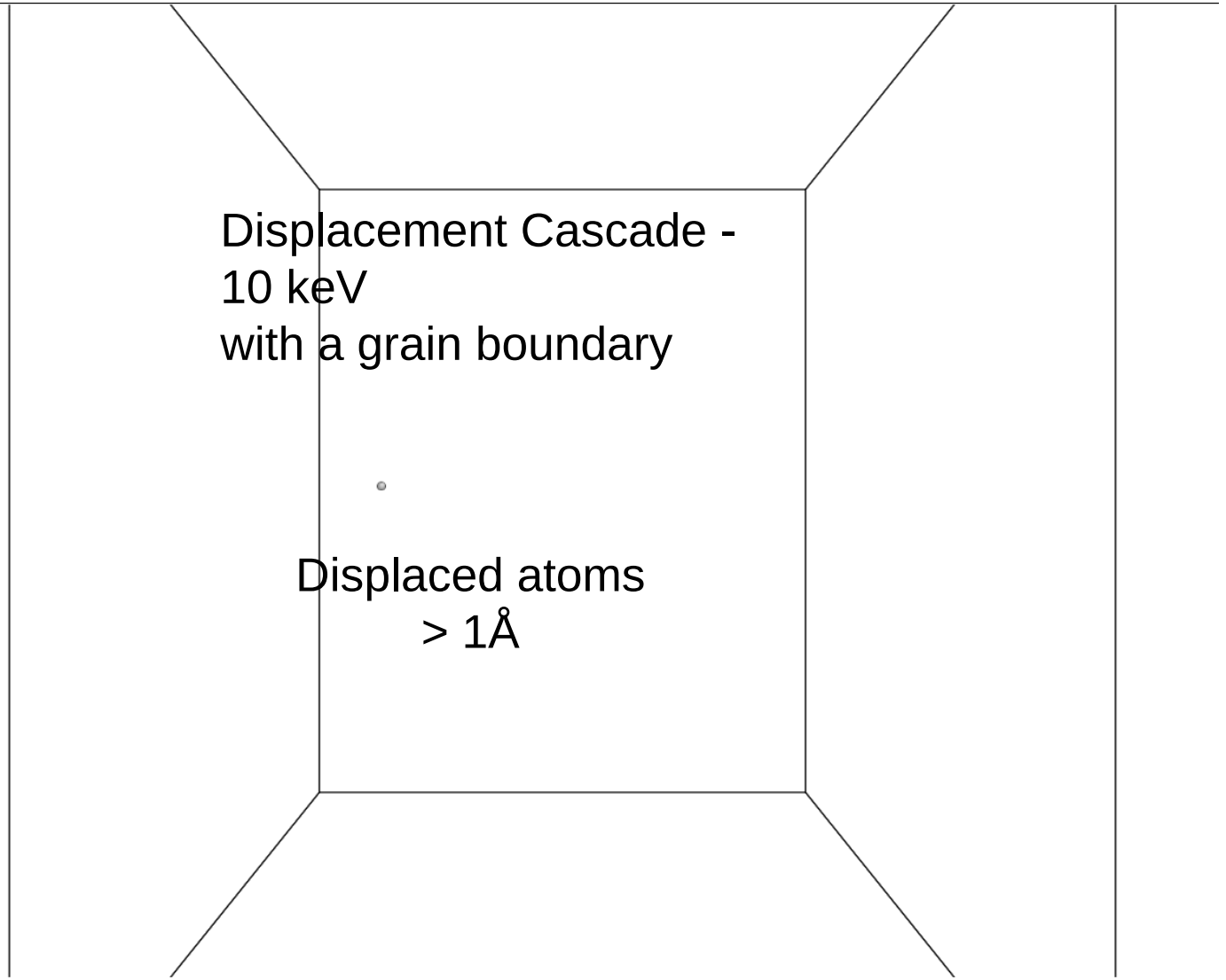




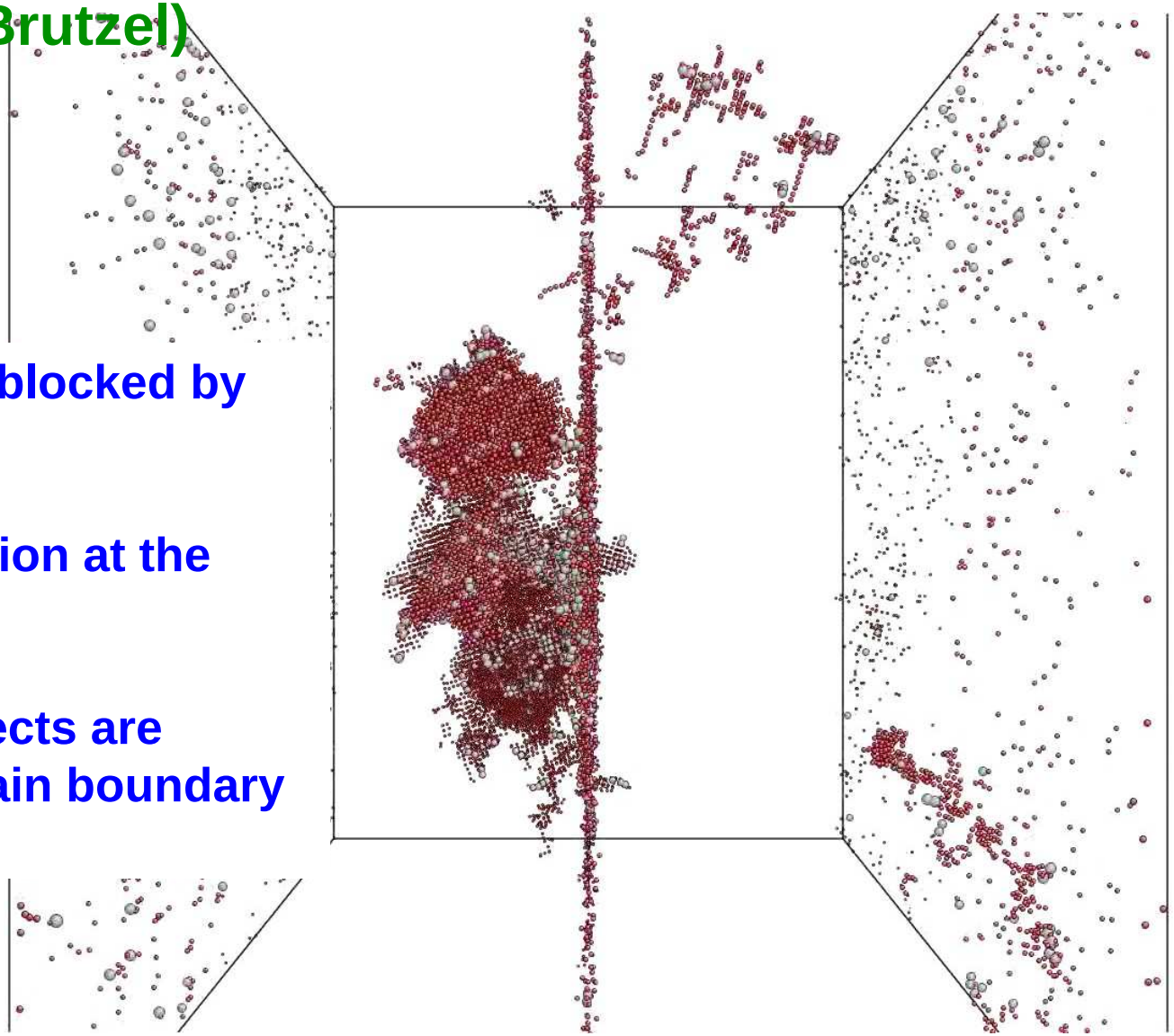
Pattern of Schottky defects = experimental observations

Grain boundaries influence in UO_2

(L. van Brutzel, CEA Saclay)



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**

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 (KMC, performance code...)

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