Neutron diffraction experiment and data analysis of UO_2 + x sample

Y. Ma, P. Garcia, L. Desgranges, G. Baldinozzi, H. Fischer, D. Simeone, J. Léchelle

DE LA RECHERCHE À L'INDUSTRIE

cea den

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

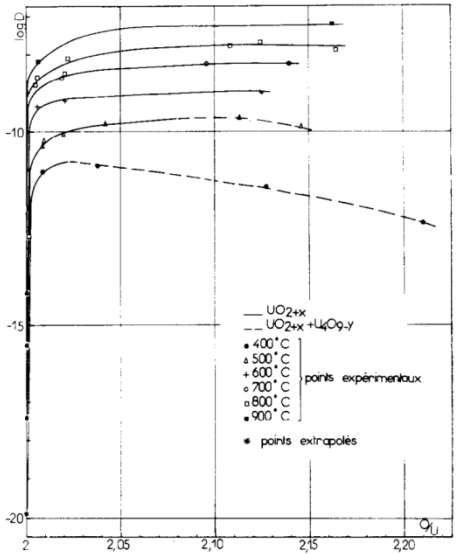
Y. MA, P. Garcia, L. Desgranges, G. Baldinozzi, H. Fischer, D. Simeone, J. Lechelle

BACKGROUND AND MOTIVATIONS

Contents

➢ Background and motivations

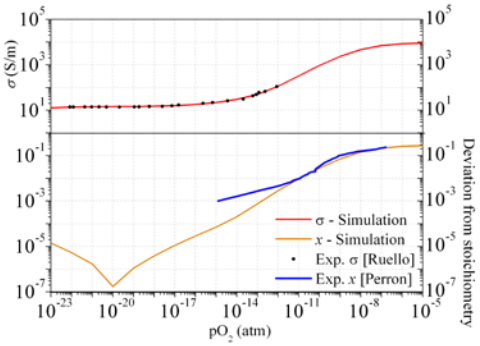
- Uranium dioxide – the major fuel materials → Improve the capacity to understand fuel properties
- The periodic structure of UO_2 crystal is always disturbed by different types of defects (associates and clusters), which determine essential engineering properties: ion diffusivity Do, electrical conductivity σ and creep.

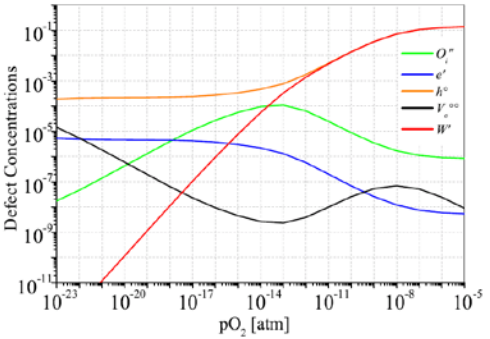


Oxygen self diffusion coeffi. as a func. of x [1]

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

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





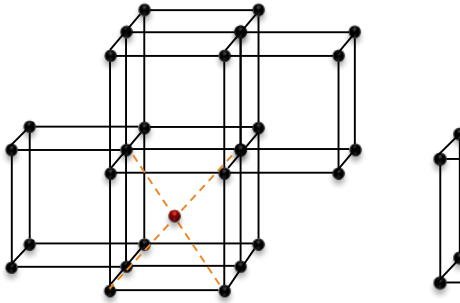
- → Understanding the nature and behavior of point defects!

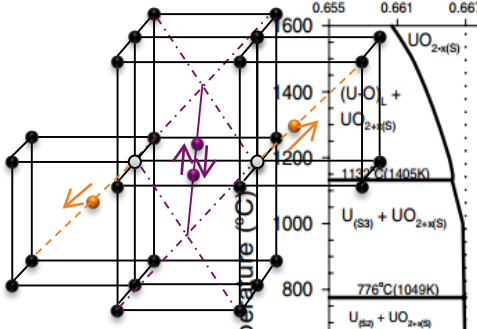
[1]Contamin, *et al.*, 1972, *J. Nucl. Mat.*, 42; [2]Dorado, *et al.*, 2011, *Phys. Rev. B 83*

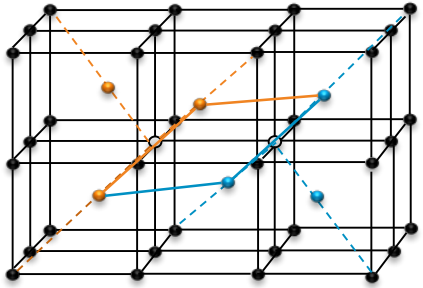
OXYGEN DEFECTS (CLUSTER)

Contents

- 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]
  - Cuboctahedron cluster [3]







[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)

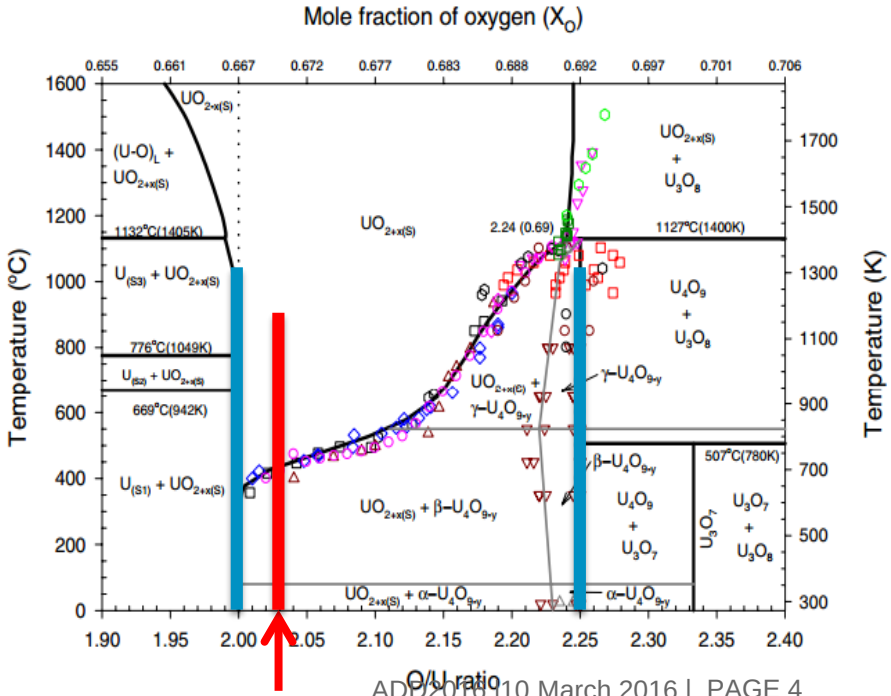
EXPERIMENT OBJECTIVES

Contents

➢ 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.



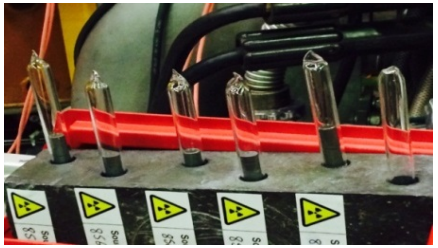
[1]Ruello, P., *et al.*, 2005, *J. Phys. Chem.* 66; [2]Desgranges, L., *et al.*, 2011, *Inorg. Chem*, 50(13)

EXPERIMENTS AND DATA REFINEMENT

Contents

➢ Experiments at ILL D4c diffractometer

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



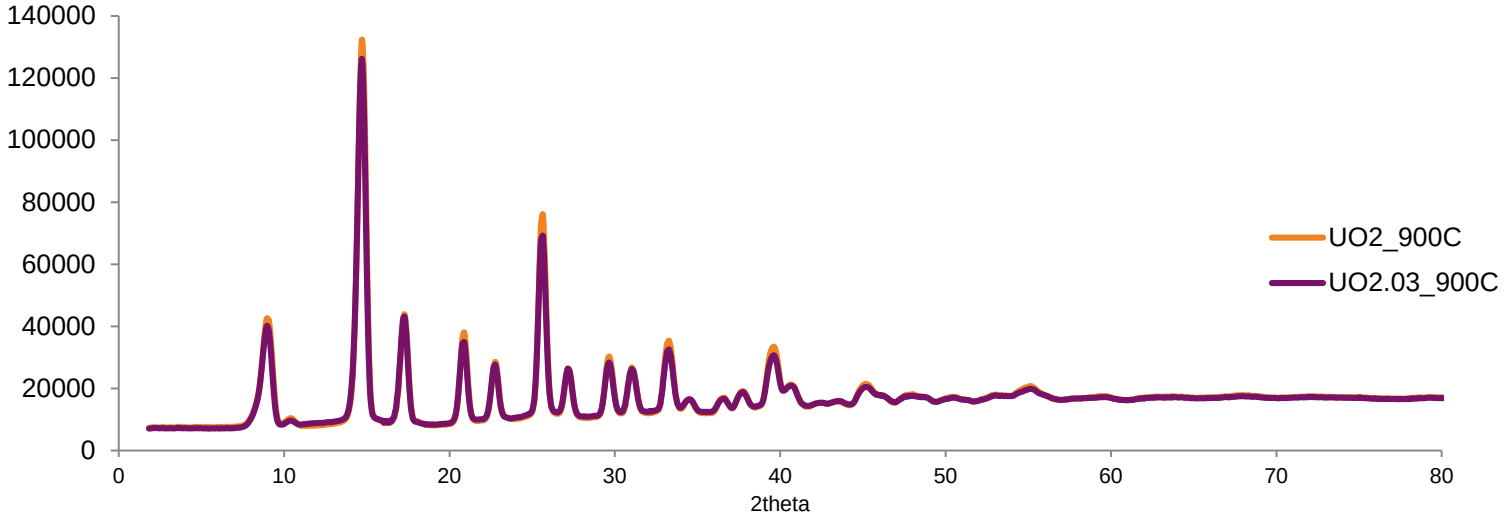
➢ Diffraction pattern analysis: Rietveld and Pair Distribution Function methods

	Rietveld Analysis (by JANA)	Pair Distribution Function Analysis (by PDFGui)
Principle	Non-linear mean square algorithm (reciprocal - space data) -> **average structure**	Pair distribution function (real-space) -> **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	

OXIDATION EFFECTS ON DIFFRACTION PATTERNS

Contents

➢ Diffraction patterns S(Q) in reciprocal space



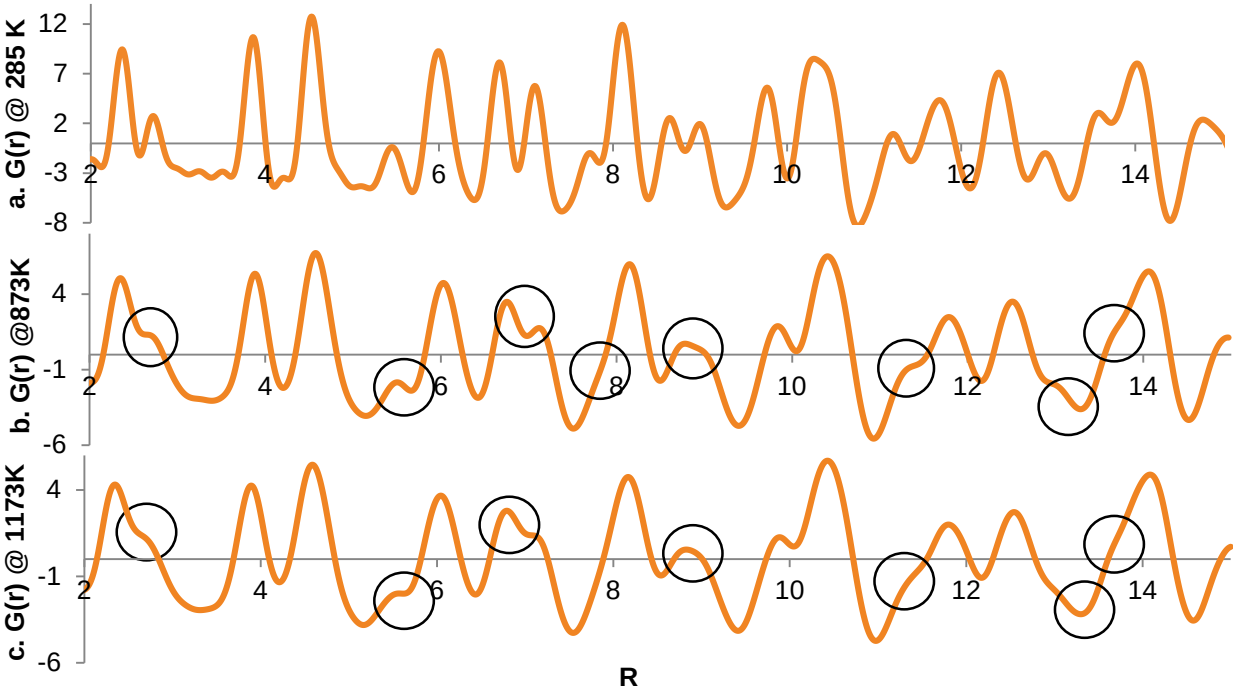
- The major difference in S(Q) of UO_2 and UO_{2+x} at low temperature (before phase transition) lies in the third peak relative to the U_4O_9 structure in two-phase stage. Such peak disappears when sample is heated and transformed to the single-phase.
- → To identify the defects leading to the small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

OXIDATION EFFECTS ON DIFFRACTION PATTERNS

Contents

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

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



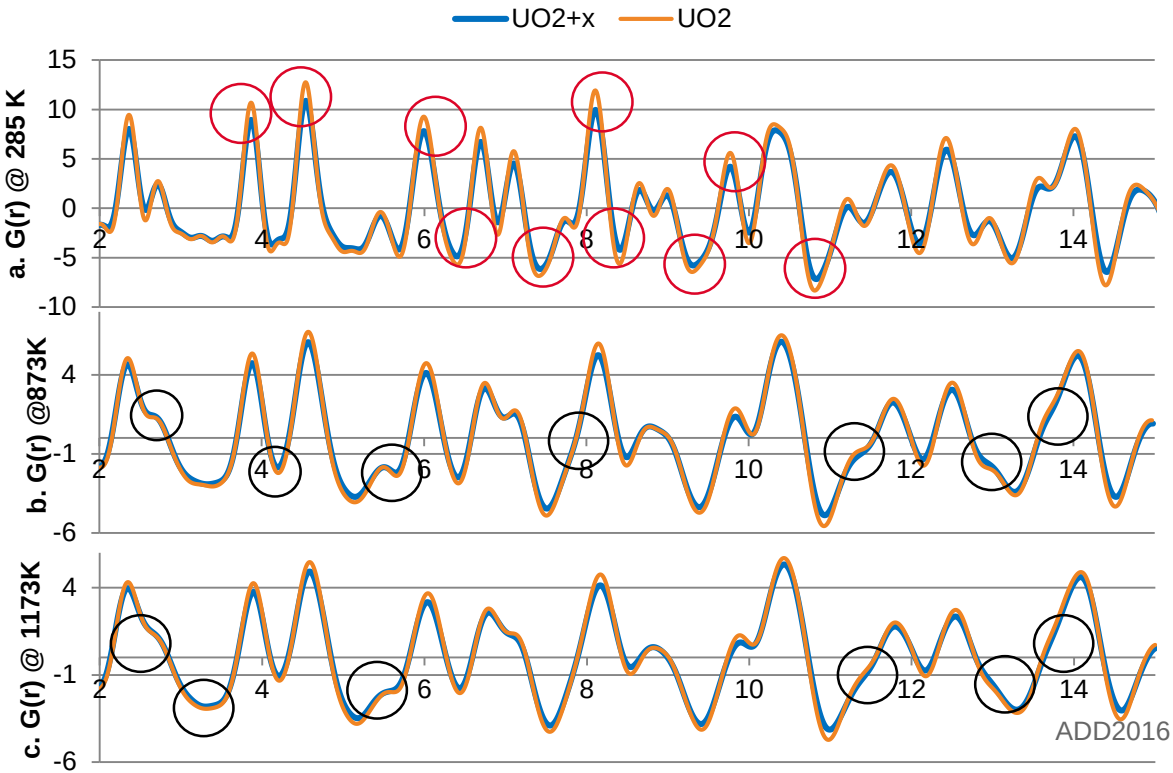
Temperature effect

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

OXIDATION EFFECTS ON DIFFRACTION PATTERNS

Contents

➢ 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

PDF ANALYSIS OF UO_{2+X}

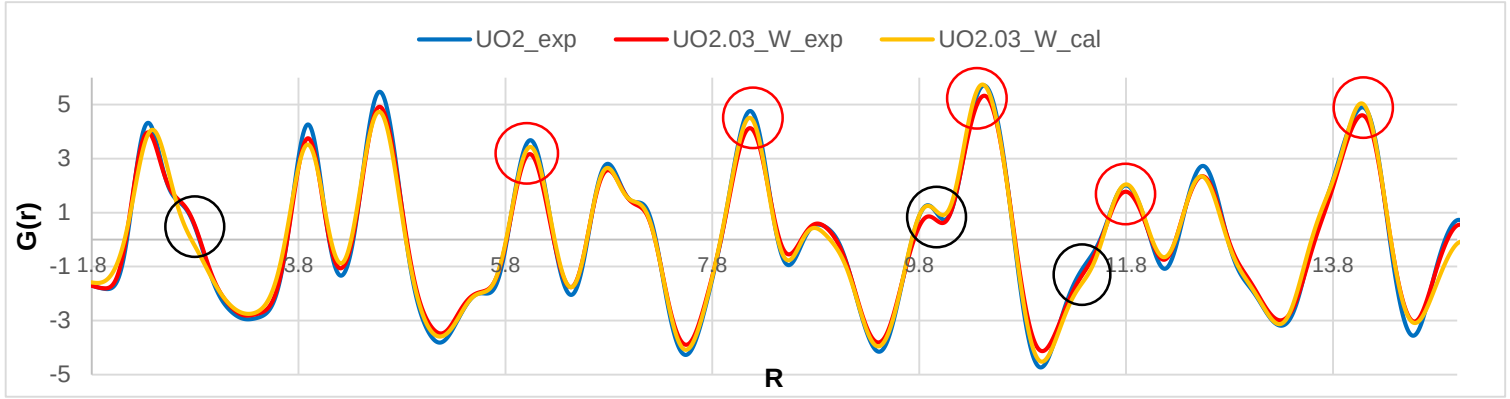
Contents

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

- Defect model: 1)Willis'2:2:2 defects I_2^w
- Model of U4O8 lattice cell ($Fm\bar{3}m$)
- Site occupancies control → stoichiometry of sample: 2,04

I_2^w: 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



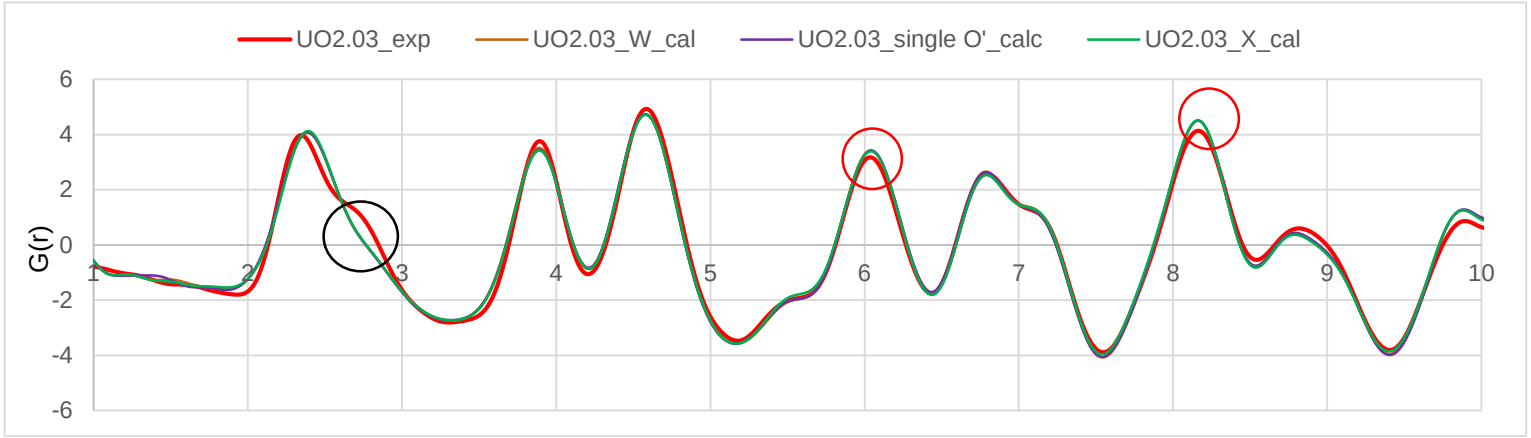
- PDFgui simulation has reproduced much features related to temperature effect.
- <u>The oxidation effect it does not reproduce belongs to peaks of U-O and O-O pairs at that distance at high temperature.</u>

PDF ANALYSIS OF UO_{2+X}

➢ Local structure analysis with PDFgui – @ 900°C, with U4O8 models

•Defects models:

Isolated interstitials I_1	Rwp= 12,16%	Composition: 1.96/0.08
Willis'2:2:2 defects I_2^w	11,98%	1,96/0,04/0,04
Split di-interstitial I_2^X	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.

PDF ANALYSIS OF UO_{2+X}

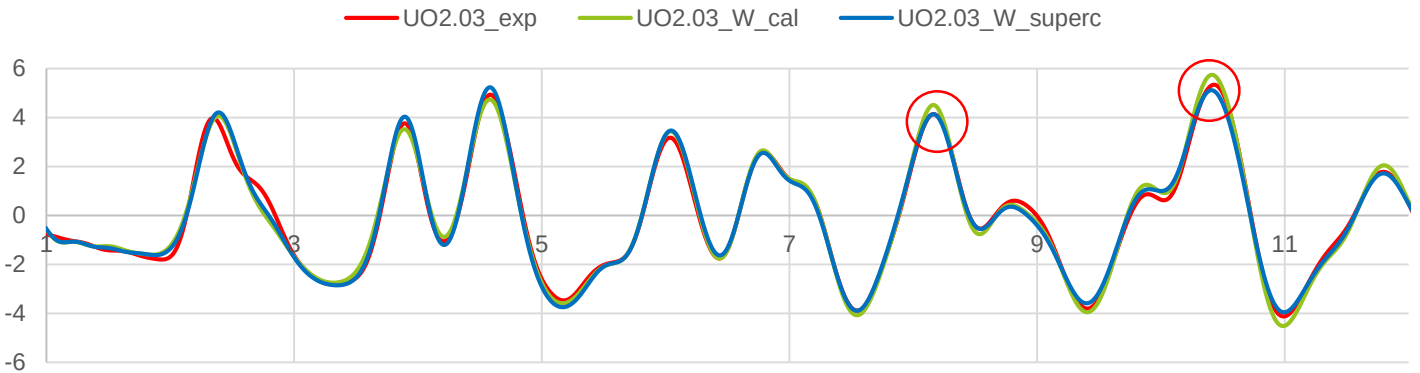
Contents

➢ Local tructure 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

RIETVELD ANALYSIS OF UO_{2+X}

➢ 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)Å, w=1,3(1)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	1.88/0.14/0.12	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

CONCLUSION AND PROSPECTS

Contents

- 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 $UO_{2.03}$ 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~0.1)
    - dopants

Thank you for listening!

Commissariat à l'énergie atomique et aux énergies alternatives
DEC/SFER/LCU
Centre de Cadarache
13108 Saint Paul lez Durance, France