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NEUTRON DIFFRACTION EXPERIMENT AND DATA ANALYSIS OF UO_{2+x} SAMPLE

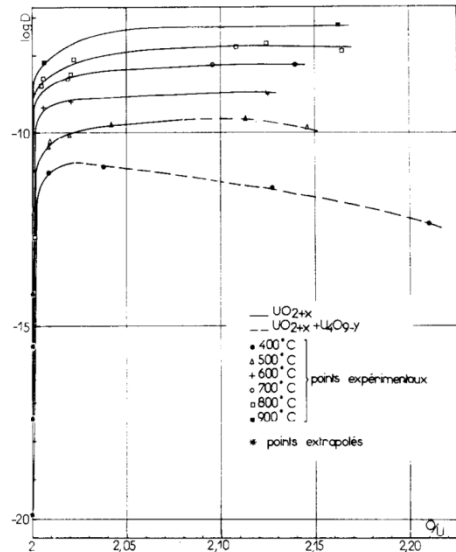
**Y. MA, P. Garcia, L. Desgranges, G. Baldinozzi,
H. Fischer, D. Simeone, J. Lechelle**

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➤ Background and motivations

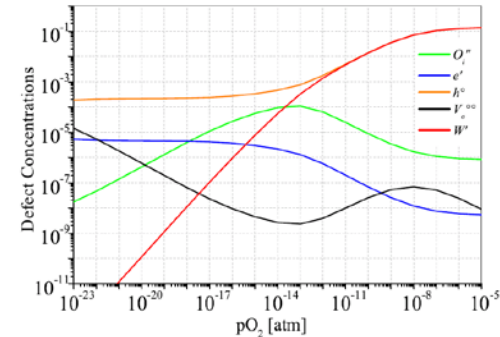
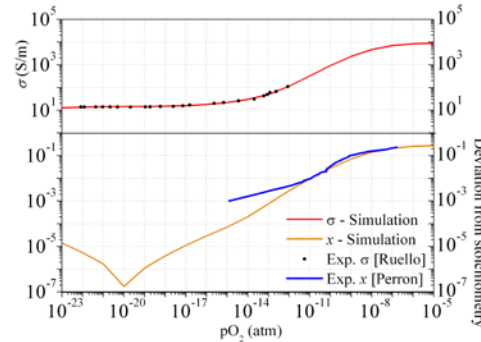
- Uranium dioxide – the major fuel materials → Improve the capacity to understand fuel properties
- The periodic structure of UO₂ crystal is always disturbed by different types of defects (associates and clusters), which determine essential engineering properties: ion diffusivity D_o, electrical conductivity σ and creep.



Oxygen self diffusion coeffi. as a func. of x [1]

- Point defects: e.g. PD model for σ and non-stoichiometry x study [2]

$$\sigma, x \propto p_{O_2}^{\frac{1}{2} \frac{n}{m+1}}$$



- → Understanding the nature and behavior of point defects!

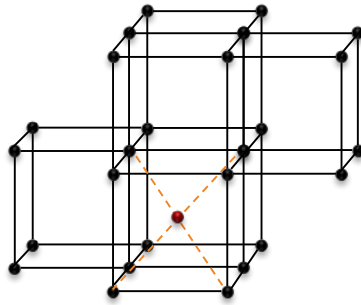
[1]Contamin, et al., 1972, J. Nucl. Mat., 42; [2]Dorado, et al., 2011, Phys. Rev. B 83

OXYGEN DEFECTS (CLUSTER)

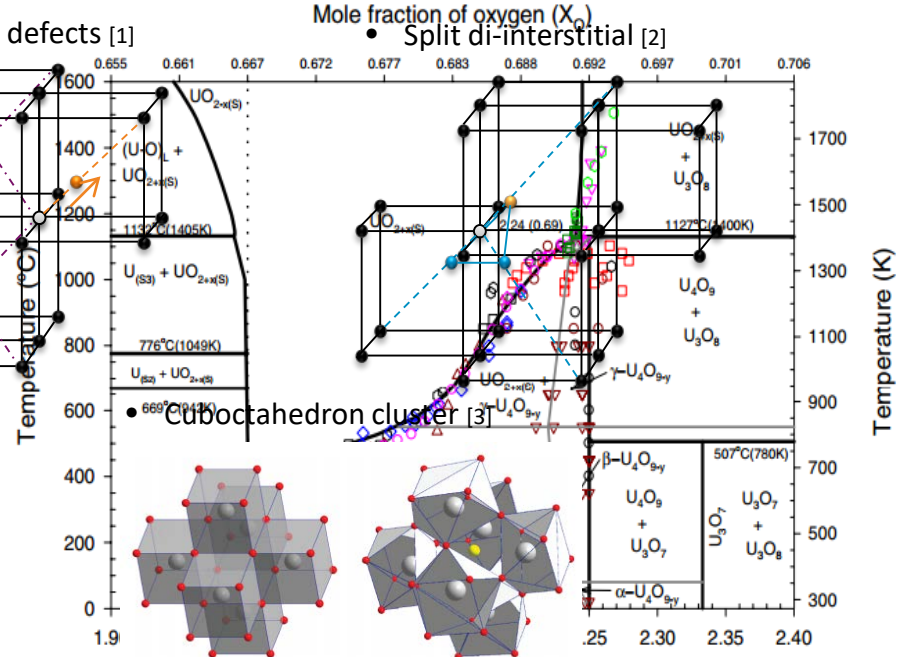
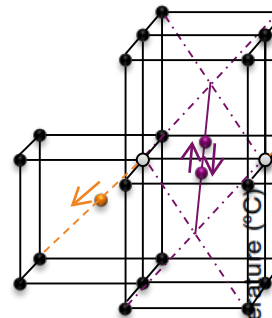
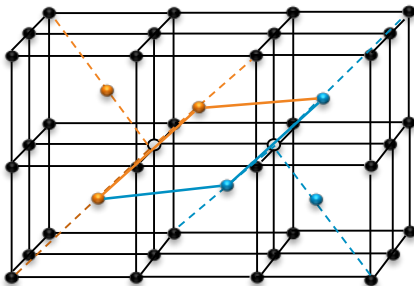
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- UO_{2+x} ($0 < x < 0.25$): experience a transformation from two-phase ($UO_{2+x} + U_4O_9$) to a homogeneous single phase as T increases;
- Oxygen defects (cluster) in this study from previous experiments and DFT calculations
 - Isolated interstitial
 - Willis 2:2:2 defects [1]
 - Split di-interstitial [2]
 - Cubooctahedron cluster [3]



• Split-quad interstitial [2]

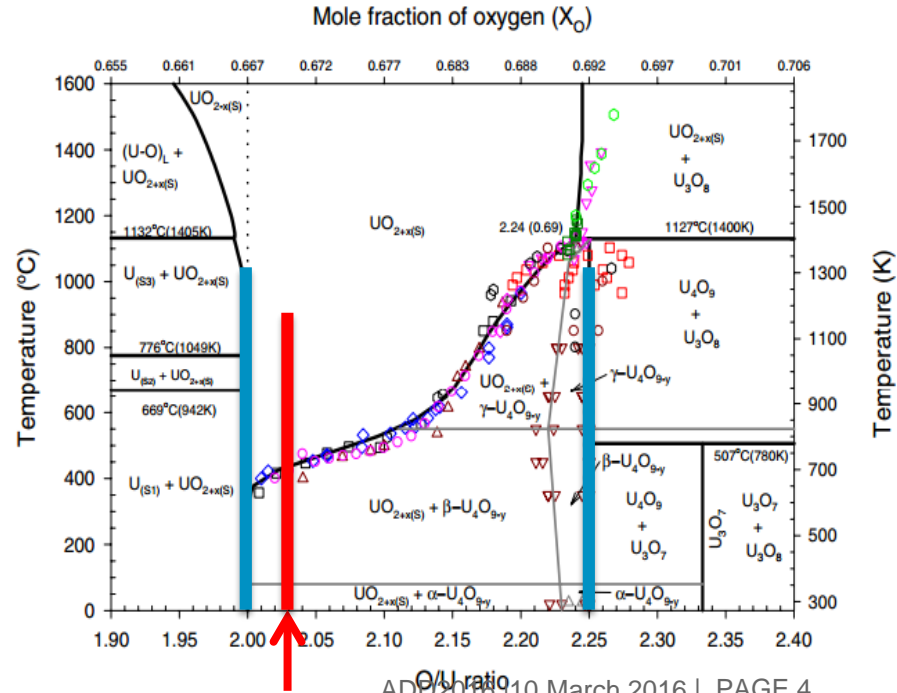


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➤ Objectives

- Neutron diffraction: UO_2 [1] and U_4O_9 [2]
 - The neutron diffusion length for O is half that for U → more accurate determination of anion sublattice (comp. to X-ray Diff.)
 - Large penetration depth
- Followed properties measurement experiment, we aim to identify the type of defect (cluster) in UO_{2+x} with small x.



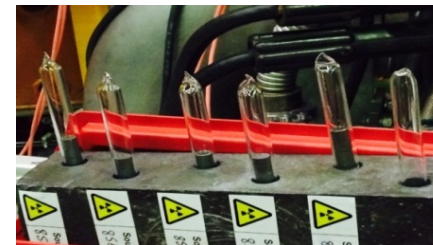
[1]Ruello, P., et al., 2005, *J. Phys. Chem.* 66; [2]Desgranges, L., et al., 2011, *Inorg. Chem.*, 50(13)

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➤ Experiments at ILL D4c diffractometer

- Samples: sintered UO_2 and $\text{UO}_{2.04}$ pellets
- Temperature range: 12°C (285 K) – 1000°C (1273 K)
- $S(Q)$ and Fourier transform $\rightarrow G(r)$
- Wavelength: $\lambda=0,4980\text{\AA}$ \rightarrow small λ for larger Q range and a higher resolution of the real space diffraction data ($d = 2\pi\sin\theta/\lambda$).



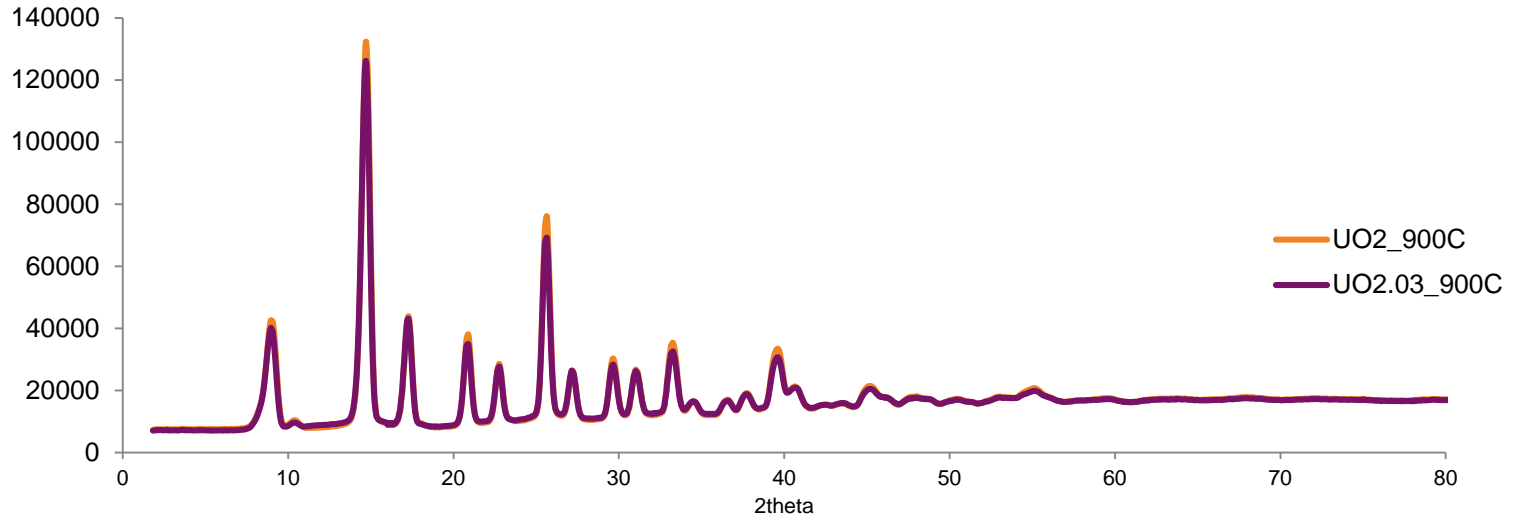
➤ Diffraction pattern analysis: Rietveld and Pair Distribution Function methods

	Rietveld Analysis (by JANA)	Pair Distribution Function Analysis (by PDFGui)
Principle	Non-linear mean square algorithm (<u>reciprocal - space data</u>) \rightarrow average structure	Pair distribution function (<u>real-space</u>) \rightarrow local ordering
Parameters for refinement on the peaks of the diffraction patterns	U, V, W : Peak shape calculation H/L, S/L : Peak symmetry Shift : Peak position Atom thermal mode and site occupancies	Delta 1, 2 : Peak width calculation Qdamp and Qbroad : Peak damping and broadening (fixed) Model size/Space group
Outcomes	Lattice parameters, atom displacement factors, atom positions, model reliabilities	

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➤ Diffraction patterns $S(Q)$ in reciprocal space

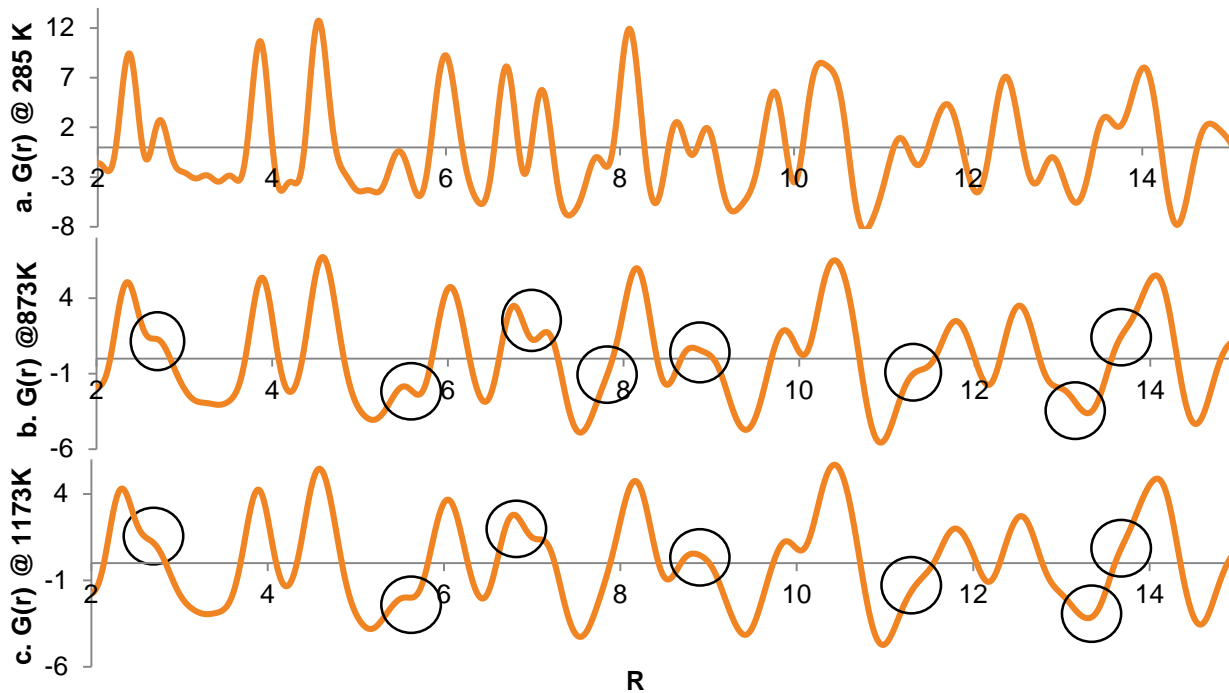


- The major difference in $S(Q)$ of UO₂ and UO_{2+x} at low temperature (before phase transition) lies in the third peak relative to the U₄O₉ structure in two-phase stage. Such peak disappears when sample is heated and transformed to the single-phase.
- → To identify the defects leading to the small change in average structure

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➤ Pair distribution function $G(r)$ in real space – UO_2



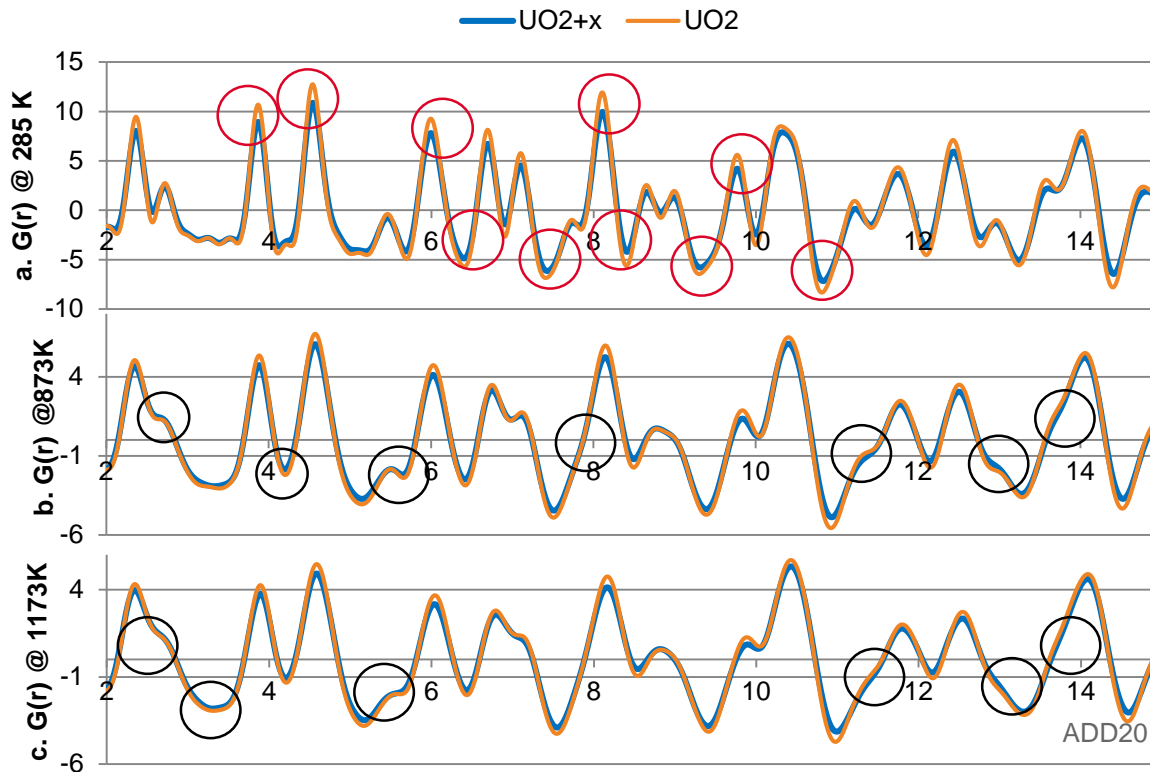
Temperature effect

- Peak (width) broadening
- Peaks merging together -> becomes shoulders
- Peak amplitude drops -> the integral of the peak equals to No. of atoms (i.e. const.)

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➤ Pair distribution function $G(r)$ in real space – UO_2 and UO_{2+x}



- Temperature effects on UO_2 PDF data can also be observed on UO_{2+x} (black circles)
- Decreasing amplitude of peaks -> oxidation effect (red circles)
- The temperature effect overwrites the oxidation contribution to the PDF data.
- → To study the evolution of defects (cluster?) upon temperature

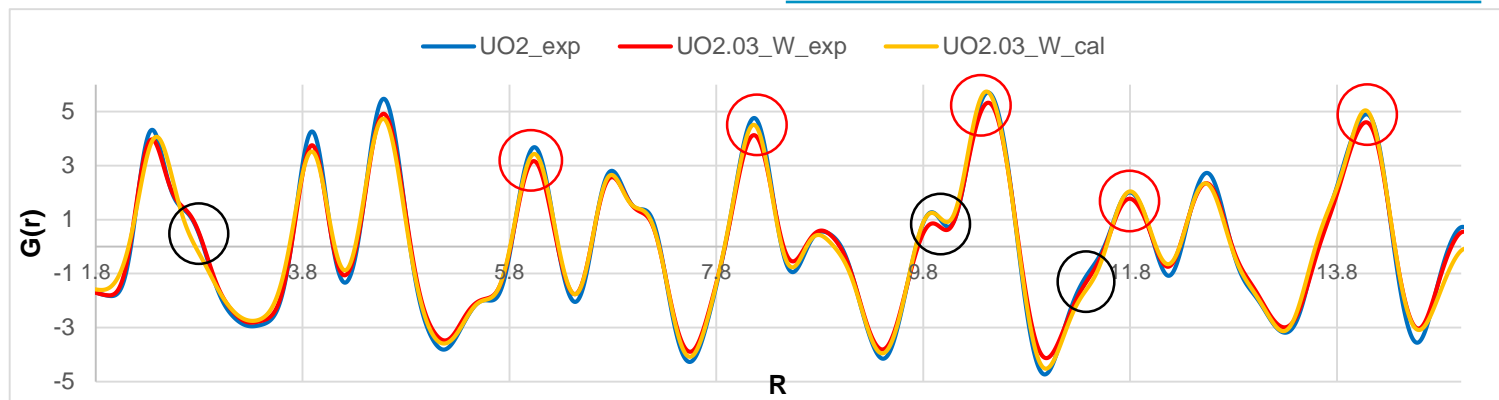
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➤ Local structure analysis with PDFgui – @ 900°C single phase

- Defect model: 1) Willis' 2:2:2 defects I_2^W
 - Model of UO_8 lattice cell ($Fm\bar{3}m$)
 - Site occupancies control → stoichiometry of sample: 2,04
- I_2^W : Rwp = 11.9%;
 $v=1,21(5)\text{Å}$, $w=1,17(1)\text{Å}$

Atom	Coordinates	Composition
Uranium	0,0,0	1.00
Lattice Oxygen O	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	1.96
Interstitial O' <110>	$\frac{1}{2}, \frac{1}{2} + v, \frac{1}{2} + v$	0.04
Interstitial O'' <111>	$\frac{1}{2} + w, \frac{1}{2} + w, \frac{1}{2} + w$	0.04



- PDFgui simulation has reproduced much features related to temperature effect.
- The oxidation effect it does not reproduce belongs to peaks of U-O and O-O pairs at that distance at high temperature.

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➤ Local structure analysis with PDFgui – @ 900°C, with U_4O_8 models

• Defects models:

Isolated interstitials I_1

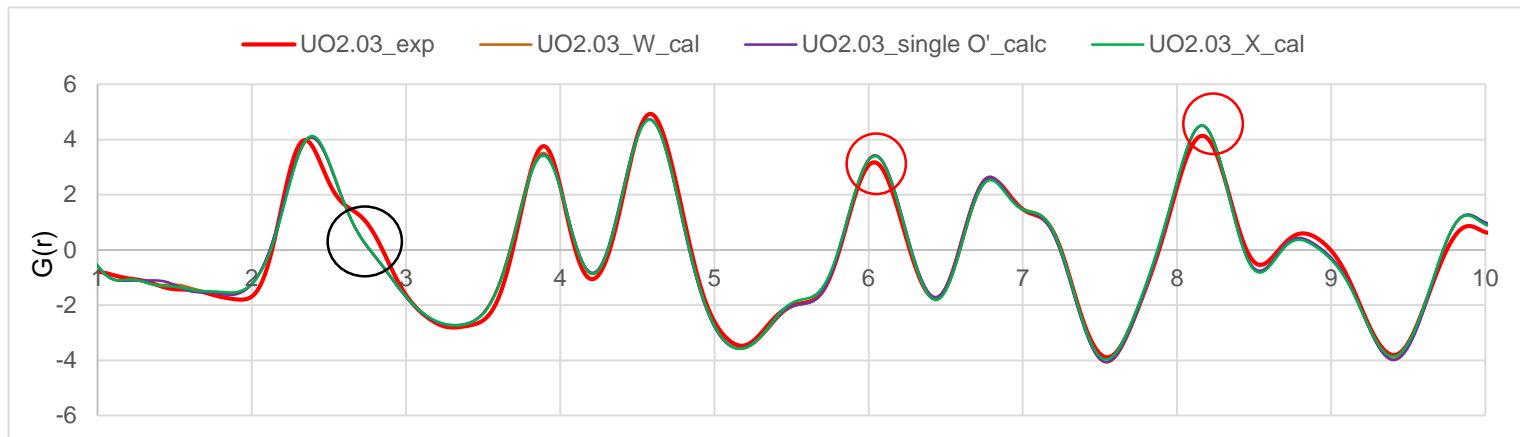
Willis' 2:2:2 defects I_2^W

Split di-interstitial I_2^X

Rwp= 12,16% Composition: 1.96/0.08

11,98% 1,96/0,04/0,04

12,22% 1.94/0.33/0.33/0.33



- Three defect models all have reproduced much features related to both the oxidation and temperature effect, and failed to interpret the same U-O and O-O bonds.

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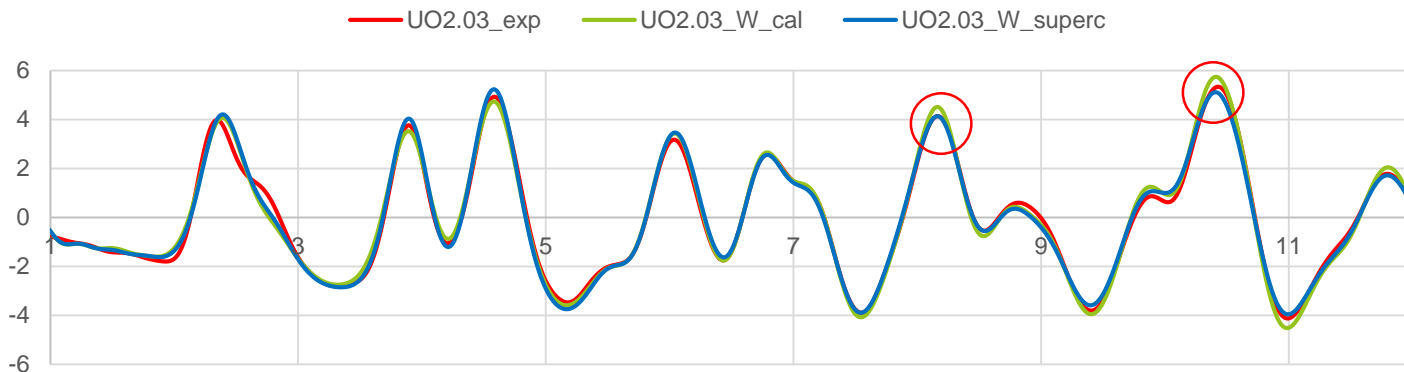
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➤ Local structure analysis with PDFgui – @ 900°C, with U32O64, U72O144 and U108O216 models

- Modelling the non-correlated defects, stoichiometry retained at 2.03 to 2.04.

- Defect models ($Fm\bar{3}m$ remains):

Isolated interstitials I_1	Rwp= 13.6%
Willis' 2:2:2 defects I_2^W	14.5%



- Supercell model actually can better interpret some U-O and O-O pairs at a longer range than small-size model of same oxygen defects.
- Current task: applying defect model with lower symmetry: P222 or P1

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➤ Rietveld analysis– @ 900°C single phase, average structure

- Defects models: isolated interstitials I_1 Willis' 2:2:2 defects I_2^W

- Refinement results:

Stoichiometry of sample: 2,03 - 2,04.

a. I_1 : Rwp = 2,61%

b. I_2^W : Rwp = 2,59%;

$v=0,6(1)\text{Å}$, $w=1,3(1)\text{Å}$

- Willis defect: comparison to our PDF and literature

Temperature (K)	1173K Rietveld	1173K PDF	973K, $UO_{2.11}$ [1]	1200K, $UO_{2.06}$ [2]
O/O'/O''	1.96/0.04/0.04	1.96/0.04/0.04	1.88/0.14/0.1 2	1.95/0.05/0.06
$v <110>$ (Å)	0.6 (0.1)	1.21 (0.1)	1.1 (0.1)	0.7 (0.2)
$w <111>$ (Å)	1.3 (0.1)	1.17 (0.1)	1.3 (0.1)	0.9 (0.2)

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- Oxidation effect on real-space diffraction patterns:
 - For UO_{2+x} with small deviation-from-stoichiometry: oxidation contribution is not as significant as the temperature.
- PDF refinement on $\text{UO}_{2.03}$ diffraction data at high temperature single phase:
 - Willis 2:2:2 defect structure model is more applicable for our UO_{2+x} with smaller deviation-from-stoichiometry in small-size model.
 - Increasing the PDF defect model size may improve the refinement.
 - The PDFgui refinement results are consistent with the Rietveld average structure analysis and are agreed with the literature as well.
- Prospects:
 - Test other defect models with PDFgui (*e.g. cuboctahedron cluster and split quad-interstitials*)
 - *G(r) based on DFT calculations*
 - Next neutron diffraction experiments:
 - UO_{2+x} with higher x ($x \sim 0.1$)
 - dopants

Thank you for listening!

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