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DE LA RECHERCHE À L'INDUSTRIE



NANODOMAINS IN 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

APRIL 6, 2018

WHY IS 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)

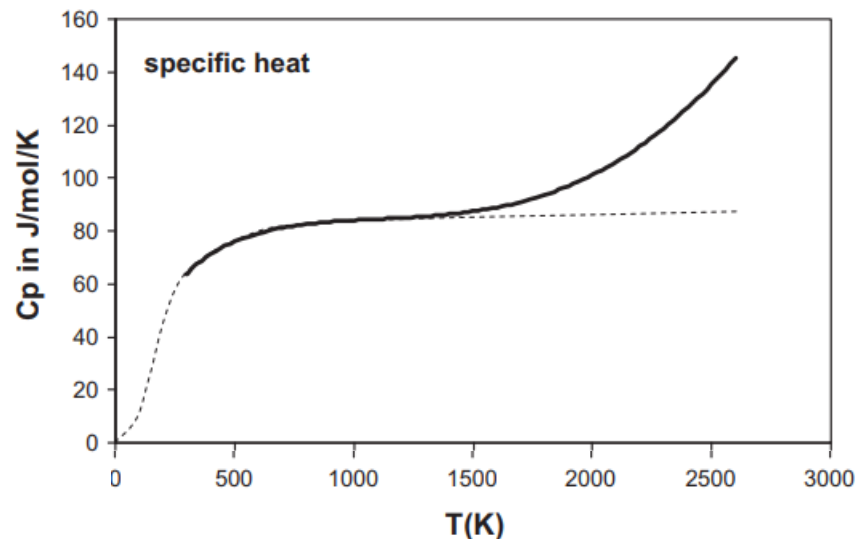
What about UO_2 ?

Irradiation resistant

A simple crystalline structure



With disordering tendency



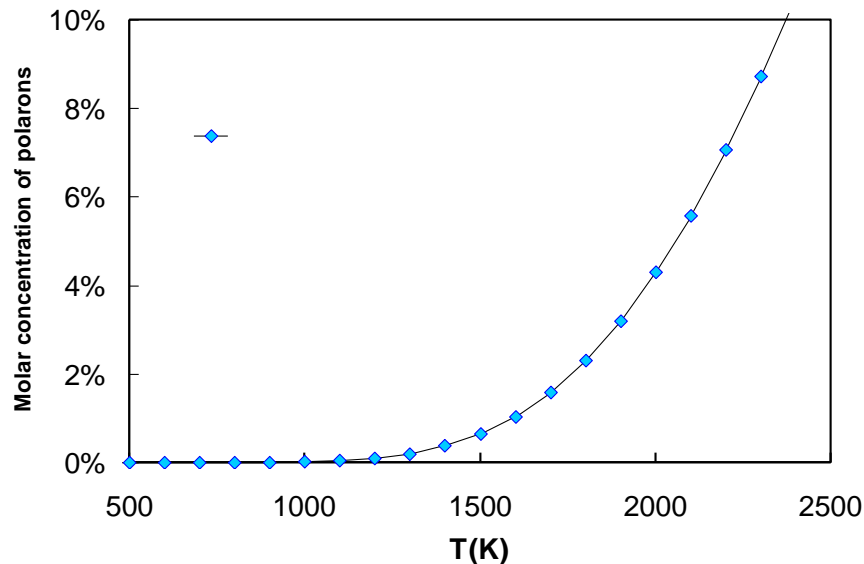
A FIRST TENTATIVE INTERPRETATION

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

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

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

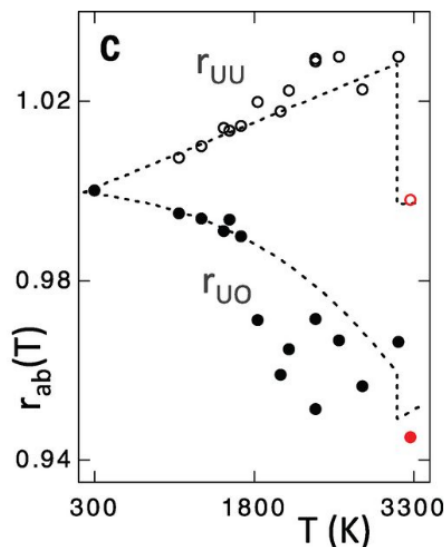


But

Unrealistic
defect concentration

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

ANOTHER EXPLANATION?



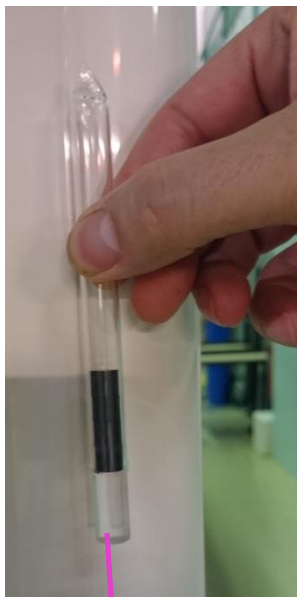
The U-O distance in UO_2 measured by X-Ray diffraction and PDF analysis is not consistent with Fm-3m crystalline structure

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

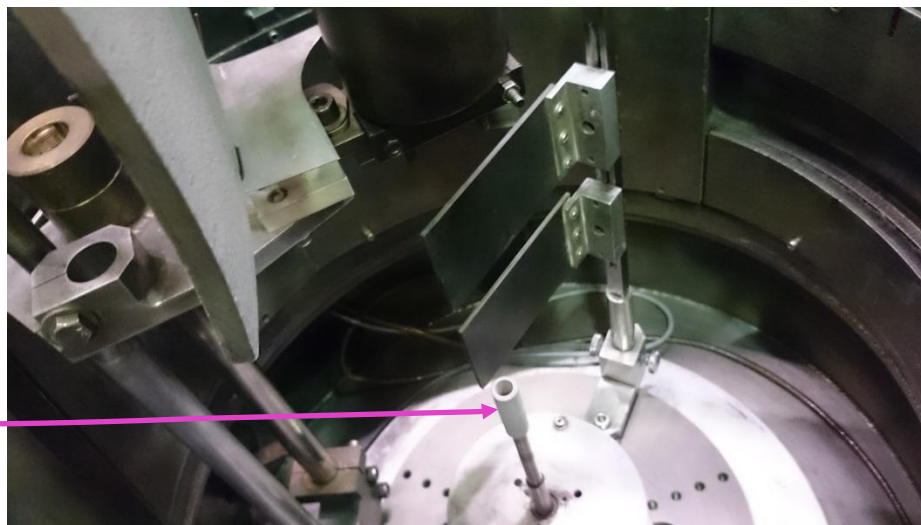
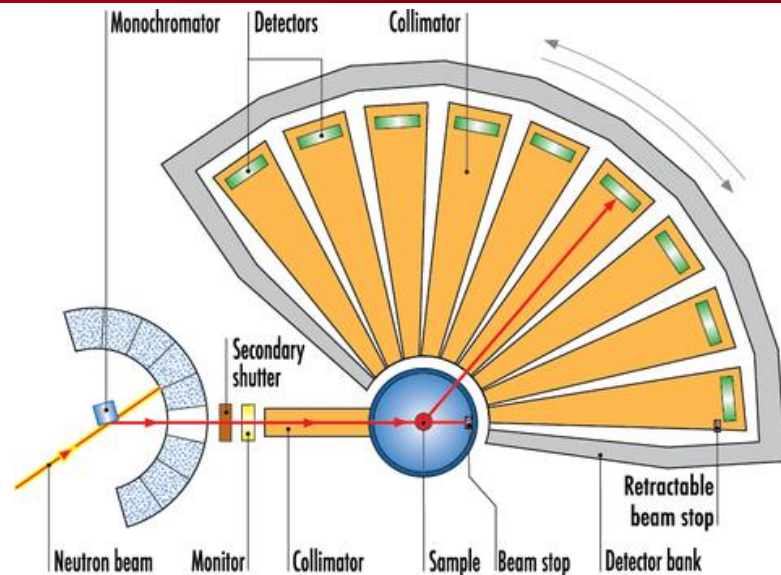
Atom	$\sigma_{\text{X-Ray}}$	σ_{neutron}
O	0.64	4.232
U	84.85	8.906

NEUTRON DIFFRACTION WITH UO_2 ON D4 AT ILL

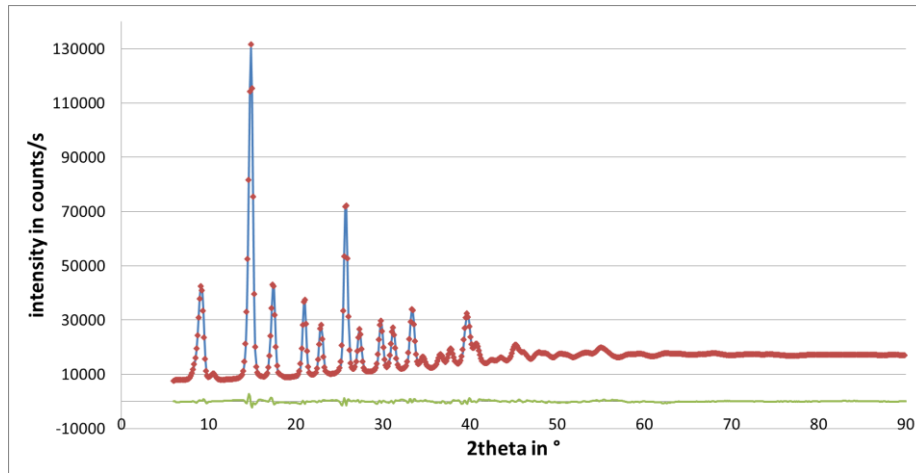


A two UO_2 pellet stack set in a airtight glass tube

Installed inside the sample holder of D4 furnace

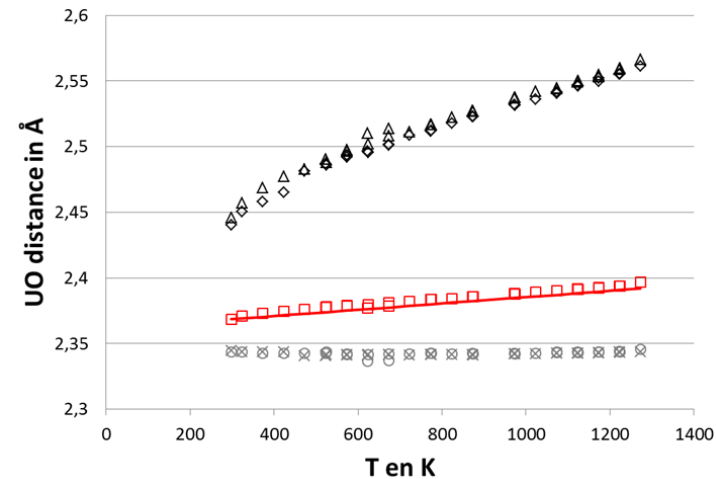
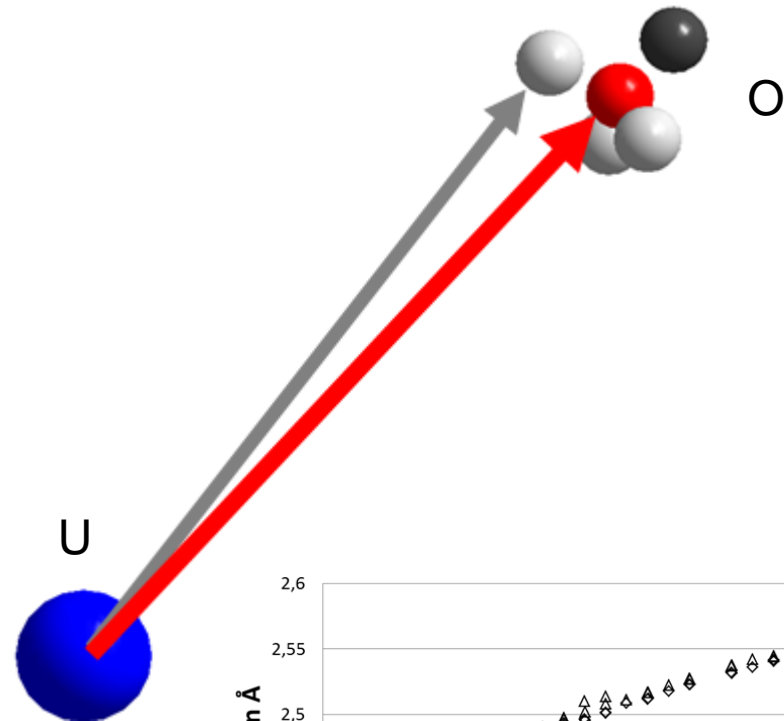


Data analyzed in reciprocal and real space

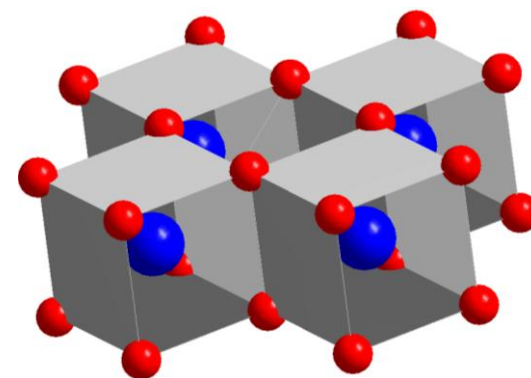
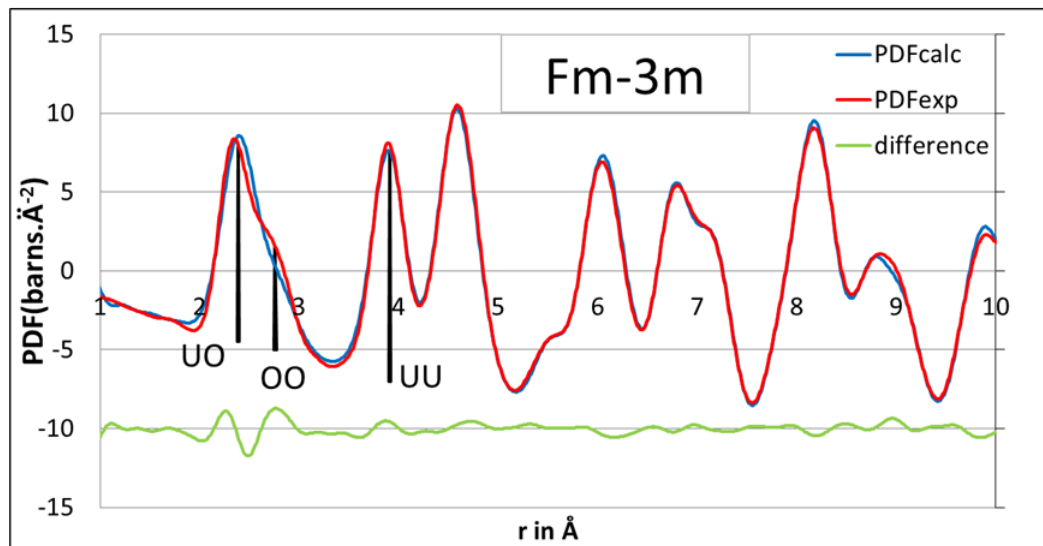


Best fit with a 4-site model
for oxygen atom

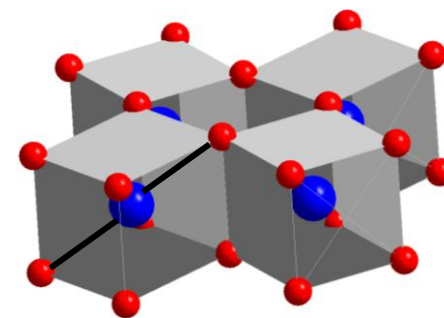
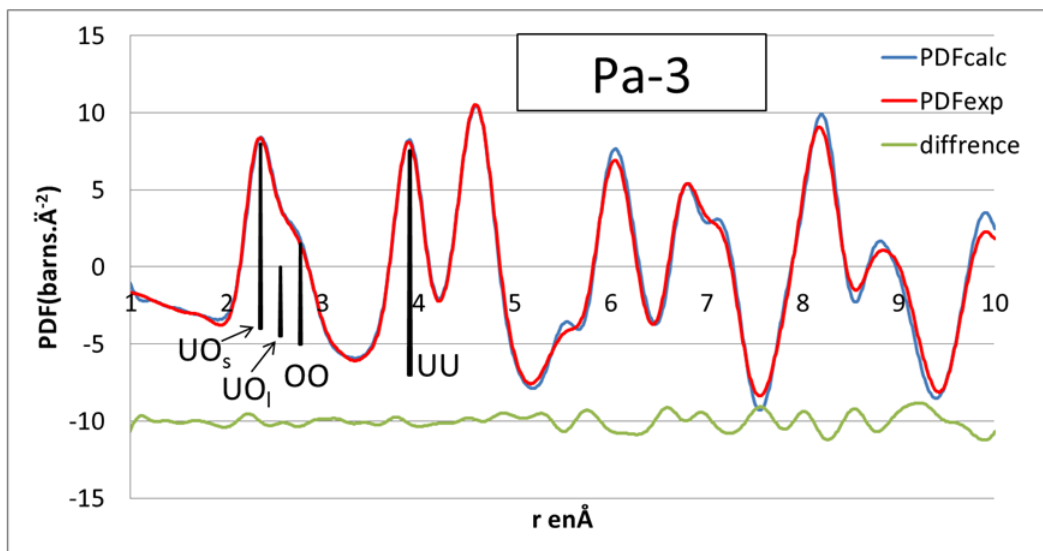
An explanation for the existence
of shorter UO distances but only
an average description



FIRST PDF ANALYSIS

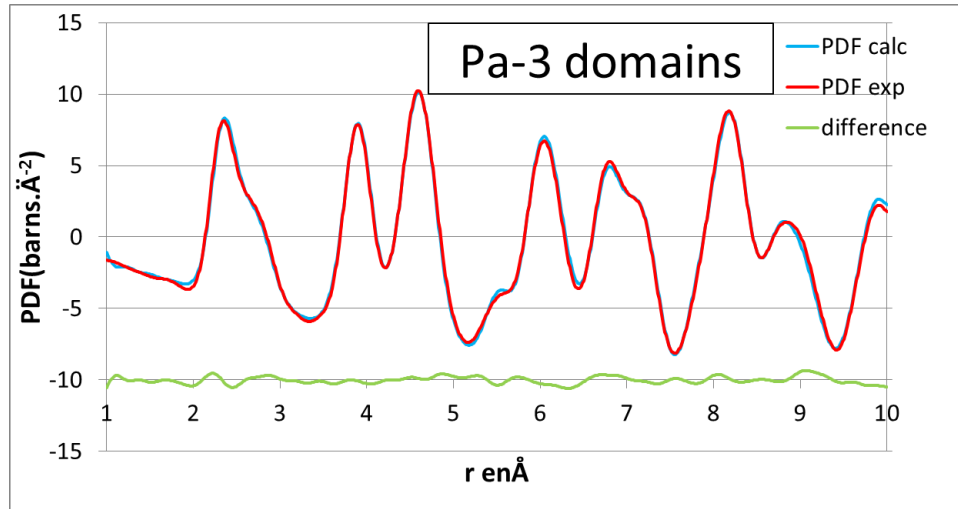


Local order badly fitted



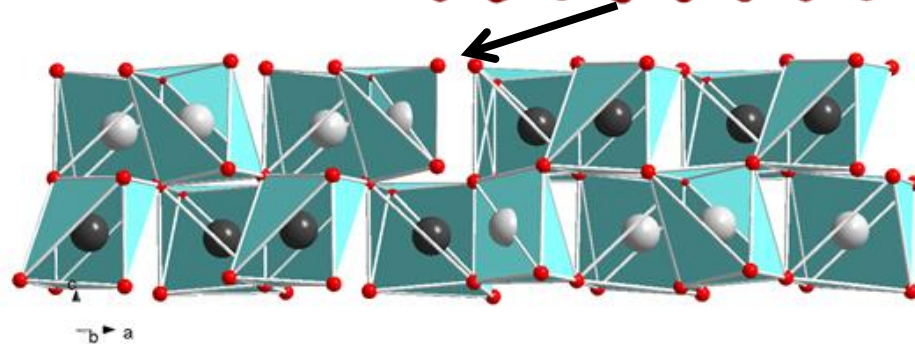
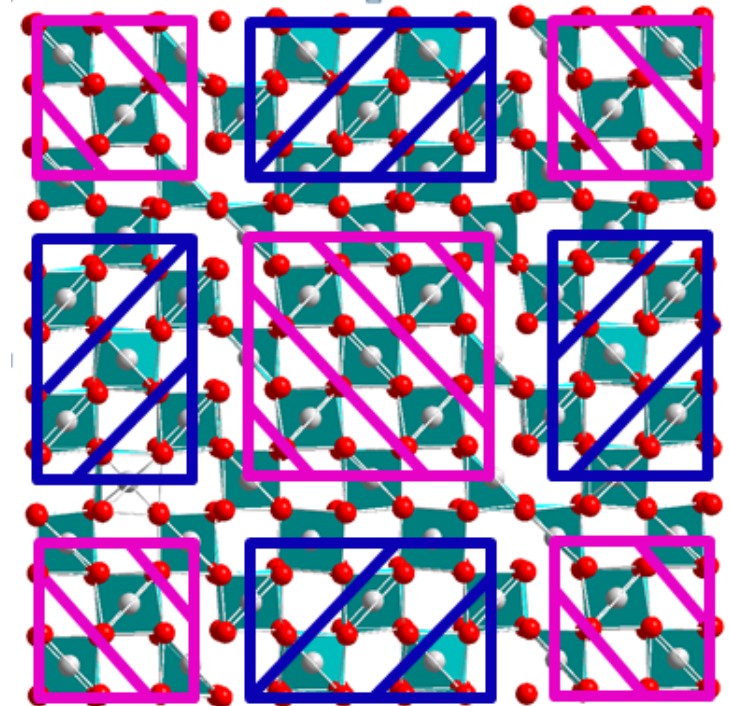
Local order better fitted
but not long range order

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

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 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 UO₂ properties
- Its irradiation resistance
- Irradiation resistance in general (explanation applicable to AmO₂, ZrO₂, MgO ..)

Thank You for your attention

Commissariat à l'énergie atomique et aux énergies alternatives
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