

# HIGH TEMPERATURE NEUTRON DIFFRACTION EXPERIMENTS OF $\text{UO}_2$ AND $\text{UO}_{2+x}$ SAMPLES

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1. **EXPERIMENT BACKGROUND AND MOTIVATIONS**
2. **EXPERIMENT METHODOLOGIES**
3. **RESULTS**
  - 1) **RIETVELD AND PDF ANALYSIS OF  $\text{UO}_2$**
  - 2) **SPLIT ATOM MODEL RELATED TO  $\text{UO}_2$  THERMAL MOTION**
  - 3) **PRELIMINARY ANALYSIS OF  $\text{UO}_{2+x}$  DEFECT CLUSTER STRUCTURE**
4. **CONCLUSIONS AND PROSPECTS**

## ➤ Background and motivations

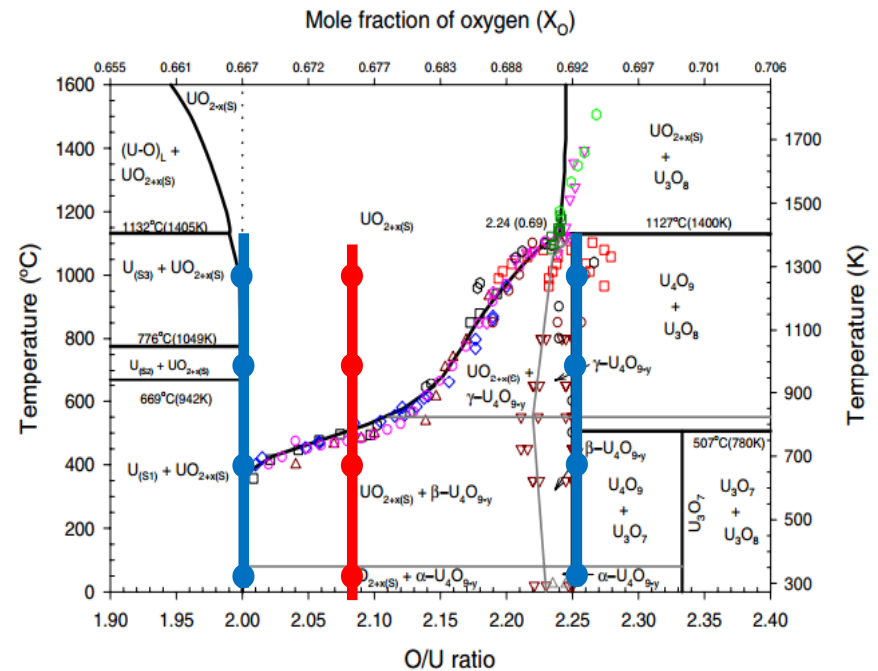
- $\text{UO}_2$  and  $\text{UO}_{2+x}$ : **fuel oxidation** – necessary for the fuel cycle study
- Key synthesis of oxidation: **oxygen interstitial defects** in uranium oxides
- **Defects** (clusters) in uranium oxides:
  - $\text{UO}_{2+x}$ : Willis' 2:2:2 cluster [1]
  - $\text{U}_4\text{O}_9$ : cuboctahedron cluster structure [2]
  - $\text{D}_\text{o}$ : defects start to cluster at small deviation-from-stoichiometry [3]

## • Objectives:

1. Basic research on  $\text{UO}_2$  crystalline structure as a function of temperature
2. Defects (clusters) – change along with phase transition: i.e. @HT the **dissolving of long-range ordering of cuboctahedron** or **Willis' structure** for **large-x** samples ( $\text{UO}_{2.12}$ )?

## ➤ Why neutron diffraction?

- **Relatively more accurate determination of O positions** (comp. to readily available X-ray Diff.) [4]

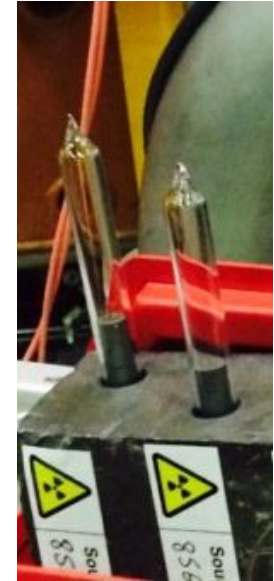


[1] Willis, B.T.M., 1978, *Acta. Cryst.*, A34; [2] Bevan, D.J.M., 1986, *J. Solid Sta. Chem.* 61;

[3] Garcia, P., 2015, MRS Conference; [4] Hutchings, M.T., 1987, *J. Chem. Soc.* 83;

## ➤ Experiment details

- $\text{UO}_{2+x}$ ,  $x \approx 0.03$ , **sintered** samples, 27 1mm-disks prepared in CEA Cadarache with  $\text{H}_2/\text{H}_2\text{O}$  equilibrium of an oxidizing environment
- D4c diffractometer at the Institute Laue-Langevin (ILL), Grenoble, France
- Furnace temperature range: ambient to  $1000^\circ\text{C}$ ; Goniometer range:  $0 < 2\theta < 138^\circ$
- New measurements on  $\text{UO}_2$ ,  $\text{UO}_{2+x}$
- Preliminary data process: diffraction pattern collection, background subtraction, Placzek correction, Fourier transform to real space data



## ➤ Diffraction data refinement plan

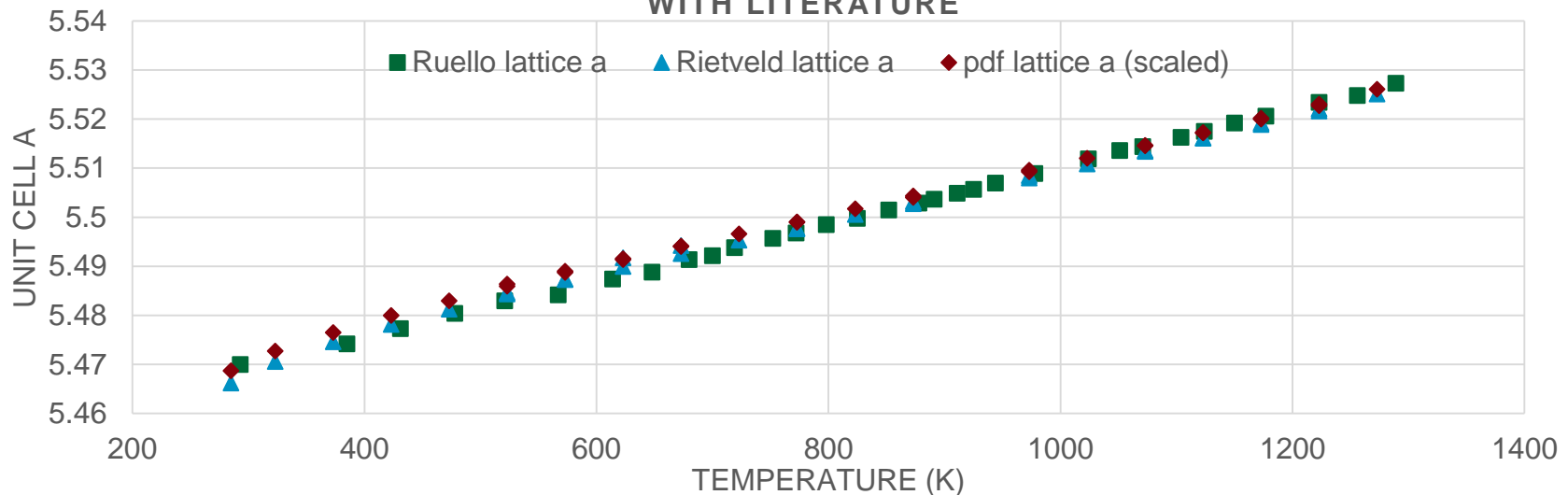
|                                    | Rietveld method<br>(JANA2006) [1]  | Pair Distribution Function<br>(PDFGui) [2]  |
|------------------------------------|--|---|
| Principle                          | Non-linear mean square algorithm<br>(atomic average structure from<br>diffraction peaks in reciprocal space) | Pair distribution function<br>(local and average structure<br>refinement in real space [2]) |
| Nature of information<br>retrieved | Unit cell parameter, O&U positions and Temperature factor / Atomic<br>Displacement Parameter                 |   |

➤ Rietveld refinement results of  $\text{UO}_2$  - Structural parameters

1. Structure information

- Unit cell parameter
- Temperature factor (atomic displacement factor)

UO<sub>2</sub> LATTICE PARAMETER BY RIETVELD AND PDF METHOD COMPARED WITH LITERATURE



- Same lattice para. Obtained from both Rietveld and PDF
- A linear thermal expansion between RT and 1000°C – consistent with previous result<sup>[1][2]</sup>.

➤ Rietveld refinement results of  $\text{UO}_2$  - Thermal motion (Debye-Waller factors)

Structural factor [1]:

$$V(x, y, z) = V_0 + \frac{\alpha_0}{2} (x^2 + y^2 + z^2) + \beta_0 xyz$$

← harmonic
← anharmonic

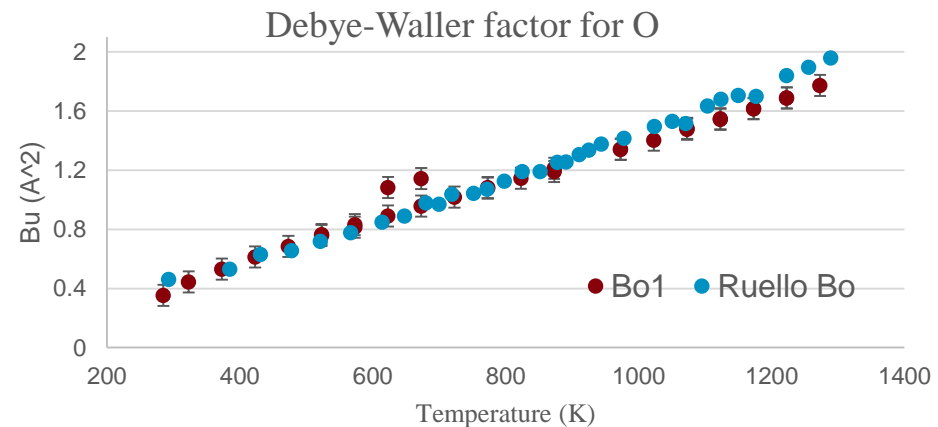
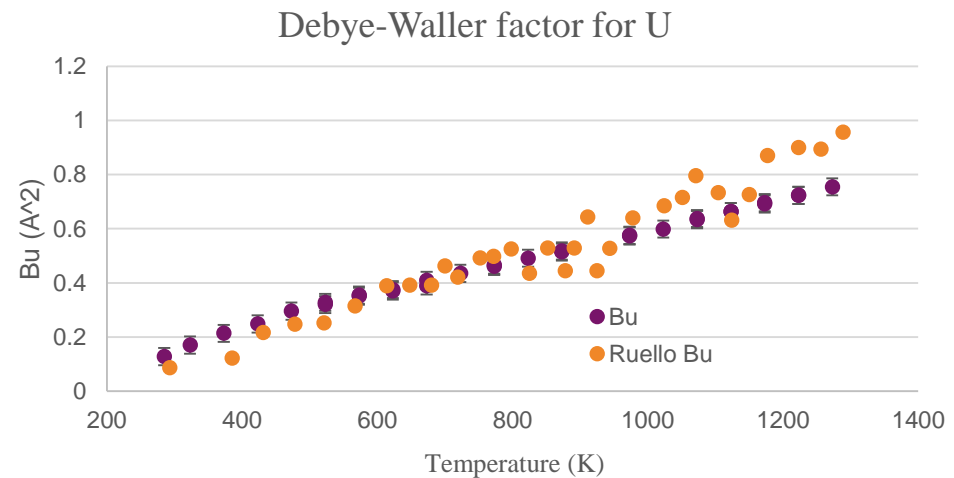
- An isotropic harmonic potential characterized by the harmonic constant  $\alpha$  to predict atom harmonic thermal motion:

$$B_0 = \frac{8\pi^2 kT}{\alpha_0} = \frac{8\pi^2}{3} \langle u^2 \rangle$$

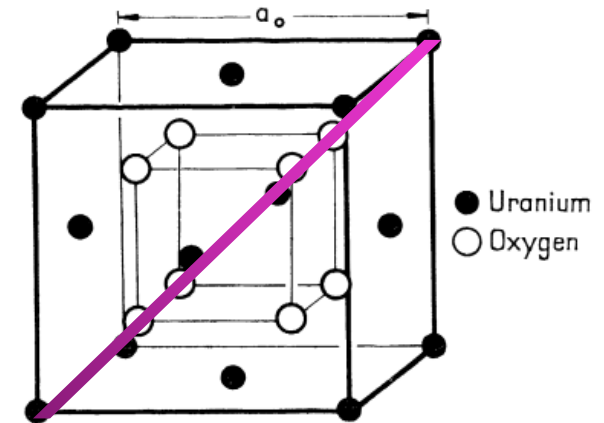
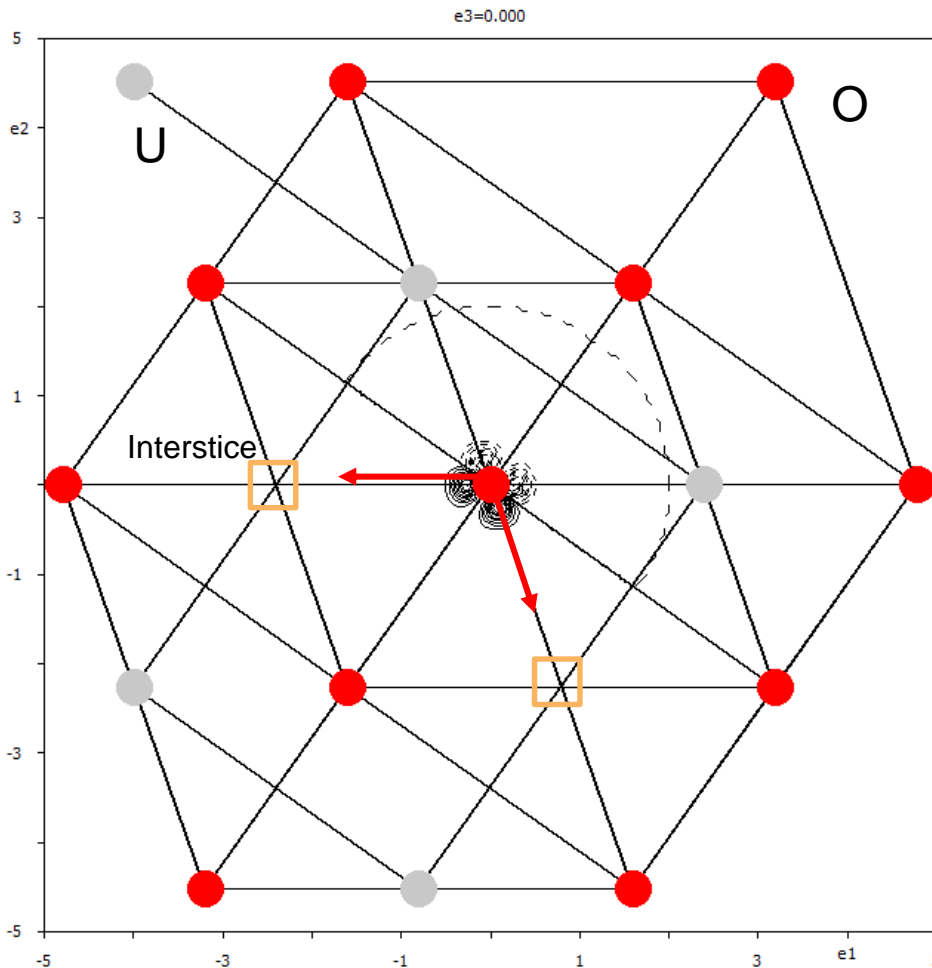
- Uranium: linear temperature-dependent Bu – consistent with previous research [2].
- Oxygen atom: involve the consideration of an **anharmonic** component for the odd reflections

$$c_{123}^0 = \frac{8\pi^3 k_B^2 T^2}{a_0^3 \alpha_0^3} \beta_0$$

- Atomic displacement factors with **PDF** method – unavailable now with the PDFgui

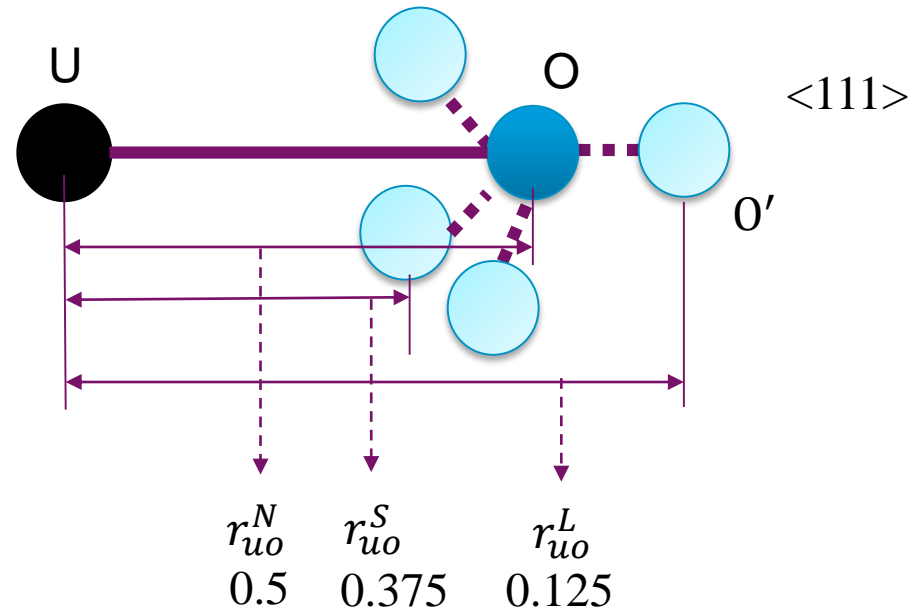
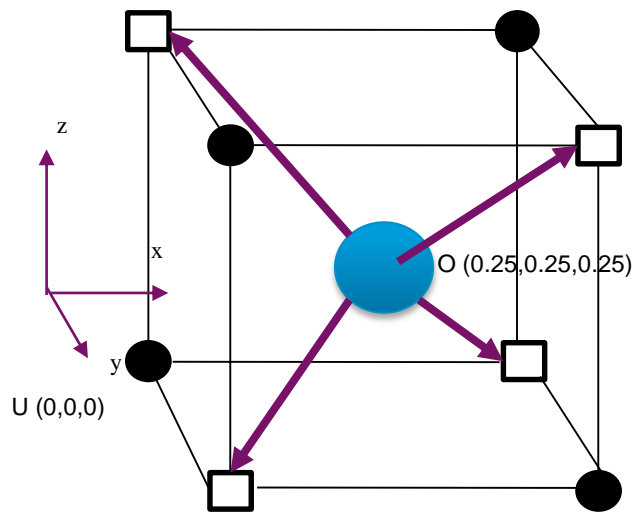


- Rietveld refinement results of UO<sub>2</sub> - Oxygen Probability Density Function map of 3<sup>rd</sup>-order anharmonic thermal motion of (110) plane



- Oxygen is expected to move to the **interstice** site in **<111>** direction
- To understand the oxygen thermal behaviour by modelling the bond lengths of U-O and O-O with Rietveld method
- To verify the knowledge obtained with the Radial Distribution of lattice measured in real-space PDF

- In real space within harmonic approximation, the thermal vibration effect can be described as a convolution of atom potential at equilibrium state and a Gaussian statistic distribution of atomic displacement. [1]
- ∴ Anharmonic – a convolution of equilibrium potential and distorted Gaussian function → mathematically difficult to calculate
- ∴ Split the O atom of one site to two sites and assuming both have isotropic thermal motion and the O' at the second site moves along <111> direction.



Q-space split-atom model – two isotropic O and O'

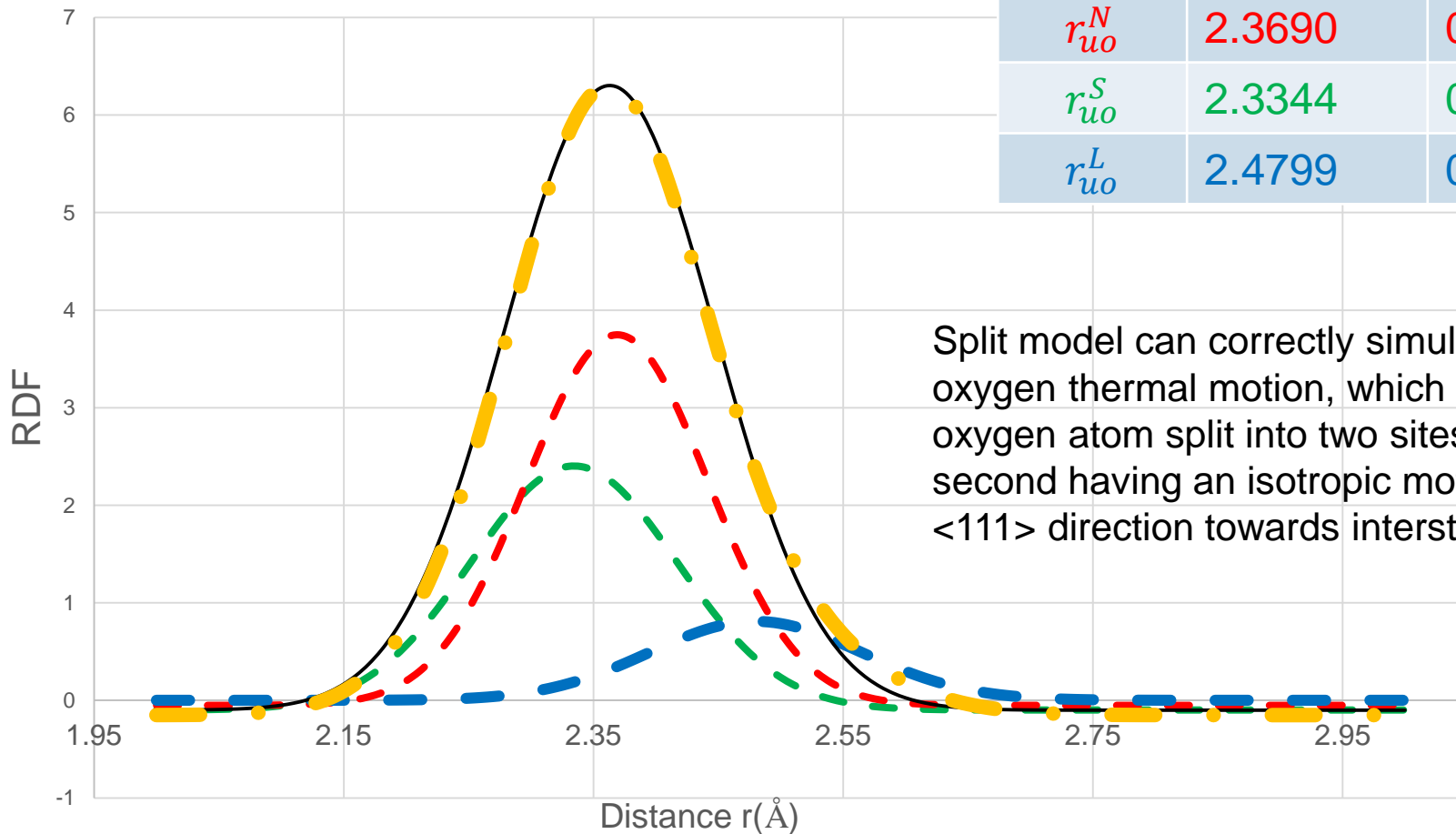
Relative occupancy and position of O'

Real space UO, UO' distance with probability p

Gaussian Function – Integrated area = Probability



Radial Distribution Function of UO bond @RT

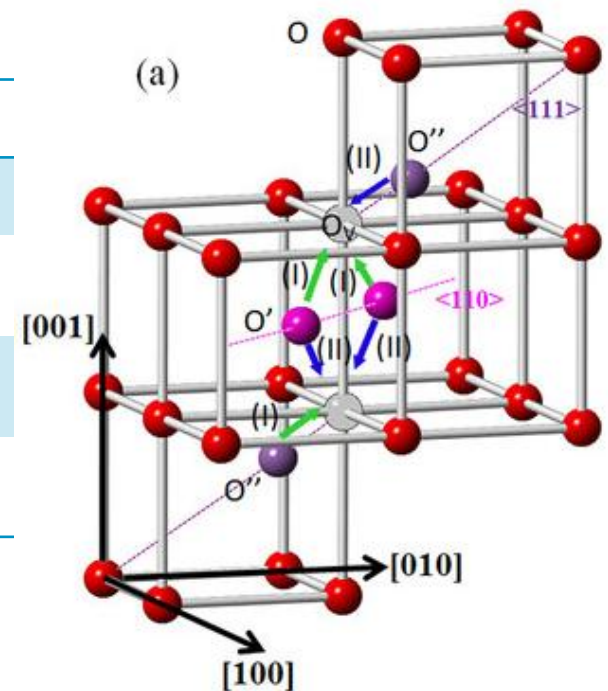


Split model can correctly simulate the oxygen thermal motion, which is an oxygen atom split into two sites with the second having an isotropic motion along  $\langle 111 \rangle$  direction towards interstices.

- Willis [1] and Murray [2] : UO<sub>2+x</sub>, x=0.12, 0.13, 0.14
  - Expect to determine the type of defect structure – cuboctahedron/Willis'
  - Conclusion: defect cluster type is highly dependent on the sample treatment
- Rietveld refinement results of UO<sub>2+x</sub>, with small deviation-from-stoichiometry
  1. Willis' cluster structure built-up [1]

| Atom             | Coordinates   | Composition |
|------------------|---|-------------|
| Uranium          | 0,0,0   | 1.00        |
| Lattice Oxygen O | $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$             | 1.97        |
| Interstitial O'  | $\frac{1}{2}, \frac{1}{2} + v, \frac{1}{2} + v$     | 0.0148*     |
| Interstitial O'' | $\frac{1}{2} + w, \frac{1}{2} + w, \frac{1}{2} + w$ | 0.0148*     |

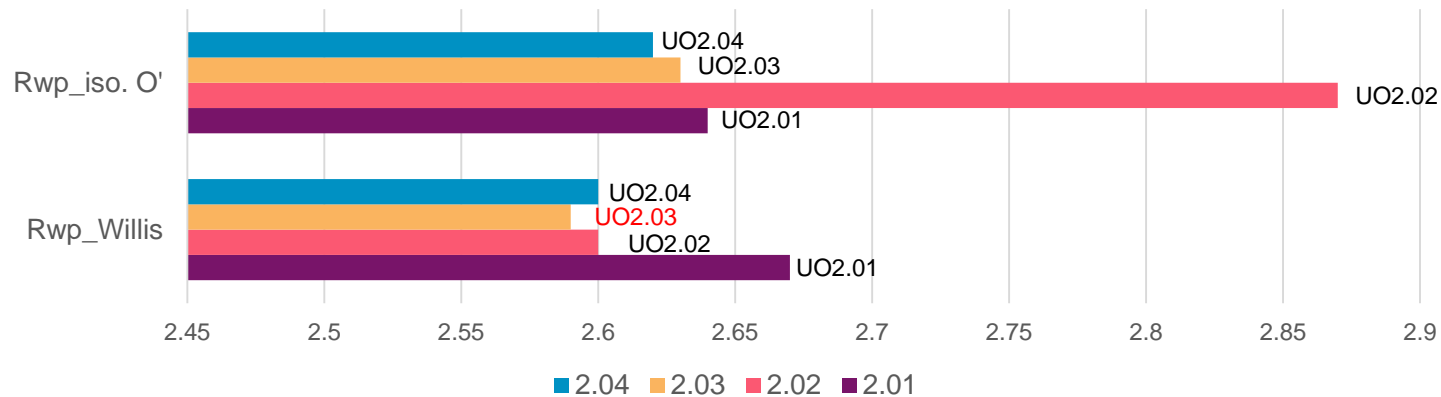
$$v = 0.02064, w = 0.121$$



➤ Rietveld refinement results of UO<sub>2+x</sub>, with small deviation-from-stoichiometry

2. Determination of the stoichiometry  
Sample preparation condition → estimated O/M ration ~ 0.03
3. Check the possibility of isolated mobile interstitial oxygen model

Refinement quality (Rwp) for models with different O/Ms and different defect structures (smaller Rwp = better refinement)



4. Refine the composition between O' and O''
5. Check the possibility of dissolved cuboctahedron cluster - poor refinement
6. Rebuild the model with supercells - similar refinement results

| Atom             | Coordinates   | Composition |
|------------------|---|-------------|
| Uranium          | 0,0,0   | 1.00        |
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| Interstitial O'' | $\frac{1}{2} + w, \frac{1}{2} + w, \frac{1}{2} + w$ | 0.0148*     |

- Rietveld and PDF refinement results of  $\text{UO}_2$ 
  - Results of atomic structure and temperature factors are consistent with literature
  
- RDF and Split-atom model study of  $\text{UO}_2$  oxygen atom thermal motion
  - Rietveld PD map illustrates the anharmonic thermal vibration
  - Split-atom model to solve the difficulties of simulating atom anharmonic motion.
  - Split-atom model results shows the consistency with the Radial Distribution Function measurement
  
- Rietveld refinement on  $\text{UO}_{2.03}$  diffraction measurements at high temperature
  - Willis 2:2:2 defect structure model is applicable for our  $\text{UO}_{2+x}$  with smaller deviation-from-stoichiometry
  - We performed refinement with different defect structures and modelled different composition ratios between U and O, and O' and O'' to find the best fit
  
- Prospects
  - Continued refinement with  $\text{UO}_{2.03}$  at low T (two-phase zone)
  - Neutron diffraction experiments on  $\text{UO}_{2+x}$  with different x and dopants

# Thank you for listening!

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