

# Neutron diffraction experiment and data analysis of $UO_2 + x$ sample

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#### DE LA RECHERCHE À L'INDUSTRIE

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# NEUTRON DIFFRACTION EXPERIMENT AND DATA ANALYSIS OF UO2+X SAMPLE

<u>Y. MA</u>, P. Garcia, L. Desgranges, G. Baldinozzi, H. Fischer, D. Simeone, J. Lechelle

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### **BACKGROUND AND MOTIVATIONS**

#### Contents

- Background & motivations
- Oxygen defect (clusters)
- Objectives
- Experiments
   & data
   refinement
- Oxidation effect on diffraction pattern
- PDF models
- Comparison to Rietveld analysis
- Conclusion & Prospect

#### Background and motivations

- Uranium dioxide the major fuel materials  $\rightarrow$  Improve the capacity to understand <u>fuel properties</u>
- 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: <u>ion diffusivity Do, electrical conductivity σ and creep.</u>



• Point defects: e.g. PD model for  $\sigma$  and non-stoichiometry x study [2]



→ Understanding the nature and behavior of point defects!

# Ceaden 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 <u>homogeneous</u> single phase as T increases;
- Oxygen defects (cluster) in this study from previous experiments and DFT calculations



emperature

[1]Willis, et al., 1978, Acta Cryst A34; [2]Andersson, et al., 2012, J. Chem. Phys. 136; [3]Desgranges, et al., 2011, Inorg. Chem, 50(13)

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### **EXPERIMENT OBJECTIVES**

0.654

1600

1400 -

0.661

(U-O), +

0.667

UO<sub>2•x(S)</sub>

0.672

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- **Objectives**
- Neutron diffraction: UO<sub>2</sub> [1]and U<sub>4</sub>O<sub>9</sub> [2] ٠ •The neutron diffusion length for O is half that for  $U \rightarrow$  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<sub>2+x</sub> with small x.



Mole fraction of oxygen  $(X_{0})$ 

0.688

0.697

0.692

0.701

UO<sub>2+x(S)</sub>

0.706

1700

1500

1300

1100

900

700

500

300

S

emperature

### **EXPERIMENTS AND DATA REFINEMENT**

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- Experiments at ILL D4c diffractometer
  - Samples: sintered UO<sub>2</sub> and UO<sub>2.04</sub> pellets
  - Temperature range: 12°C (285 K) 1000 °C (1273 K)
  - S(Q) and Fourier transform  $\rightarrow$  G(r)
  - Wavelength:  $\lambda = 0,4980 \text{\AA} \rightarrow \text{small } \lambda$  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 -</u> space data) -> <b>average structure</b>	Pair distribution function ( <u>real</u> -space) -> <b>local ordering</b>
	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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### Ceaden OXIDATION EFFECTS ON DIFFRACTION PATTERNS



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PDF models

Comparison

**Conclusion &** 

to Rietveld

analysis

Prospect

- The major difference in S(Q) of UO<sub>2</sub> and UO<sub>2+x</sub> at low temperature (before phase transition) lies in the third peak relative to the <u>U4O<sub>9</sub> structure</u> in two-phase stage. Such peak disappears when sample is heated and transformed to the single-phase.
  - $\rightarrow$  To identify the defects leading to the small change in average structure

### Ceaden OXIDATION EFFECTS ON DIFFRACTION PATTERNS



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### **OXIDATION EFFECTS ON DIFFRACTION PATTERNS**

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Pair distribution function G(r) in real space – UO<sub>2</sub> and UO<sub>2+x</sub>



- Temperature effects on UO2 PDF data can also be observed on UO2+x (black circles)
- <u>Decreasing amplitude of</u> <u>peaks -> oxidation effect</u> (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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### Ceaden PDF ANALYSIS OF UO2+X

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

•Defect model: 1)Willis'2:2:2 defects I<sub>2</sub><sup>w</sup>
•Model of U4O8 lattice cell (Fm3m)
•Site occupancies control → stoichiometry of sample: 2,04
I<sub>2</sub><sup>w</sup>: Rwp = 11.9%; v=1,21(5)Å, w=1,17(1)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.
- <u>The oxidation effect it does not reproduce belongs to peaks of U-O and O-O pairs at that distance</u> <u>at high temperature.</u>
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### Ceaden PDF ANALYSIS OF UO2+X

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• 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.

## Ceaden PDF ANALYSIS OF UO2+X

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- Supercell model actually can better interpret some U-O and O-O pairs at a longer range than smallsize model of same oxygen defects.
- Current task: applying defect model with lower symmetry: P222 or P1 ADD2016 |10 March 2016 | PAGE 11

## Ceaden RIETVELD ANALYSIS OF UO2+X

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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<sub>2</sub><sup>w</sup>: Rwp = 2,59%; v=0,6(1)Å, w=1,3(1)Å
- Willis defect: comparison to our PDF and literature

Temperature	1173K	1173K	973K,	1200K, UO <sub>2.06</sub>
(K)	Rietveld	PDF	UO <sub>2.11</sub> [1]	[2]
0/0'/0''	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)

[1]Murray & Willis, 1990, J. Sol. Sta. Chem., 84, 52-57; [2] Wang, 2014, Scientific Reports, 4, 4216

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### **CONCLUSION AND PROSPECTS**

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- Oxidation effect on real-space diffraction patterns:
  - For UO<sub>2+x</sub> with small deviation-from-stoichiometry: oxidation contribution is not as significant as the temperature.
- > PDF refinement on UO<sub>2.03</sub> diffraction data at high temperature single phase:
  - Willis 2:2:2 defect structure model is more applicable for our UO<sub>2+x</sub> 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 quadinterstitials)
  - G(r) based on DFT calculations
  - Next neutron diffraction experiments:
    - $UO_{2+x}$  with higher x (x~0.1)
    - dopants

# Thank you for listening!

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