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## Neutron diffraction experiment and data analysis of $\text{UO}_2 + x$ sample

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# NEUTRON DIFFRACTION EXPERIMENT AND DATA ANALYSIS OF $\text{UO}_{2+x}$ SAMPLE

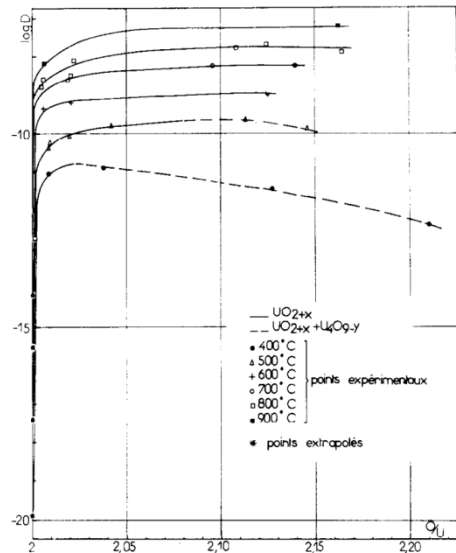
**Y. MA, P. Garcia, L. Desgranges, G. Baldinozzi,  
H. Fischer, D. Simeone, J. Lechelle**

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## ➤ Background and motivations

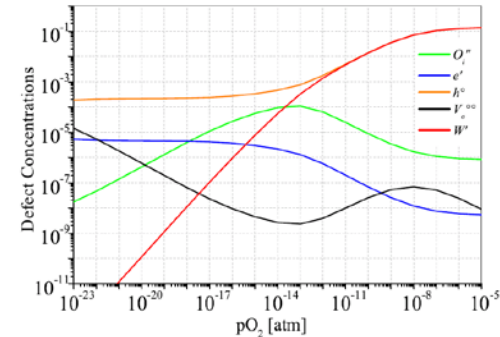
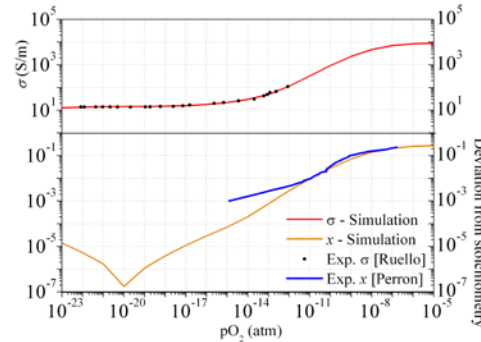
- Uranium dioxide – the major fuel materials → Improve the capacity to understand fuel properties
- The periodic structure of UO<sub>2</sub> crystal is always disturbed by different types of defects (associates and clusters), which determine essential engineering properties: ion diffusivity D<sub>o</sub>, electrical conductivity σ and creep.



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

- Point defects: e.g. PD model for  $\sigma$  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

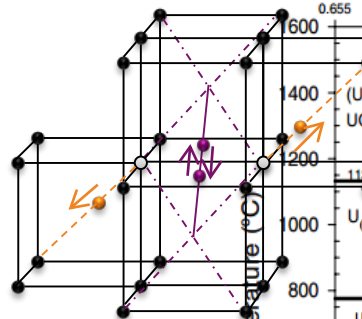
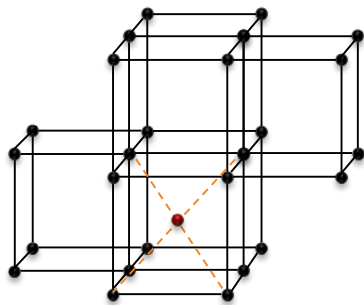
# OXYGEN DEFECTS (CLUSTER)

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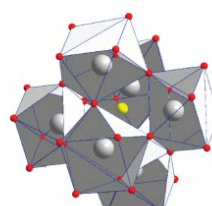
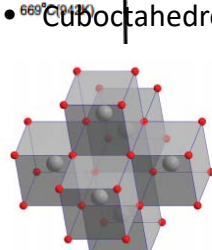
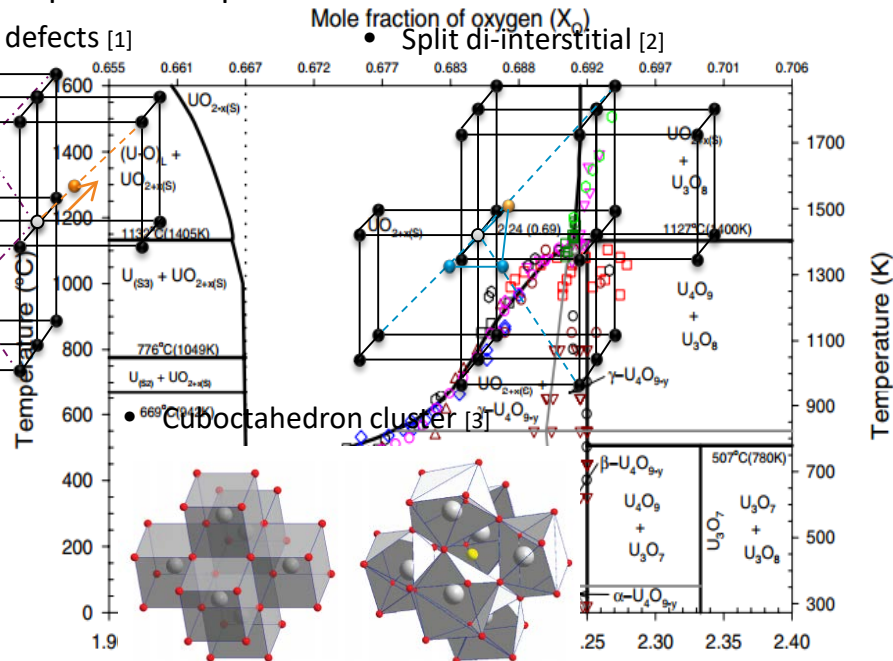
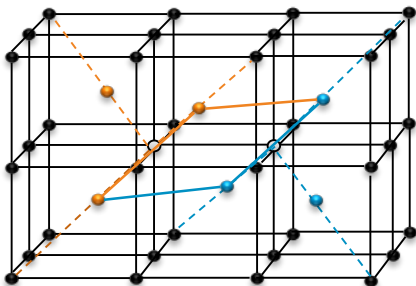
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- $UO_{2+x}$  ( $0 < x < 0.25$ ): experience a transformation from two-phase ( $UO_{2+x} + U_4O_9$ ) to a homogeneous single phase as T increases;

- Oxygen defects (cluster) in this study from previous experiments and DFT calculations
- Isolated interstitial
- Willis 2:2:2 defects [1]
- Split di-interstitial [2]



- Split-quad interstitial [2]

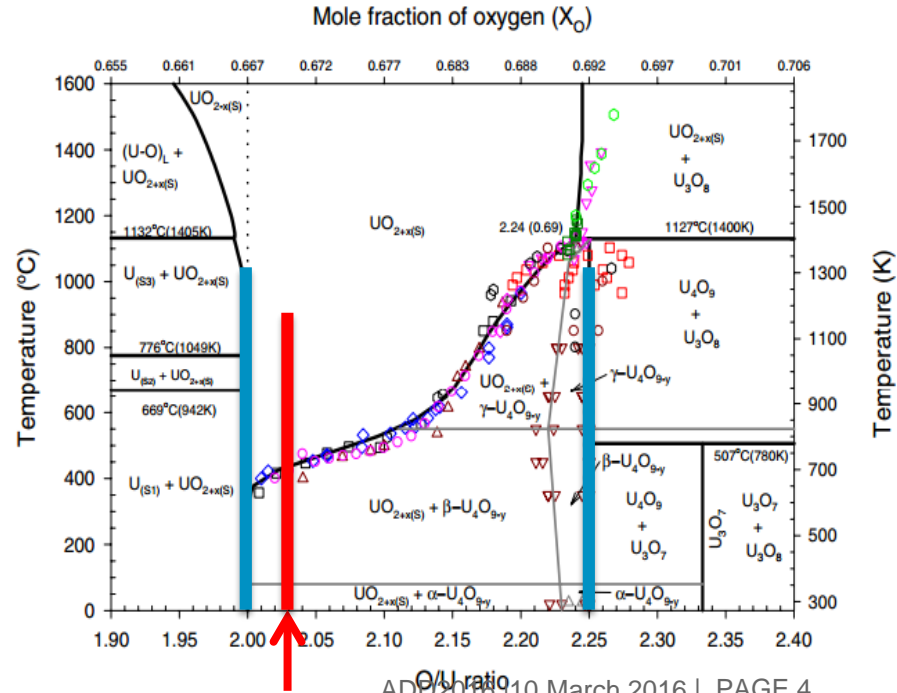


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## ➤ Objectives

- Neutron diffraction:  $\text{UO}_2$  [1] and  $\text{U}_4\text{O}_9$  [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  $\text{UO}_{2+x}$  with small x.



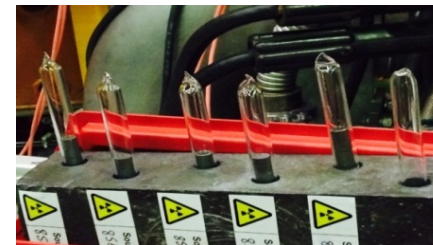
[1]Ruello, P., et al., 2005, *J. Phys. Chem.* 66; [2]Desgranges, L., et al., 2011, *Inorg. Chem.*, 50(13)

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### ➤ Experiments at ILL D4c diffractometer

- Samples: sintered  $\text{UO}_2$  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  $\lambda$  for larger  $Q$  range and a higher resolution of the real space diffraction data ( $d = 2\pi\sin\theta/\lambda$ ).



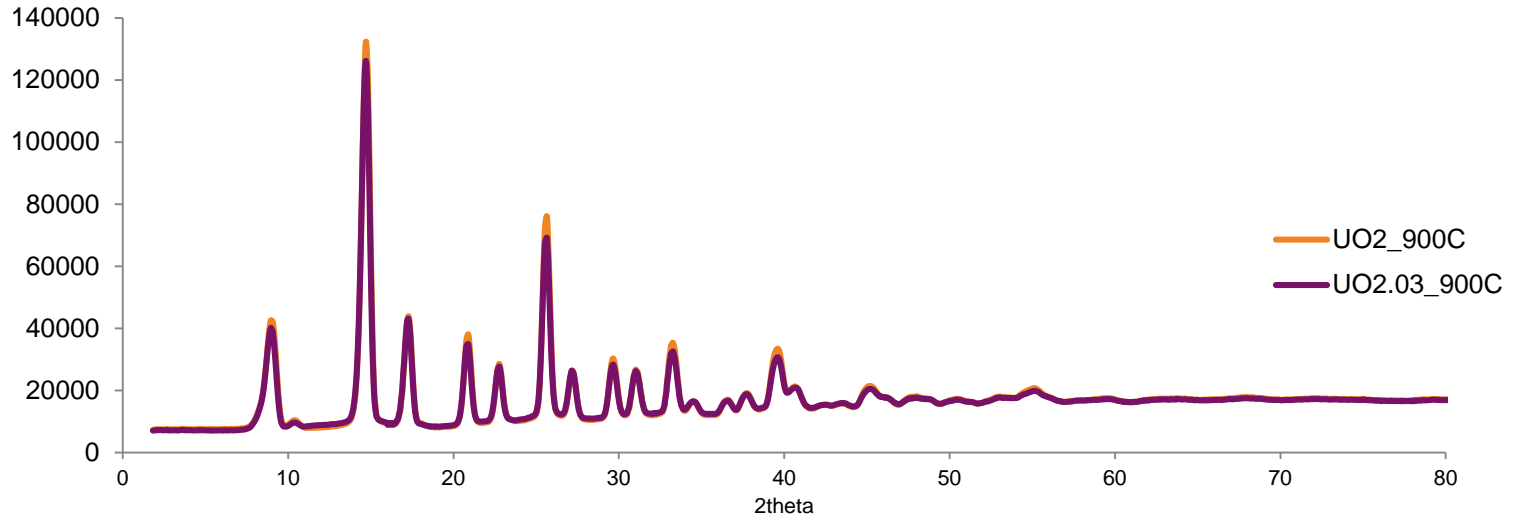
### ➤ Diffraction pattern analysis: Rietveld and Pair Distribution Function methods

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

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

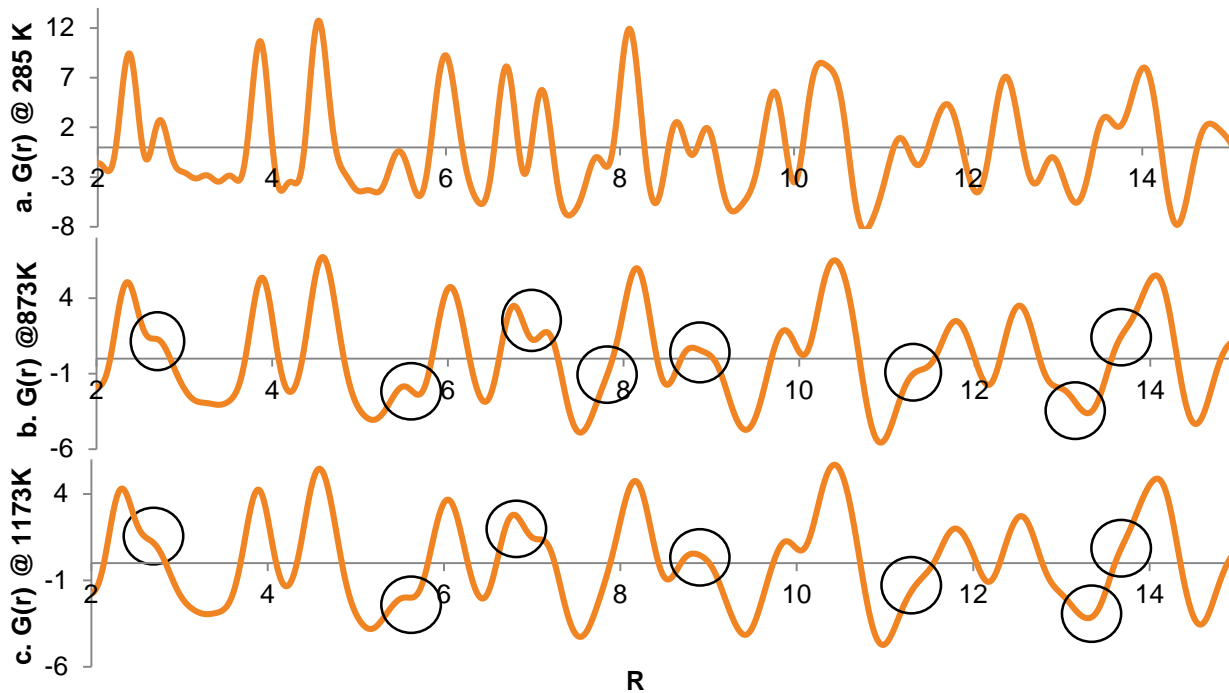


- The major difference in  $S(Q)$  of  $UO_2$  and  $UO_{2+x}$  at low temperature (before phase transition) lies in the third peak relative to the  $U_4O_9$  structure in two-phase stage. Such peak disappears when sample is heated and transformed to the single-phase.
- → To identify the defects leading to the small change in average structure

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



### Temperature effect

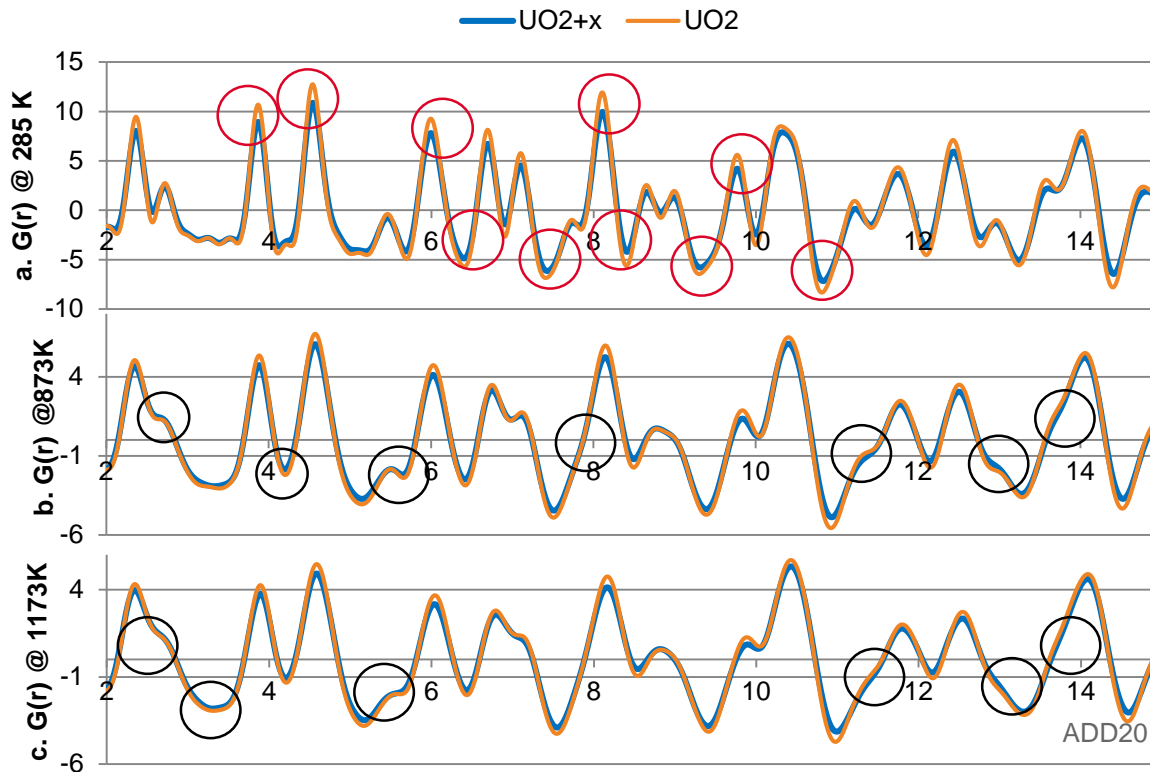
- Peak (width) broadening
- Peaks merging together -> becomes shoulders
- Peak amplitude drops -> the integral of the peak equals to No. of atoms (i.e. const.)



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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

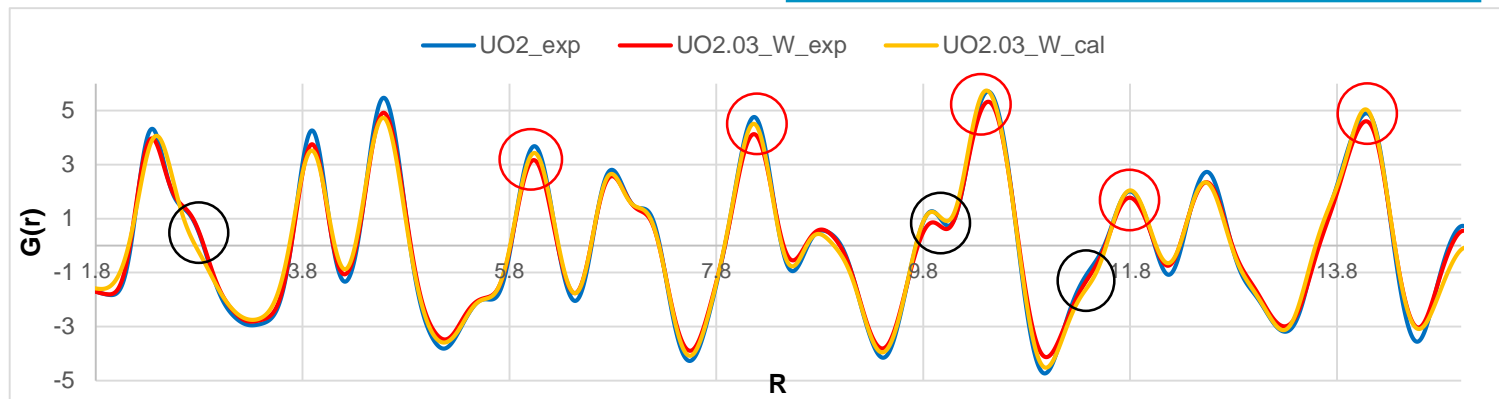
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## ➤ Local structure analysis with PDFgui – @ 900°C single phase

- 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  $I_1$

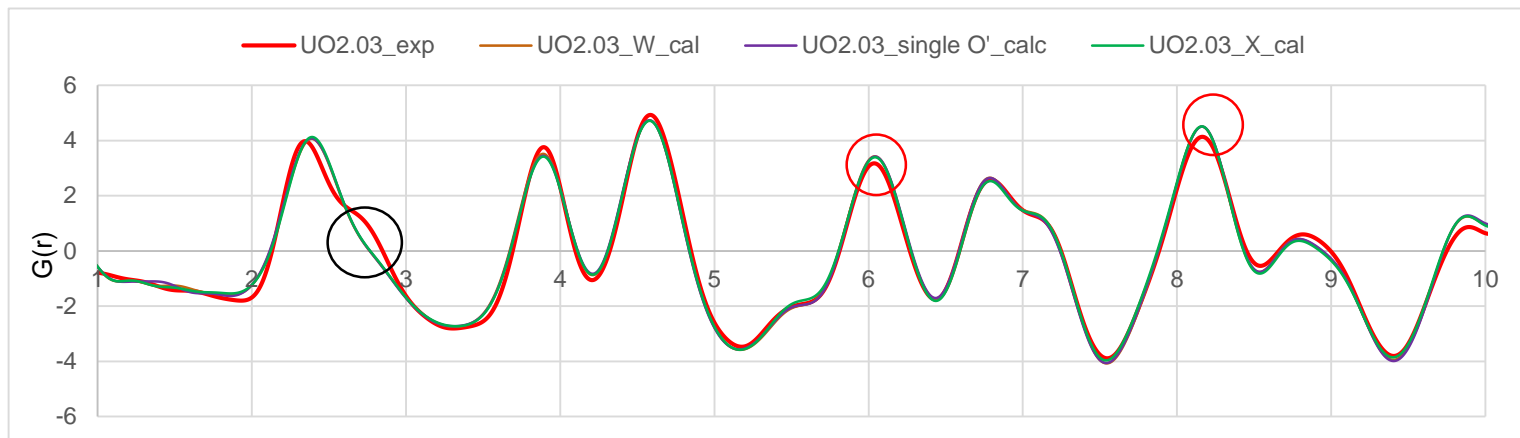
Willis' 2:2:2 defects  $I_2^W$

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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## ➤ 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.

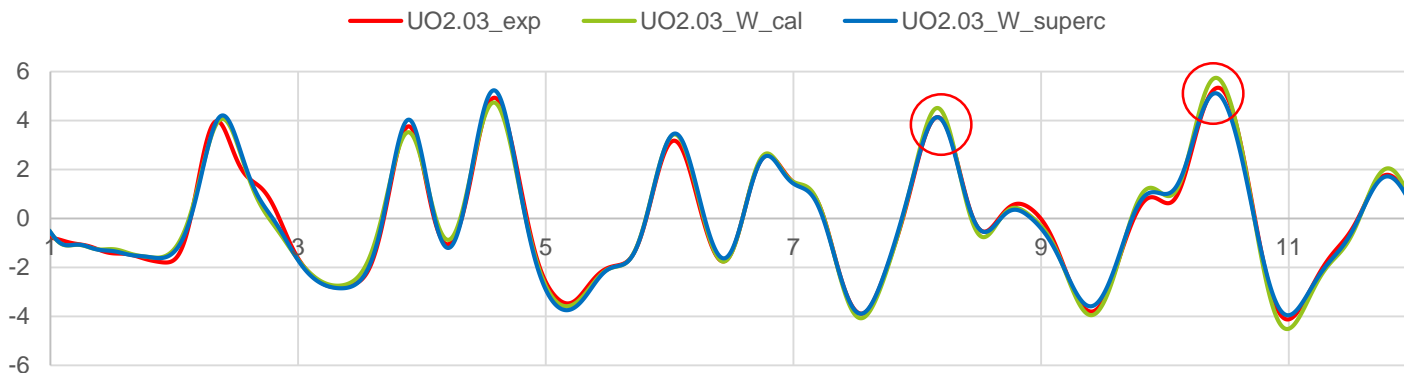
- Defect models ( $Fm\bar{3}m$  remains):

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  $\text{UO}_{2+x}$  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  $\text{UO}_{2+x}$  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:
    - $\text{UO}_{2+x}$  with higher x ( $x \sim 0.1$ )
    - dopants

# Thank you for listening!

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