Ion Beam Analysis of Nuclear Ceramics

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SCIENTIFIC GOALS

Better understanding of the behaviour of nuclear materials using energetic ion beams

- Irradiation-induced effects: radiation defects, (micro)-structural transformations
- Role played by embedded impurities: fission products, gases (He, Kr, Xe) – lattice location and behaviour (T, irradiation, solubility, chemical interaction, role of Cr)
- Oxidation, corrosion

Nuclear materials of interest: fuels, immobilization matrices, ceramics for Gen4

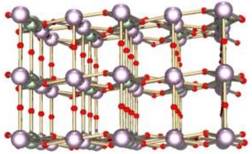
Ultra simplified system: single crystals

Parametric approach

Better understanding of the nuclear materials using energetic ion beams: towards the *Modelling of Radiation-Induced Effects in Nuclear Materials*

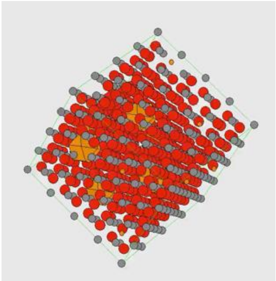
OXIDATION OF THE SPENT NUCLEAR FUEL

Structural stability towards oxidation



- High O/U $\in$[2.5; 3]: *layered* structure with linear 'uranyl' groups (trans dioxo geometry) (e.g. U_3O_8, UO_3)
- Low O/U $\in$[2; 2.5]: *distorted fluorite-type* structure (e.g. UO_{2+x}, U_4O_{9-y}, U_3O_7)
- Transition from distorted (UO_2) to layered (U_3O_8) deleterious for the fuel stability: from pellet to powder !
- Strong need to understand the transition mechanisms at the atomic scale

Investigation the crystalline structure of U_4O_9: distorted fluorite-type structure – crystallography using ion beams



- Extra O atom form anionic clusters embedded in the fluorite-type matrix
- Clusters are known to exist in UO_{2+x} and U_4O_{9-y} (Willis-type; anti-prism type cuboctahedral aggregates) based on neutron diffraction experiments
- Spectroscopic methods (EXAFS) favour the formation of oxo groups associated with U^{6+} (short $d_{U\text{-}O}$ bonds as seen in coordination chemistry) and glassy part

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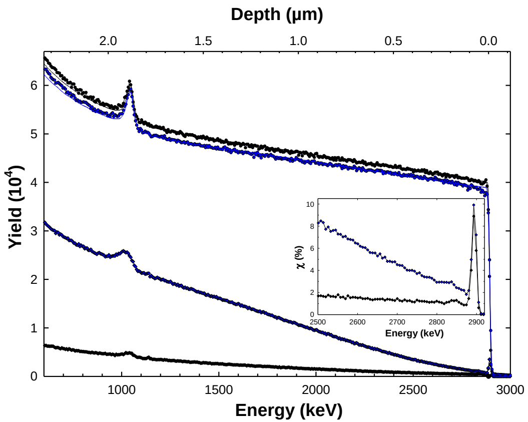
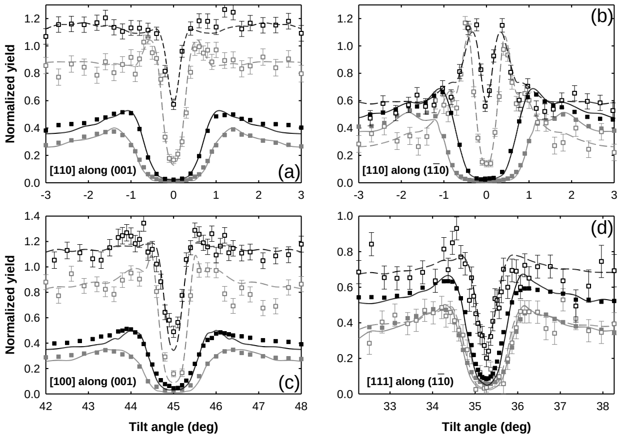
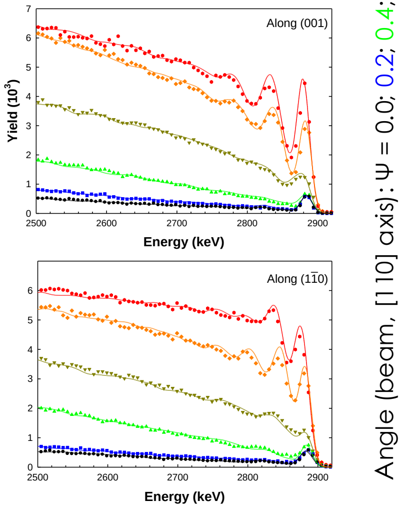
OXIDATION OF THE SPENT NUCLEAR FUEL

The two descriptions are fundamentally irreconcilable - Ion channelling applied to solve the puzzle

- Crystallography by ion channelling (MOSAIC facility) and Monte Carlo simulations (McChasy code)
  - Single crystal synthesis U_4O_9 (UO_2 single crystal + U_3O_8 powder)
  - Sensitivity to distortions of atomic rows and planes (medium and long-range order)
  - Sensitivity to atoms displaced off regular crystallographic positions (short-range order)

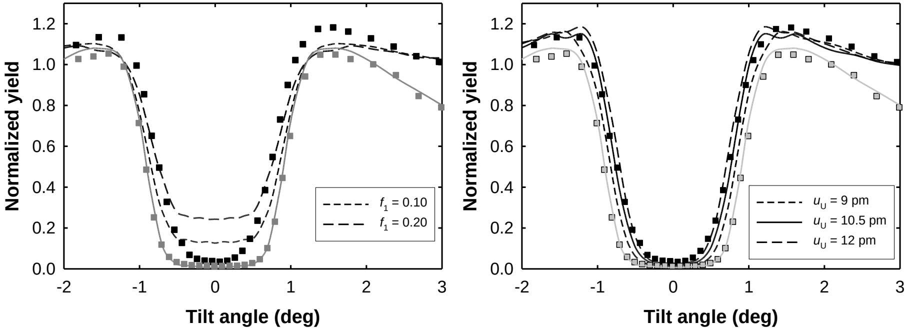






OXIDATION OF THE SPENT NUCLEAR FUEL

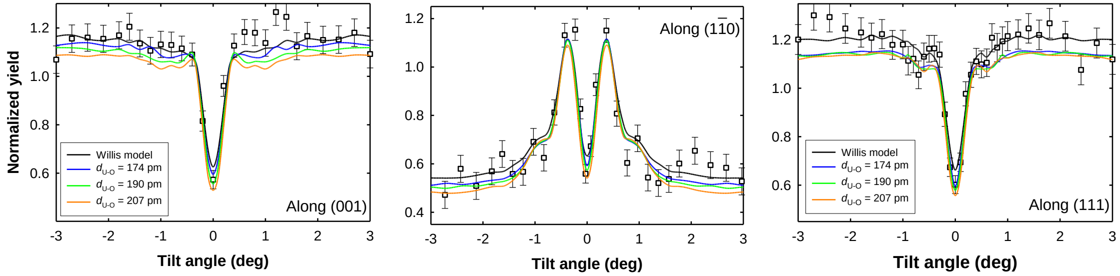
Searching for an amorphous fraction



Scan recorded at 13° from (1-10) plane across [110]

No glassy part !

Anionic clusters (oxygen sublattice): oxo bonds and Willis-type



No short U-O bonds: no oxo groups

Good agreement with Willis clusters

Willis clusters: O′ (½ + v, ½ + v, ½) and O″ (½ + w, ½ + w, ½ + w)
Best agreement: v = 0.10; w = 0.125 (good agreement with neutrons: v = 0.10-0.14; w = 0.06-0.15

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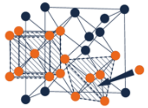
OXIDATION OF THE SPENT NUCLEAR FUEL



Crystallographic description

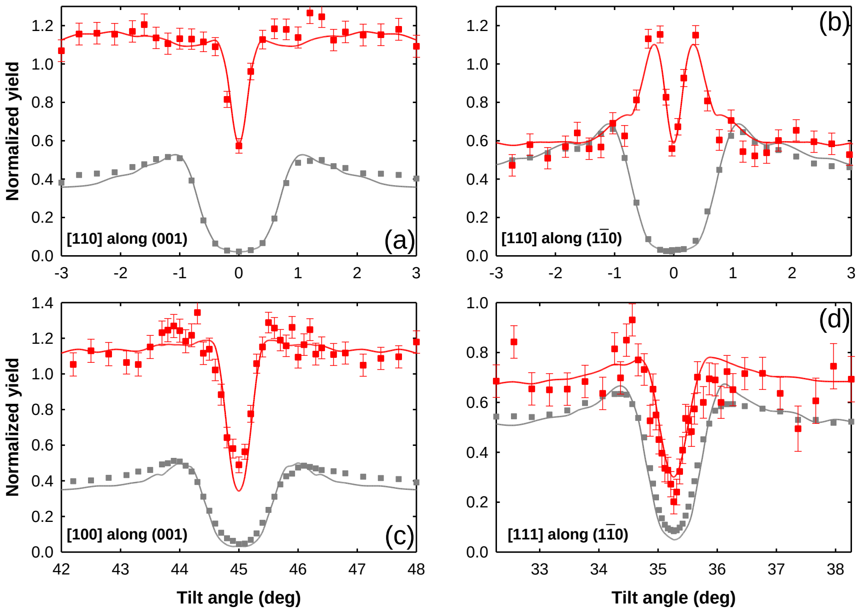
Variable positional parameters are a_1–a_4 and b_1–b_8.

Atom	Site	x	y	z
U1	16(c)	0	0	0
U2	24(d)	$1/4+a_1$	0	1/4
U3	48(e)	1/8	$1/8-a_1$	1/4
U4	24(d)	a_2	0	1/4
U5	48(e)	7/8	0	$1/8-a_2$
U6	48(e)	$-a_3$	$1/8-a_3$	$3/8-a_3$
U7	48(e)	$-a_4$	$1/8-a_4$	$1/8+a_4$
O1	48(e)	$7/8+b_1$	b_1	$1/4+b_2$
O2	48(e)	$7/8+b_1$	b_2	$1/4+b_1$
O3	48(e)	$7/8+b_2$	b_1	$1/4+b_1$
O4	16(c)	1/16	1/16	1/16
O5	16(c)	3/16	3/16	3/16
O6	48(e)	$1/16-b_3$	$3/16-b_3$	$3/16+b_3$
O7	48(e)	$1/16+b_4$	$1/16+b_5$	$3/16-b_5$
O8	48(e)	$15/16+b_5$	$1/16+b_5$	$1/16-b_4$
O9	48(e)	$15/16-b_6$	$1/16-b_6$	$7/16+b_4$
O10	48(e)	$15/16+b_5$	$3/16+b_4$	$3/16-b_5$
O11	48(e)	$15/16-b_6$	$3/16+b_4$	$5/16-b_6$
O12	48(e)	$1/16+b_4$	$1/16-b_6$	$5/16-b_6$
O13	48(e)	$15/16-b_7$	$3/16-b_7$	$7/16+b_7$
Empty	12(b)	7/8	0	1/4
O15	48(e)	$7/8+b_8$	b_8	$1/4+b_8$

Free parameters

- 4 for U
- 8 for O

Positional parameters q_U, q_O, r_O (multiplying factors, radius of cuboctahedron)



$q_U = 1.8 \pm 0.1$; $q_O = 2.0 \pm 0.2$; $r_O = 308$ pm

U_4O_9 is a conventional crystalline compound

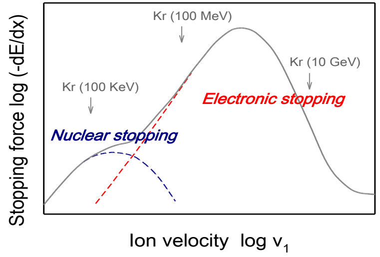
- Absence of glassy part in the structure
- No evidence of short U-O bonds (oxo groups)
- Good agreement with neutron diffraction investigation assuming $q_U = 1.8 \pm 0.1$; $q_O = 2.0 \pm 0.2$; $r_O = 308$ pm

EXPERIMENTAL SIMULATION OF IRRADIATION INDUCED EFFECTS

Nuclear fuel exhibits the fluorite-type structure

- Structure of UO_2, PuO_2 (MOX) and in reactor transmutation matrices: (Zr, *An*)O_2

Single crystals as a simplified model of nuclear fuel or transmutation matrix



Simulation of radiation-induced damage

- Atomic collisions (MOSAIC platform IJCLab); electronic excitations (GANIL)
- Doping – chemical contribution – role played by soluble versus insoluble specie (fission products)

EXPERIMENTAL SIMULATION OF IRRADIATION INDUCED EFFECTS

Investigating the High Burnup Structure of spent nuclear fuels

- Microstructural phase transformation occurring at the rim of fuel pellets: grain subdivision (100 nm) and high porosity
- Related to the local enrichment in ^{239}Pu (neutron capture cross section in the resonance region up to 1 eV)
- Atomic mechanisms not understood; possible parameters include low T, higher concentration of impurities, radiation damage (atomic and electronic)
- Parametric approach: burnup, T, chemistry of impurities, radiation defects

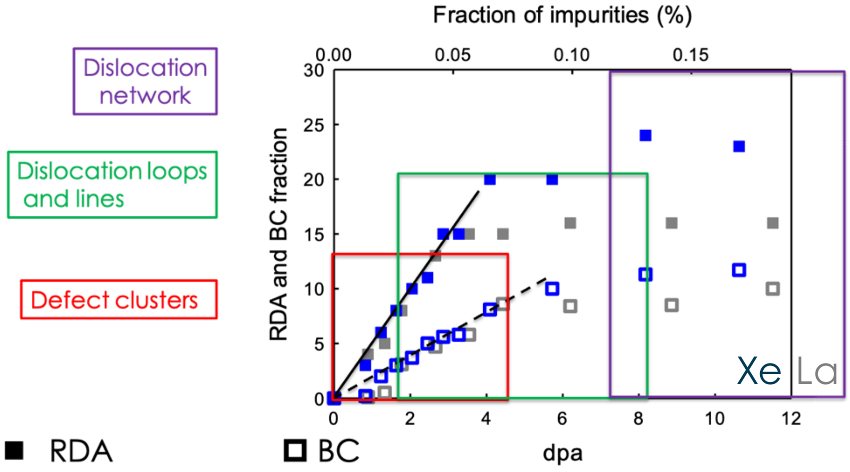
In situ channelling and TEM experiments coupled to implantation at 773 K – Role of insoluble versus soluble fission products

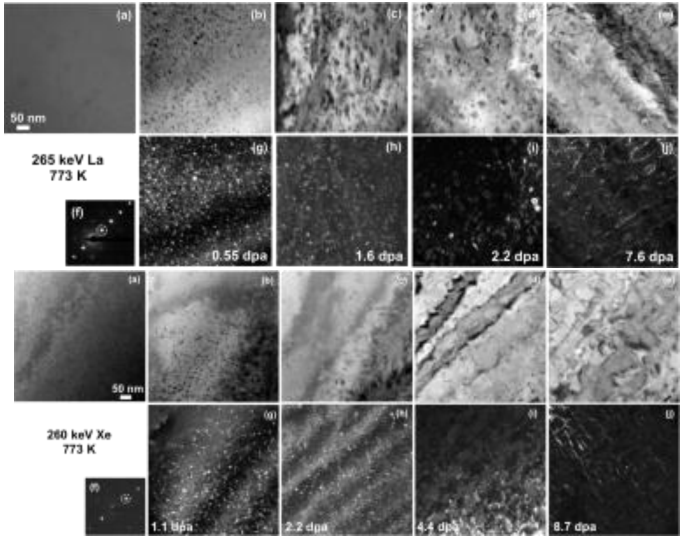
Swift ion irradiation coupled to channelling and TEM experiments – Role of electronic stopping

EXPERIMENTAL SIMULATION OF IRRADIATION INDUCED EFFECTS

In situ channelling and TEM experiments coupled to implantation at 773 K – Role of insoluble versus soluble fission products

- Direct comparison between the fate of Xe and La (Z =54, insoluble in UO_2; Z = 57, fully soluble) - In situ evolution at 773 K
- Defect model: RDA (obstruction) & BC (distortion)





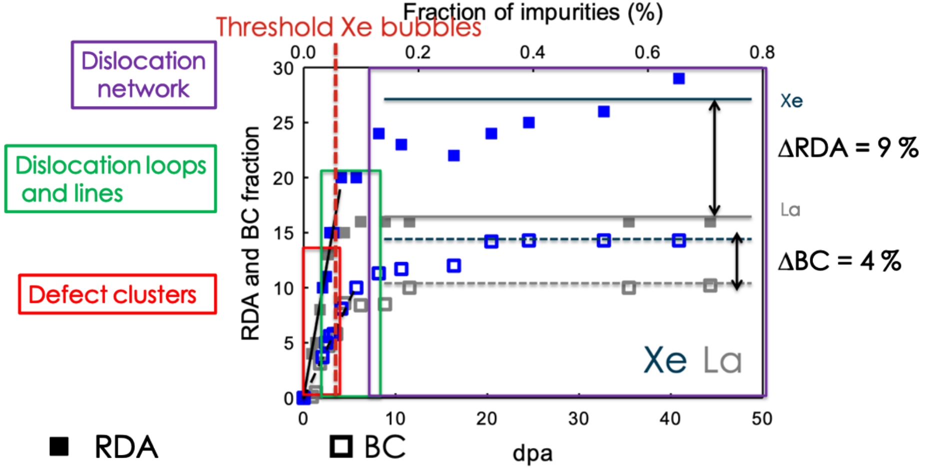
- Same evolution for both specie: sequential evolution from black dots to dislocation loops and lines

EXPERIMENTAL SIMULATION OF IRRADIATION INDUCED EFFECTS

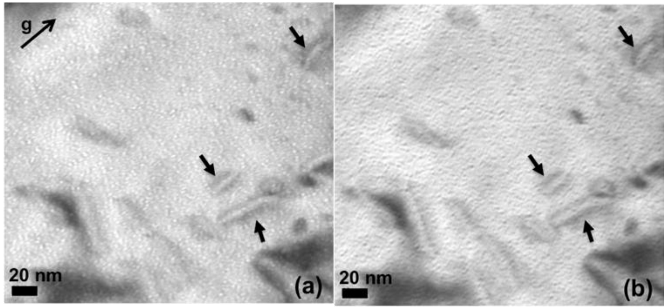
In situ channelling and TEM experiments coupled to implantation at 773 K – Role of insoluble versus soluble fission products

- Direct comparison between the fate of Xe and La (Z =54, insoluble in UO_2; Z = 57, fully soluble) - In situ evolution at 773 K

- Channelling



- TEM



Images recorded in situ at 773 K at 5 dpa; mean bubble size is (2.0 ± 0.5) nm

- Formation of Xe bubbles homogeneously distributed (no bubble or cavity for La)

WORK IN PROGRESS – LATTICE LOCATION OF CHROMIUM

Investigating the role of chromium in Accident Tolerant Fuels – BENEFICIA ANR project (IP2I Lyon, CEA, Framatome, IRSN)

- Fuels with large grain size (~ 100 µm): Cr_2O_3 addition during the sintering process
- Role of Cr not well understood – lattice location of Cr unknown
- Coupling RBS and PIXE in channelling mode across major crystallographic directions and along major planes to reveal Cr by triangulation

Implanted UO_2 single crystal as a model system

- Cr incorporated by ion implantation: 170 keV; typically, 10^{15}-10^{16} cm^{-2}; Cr concentration 0.1-1%)
- Cr presence revealed by PIXE
- Information on U and O sublattice obtained via backscattered probing ions

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ION BEAM ANALYSIS OF NUCLEAR CERAMICS

Crystallography in direct space using ion channelling – Investigation of the structure of uranium oxides

Coupling In situ channelling and TEM experiments coupled to implantation at 773 K – Role of insoluble versus soluble fission products

Swift ion irradiation coupled to channelling – Investigating the role of electronic stopping in fluorite type oxides

Investigating the role of chromium in Accident Tolerant Fuels – Lattice location of foreign elements

Experiments at MOSAIC are possible thanks to the skills and dedication of technicians, engineers and physicist and chemists

I am particularly indebted to my colleagues