

**IRSN**

INSTITUT  
DE RADIOPROTECTION  
ET DE SÛRETÉ NUCLÉAIRE

# “Modelling of Fission Products (FPs) in UC, a first principles study”

2010/10/06 / IRSN

Emile BEVILLON, Roland DUCHER, Roland DUBOURG,  
Marc BARRACHIN and ALAIN PASTUREL

DPAM/SEMIC/LETR

NuMAT 2010 - MMSNF

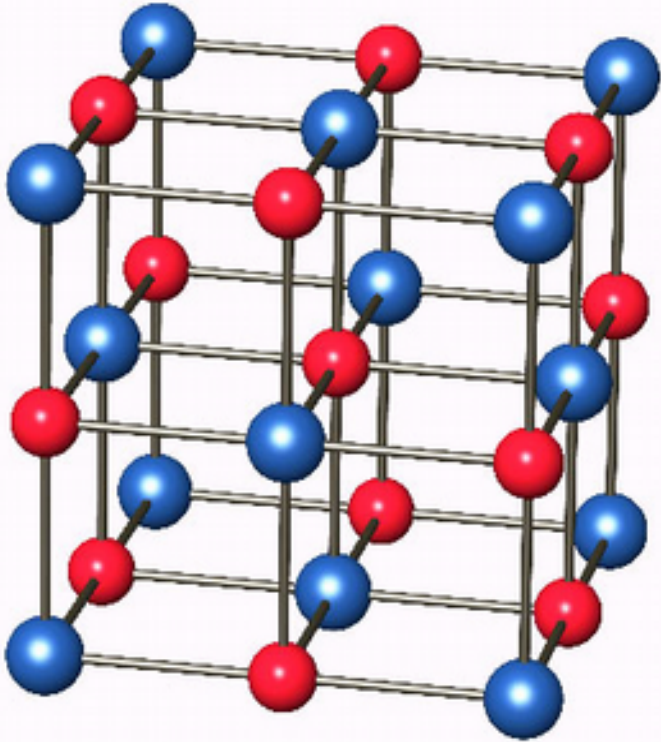
# Outline

- Introduction
- The UC structure
- Calculation Methods
- Stability of Fission Products in UC
  - Sites considered for the incorporation
  - Method for computing incorporation energies
  - Incorporation energies of FPs in UC
  - Incorporation energies - Assessment
- Mobility of Fission Products in UC
  - Displacements considered for the mobility
  - Method for computing migration energies
  - Migration energies of FPs in UC
  - Migration energies - Assessment

# Introduction

- UC is still under consideration for Sodium Fast Reactors (genIV)
  - Interesting properties (high thermal conductivity, high density of metallic atoms ...)
- UC is highly symmetric and is thus an ideal subject of study
- The study of UC may lead to interesting comparisons with  $\text{UO}_2$
- UC and defects in UC were previously studied by Roland Ducher (see poster session)
- The study of FPs in UC is of importance since :
  - They will modify the thermomechanical properties of the fuel
  - Their release is relevant for the source term issue

# The UC structure



Uranium



Carbon

- NaCl structure, cubic, SG: Fm3m. Highly symmetric
- U, inside a C octahedral environment (coordinated 6)
- C, inside a U octahedral environment (coordinated 6)
- Interstitial site: formed by two tetrahedral of U and C atoms.

# Calculation methods

- Use of the VASP code
- DFT calculations, based on the GGA PW91 functional
- Pseudopotentials in the PAW form
- Use of a defective UC supercell (2x2x2, around 64 atoms)
- K-point grid: 4x4x4; Cut off energy: 400 eV
  
- Spin polarisation and spin-orbit coupling neglected
- No use of Hubbard potential (see poster session)
- Geometry optimizations were done at constant volume

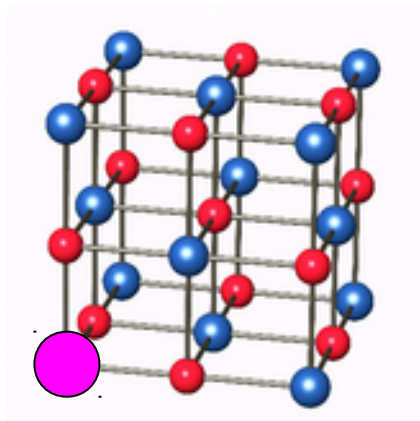


# Stability of Fission Products in UC

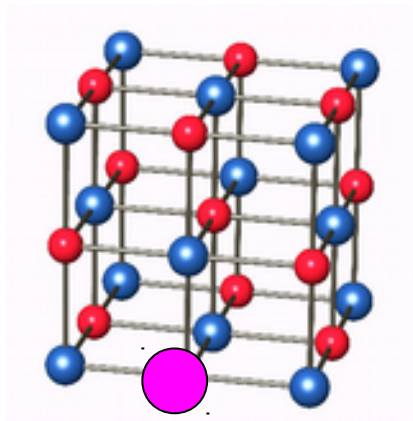
- Sites considered for the incorporation
- Method for computing incorporation energies
- Incorporation energies of FPs in UC
- Incorporation energies - Assessment

# Sites considered for incorporation

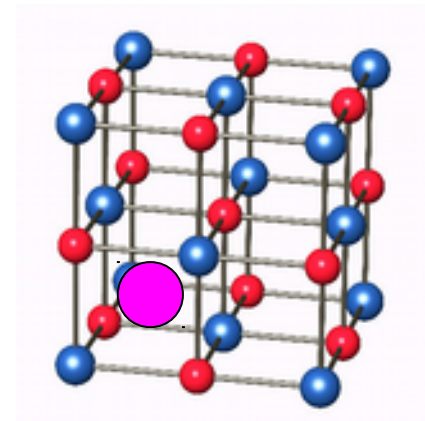
- FPs are possibly located in every sites in UC...
- Investigation of the most simple sites: the lattice sites



FPs on VacU  
(U site)



FPs on VacC  
(C site)



FPs in interstitial position  
(interstitial site)

● Uranium    ● Carbon    ● FPs

# Method for computing incorporation energies



- The reservoir should be consistent with the studied reaction
  - Isolated FPs in the present case

$$E_{inc}(FP) = E_{TOT}(FP) - E_{TOT}(VAC) - E_{FP}$$

- The more the incorporation energy is negative the more the incorporation is favorable, and vice versa.



# Incorporation energies of Noble Gases in UC (eV)

Elements	Incorporation energies (eV)		
	Vac U	Vac C	Interstitial
He	0.66	2.73	2.97
Kr	3.57	6.38	10.55
Xe	4.26	8.87	12.81
Zr	-12.28	-2.59	-3.37
Mo	-11.24	-4.19	-2.83
Ru	-9.86	-5.70	-2.37
Rh	-8.06	-4.46	-1.41
Pd	-5.43	-0.94	1.48
La	-9.03	-1.46	0.61
Ce	-7.88	0.68	0.85
Nd	-8.38	0.24	0.33
I	-0.33	3.03	7.78
Cs	1.55	7.45	9.68
Ba	-2.55	5.19	5.78

- Positive values... Noble Gases are never stable in these sites.
- Dependent on the available space and on the size of the elements.
- Nonetheless the U site is the less unstable site

# Incorporation energies of Solid FPs in UC (eV)

Elements	Incorporation energies (eV)		
	Vac U	Vac C	Interstitial
He	0.66	2.73	2.97
Kr	3.57	6.38	10.55
Xe	4.26	8.87	12.81
Zr	-12.28	-2.59	-3.37
Mo	-11.24	-4.19	-2.83
Ru	-9.86	-5.70	-2.37
Rh	-8.06	-4.46	-1.41
Pd	-5.43	-0.94	1.48
La	-9.03	-1.46	0.61
Ce	-7.88	0.68	0.85
Nd	-8.38	0.24	0.33
I	-0.33	3.03	7.78
Cs	1.55	7.45	9.68
Ba	-2.55	5.19	5.78

- Strong and negative values on the U site. Strong decrease on the C site and in interstitial position
- Due to the lack of available space
- Due to the change of the chemical environment.
  - U site : M-C bonds highly stabilizing
  - C site : M-U bonds less stabilizing
  - Interstitial: intermediate environment

# Incorporation energies of Volatile FPs in UC (eV)

Elements	Incorporation energies (eV)		
	Vac U	Vac C	Interstitial
He	0.66	2.73	2.97
Kr	3.57	6.38	10.55
Xe	4.26	8.87	12.81
Zr	-12.28	-2.59	-3.37
Mo	-11.24	-4.19	-2.83
Ru	-9.86	-5.70	-2.37
Rh	-8.06	-4.46	-1.41
Pd	-5.43	-0.94	1.48
La	-9.03	-1.46	0.61
Ce	-7.88	0.68	0.85
Nd	-8.38	0.24	0.33
I	-0.33	3.03	7.78
Cs	1.55	7.45	9.68
Ba	-2.55	5.19	5.78

- Incorporation energies weakly stabilizing or positive on U site.
- Strongly positive on other sites
- Low stability inside UC, behavior likely similar to Noble Gases

# Incorporation energies - Assessment

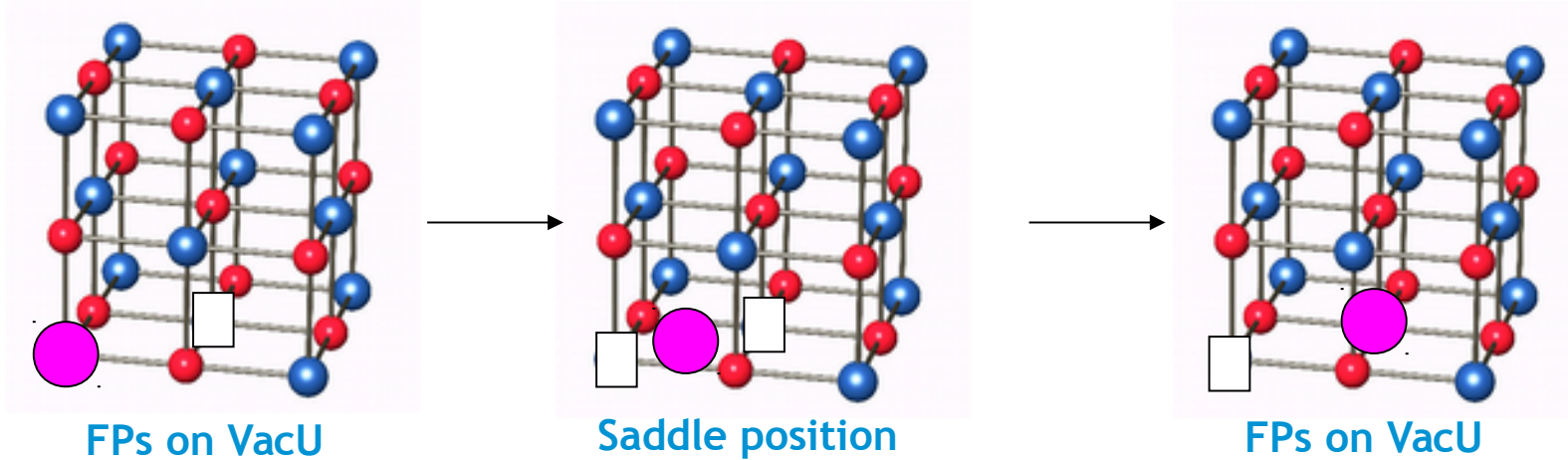
- FPs are always more stable on the U site in UC
- Generally the stability of FPs in UC follows the order : U site > C site > Interstitial. This trend is attributed to:
  - The change of the available space. This is unfavorable to big atoms (Noble Gases, Rare Earths, Cs, Ba and I).
  - The change of the chemical environment. Transition metals and Rare Earths are much more stabilized in the carbide environment they find on the U site than in the metallic environment (C site - interstitial site)
- I, Cs, Ba and Noble Gases always exhibit a low stability in UC or a strong non-stability, in good agreement with their ability to form gas phases and their high release.

# Mobility of Fission Products in UC

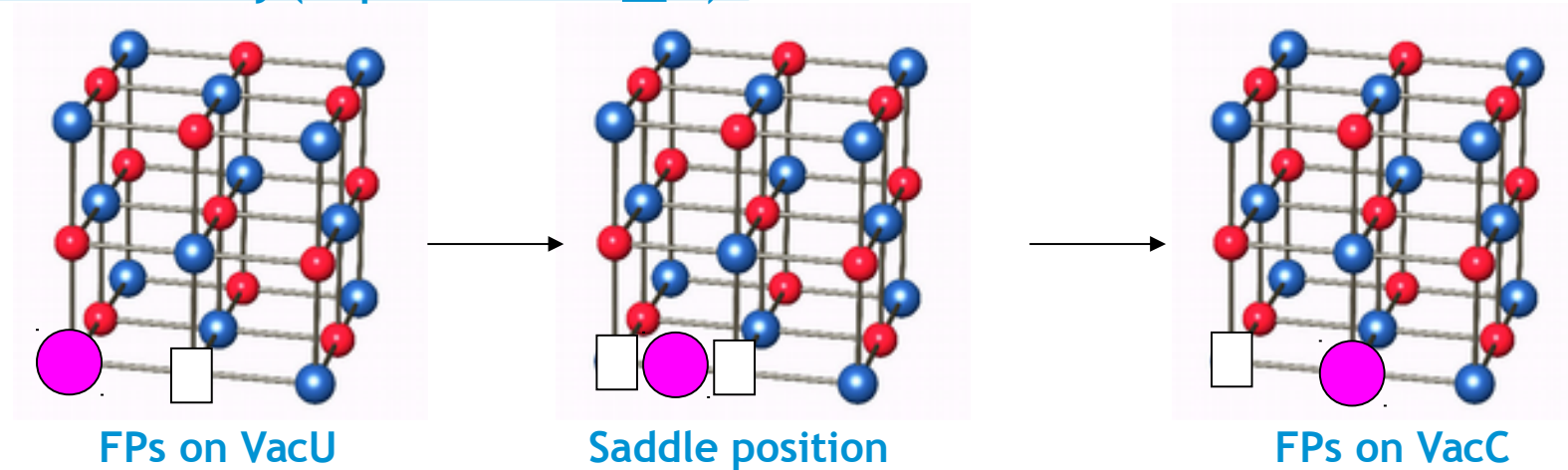
- Displacements considered for the mobility
- Method for computing migration energies
- Migration energies of FPs in UC
- Incorporation energies - Assessment

# Displacements considered for the mobility

Through a UU bi-vacancy (displacement  $U \rightarrow U$ ) :

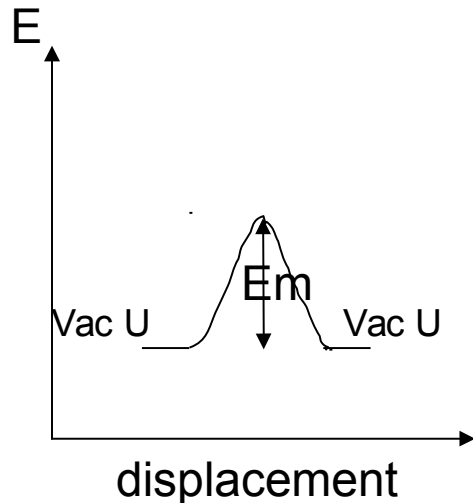


Through a UC bi-vacancy (displacement  $U \rightarrow C$ ) :



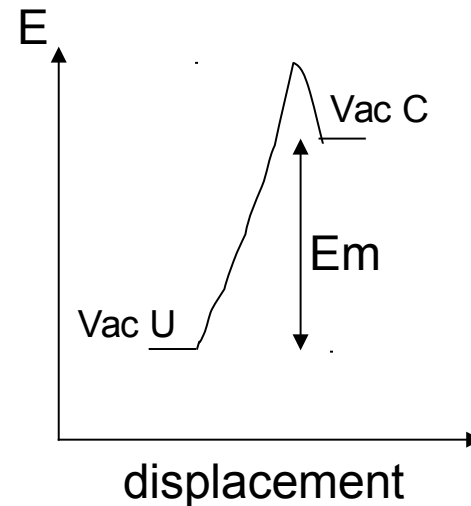
# Method for computing migration energies

- BiVac. UU <101>
- U site → U site
- Symmetric saddle position
- → NEB calculations



- The weaker is  $E_m$ , the easier is the displacement (energy)

- BiVac. UC <100>
- U site → C site
- Asymmetric saddle position
- →  $E_m$  is approximated to the energy difference between the initial and the final state of the displacement



,  $E_f$  being the defect formation energy

$$D = D_0 e^{-\frac{E_f + E_m}{kT}}$$

# Migration energies of Noble Gases in UC (eV)

BiVac UU <101>	Elements	BiVac UC <001>
U → U		U → C
0.21	He	1.23
0.46	Kr	1.66
0.76	Xe	2.79
3.42	Zr	6.91
4.23	Mo	4.80
2.51	Ru	2.60
1.15	Rh	2.20
0.63	Pd	2.36
1.55	La	5.13
2.03	Ce	6.01
2.15	Nd	6.06
0.33	I	1.81
0.77	Cs	3.66
1.20	Ba	5.05

■ U → U: weak migration energies (displacements highly favored)

■ U → C: migration energies are higher, but displacement possible for He and Kr; difficult for Xe



# Migration energies of Solid FPs in UC (eV)

BiVac UU <101>	Elements	BiVac UC <001>
U → U		U → C
0.21	He	1.23
0.46	Kr	1.66
0.76	Xe	2.79
3.42	Zr	6.91
4.23	Mo	4.80
2.51	Ru	2.60
1.15	Rh	2.20
0.63	Pd	2.36
1.55	La	5.13
2.03	Ce	6.01
2.15	Nd	6.00
0.33	I	1.81
0.77	Cs	3.66
1.20	Ba	5.05

## ■ Inhomogeneous trend

### ■ U → U, three kinds of FPs:

- lowly mobile : Zr and Mo
- mobile : Ru and Rare Earths
- highly mobile : Rh and Pd

### ■ U → C, only two kinds of FPs

- Em incompatible with displacement: Zr, Mo and Rare Earths
- Em compatible with displacement : Ru, Rh and Pd

# Migration energies of Volatile FPs in UC (eV)

BiVac UU <101>	Elements	BiVac UC <001>
U → U		U → C
0.21	He	1.23
0.46	Kr	1.66
0.76	Xe	2.79
3.42	Zr	6.91
4.23	Mo	4.80
2.51	Ru	2.60
1.15	Rh	2.20
0.63	Pd	2.36
1.55	La	5.13
2.03	Ce	6.01
2.15	Nd	6.06
0.33	I	1.81
0.77	Cs	3.66
1.20	Ba	5.05

■ U → U: weak migration energies compatible with the displacement

■ U → C: Much higher migration energies (> 1.8 eV). Displacement possible for I, weakly probable for Cs and Ba

# Migration energies - Assessment

- **For FPs, the displacement  $U \rightarrow U$  is easier :**
  - It is very probable for Volatiles, Noble Gases as well as for small Transition Metals (Rh, Pd) and probable for Rare Earths and Ru.
  - They are difficult for Zr and Mo, both being very stable on the U site.
- **On the contrary,  $U \rightarrow C$  displacements are generally improbable or expected to have a short lifetime due to the really favored opposite displacement ( $C \rightarrow U$ , we neglected the corresponding energy barrier).**
- **Such asymmetric behavior on the UC bivacancy can be explained by the volume and the chemical changes of the environment.**
- **But... Concerted mechanism means :**
  - Long range diffusion is limited by the limiting step ( $E_m U$  is 1.8 eV)
  - Same for highly mobile FP, long range diffusion could not be less than 1.8 eV

***Thank you for your attention***