

DE LA RECHERCHE À L'INDUSTRIE



## The influence of oxygen activity on the behaviour of UO<sub>2</sub>

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Quantify the influence of oxygen activity on the behaviour of  $\text{UO}_2$ , starting from point defects ...

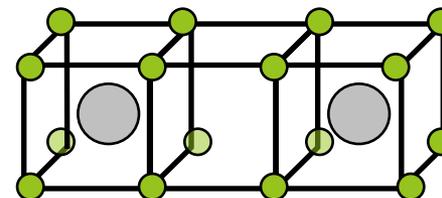
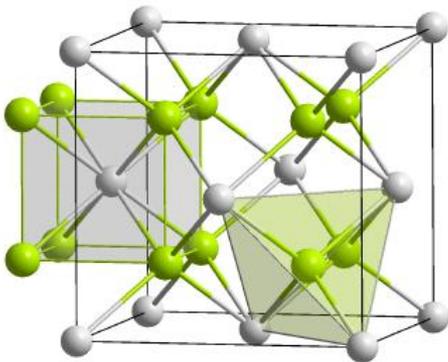
- Interpret results from out-of-pile property measurements
- Try to control, enhance or mitigate its effects:

develop materials whose properties are tailored, develop and control fuel cycle processes

- I) Oxygen potential and deviation from stoichiometry
  
- II) Point defect populations in  $\text{U-O}_2\pm x$  and their dependence upon oxygen activity
  
- III) Consequences on
  - self-diffusion properties
  - *mechanical properties*
  - *radiation environment? Some complicating factors*
  
- IV) Conclusions

# I-1 Fluorine structure of $\text{UO}_2$ and deviation from stoichiometry

## ■ Fluorine iono-covalent compound

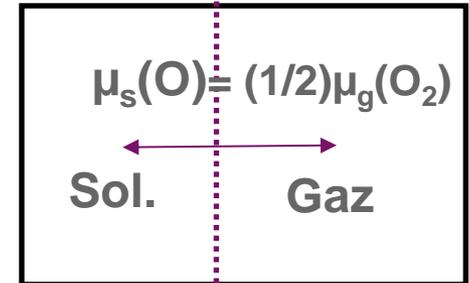


## ■ $\text{UO}_{2+x} \Rightarrow$

- Insertion of interstitial atoms in octahedral sites ( $\text{O}_i''$ )
- oxydation of cations +4 à +5 ou +6 depending on degree of non-stoichiometry...

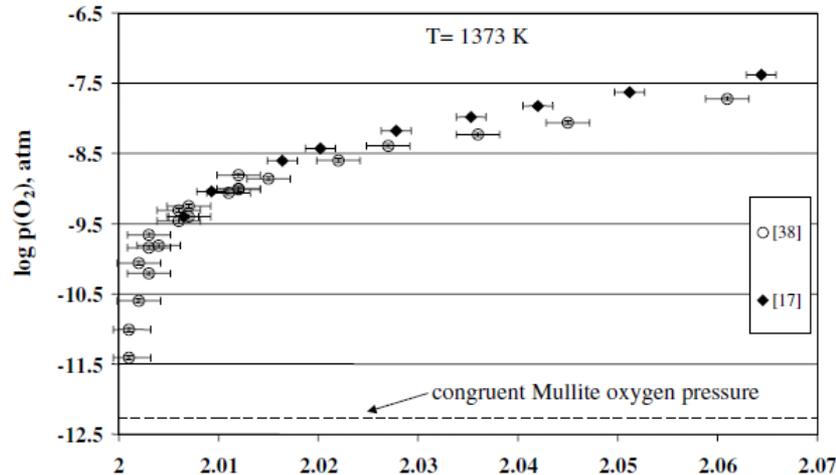
# I-2 Definition of oxygen potential

- Gibbs' rule of  $\phi$ : N of intensive parameters necessary and sufficient to determine the system
- Solid exchanging with gas phase



$v = 5 - 2 = 3$ , as a result,  $x = f(T, P, p_{\text{O}_2})$

If there  $\exists$  impurity or other actinide  $v = 6 - 2 = 4$  soit  $x = f(T, p_{\text{O}_2}, P, y)$

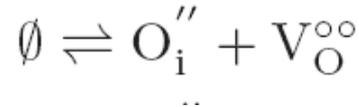
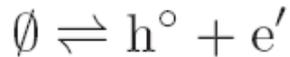


**$\Delta G(\text{O}_2) = RT \ln(p_{\text{O}_2})$  (Molar free enthalpy of oxygen or oxygen potential)**

**Intensive parameter which has to be controlled in exactly the same way as say temperature (Gerdanian, Dodé)**

# II-1 Which majority defect at « exact » stoichiometry

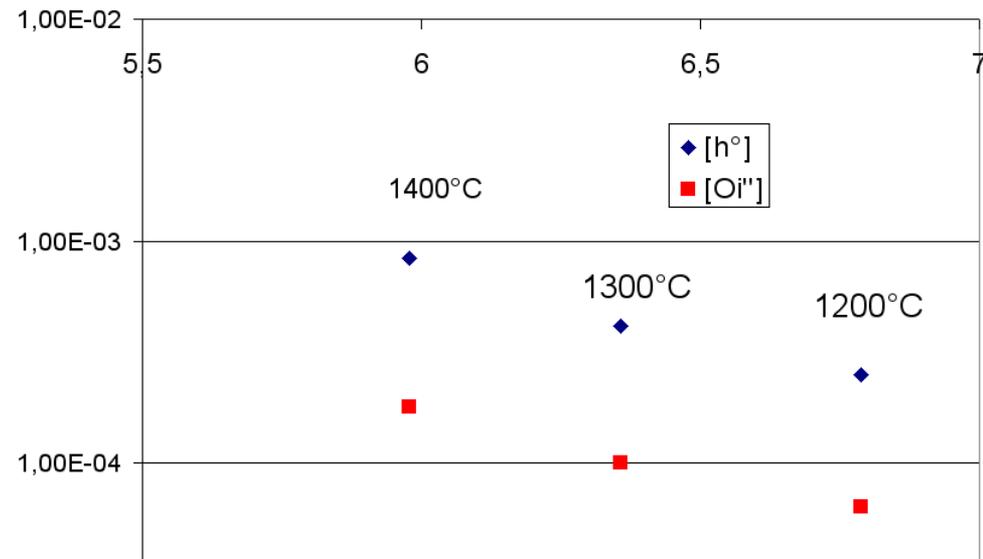
- Defects controlled transition metal oxides by basic equilibria <sup>[1]</sup> :



**■ UO<sub>2</sub> oxygen deficient/excess transition metal oxide & intrinsic ionisation<sup>[1]</sup> :**

- $[e'] \sim [h^\circ] \gg [O_i''] \sim [V_O^{\circ\circ}] \gg [V_U] - [U_i]$
- Basic reason: SC (small gap)  $\Rightarrow$  electronic conductor
- DFT+U <sup>[2]</sup> calculations:  $E_f(e' - h^\circ) \sim 1.7 \text{ eV} < E_f(V_O - O_i) \sim 3.3 \text{ eV} < E_f(V_U - U_i) \sim 11 \text{ eV}$

**■  $\sigma$  measurement, simple hyps., estimate  $[h^\circ] \sim [e']$ ,  $[O_i''] \sim [V_O^{\circ\circ}]$**

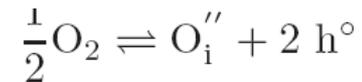
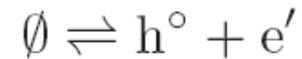


[1] P. Kofstad, *non-stoichiometry, diffusion and electrical conductivity in binary metal oxides*, 1972

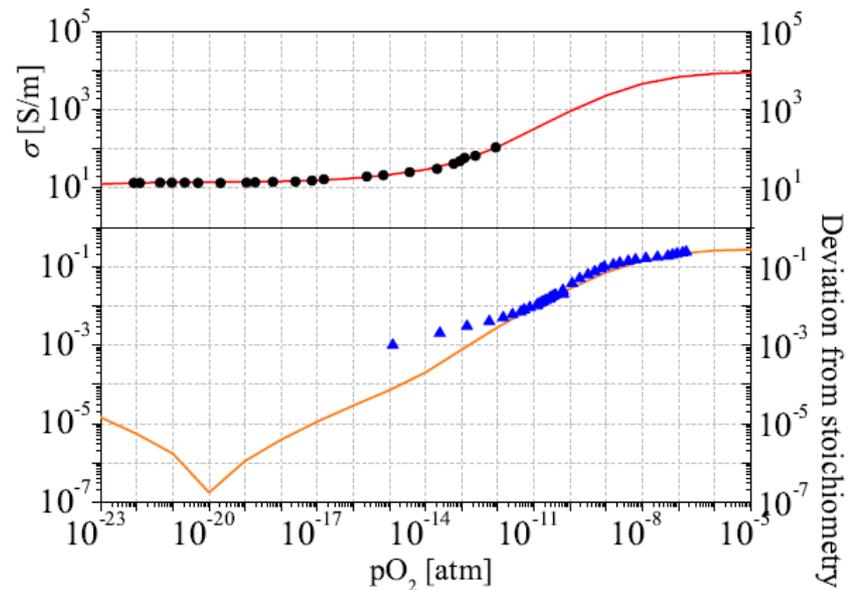
[2] Andersson et al., *Phys. Rev. B* 84 (2011)

## II-2 Defect concentrations as a function PO<sub>2</sub>?

- Model which accounts for impurities and equilibrium pO<sub>2</sub><sup>[1]</sup>



- Reproduce as many experimental data as possible as a function of oxygen activity, T, doping:  $\sigma$  <sup>[2]</sup>  $\Rightarrow [h^\circ]$ ,  $x$  <sup>[3]</sup>  $\Rightarrow [O \text{ defects}]$
- Consistency with DFT<sup>[4,5,6]</sup> calculation of formation energies



[1] To be published (2013)

[2] P. Ruello et al. JACS 88 (2005)

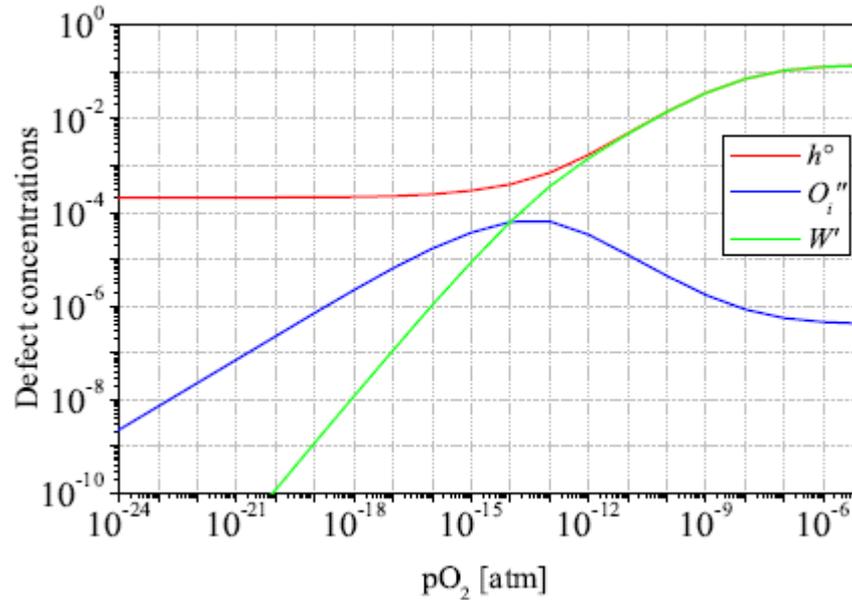
[3] P.O Perron, Report AECL-3072 (1968)

[4] Crocombette et al., Phys. Rev. B 83 (2011)

[5] Dorado et al., Phys. Rev. B 83 (2011)

[6] Andersson et al. Phys. Rev. B | 7

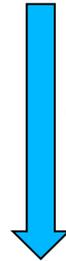
## II-3 Example of Results at 900°C



- Predominant electronic defects
- Transition from a single defect regime to a di-interstitial  $W'$  at roughly  $10^{-4}$
- $[\text{defects}] \sim PO_2^\alpha$

## III-1 Effect of PO<sub>2</sub> on oxygen self-diffusion

$$D_{\text{O}}^* = f_{\text{O}_i''} [\text{O}_i''] D_{\text{O}_i''} + f_{\text{V}_{\text{O}}^{\circ\circ}} [\text{V}_{\text{O}}^{\circ\circ}] D_{\text{V}_{\text{O}}^{\circ\circ}}$$

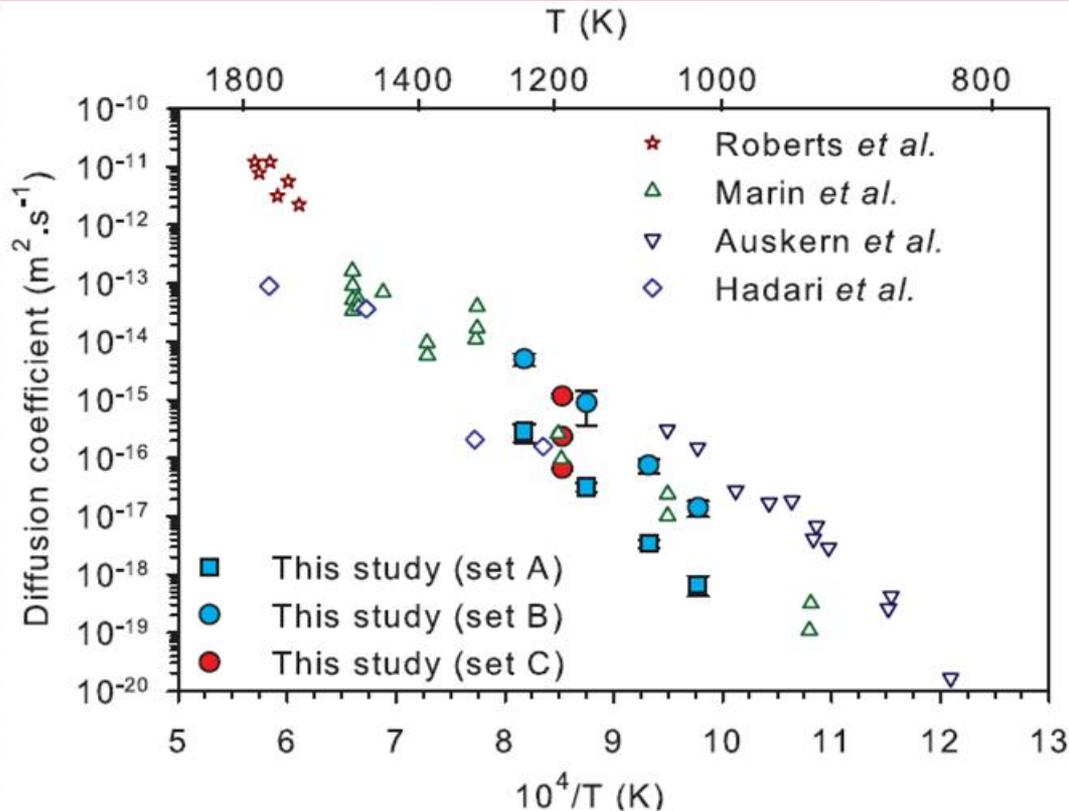


$$D_{\text{O}}^* = P_{\text{O}_2}^{\alpha} \times e^{-\frac{Em\alpha}{kT}} + P_{\text{O}_2}^{\beta} \times e^{-\frac{Em\beta}{kT}}$$



$\alpha$  and  $\beta$ ,  $E_m$  characteristic of the mediating defect

## III-2 Application to oxygen self-diffusion at $x \sim 0$ <sup>[1,2]</sup>



■ Data comparable for « stoichiometric »  $\text{UO}_2$  (But  $p(\text{O}_2)$  is neither controlled nor measured)

- X estimate impossible below  $2 \cdot 10^{-3}$
- Markin & Bones:  $\Delta x \sim 0.0025 \Rightarrow 4$  orders of mag. on  $p(\text{O}_2)$  at  $700^\circ\text{C}$

- 2 - 3 orders of magnitude in part due to:
  - Small changes in oxygen content  $\sim 2$  orders of magnitude<sup>[1]</sup>
  - Impurities  $\sim 1$ -2 orders of magnitude<sup>[2]</sup>

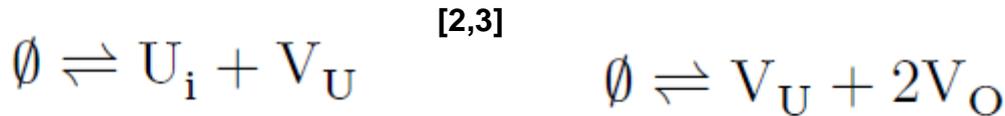
**Both  $p(\text{O}_2)$  &  $y$  must be controlled, measured**

[1] B. Dorado, *Phys. Rev. B* 83 (2011)

[2] P. Garcia *et al.*, *JNM* 400 2010

## III-3 Comparable (theoretical) approach to U self-diffusion<sup>[1]</sup>

- Near-stoichiometric region, high T
- LDA+U calculations
  - Energies associated with equilibria  $\Rightarrow$  data for point defect model
  - Migration energies (NEB)  $\Rightarrow$  (**assumed** diffusion mechanism) activation energies



$$K_{FU} = [U_i] \cdot [V_U]$$

$$K_S = [V_U] \cdot V_O^2$$

$$[V_U] = K(T) \cdot p_{O_2}$$

$$[U_i] = K'(T) \cdot p_{O_2}^{-1/2}$$

If  $e' \sim h^\circ$ , then

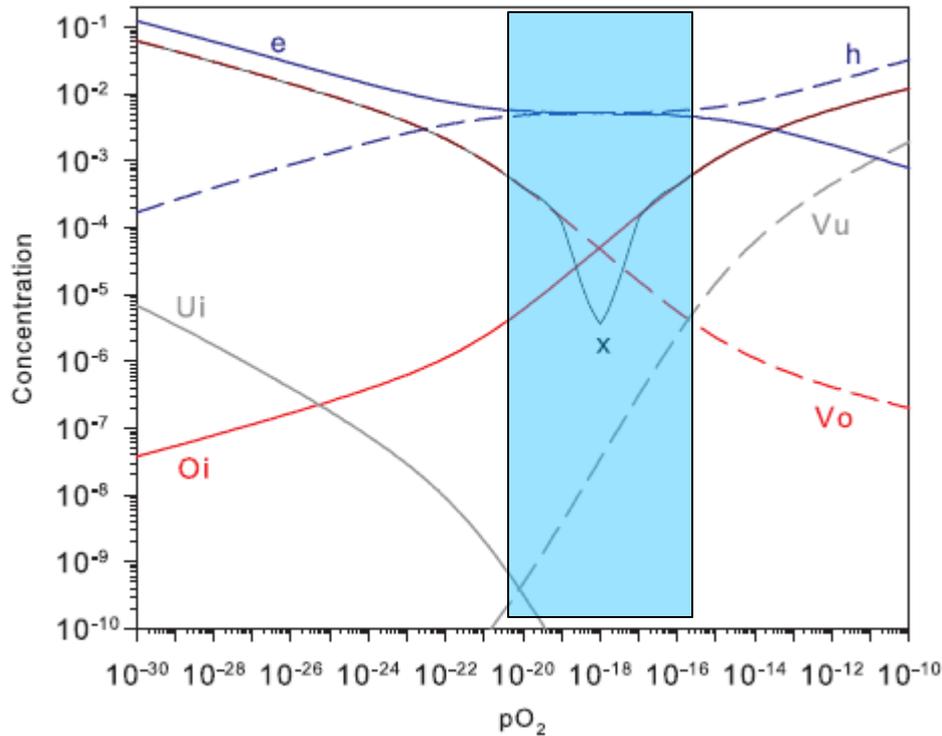
- Vacancy assisted mechanism:  $D_u \sim [V_U] e^{-E_m/kT}$ ,  $D_u \sim e^{-E+E_m/kT} p_{O_2}(T)$
- Ar/H<sub>2</sub> and residual H<sub>2</sub>O<sub>vap</sub> determine pO<sub>2</sub>  $\Rightarrow E_a \sim 4\text{eV}$
- If interstitial mechanism:  $D_u \sim [U_i] e^{-E_{mi}/kT}$ ,  $D_u \sim p_{O_2}^{-1}$  ( $E_a \sim 15\text{eV}$ )

[1] B. Dorado et al., Phys. Rev. B 86 (2012)

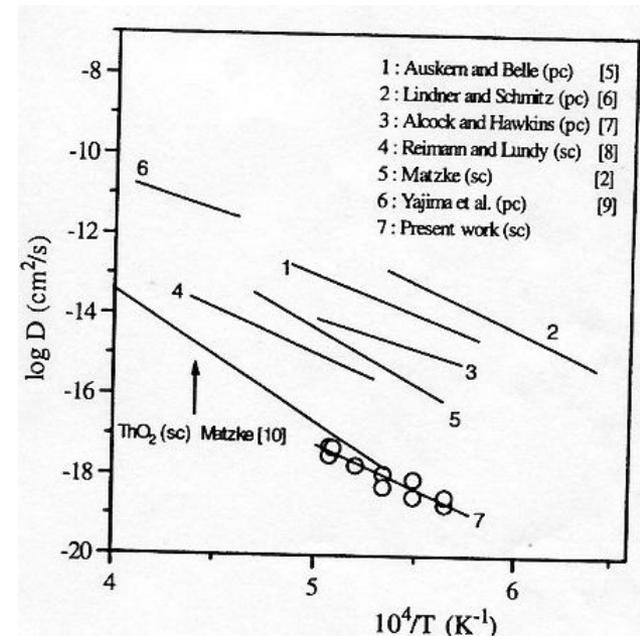
[2] Andersson et al., Phys. Rev. B 84 (2011)

[3] Crocombette et al., Phys. Rev. B 83 (2011)

# III-4 Comparison between experiment-theory



- $e' \sim h^\circ$
- $[def. U] < [def. O]$



- 3 order of magnitude dispersion
- $E_a \sim 3.6 - 5$  eV for single crystals
- $E_{atheoretical} \sim 4$  eV  $\Rightarrow$  **vacancy mechanism**

Results are rationalised based on  $PO_2$  dependence of [defect]

## III-5 Summary of results

Irrespective of temperature or composition

$$\underline{[\text{Defect}_\alpha]} \sim \underline{P_{\text{O}_2}^{q_\alpha} \times \text{Exp}(-E_\alpha/kT)}$$

$q_\alpha$ ,  $E_\alpha$  characteristic of defect (composition, charge, formation energy)

Electrical conductivity O, neutron scattering, PAS for Vu (collaboration with CNRS CEMHTI)

$$\underline{D_{\text{U/O}}} \sim \underline{P_{\text{O}_2}^{q_\alpha} \times \text{Exp}(-E_\alpha + E_m/kT)}$$

$q_\alpha$ ,  $E_\alpha + E_m$ , characteristic of diffusion mechanism (formation & migration)

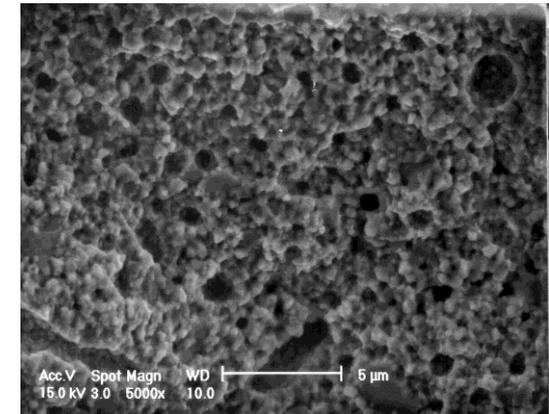
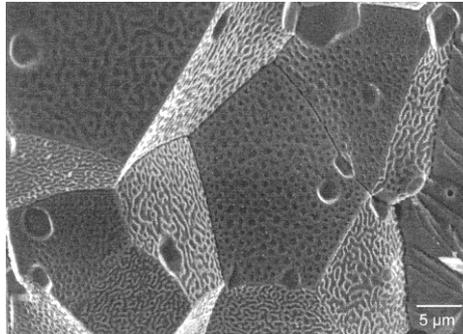
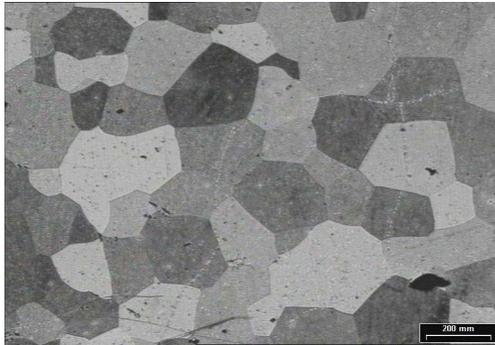
Self-diffusion

In UO<sub>2+x</sub> [electronic]>[oxygen]>[uranium]

## IV- Conclusions

### Oxygen activity controls defect concentrations hence atomic transport properties

- Sintering, mechanical properties, microstructural changes, diffusion and release of volatile fission products



- Property measurements should whenever possible be carried out under controlled atmospheres, not composition
- Means of comparing property measurements to theory (first principles)
  - Measurement of  $U/O/FP = f(T, p_{O_2}, \nabla T)$ , see announcement
  - Merge U-O defect models & use compound energy formalism?
  - *Correlation between mechanical properties and self-diffusion*

## IV- Announcement

- Hoping for a PhD position to fill at Cadarache starting October 2014
- Subject: measurement, interpretation and modelling of electrical & atomic transport properties of  $\text{UO}_{2+x}$  (doped with Nb/rare earths). Mainly U.
- Recently acquired and developed equipment ADELAIDE

