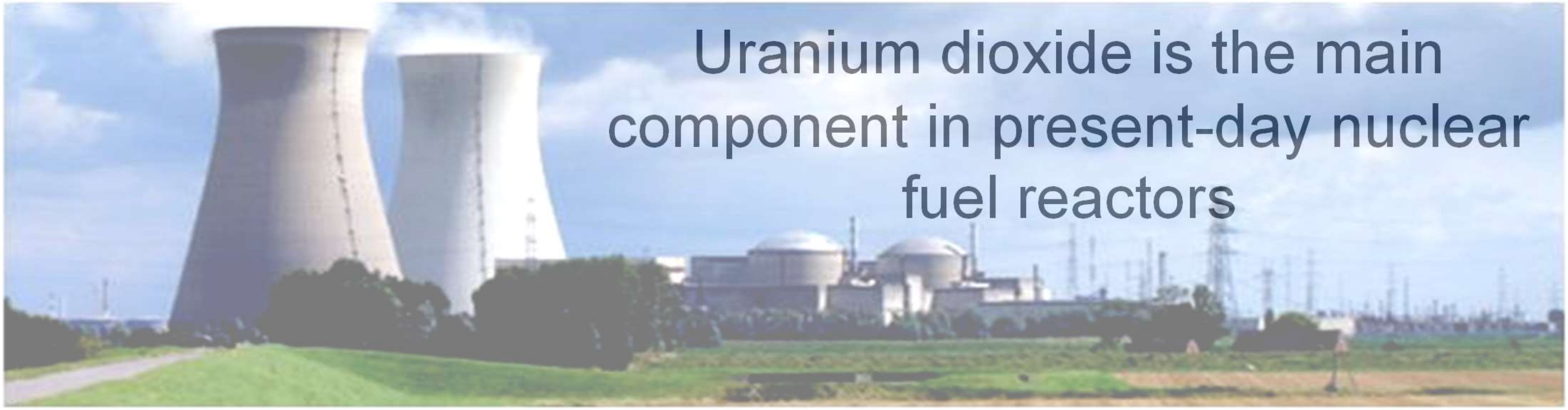
DE LA RECHERCHE À L'INDUSTRIE

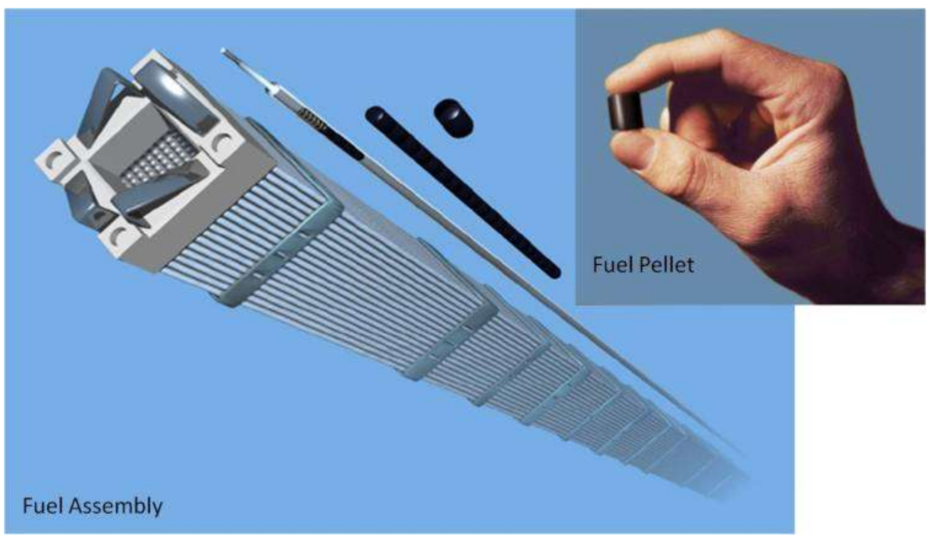
A RENEWED APPROACH OF UO_2 NUCLEAR FUEL USING PDF ANAYSIS

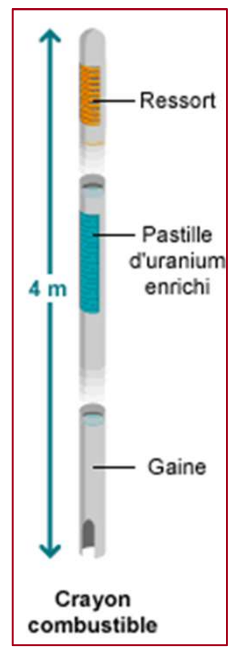
MRS EN 17| L. Desgranges,[1] Y. Ma[1], Ph. Garcia[1,] G. Baldinozzi[1], D. Siméone[1], H.E. Fischer[2]
[1] CEA,DEN France
[2] ILL, France

APRIL 6, 2018

Uranium dioxide is the main component in present-day nuclear fuel reactors

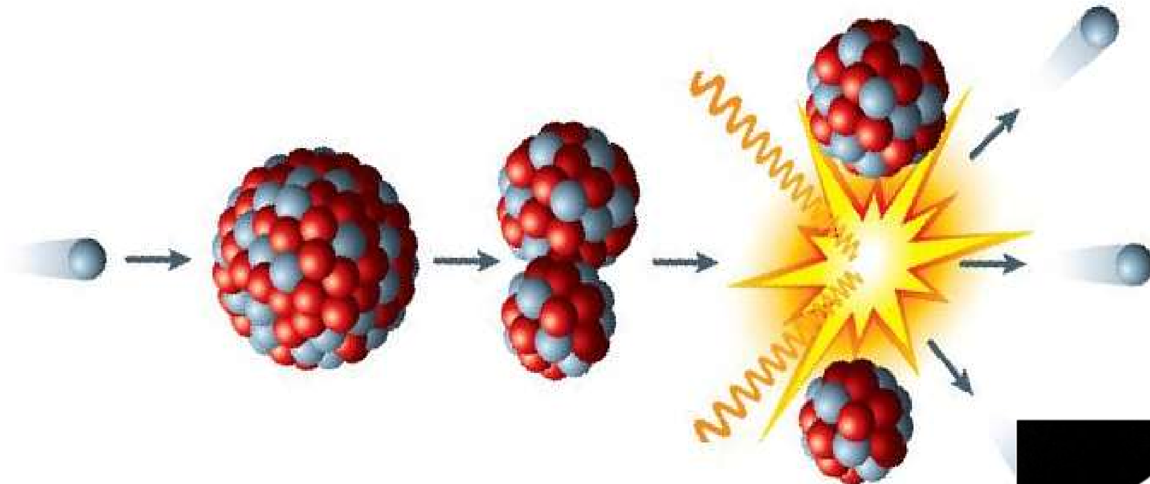




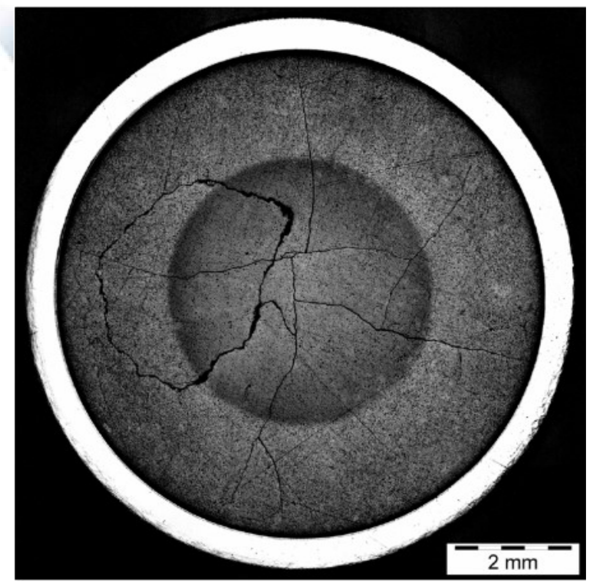


UO_2 BEHAVIOUR UNDER IRRADIATION

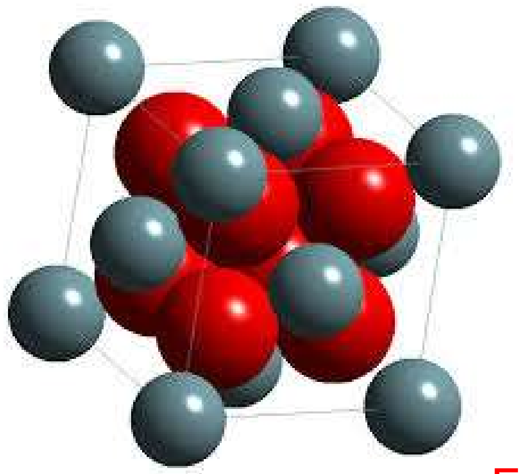
Energy production by Fission

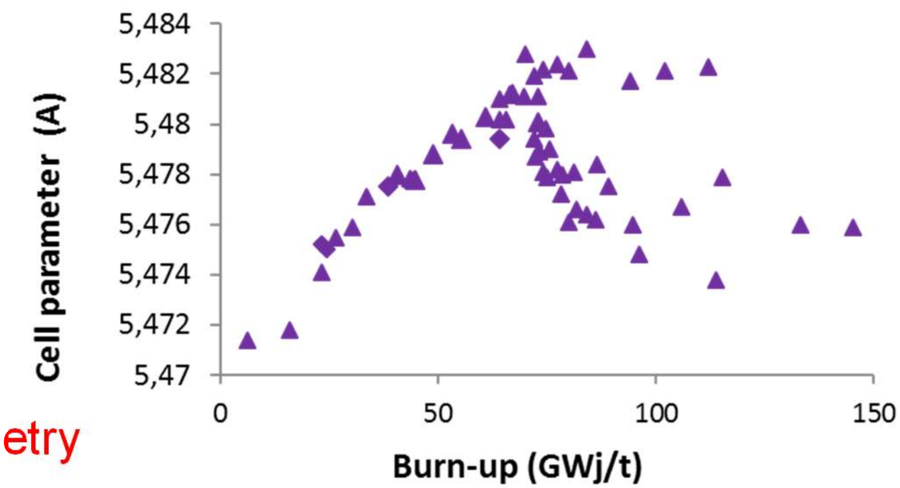


Thermal gradient
Oxygen transfer
Irradiation damage
Fission product incorporation



BUT A STABLE CRYSTALLINE STRUCTURE





Fm-3m symmetry
is kept
With slight changes of cell parameter

A simple picture of UO_2 (used in thermodynamic modelling J. Nucl. Mater.419 (2011) 145-167) :

- One crystalline structure
- Three sites : 1 cationic, 1 anionic, 1interstitial
- Different occupation fractions on each site

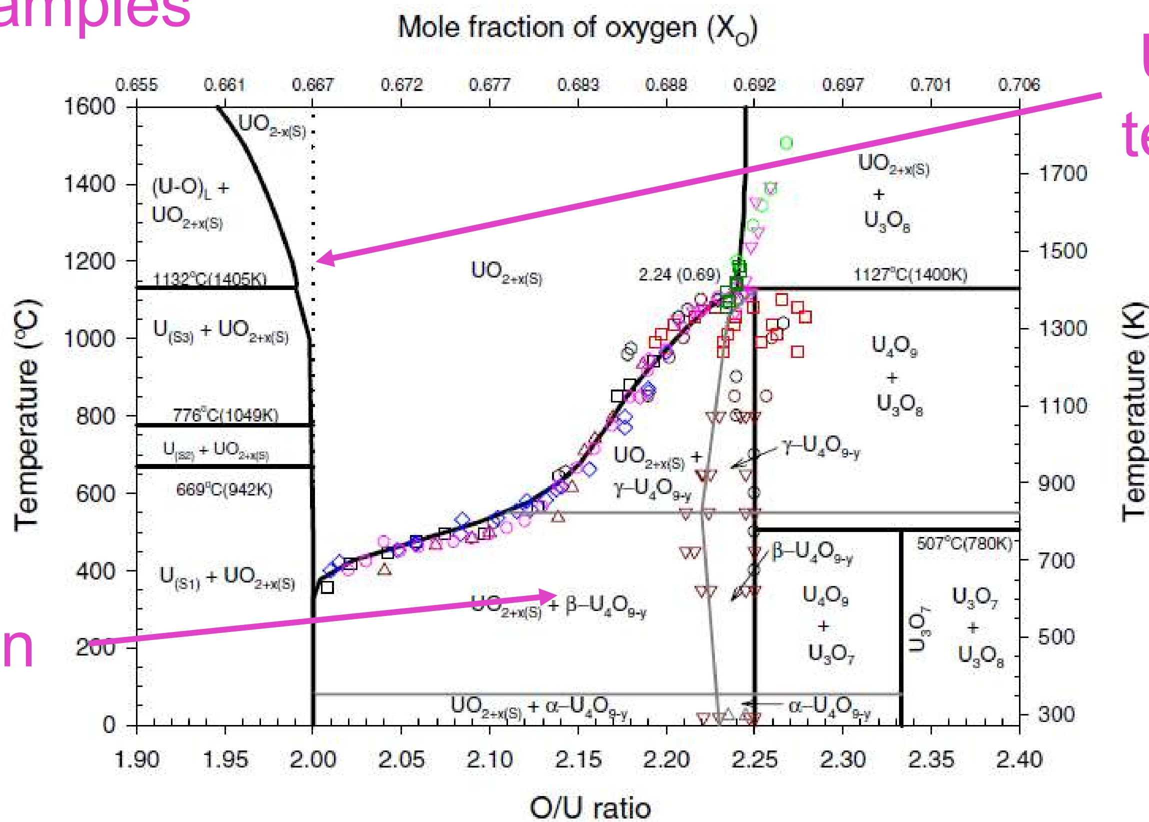
A TOO SIMPLIFIED PICTURE?

In the last 15 years, PDF analysis of UO_2 was used to improve the understanding of nuclear fuel behavior.

The obtained results contributed in proving that the ideal solid solution picture was oversimplified.

Two examples

UO_2 at high temperature



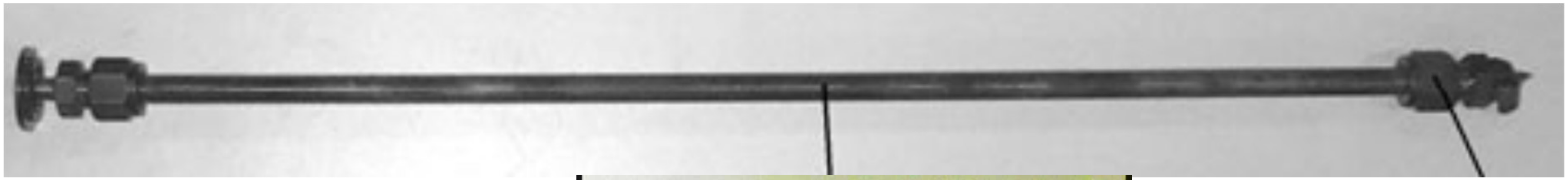
UO_2 oxidation

Example 1

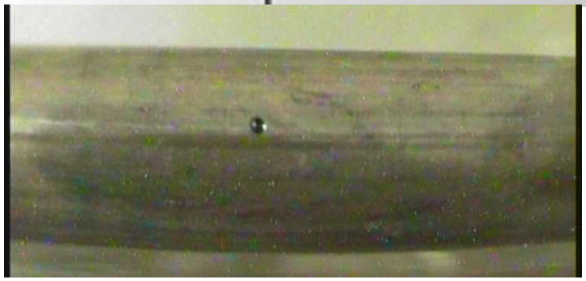
UO_2 oxidation

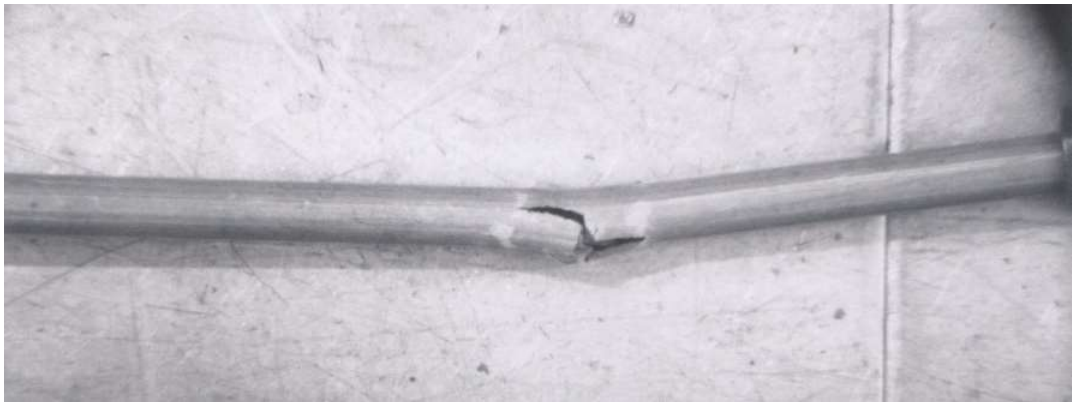
UO_2 OXYDATION: A INDUSTRIAL HAZARD

In an accidental scenario, a defect in the cladding might put UO_2 irradiated fuel in contact with atmosphere (T<400°C)



The oxidation of irradiated UO_2 could lead to the ruin of the fuel rod





Need for a better understanding of UO_2 oxidation

$UO_2 \Rightarrow U_4O_9 \Rightarrow U_3O_7 \Rightarrow U_3O_8$

Nucl. Techn 163 (2008) 252-260

U_4O_9 CRYSTALLINE STRUCTURE : AN OLD BRAIN TEASER!

- 1961 : first U_4O_9 observation using X-Ray Diffraction
- 1964 : U_4O_9 observation using neutron diffraction
- 1968 : U_4O_9 observation using electron diffraction
- 1960-1980 : evidence of α–β transition at 50°C
- First simple structural models simples : I-43d (1961) $I4_132$ (1974)
- 1980 structural models using clusters of of oxygen atoms
- 1989 : determination β phase space group, I-43d
- 2004 : first structural refinement of β-U_4O_9 using Rietveld analysis
- 2005 : EXAFS measurements of α-U_4O_9
- 2006 : First PDF measurement of α-U_4O_9
- 2011 : first structural refinement of α-U_4O_9 using PDF analysis
- 2016 : first structural refinement of γ-U_4O_9 using PDF and Rietveld analysis

why so many difficulties?

DIFFICULTIES FOR SOLVING U_4O_9 STRUCTURE

An heavy cation near to a light anion

Atom	$\sigma_{X\text{-}Ray}$	$\sigma_{neutron}$
O	0.64	4.232
U	84.85	8.906

► *neutron diffraction mandatory to evidence O atoms*

More than 100 parameters to be refined

β-U_4O_9 is a UO_2 superstructure 4x4x4 (a = 21.766 Å), 21 independent atoms

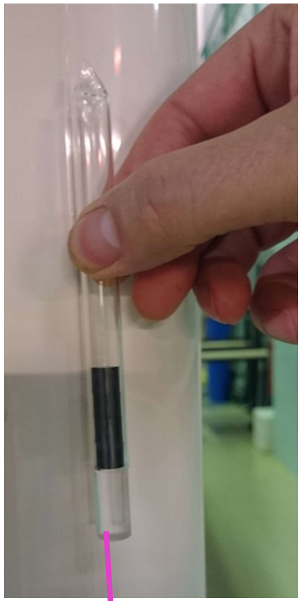
► *a large data set mandatory with numerous diffraction lines*

Need for local details

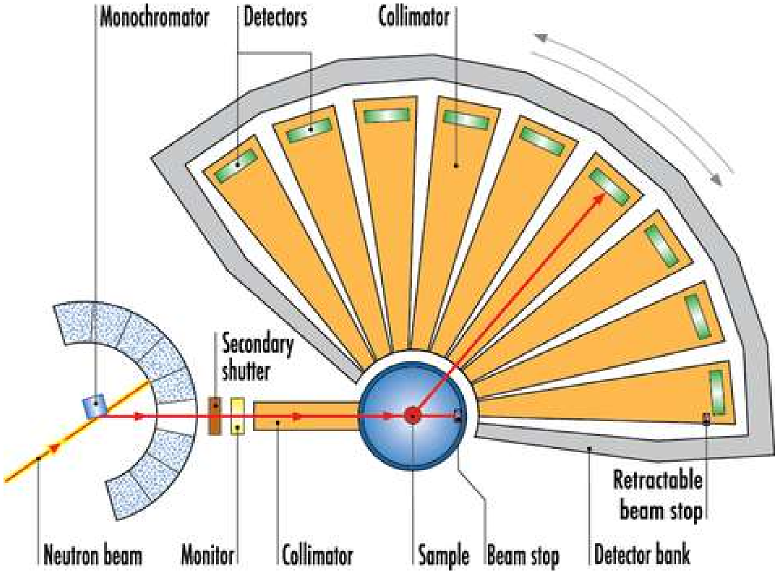
U_4O_9 contains clusters of oxygen interstitial

► *PDF analysis mandatory for the short interatomic distance determination*

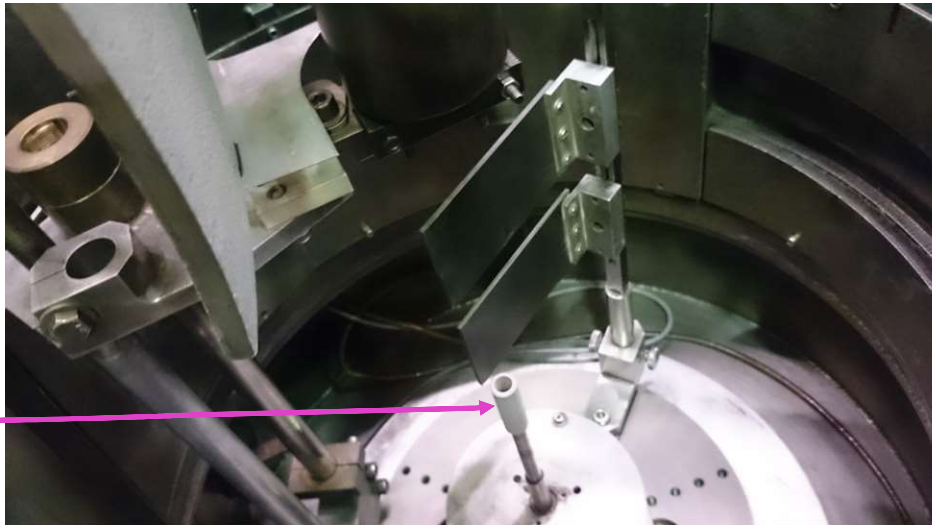
NEUTRON DIFFRACTION WITH URANIUM OXIDES AT D4, ILL



A two UO_2 pellet stack set in a airtight glass tube



Installed inside the sample holder of D4 furnace



Data analyzed in reciprocal and real space

DATA ANALYSIS

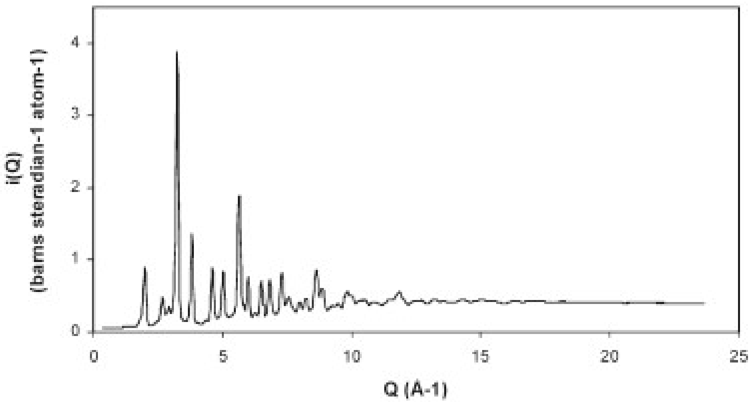
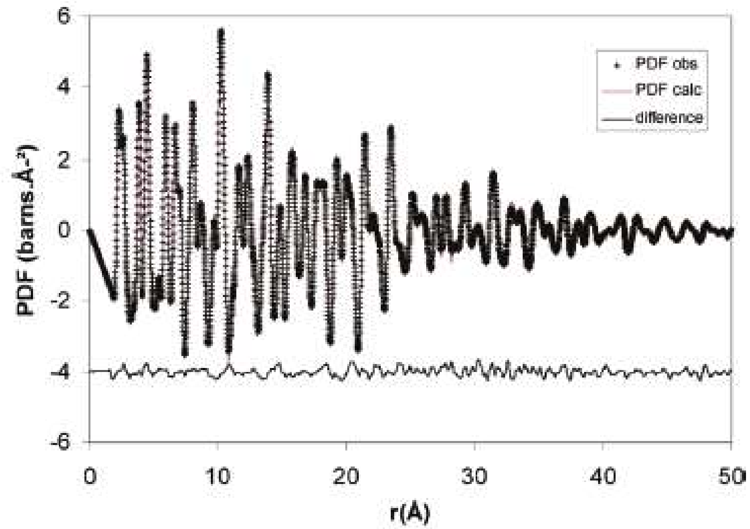
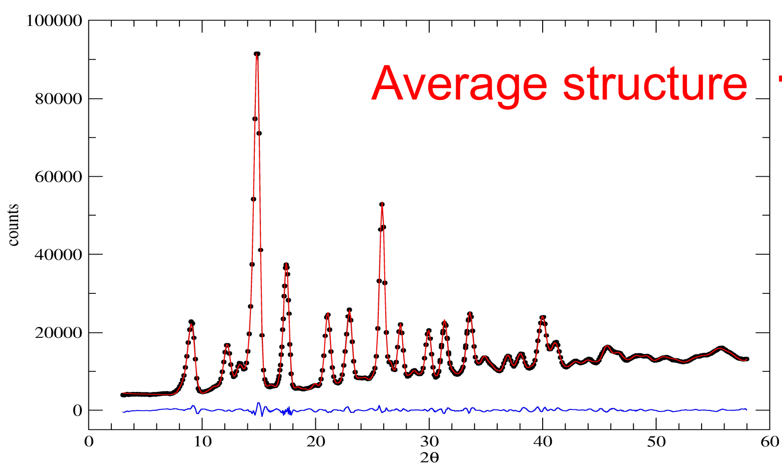


Figure 2. α-U_4O_9 neutron diffraction pattern corrected from air and sample holder diffusion.

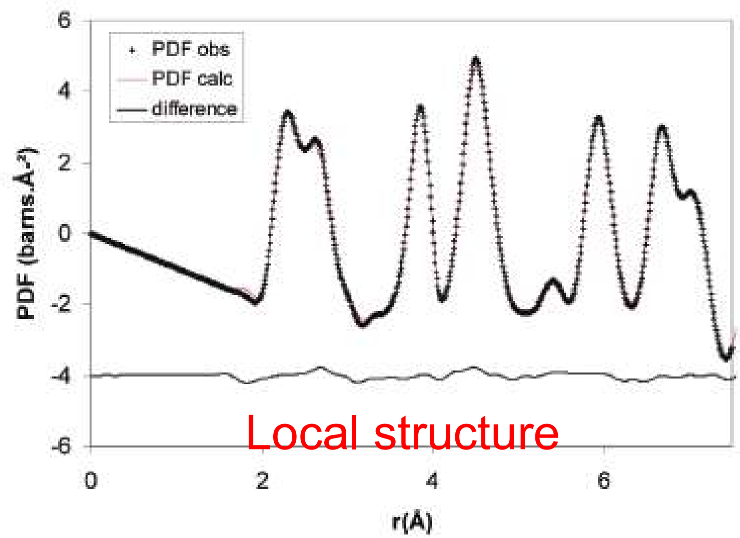
Fourier transform



Rietvelt refinement (JANA)

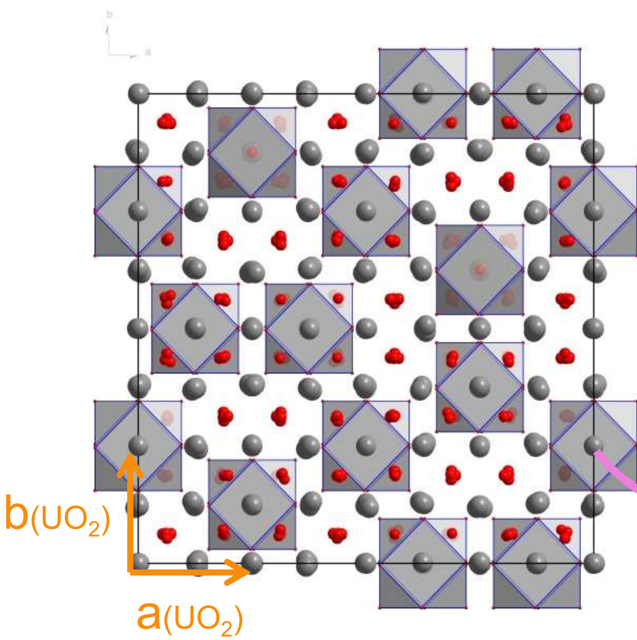


PDF refinement (PDFGUI)

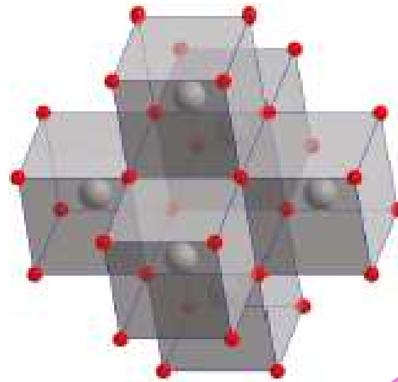


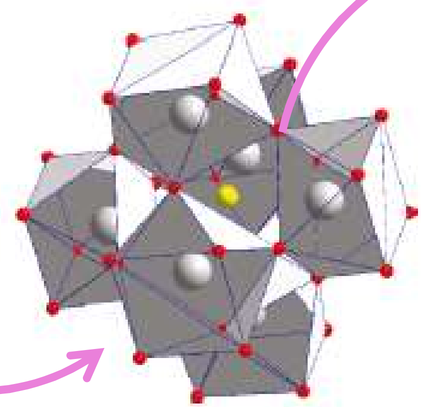
U_4O_9 AVERAGE STRUCTURE

An array of oxygen interstitial clusters in a UO_2 matrix



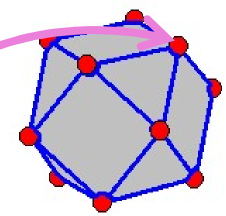
U_6O_{32} in UO_2





U_6O_{36+1}

cuboctahedron



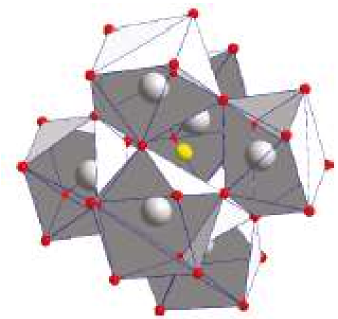
A more precise description of the cluster was achieved using PDF refinement

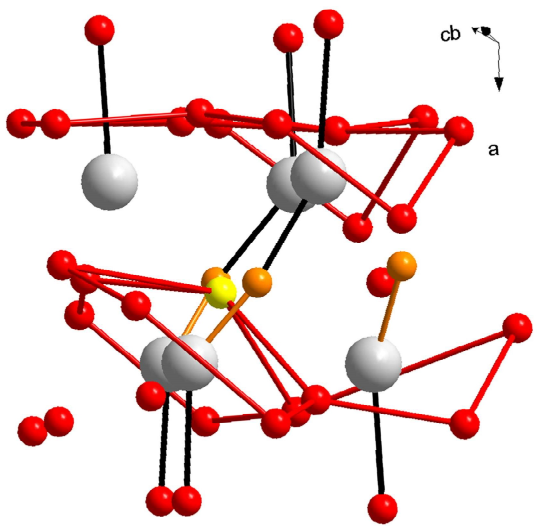
Inorg. Chem. 48 (2009) 7585-7592

CUBOCTAEDRON IN α-U_4O_9

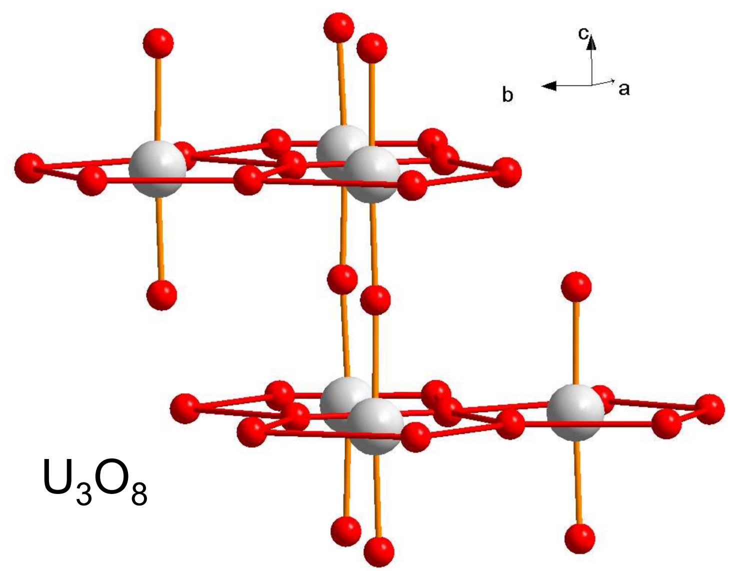
PDF refinement :

- Confirmed the existence of a the central oxygen
- Evidence the cuboctahedron as seed for higher oxide formation





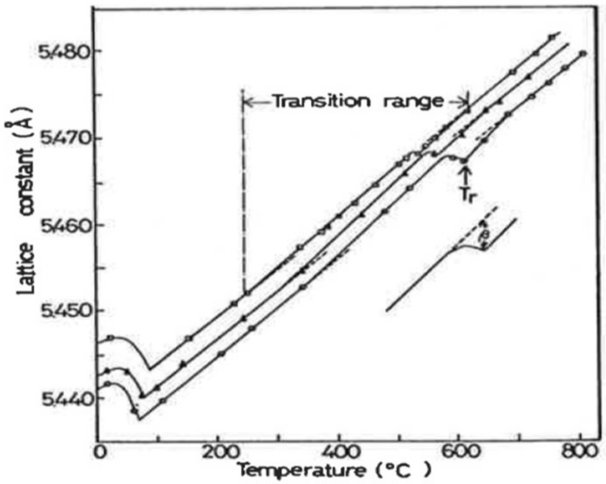
α-U_4O_9



U_3O_8

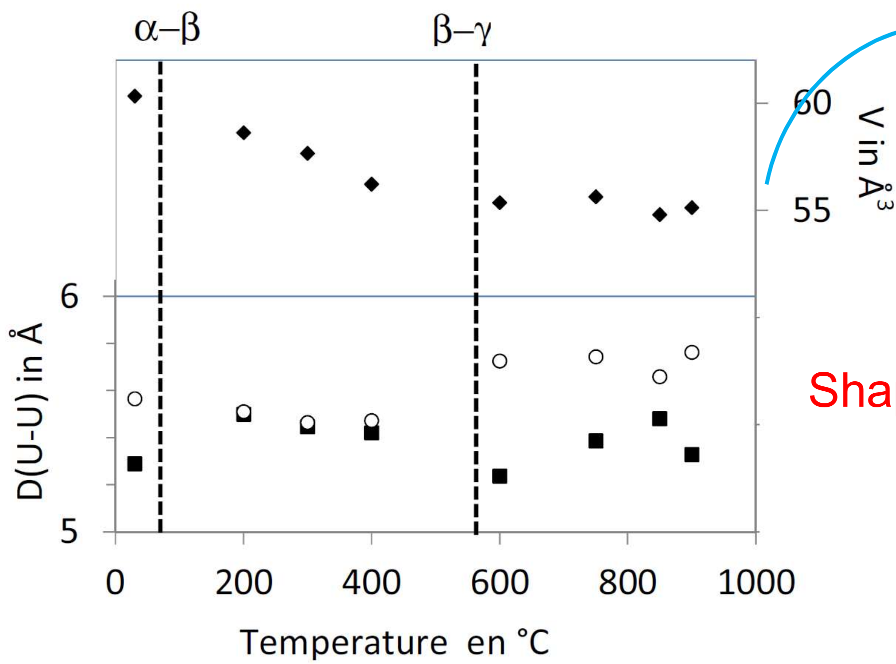
Inorg. Chem. 50 (2011) 6146-6151

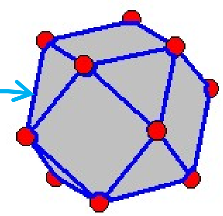
PHASE TRANSITION IN U_4O_9



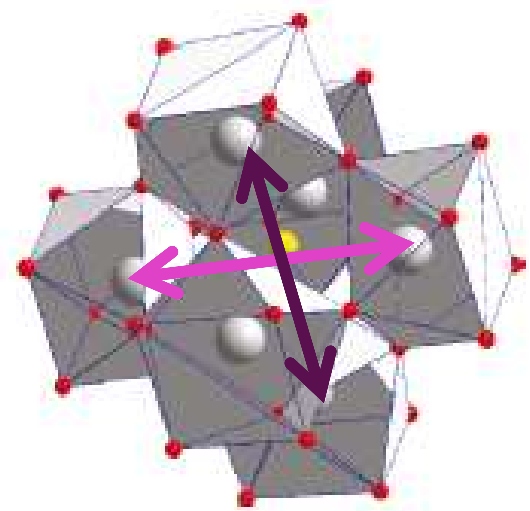
Evidence of changes in the cuboctahedron shape at the phase transition

β–γ isostructural transition





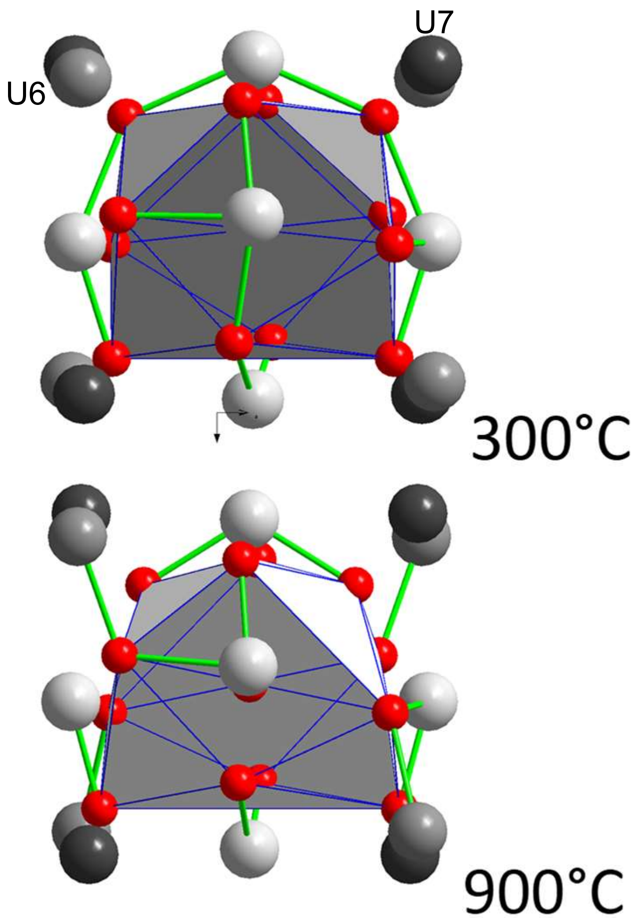
Volume decrease



Shape changes

Inorg. Chem. 55 (2016) 7485-7491

PDF INTERPRETATION OF CHANGE IN SHAPE



β-U_4O_9 :

- A nearly symmetric packing
- No difference between U6 an U7
- Steric interactions are dominant

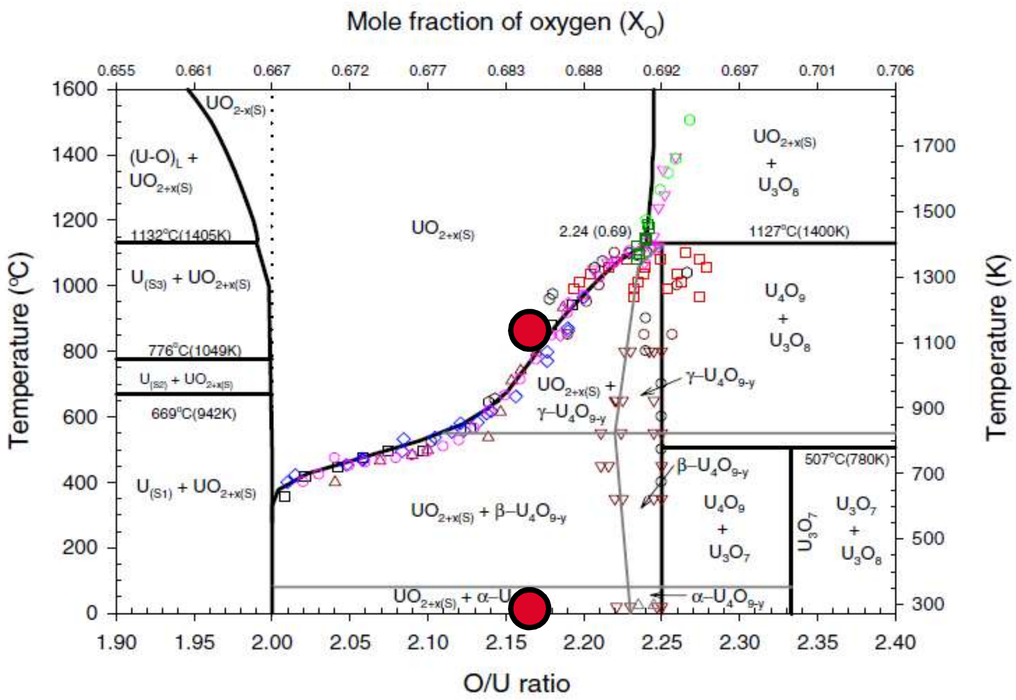
γ-U_4O_9 :

- Asymmetric packing
- U atoms with no UO bond shorter that 2.2Å, (U^{4+})
- U atoms with UO bond shorter that 2.2Å, (U^{5+})
- U6 (5+) are connected to the cuboctahedron by short bonds (in green)
- Coordination interactions are dominant

FIRST CONCLUSION UO_2 OXIDATION

Oxygen incorporation in UO_2 proceeds by the formation of oxygen interstitial clusters

This conclusion is valid for a wide range of U-O phase diagram

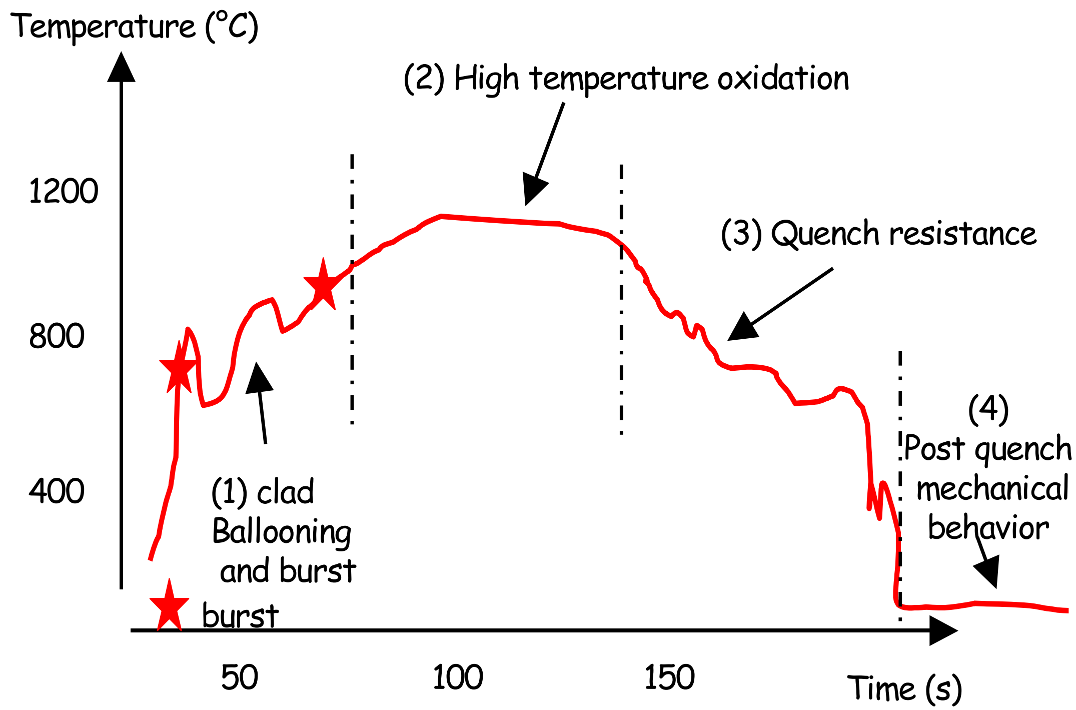


Ma et al, Inorg, Chem. 57 (2018) 7064-7076

Example 2

UO_2 at high temperature

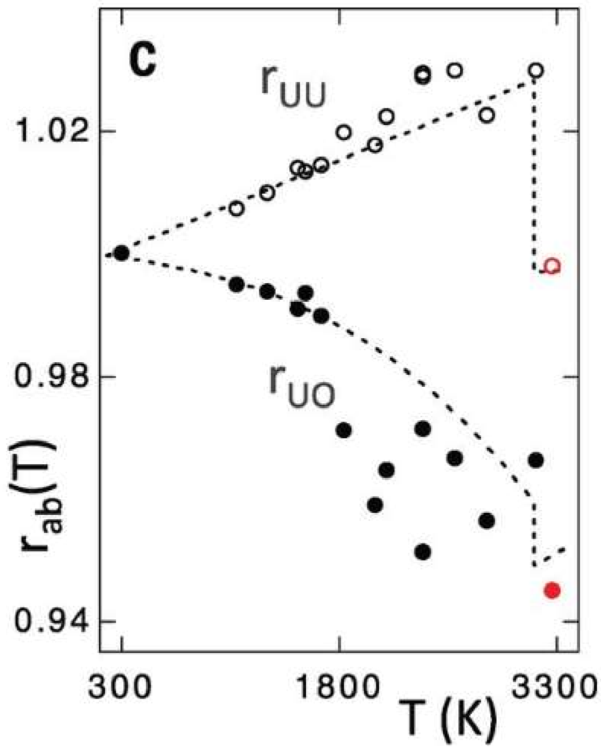
HIGH TEMPERATURE : ACCIDENTAL SCENARII



Temperature change in the case of a LOCA scenario as a function of time
The behavior of UO_2 at high temperature has to be known

No change in UO_2 crystal symmetry is expected

BUT !!



The U-O distance in UO_2 measured by X-Ray diffraction and PDF analysis is not consistent with Fm-3m crystalline structure

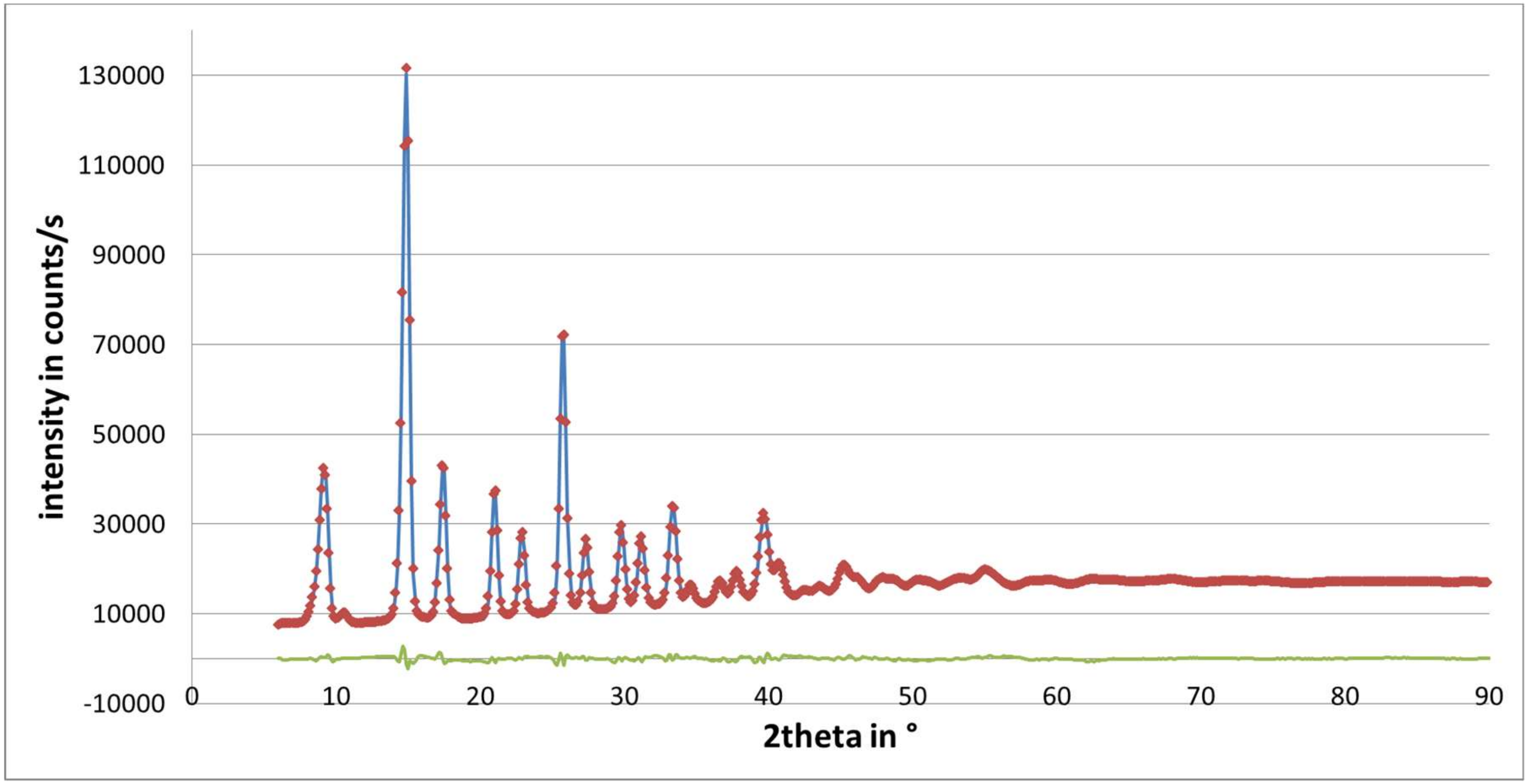
Skinner et al. Science. 2014 Nov 21;346(6212):984-7

A change in UO_2 local symmetry at high temperature ???

⇨ New experiments using neutron diffraction in order to probe O-O distance that are not visible using X-Ray diffraction

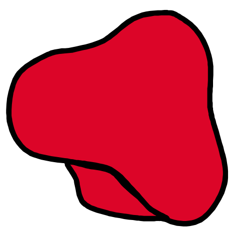
NEW EXPERIMENTAL DATA

Several diffraction patterns of UO_2 pellets measured from RT to 1000°C

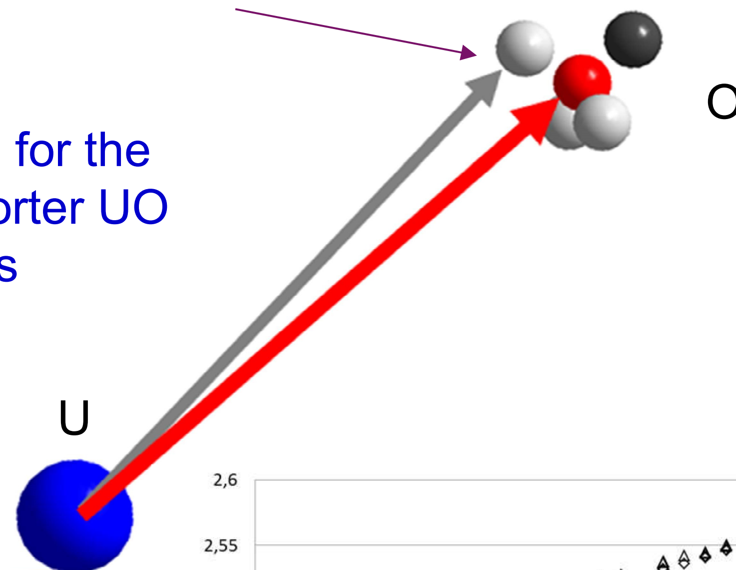


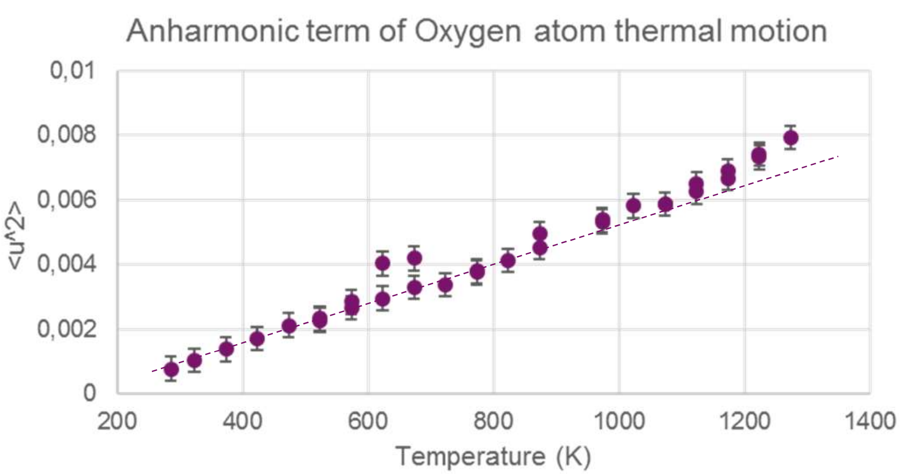
EVIDENCE OF OXYGEN DISORDER

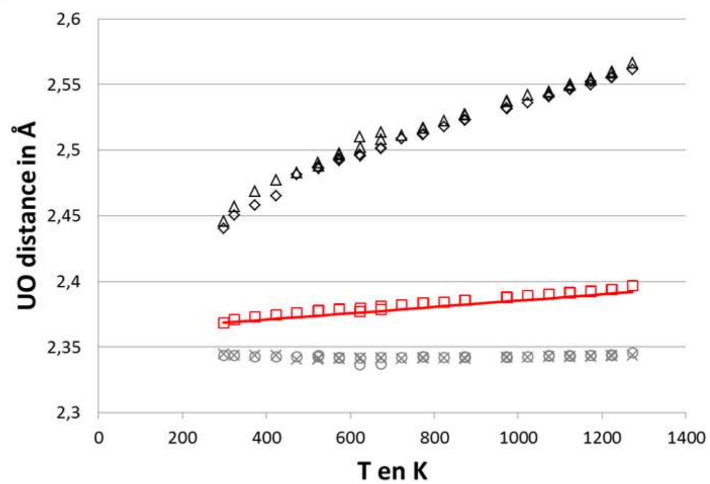
Described by Rietveld analysis,
either with anharmonic thermal motion or with a 4-site model



An explanation for the existence of shorter UO distances

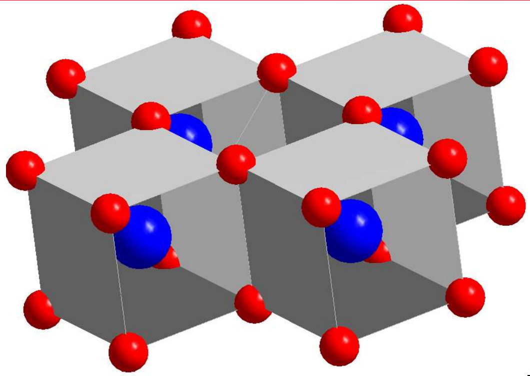






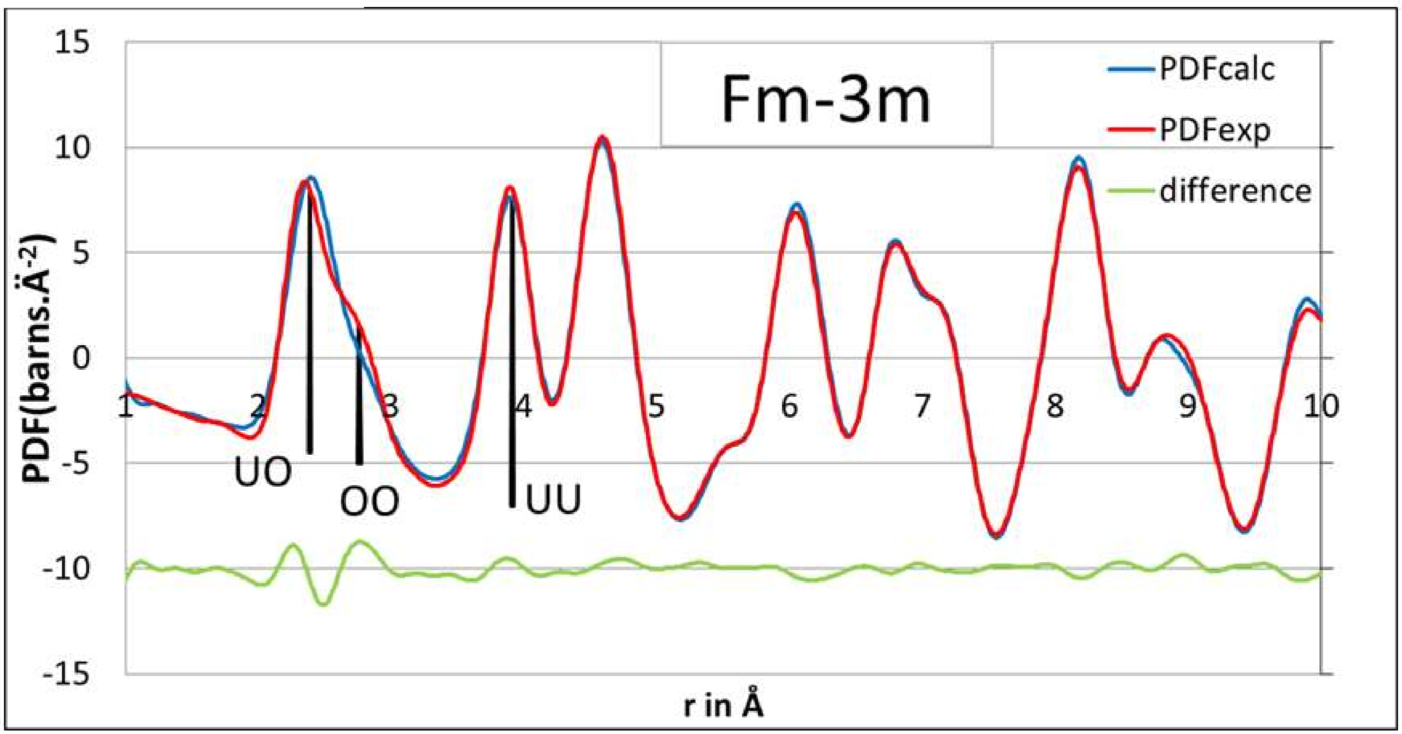
But only an average model

WHAT DOES PDF SAYS



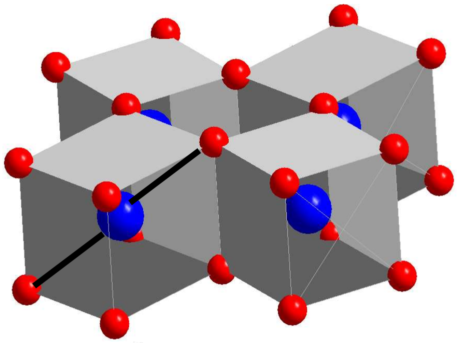
Regular Fm-3m structure does not reproduce well short distance distribution

Consistent with oxygen disorder



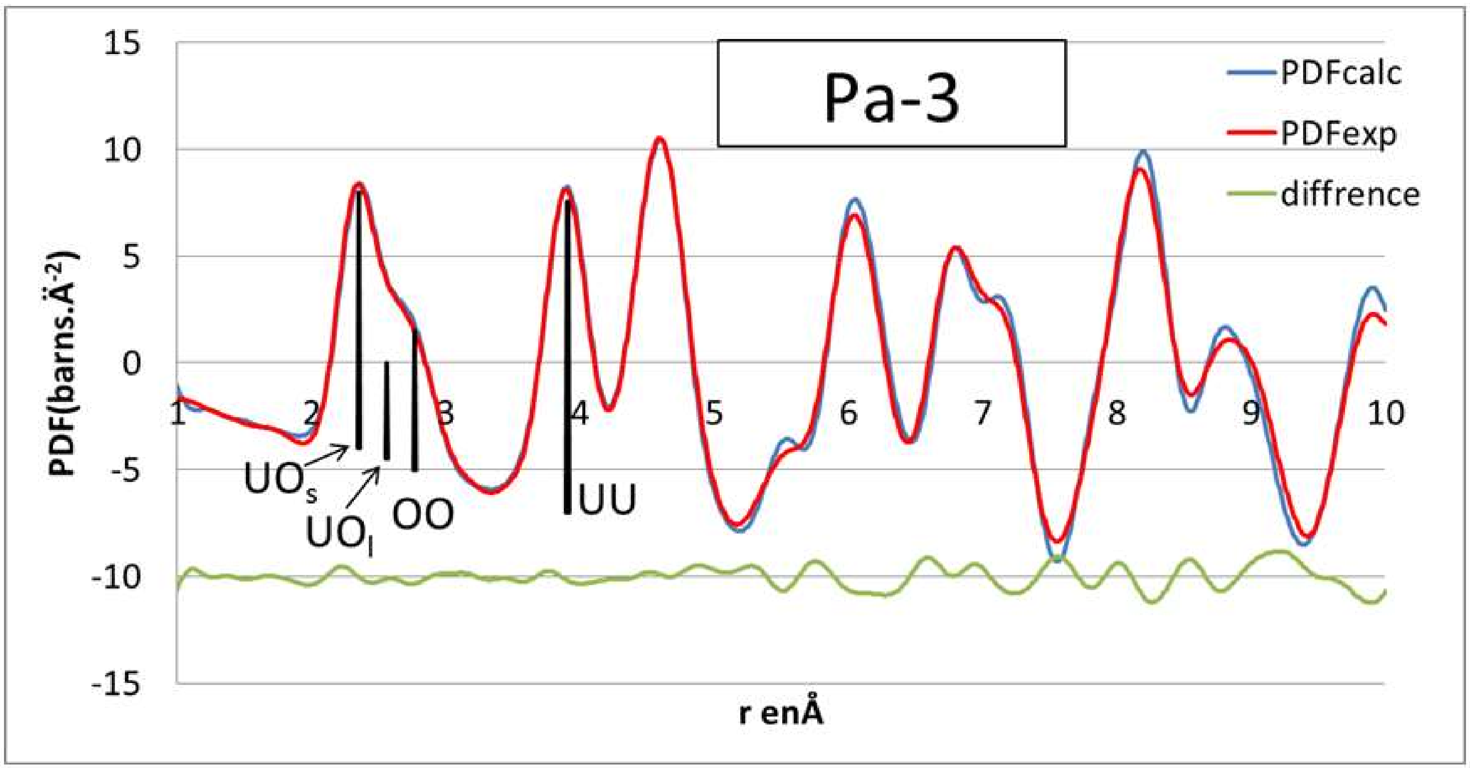
Inorg. Chem. 2017, 56, 321−326

A FIRST ATTEMPT TO DESCRIBE LOCAL ORDER



A lower symmetry structure, Pa-3, a Fm-3m subgroup having 2 short, 6 long UO and a single OO bound lengths,

fits local order better, but no more long range order

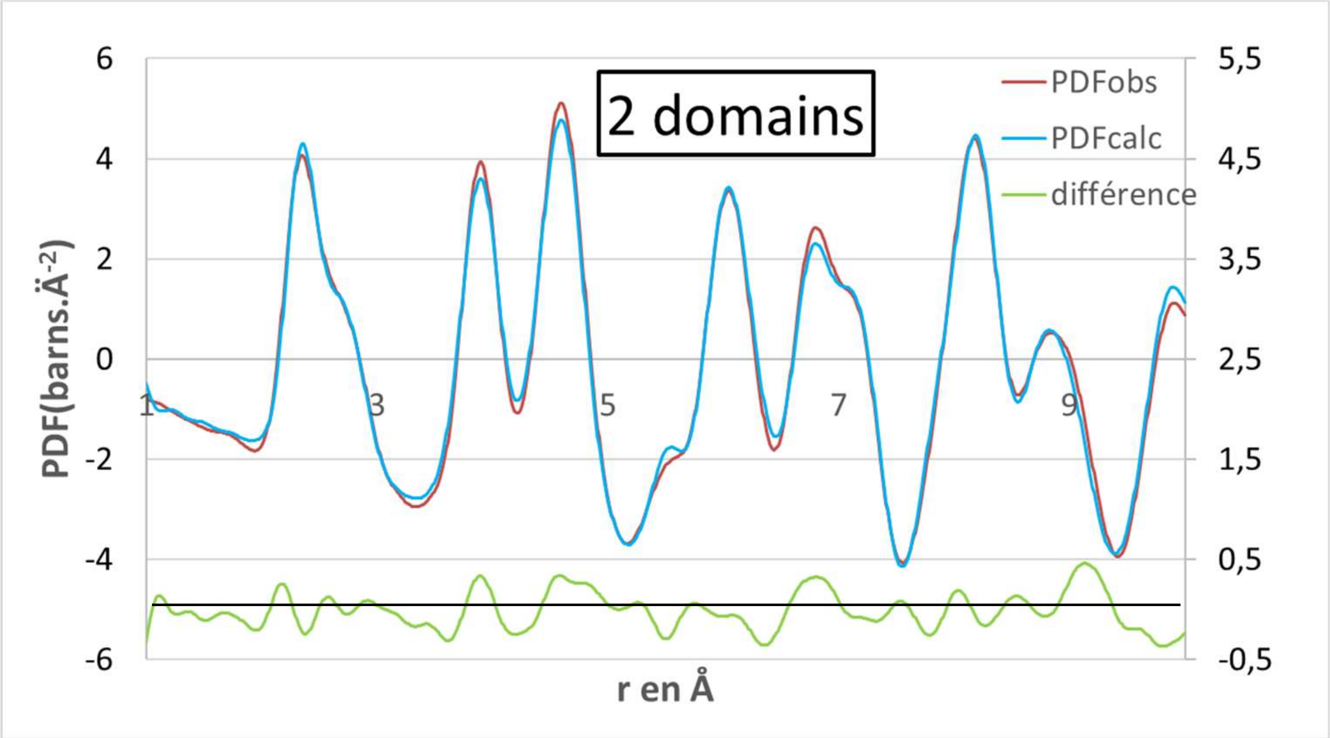


Inorg. Chem. 2017, 56, 321–326

HOW TO LINK LOCAL AND LONG RANGE ORDER?

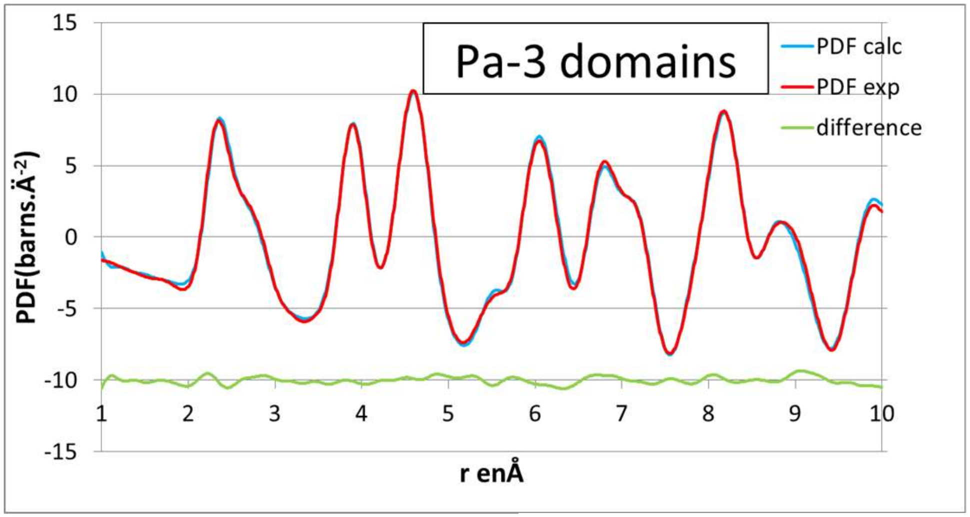
Putting domains having different orientations the ones next to the others is not enough.

Modeling box with 5 UO_2 cells and 2 domains

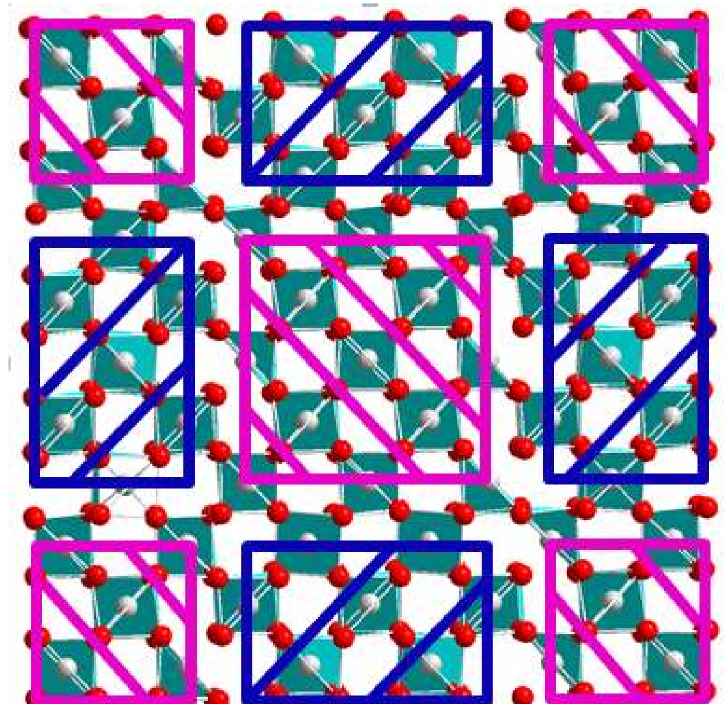


Adding more domains does not improve the fit

SYMMETRY CONSTRAINTS ARE NEEDED !!

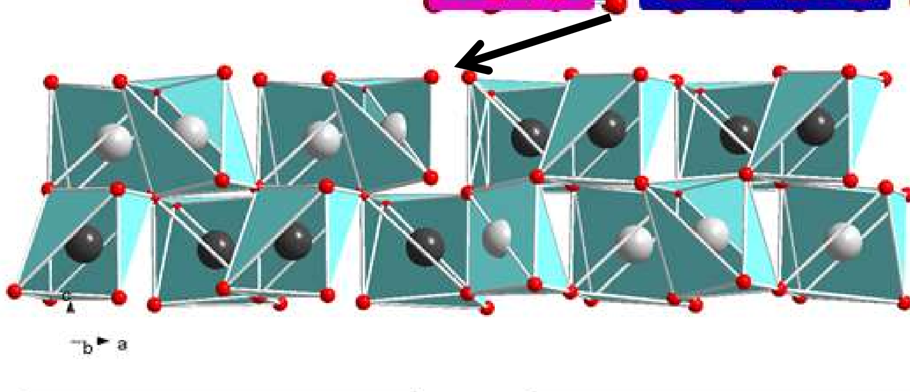


Chem. Eur. J. **2018**, *24*, 2085 – 2088



Best fit with Pa-3 nm size domain separated by coherent interfaces (compatible with average Fm-3m)

Consistent with the absence of additional diffraction lines



WHAT DOES IT MEAN?

Rietveld or PDF fits are only mathematical descriptions of the actual atomic distribution. More physics is needed for interpretation.

A static or dynamic disorder ?

- Diffraction (whether Rietveld refinement or PDF-analysis) cannot distinguish between static versus dynamic disorder, unless data are taken as a function of temperature.

Domains or somethings else ?

- Moving interfaces are also possible

The link with kinetic data would be helpful:

- What are the dynamics inside UO_2 at high temperature that could be related to oxygen motion?

FIRST CONCLUSION UO_2 AT HIGH TEMPERATURE

At least dynamically, at high temperature, the local symmetry of UO_2, Pa-3,
is lower that the regular Fm-3m regular symmetry of UO_2

Shorter UO bond length that are observed by EXAFS, X-ray and neutron diffraction
Is consistent with this lower local symmetry

GLOBAL CONCLUSION

For UO_2, the assumption : " one crystalline structure, three sites : 1 cationic, 1 anionic, 1interstitial, and different occupation fractions on each site" is oversimplified.

The understanding of UO_2 modification by irradiation requires a description at the local scale

- **2 perspectives:**
  - A new approach for the understanding of irradiated UO_2
  - A more general approach of « simple » oxides

Thank You
for your attention

Commissariat à l'énergie atomique et aux énergies alternatives
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