What does the crystallo-chemistry of UO_2 tells us to design innovative nuclear fuels?

L. Desgranges

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DE LA RECHERCHE À L'INDUSTRIE

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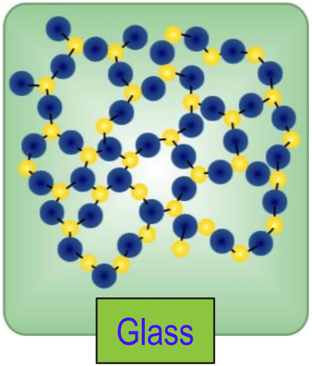
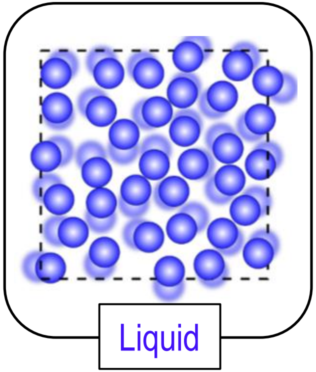
CEA-DEN-DEC

The choice of fuel has major impact on nuclear reactor design :

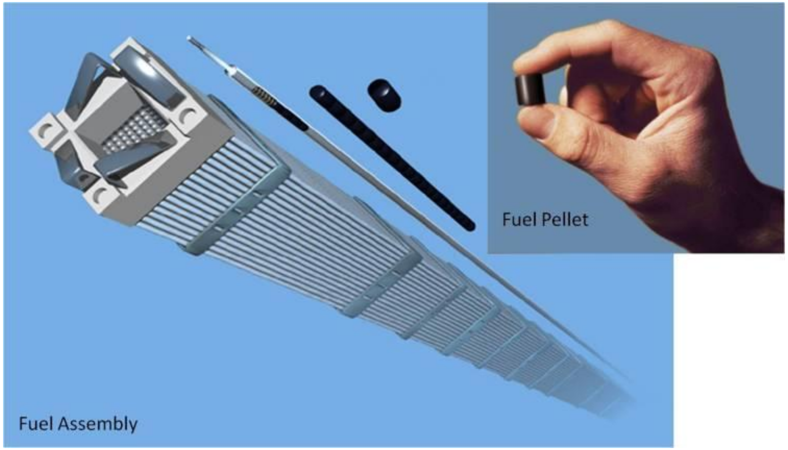
- Density of fissile atoms (neutron flux)
- Thermal conductivity (heat transfert)
- ….

Different physical states are possible :





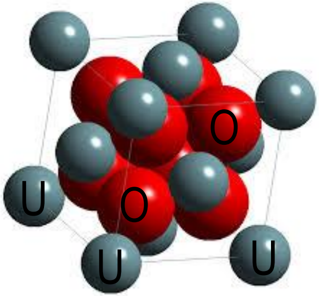
UO_2 : crystal with internal disorder



Uranium dioxide is the main component in present-day nuclear fuel reactors

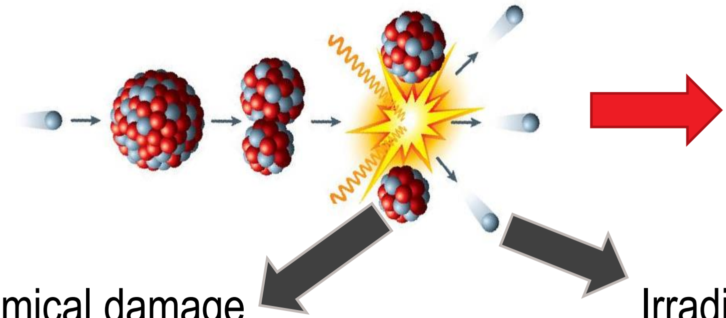
UO_2 was chosen as nuclear fuel for :

- its structural stability
- its stability with water



But UO_2 turned out to have another major property as nuclear fuel

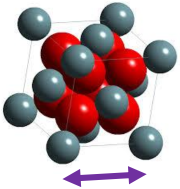
Nuclear fission

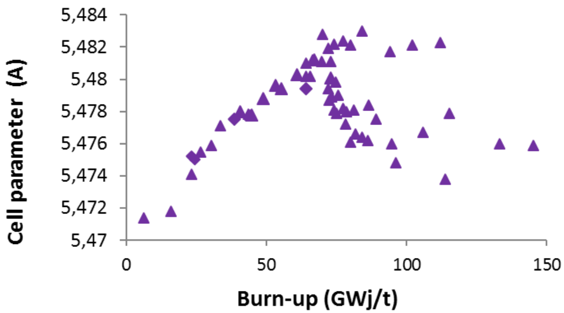


Heat for energy production

Chemical damage

Irradiation damage





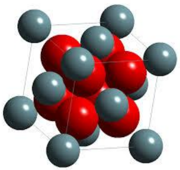
No change of UO_2 crystalline structure under irradiation up to at least 6-7 at% fission rate

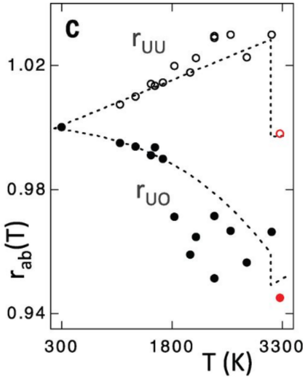
Still an open question

Recent results on the existence of internal disorder in UO_2

- Stoichiometric UO_2
  - Evidence of local symmetry disorder
- Hyper-stoichiometric UO_{2+x}
  - Evidence of clusters made of oxygen interstitials
  - Lanthanide dopants around these clusters
- Hypo-stoichiometric UO_{2-x}
  - Planar defects
  - Miscibility gap in doped UO_2

Stoichiometric UO_2

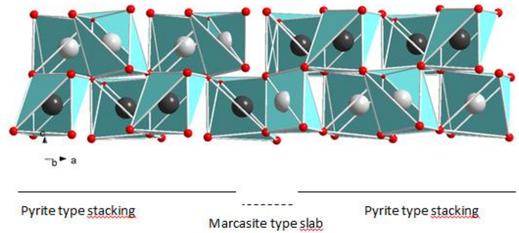




Skinner et al. Science. 2014 Nov 21;346(6212):984-7

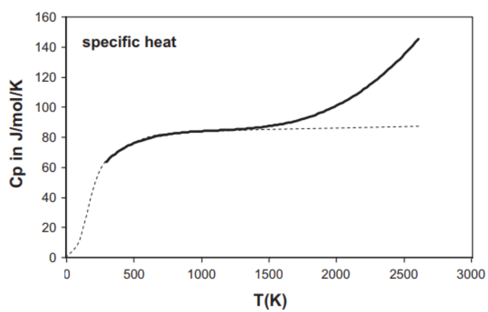
The U-O distance in UO_2 measured by X-Ray diffraction and PDF analysis is not consistent with Fm-3m crystalline structure

An interpretation with low symmetry Pa-3 nm size domains separated by coherent interfaces (compatible with average Fm-3m) *Chem. Eur. J.* **2018**, *24*, 2085 – 2088



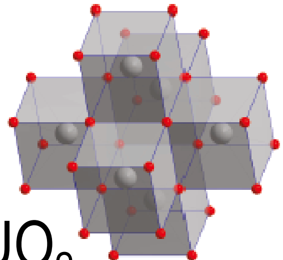
Mesoscale disorder

that increases with temperature

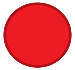


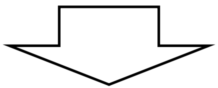
Irradiation resistance

Journal of Nuclear Materials 420 (2012) 334–337



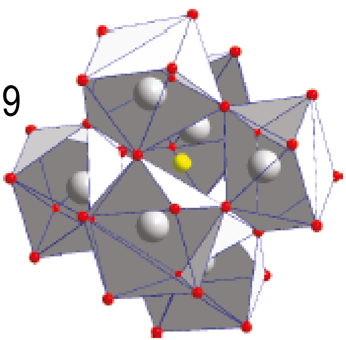
UO_2

+ 5 



oxygen interstitial cluster embedded in UO_2 crystalline lattice

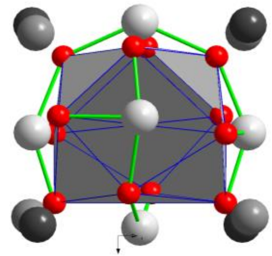
U_4O_9



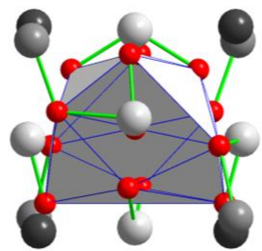
Inorg. Chem. 48 (2009) 7585-7592

Encapsulation of interstitial clusters with some chemical plasticity

Change of the shape of the cluster as a function of temperature



300°C



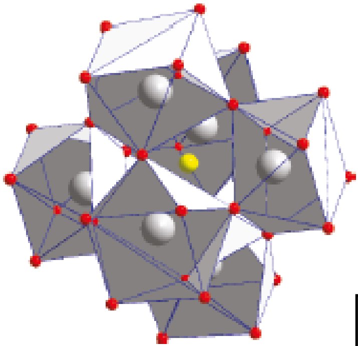
900°C

An interpretation with modification of chemical bounding and charge state

Inorg. Chem. 55 (2016) 7485-7491

doped hyper-stoichiometric UO_2 : $(U,Ln)O_{2+x}$

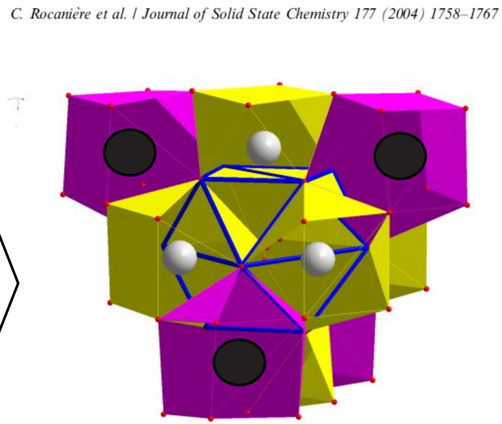
U_4O_9



\+

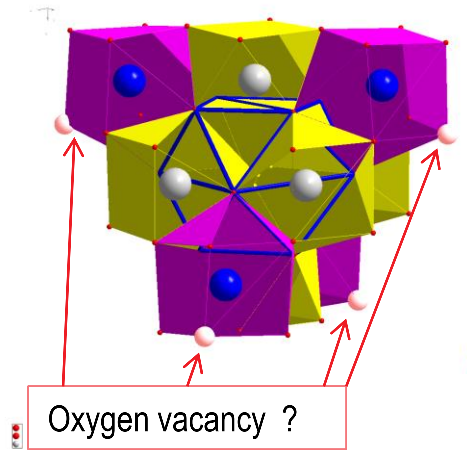
4 ● Ce

$(U_{0,9}Ce_{0,1})_4O_{9-\delta}$



Specific incorporation sites with some chemical and size adaptability

$(U,Nd)O_2$?



Consistent with U^{5+} formation in $(U,Nd)O_2$ (J. Nucl. Mater. 507 (2018) 145-150)

Evidence of planar defects in $UO_{1.98}$

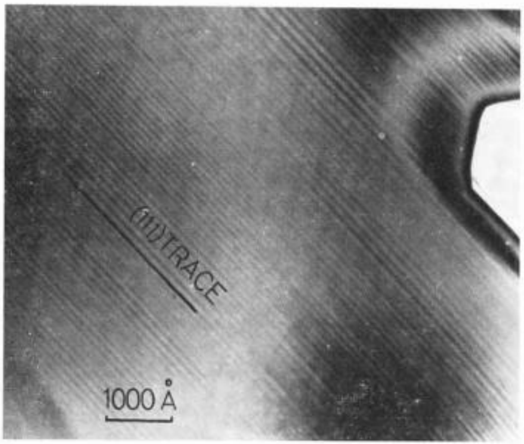
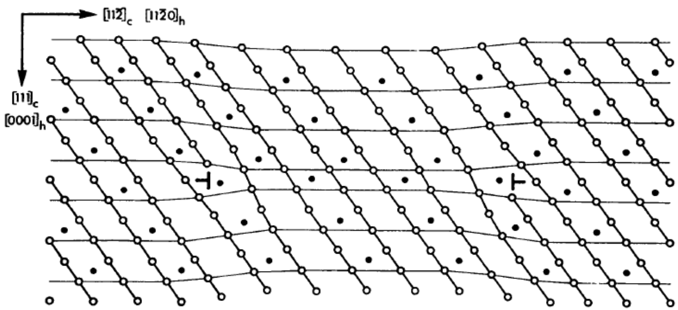


FIG. 3. – Transmission electron micrograph of a UO_2 sinter annealed in commercial H_2 in a reducing environment at 1 500 °C for only 5 min.

Phil. Mag. 26 (1972) 1395-1407

An interpretation with Magneli type defects



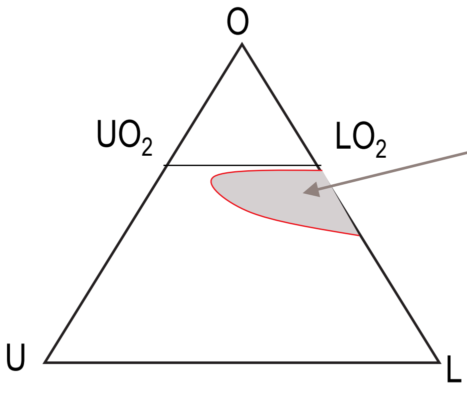
Hyde (Acta Cryst A **27** 617 1971)

Vacancy clusters as stacking faults ??

Hypostochiometry for doped UO_2

Existence of a 2 phase domain in many (U,L)O2-x compounds

L = Pu, Ce, Nd, …



A miscibility gap as stated in literature ?

On going research to check the possible existence of crystalline phases different from fluorite

J. Nucl. Mater. 458 (2015) 394-405

Formation of different crystalline phases in the hypostoichiometric range

Conclusion

UO_2 irradiation resistance can, at least partially, be explained by:

- Its internal disorder with lower local symmetry
- Its various defects for the incorporation of dopants

A driving force for the search of other ***crystals with internal disorder*** to be used as nuclear fuel :

- Non stoichiometric compounds
- Encapsulating material (layered compounds?)
- ..

Thank you for your attention