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## Nanodomains in UO<sub>2</sub> Some New Degrees of Freedom for Nuclear Fuel

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► **To cite this version:**

L. Desgranges, Y. Ma, P. Garcia, D. Simeone, G. Baldinozzi, et al.. Nanodomains in UO<sub>2</sub> Some New Degrees of Freedom for Nuclear Fuel. MRS Spring 2018, Apr 2018, Phoenix, United States. cea-02339073

**HAL Id: cea-02339073**

**<https://cea.hal.science/cea-02339073v1>**

Submitted on 13 Dec 2019

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DE LA RECHERCHE À L'INDUSTRIE



# NANODOMAINS IN $\text{UO}_2$ : SOME NEW DEGREES OF FREEDOM FOR NUCLEAR FUEL

MRS EN 17 | L. Desgranges, Y. Ma, Ph. Garcia, G. Baldinozzi, D. Siméone, H.E. Fischer

[www.cea.fr](http://www.cea.fr)

APRIL 6, 2018

# WHY IS $\text{UO}_2$ IRRADIATION RESISTANT ?

Our results indicate that complex oxides with natural atomic disordering tendencies are the most likely compounds to possess good resistance to radiation damage.

K. Sickafus et al. *Nature Materials* **volume 6**, pages217–223 (2007)

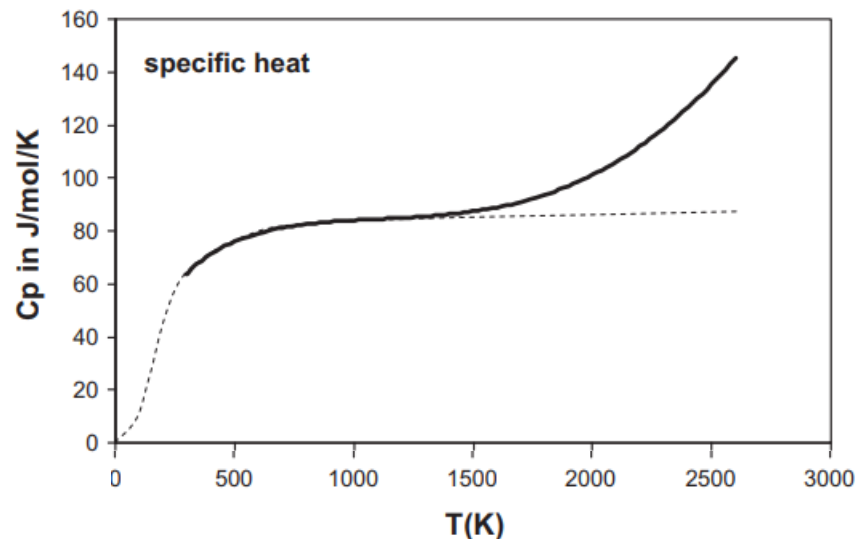
## What about $\text{UO}_2$ ?

Irradiation resistant

A simple crystalline structure



With disordering tendency



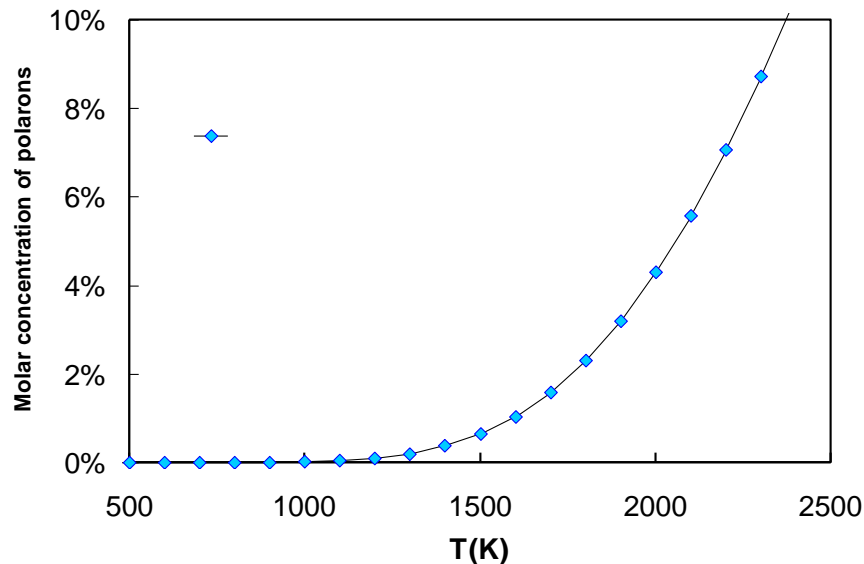
# A FIRST TENTATIVE INTERPRETATION

$C_p$  increase can be described by point defect formation

*P. Ruello et al. / Journal of Physics and Chemistry of Solids 66 (2005) 823–831*

$$C_p = C_{v \text{ phonon}} + C_{\text{thermal expansion}} + C_{\text{Schottky}} + C_{\text{electronic defects}} + C_{\text{oxygen Frenkel pair}}$$

$$C_e = N \frac{k}{2} \left( \frac{\Delta H_p}{kT} \right)^2 \exp \left( -\frac{\Delta H_p}{2kT} + \frac{\Delta S_p}{2k} \right)$$

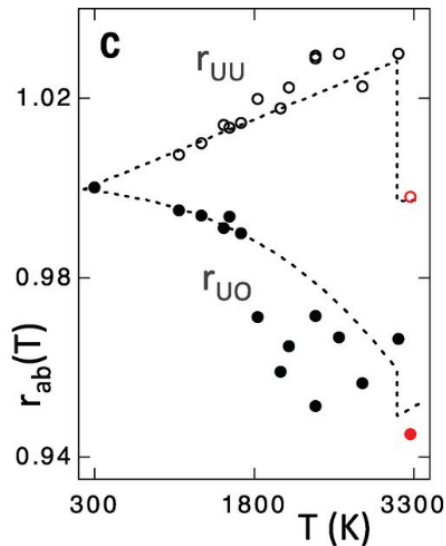


But

Unrealistic  
defect concentration

Nucl.Instrum. Methods B 277 (2012) 109–111

## ANOTHER EXPLANATION?



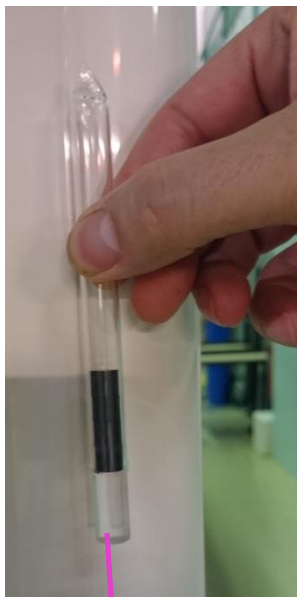
The U-O distance in  $UO_2$  measured by X-Ray diffraction and PDF analysis is not consistent with Fm-3m crystalline structure

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

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

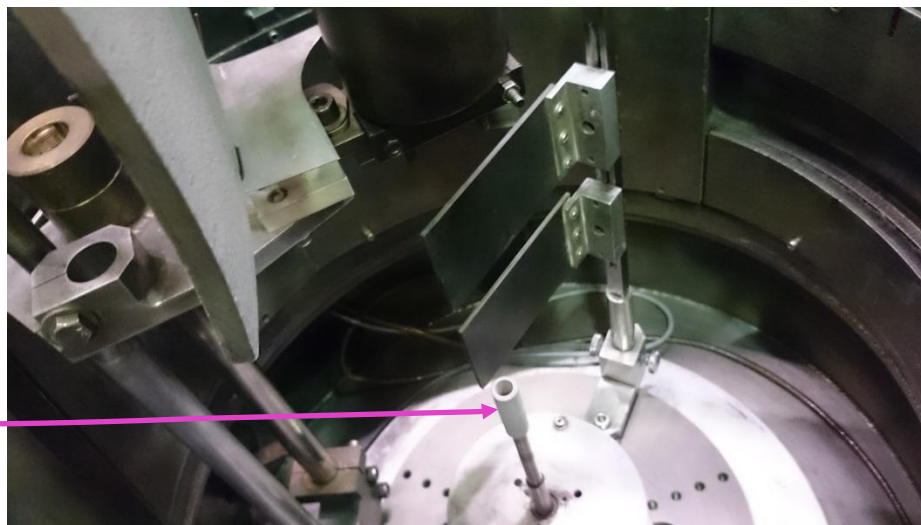
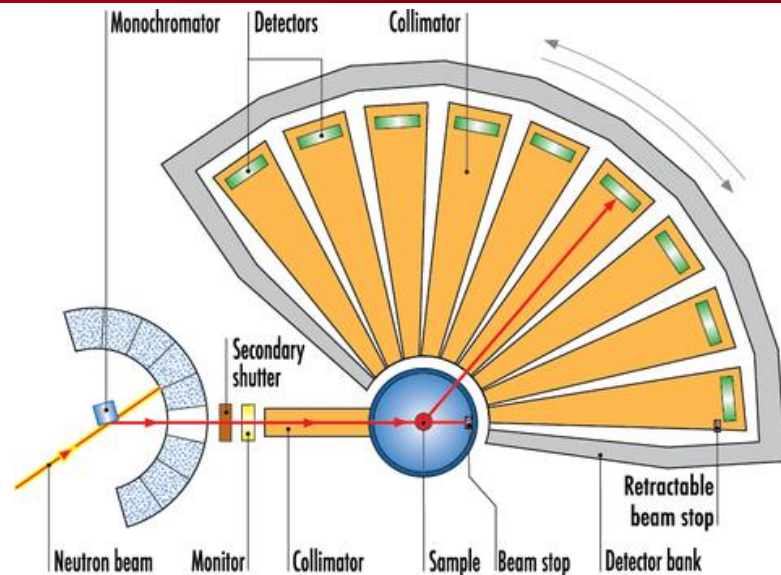
Atom	$\sigma_{X\text{-Ray}}$	$\sigma_{\text{neutron}}$
O	0.64	4.232
U	84.85	8.906

# NEUTRON DIFFRACTION WITH $\text{UO}_2$ ON D4 AT ILL

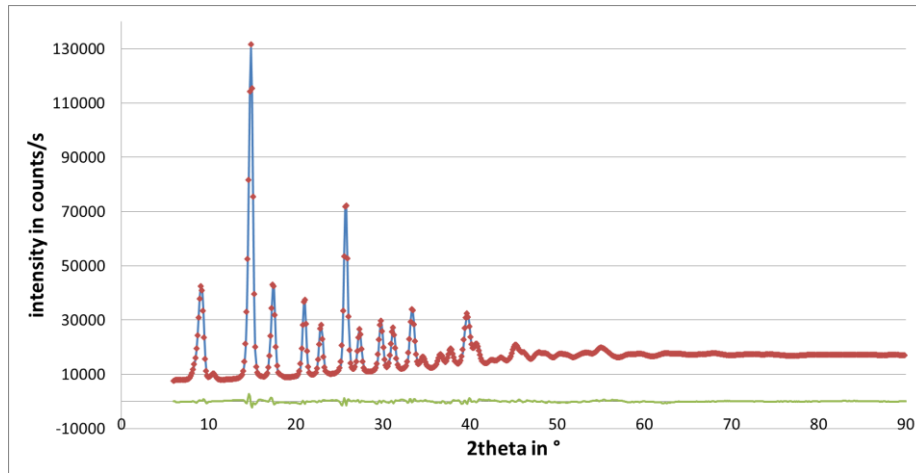


A two  $\text{UO}_2$  pellet stack set in a airtight glass tube

Installed inside the sample holder of D4 furnace

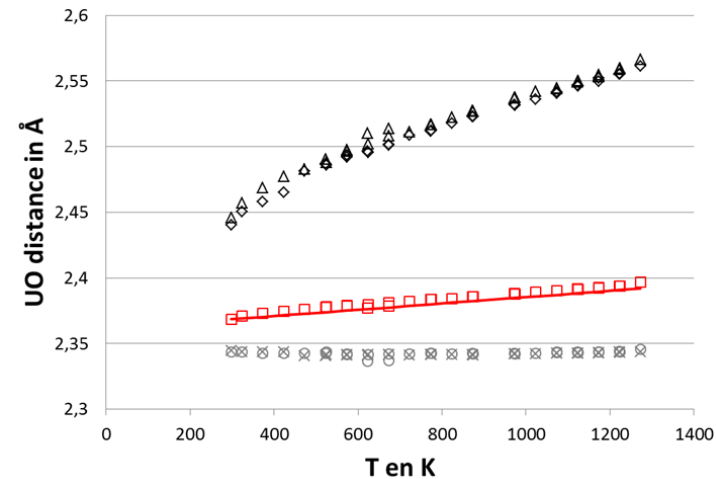
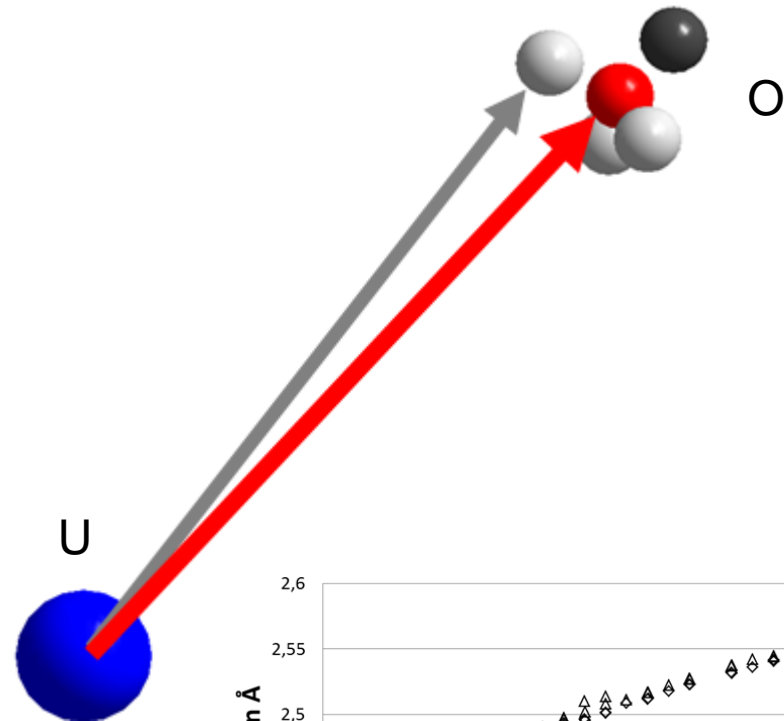


Data analyzed in reciprocal and real space

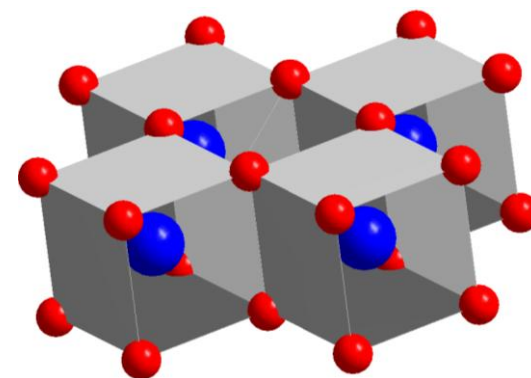
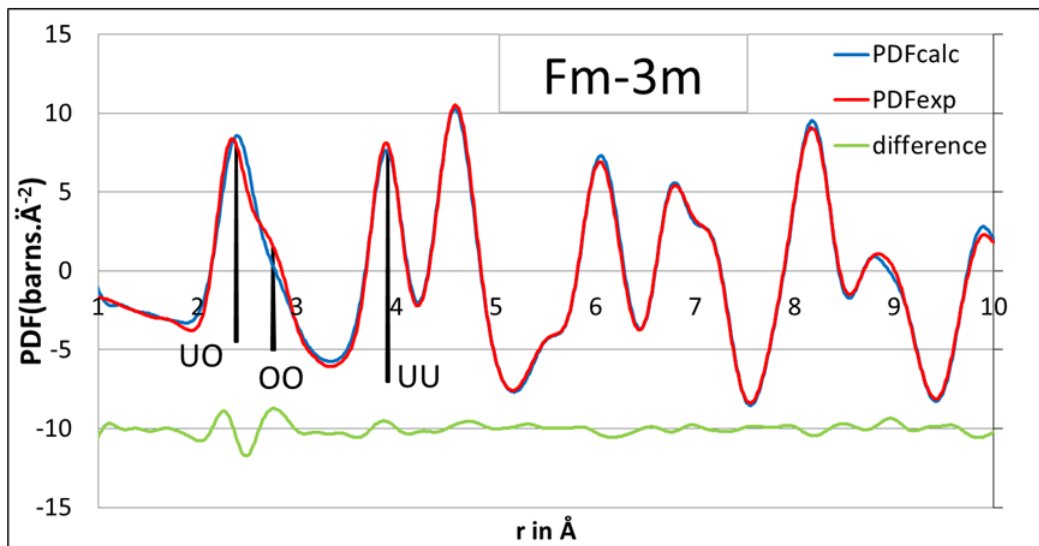


Best fit with a 4-site model for oxygen atom

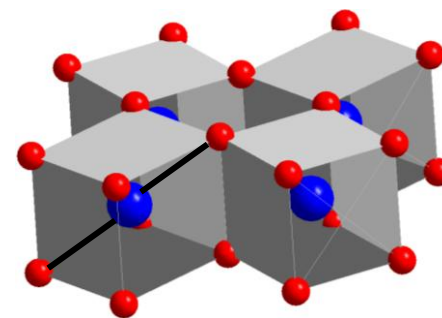
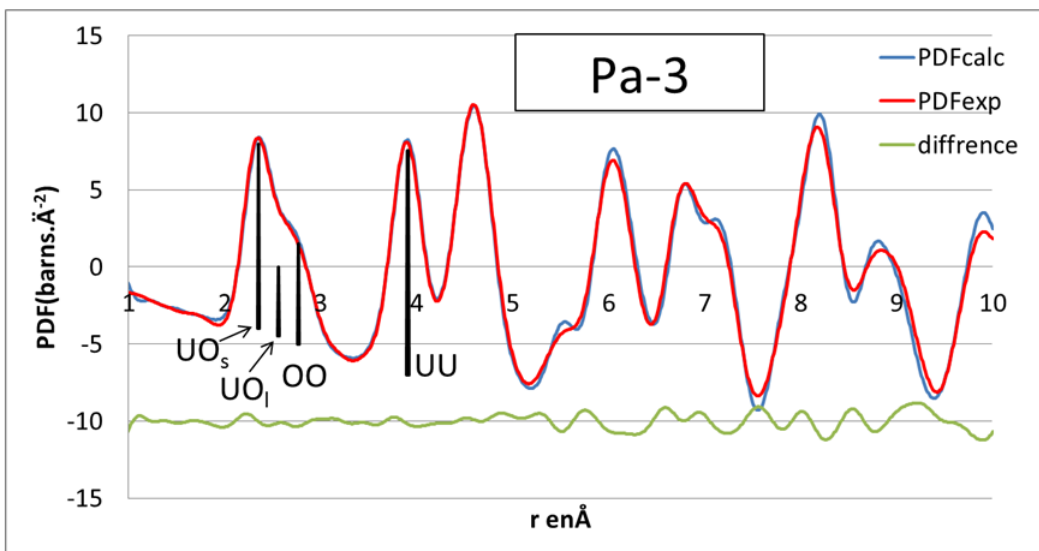
An explanation for the existence of shorter UO distances but only an average description



# FIRST PDF ANALYSIS



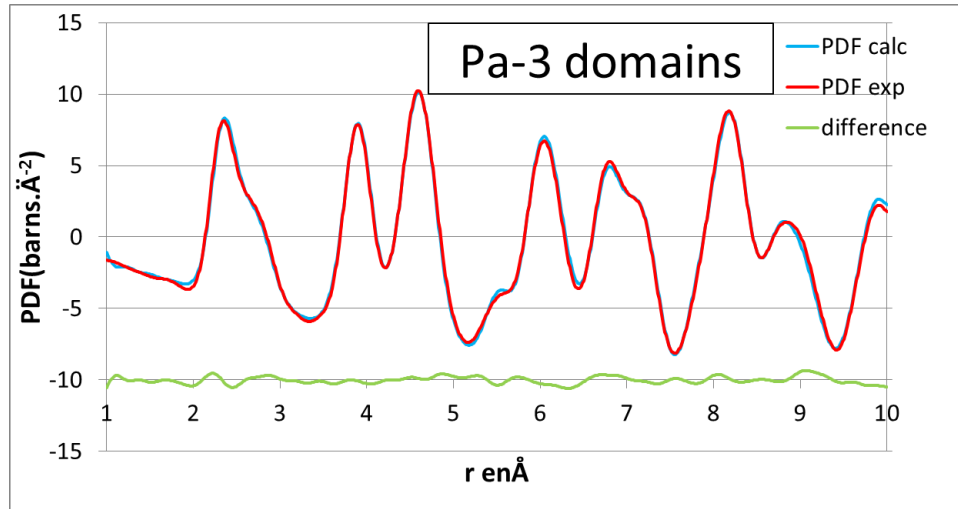
Local order badly fitted



Local order better fitted  
but not long range order

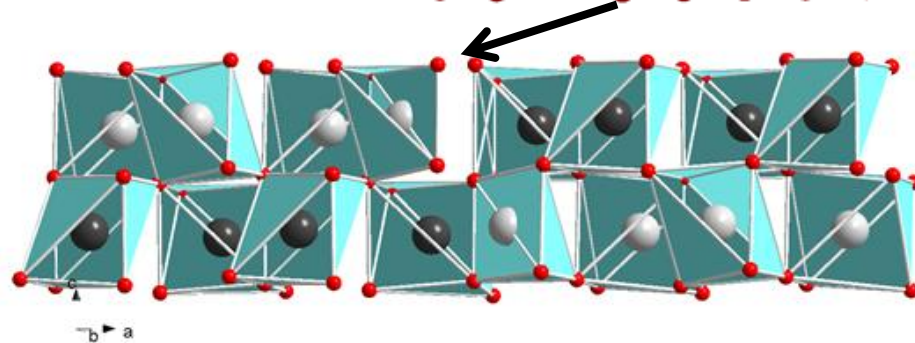
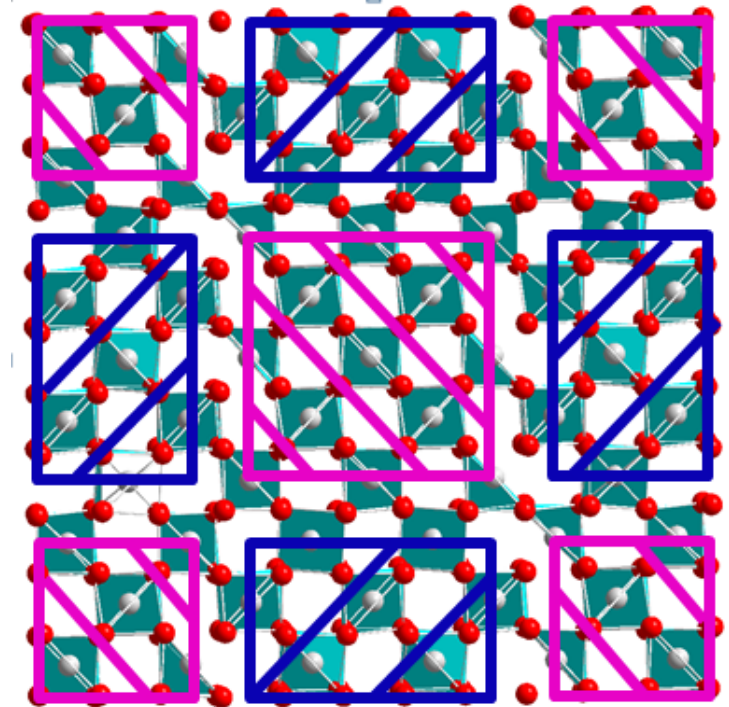


# MORE WORKED-OUT PDF ANALYSIS



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

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



Pyrite type stacking

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Marcasite type slab

Pyrite type stacking

## 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.
- Very small domain size would indicate dynamic

## What is the relationship between structural disorder and :

- Heat capacity
- Polarons (point defects)

## Is it the right way to consider $\text{UO}_2$ as:

- “A complex oxide with natural atomic disordering tendencies”
- An irradiation resistant material

## PDF and Rietveld analyses evidence:

- Local disorder at Oxygen site in Fm-3m
- Consistent with a local symmetry lower than Fm-3m

## PDF analysis allows to propose :

- A local Pa-3 symmetry
- A domain like arrangement of the domains

## A new track for the interpretation:

- Of UO<sub>2</sub> properties
- Its irradiation resistance
- Irradiation resistance in general (explanation applicable to AmO<sub>2</sub>, ZrO<sub>2</sub>, MgO ..)

# Thank You for your attention

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