

# Neutron Scattering Experiments and Electronic Structure Calculations on $\text{U}_3\text{O}_7$ and $\text{U}_3\text{O}_8$

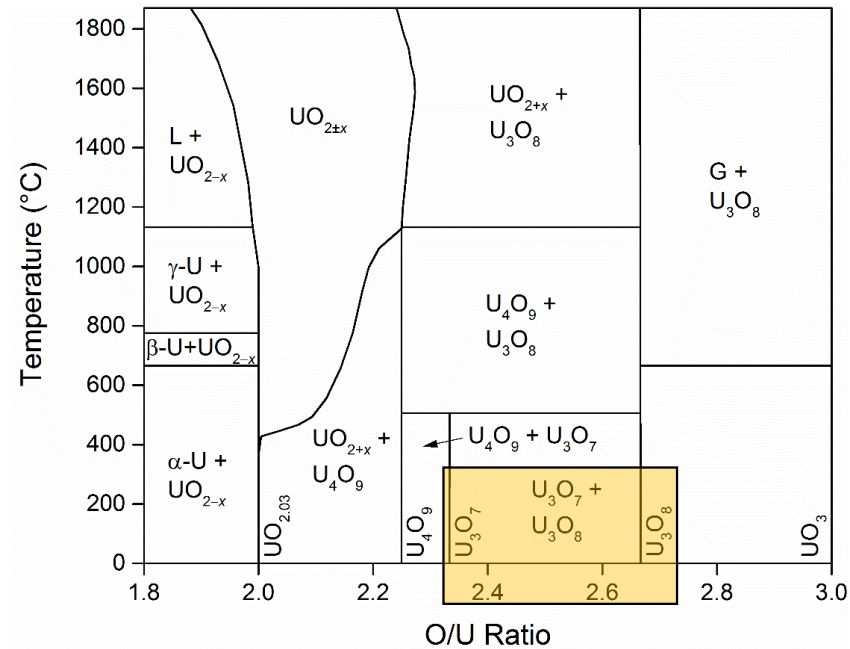
Gregory Leinders,<sup>a</sup> Gianguido Baldinozzi,<sup>b</sup> Clemens Ritter,<sup>c</sup> Henry Fischer,<sup>c</sup> Rolando Saniz,<sup>d</sup> Ine Arts,<sup>d</sup> Dirk Lamoen,<sup>d</sup> Marc Verwerft<sup>a</sup>

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<sup>b</sup> Université Paris-Saclay, CentraleSupélec

<sup>c</sup> Institut Laue-Langevin

<sup>d</sup> UAntwerpen, Department of Physics



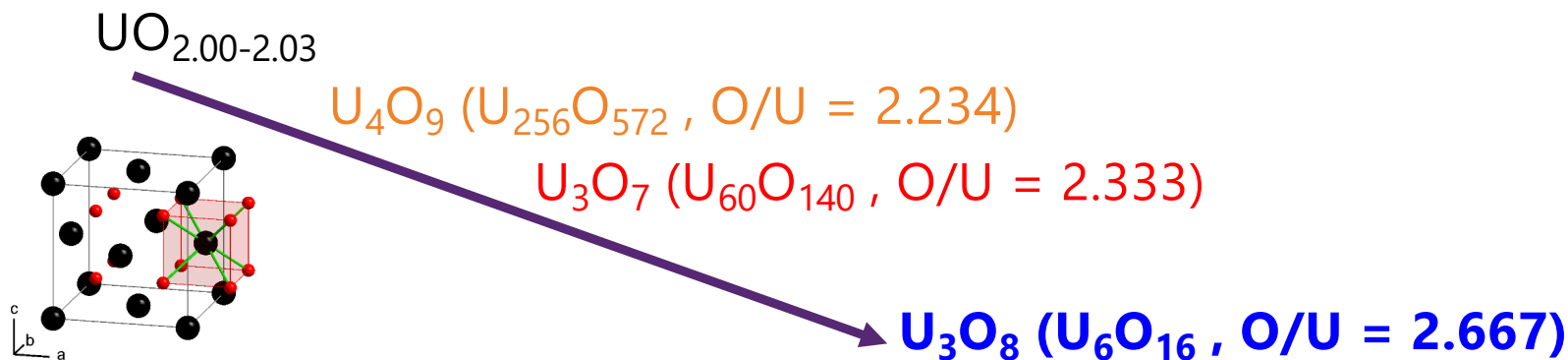
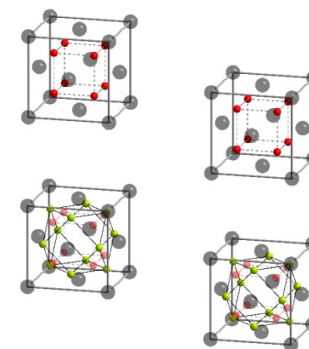
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# The U-O system

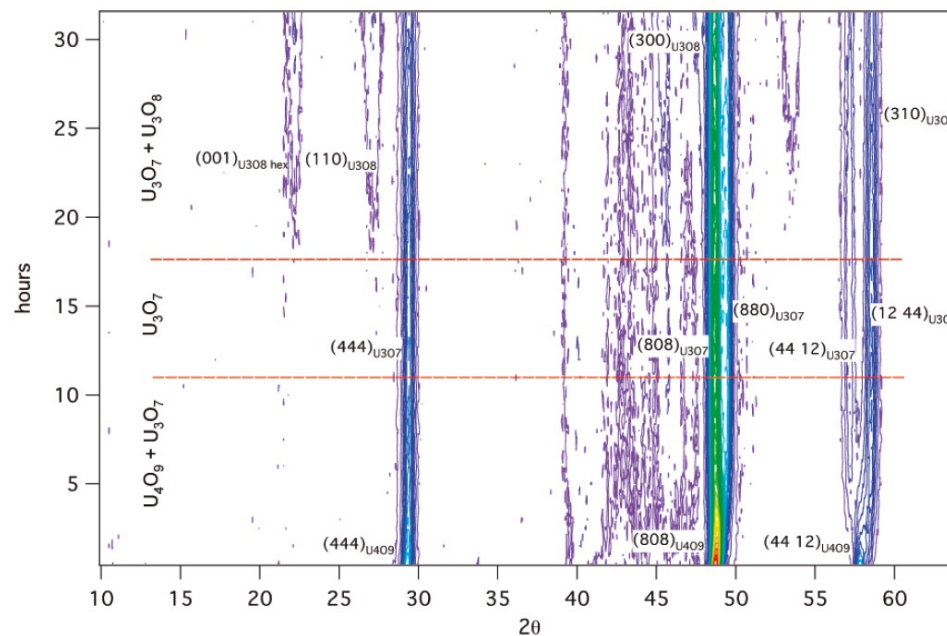
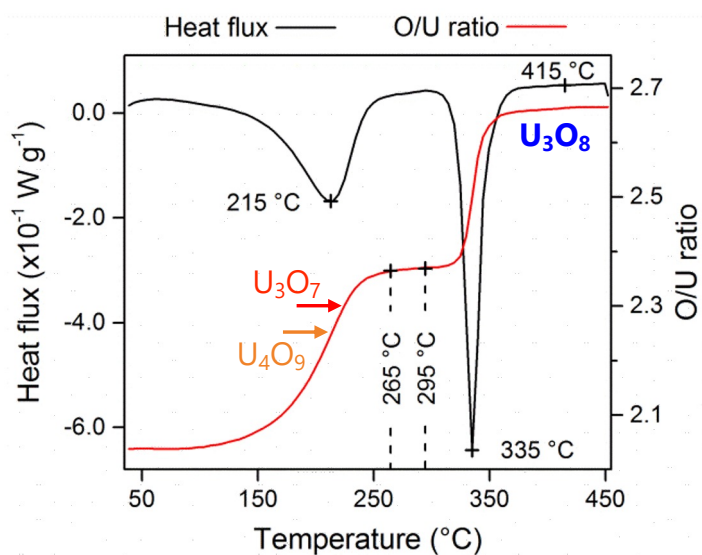
Oxidation pathway at temperatures < 500 °C

1. Incorporation of excess oxygen as point defects
2. Formation of defect clusters
3. Periodic (long-range) ordering of clusters
4. Formation of anion-excess fluorites
5. **Morphotropic phase transitions to  $U_3O_8$  [1,2]**



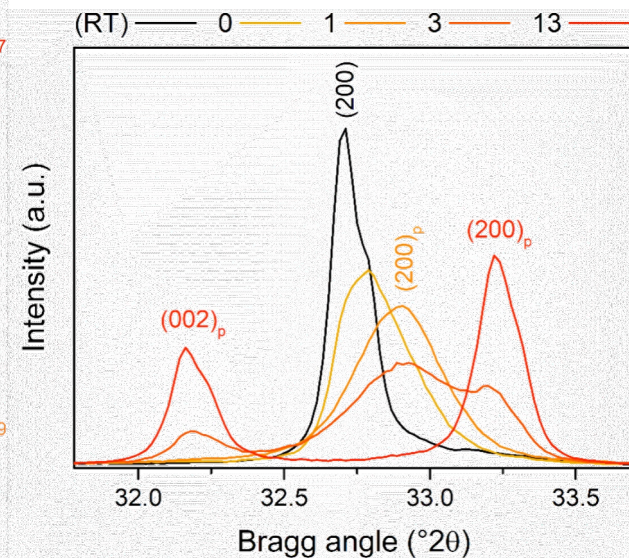
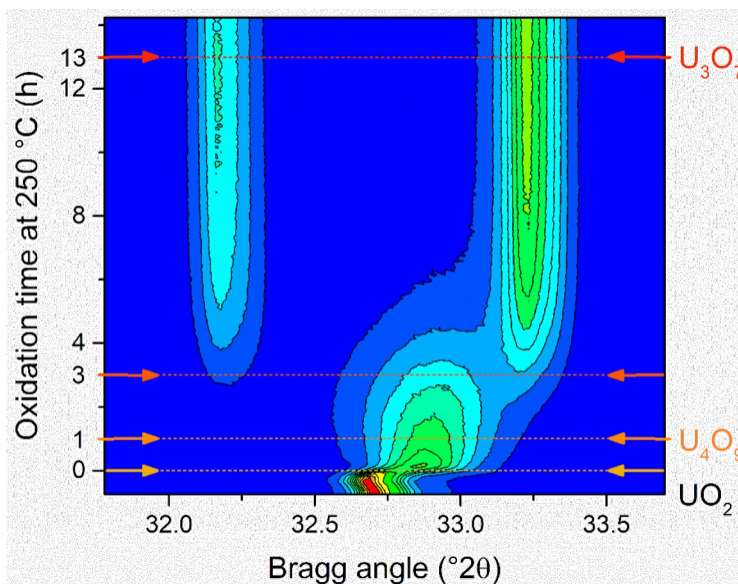
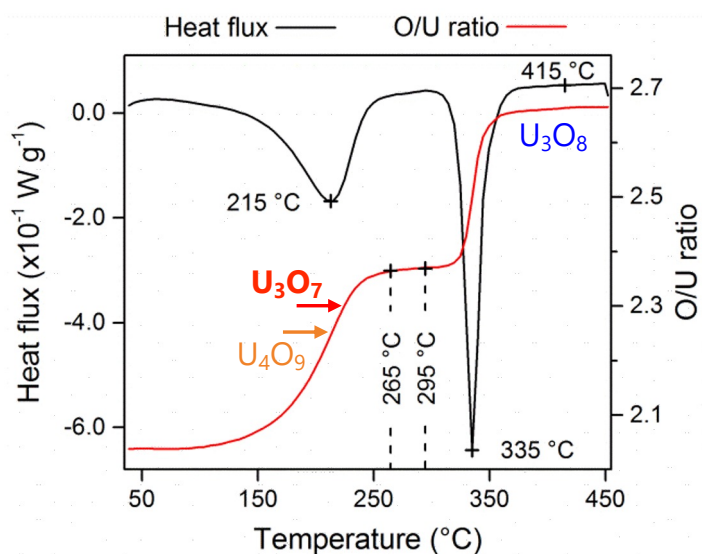
# Successive oxidation to $U_3O_8$

In-situ neutron diffraction [1]



# Formation of $U_3O_7$ from $UO_2$

In-situ TG-DSC and XRD [1,2]





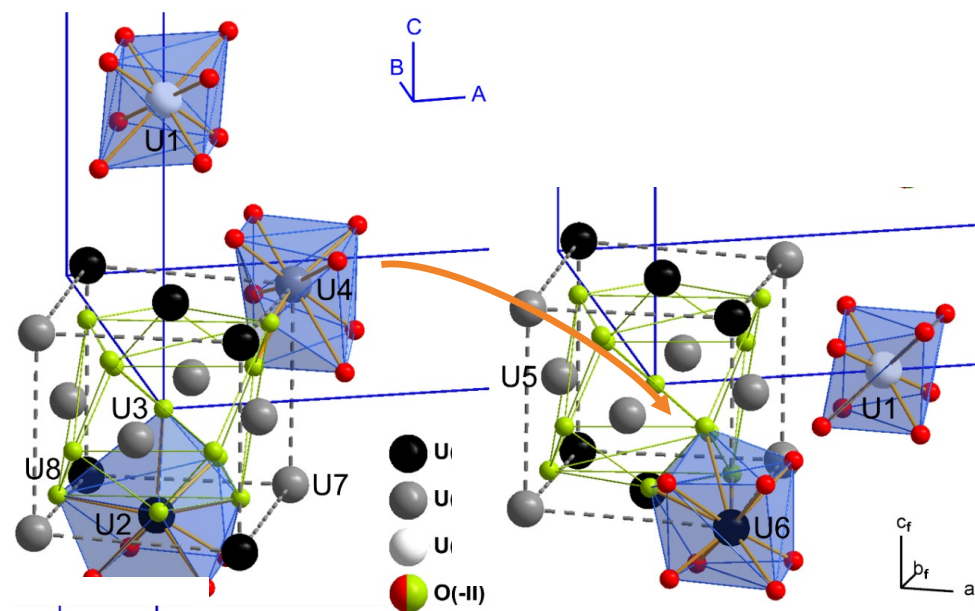
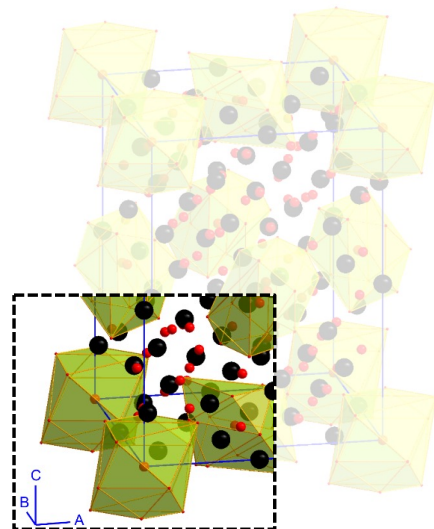
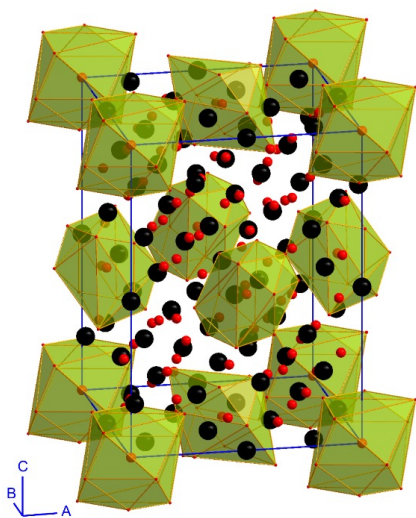
# Structural characterization: $U_3O_7$

Anion-excess fluorite with long-range periodic order, SG  $P4_2/n$  [1]

- Type of defect motif: " cuboctahedral oxygen clusters " cf.  $U_4O_9$  [2]

→ U remain close to their original, fluorite-type positions

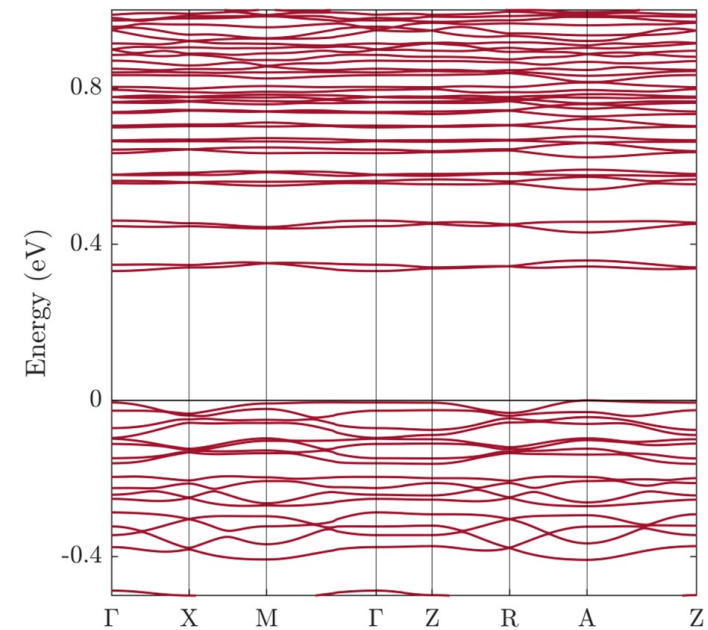
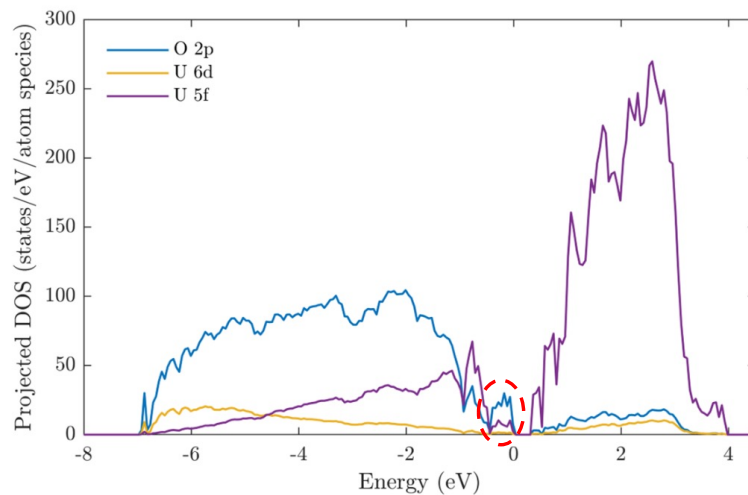
→ O deviate irregular environments



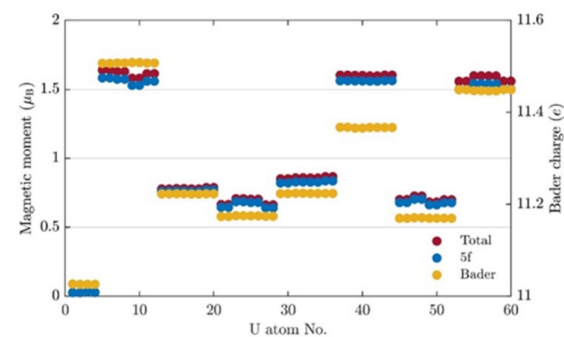
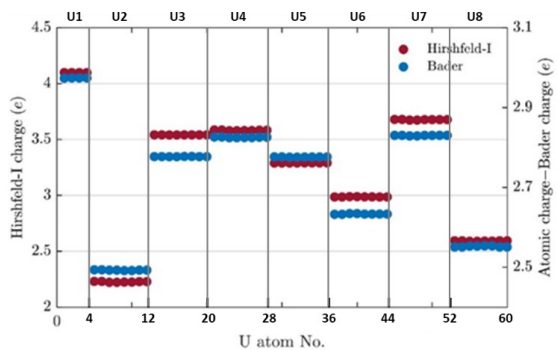
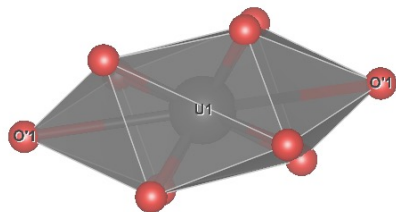
# Electronic structure calculations

PBE+ $U$  approximation, including SOC

- Semiconductor band structure predicted
  - 0.32 eV band gap
- Charge-transfer insulator
  - Valence band top: O 2p  $\leftrightarrow$  Conduction band U 5f

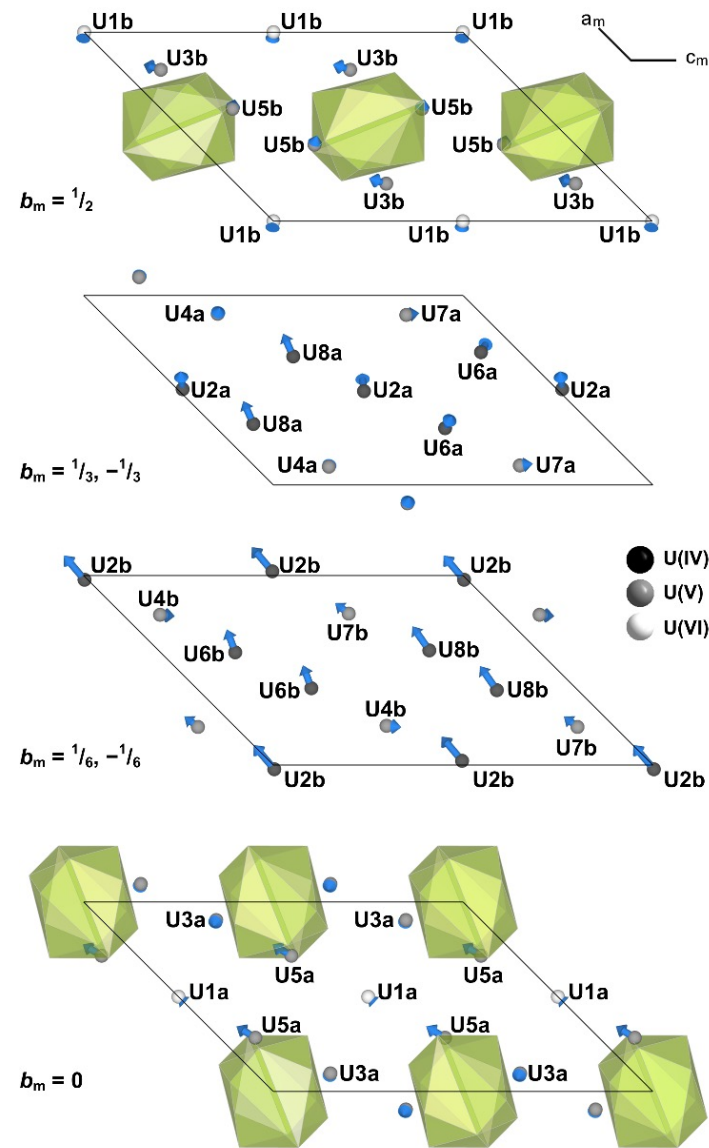


# Charge and spin localisation



- Change x-axis labels
- Use vertical gridlines
- Add U1-U8 labels
- Delete horizontal gridlines

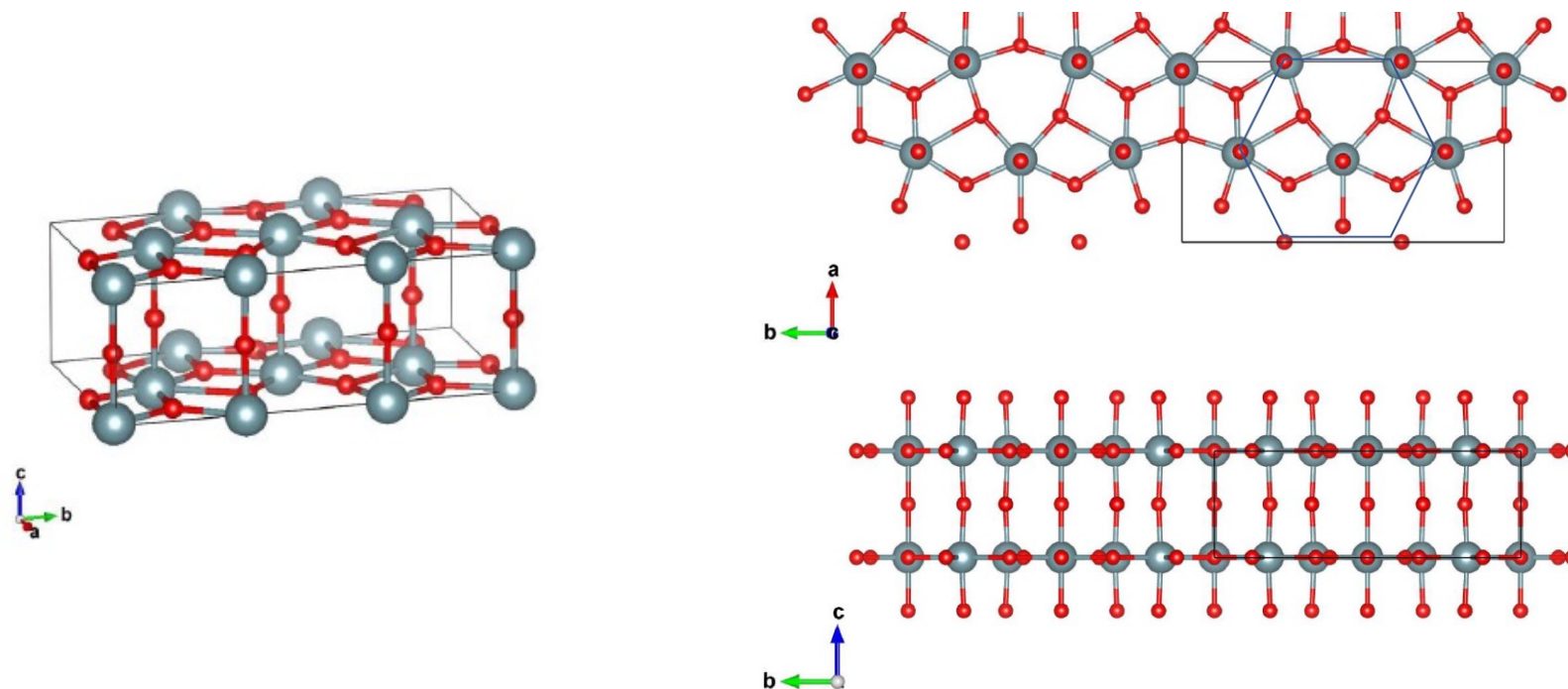
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# Structural characterization: $U_3O_8$

Uranium atoms in 7-fold (pentagonal bipyramid) coordination

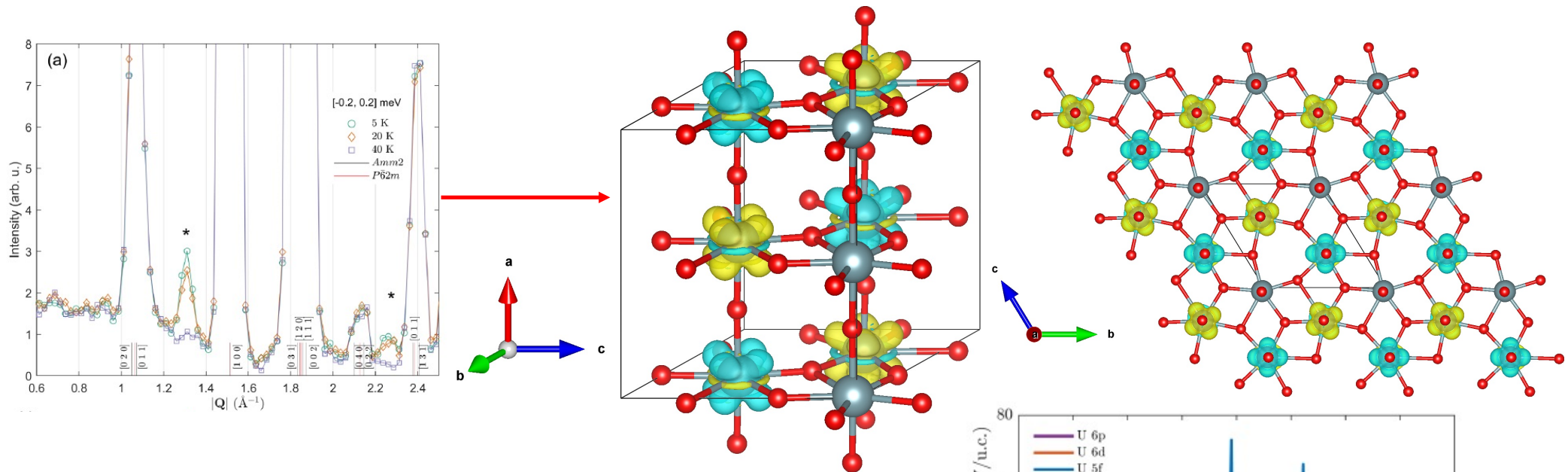
- Layered structure ( $C2mm$ ) along c-axis: oxygen atoms bridging between planes [1]





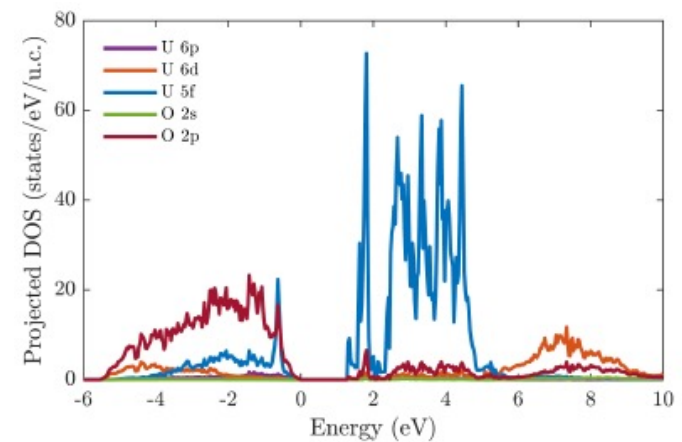
# Magnetic ground state

Recent neutron scattering experiments [1]: AFM order observed



PBE+ $U$  approximation, including SOC [2]

- Indirect band-gap insulator
- Charge-transfer insulator
- Gap opening between O 2p and U 5f states

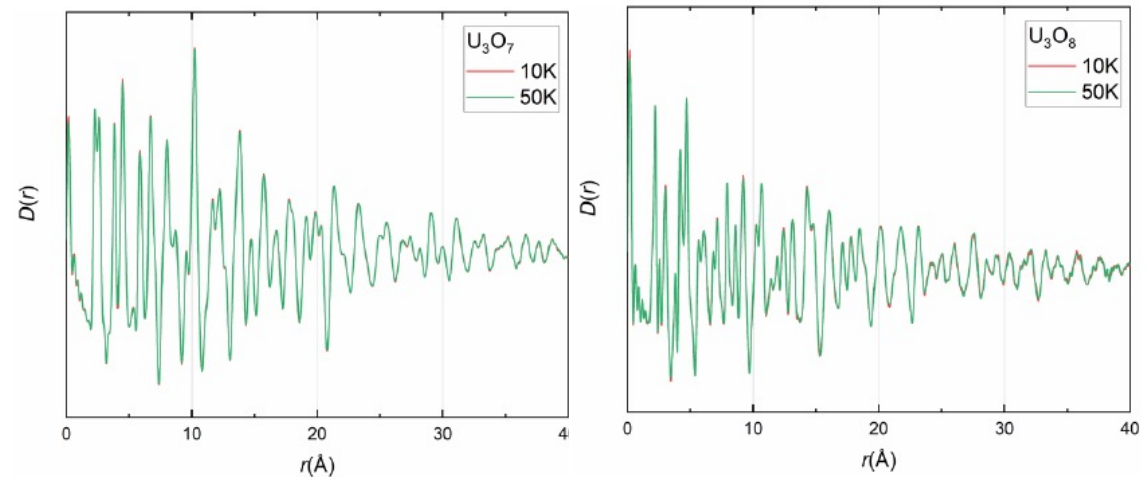


# Conclusion and outlook

Major steps forward in characterization of the mixed-valence oxides  $U_3O_7$  and  $U_3O_8$  using neutron scattering techniques and calculations

Detailed structure assessment ongoing to find phase relation between the  $U_3O_7 \leftrightarrow U_3O_8$  transition

- Local structure evaluation from neutron scattering (PDF)
- Oxidation state evolution from anomalous X-ray diffraction



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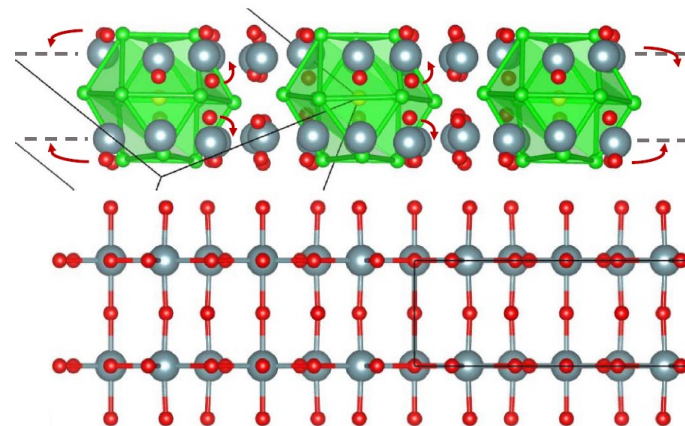
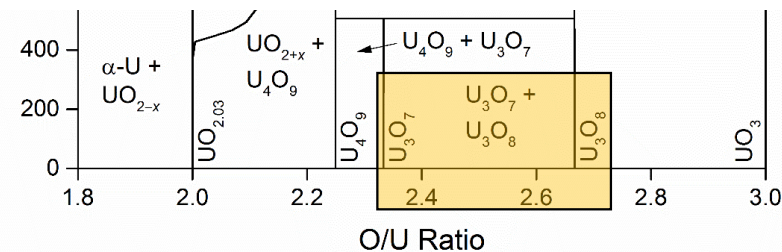
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## Thank you for your attention

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