Atomic scale investigation of the diffusion of defects and fission gases in uranium dioxide

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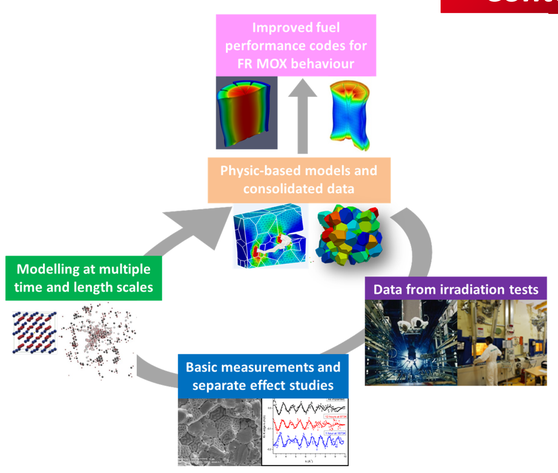
Context



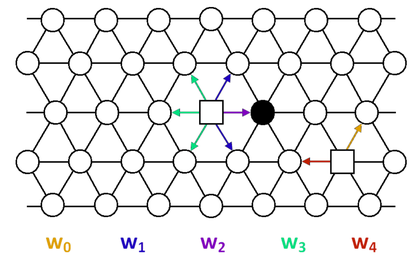
- Basic research approach applied to oxide nuclear fuels
- Actinide fission in reactor produces large quantities of defects and fission products, in particular fission gases (e.g. Xe, Kr), which have low solubility in the material
- Important consequences for fuel behaviour: swelling, decrease of thermal conductivity, release of radioactivity
- Further insight still needed into all stages of fission gas behaviour, starting with elementary diffusion mechanisms active in segregation and bubble formation
- Atomic xenon behaviour in UO_2 quite extensively studied
- Fewer data on Kr atomic diffusion
  - 2 experiment studies: Auskern 1960 [1], Michel 2011 [2]
  - Only 1 empirical potential study: Catlow 1978 [3]

Objective of present work

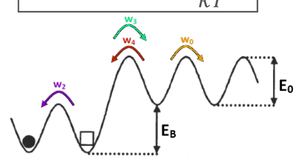
Study of krypton diffusion in UO_2 using atomic scale calculations combined with diffusion models adapted to the system studied [4]

Investigation of solute diffusion in solids using five-frequency model

- In crystals, diffusion occurs by succession of atomic hops between neighbouring sites in the lattice
- Diffusion models: link between elementary mechanisms at the atomic scale and macroscopic diffusion (Mehrer [5])
- Data needed: theoretically all elementary mechanisms
- Approximation to limit the number of mechanisms: no interaction beyond 2nd neighbours ⇨ 5-frequency model
- Elementary mechanisms considered
  - ω_0 (E_0, ν_0): vacancy migration between adjacent lattice positions in absence of impurity
  - ω_1 (E_1, ν_1): vacancy migration between first neighbour sites of the impurity
  - ω_2 (E_2, ν_2): vacancy-impurity exchange
  - ω_3 (E_3, ν_3): transition of the vacancy from a 1st neighbour site to a 2nd neighbour site (dissociation)
  - ω_4 (E_4, ν_4): reverse transition of ω_3 (association)
- Diffusion coefficient D can be obtained from atomic scale calculations of elementary mechanisms



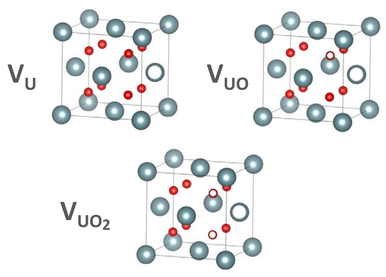
$$\omega_i = \nu_i \exp(-\frac{E_i}{kT})$$



$$D = D_0 \exp(-\frac{E_a}{kT})$$

Study of Kr diffusion in UO_2

- UO_2: binary compound ⇨ Further approximations needed to apply the 5-frequency model
- Kr: large impurity and high incorporation energy on O sublattice
  - ⇨ **Application of five-frequency model to U sublattice only, also a fcc lattice**
  - Reorganization of O sublattice taken into account in pathway calculations
- U atoms are then considered to be first nearest neighbours
- Distance between 2nd nearest neighbours in U lattice is large enough so that defect and impurity are non-interacting as 2nd nearest neighbours
- Traps considered: most stable vacancies in UO_2 and most favourable for Kr incorporation depending on non-stoichiometry in their most stable charge states; assisting vacancy: V_U



- Interstitial migration also considered

Atomic scale calculations

DFT+U using functional enabling description of Van der Waals interactions (VdW-DF) [6] combined to occupation matrix control to avoid convergence to metastable states

- Defect formation and Kr solution energies
- Elementary migration energies calculated using NEB: static method for pathway and saddle-point determination

Pair empirical potential: Buckingham form

Attempt frequencies obtained from phonon modes of defect at initial and saddle points

Calculating diffusion coefficient for impurity migration

General expression for defect-assisted diffusion of an impurity in a cubic structure

$$D = \frac{1}{6} * {d_2}^2 * f_2 * p * \omega_2$$

- d_2: jump distance of the impurity (a/$\sqrt{2}$, with a UO_2 cell parameter)
- p: probability of assisting defect located in neighbouring site of impurity

$$p = n e^{-\frac{(E_f + E_B + E_R)}{kT}}$$

n number of possible adjacent sites
E_f formation energy of vacancy in the bulk
E_B binding energy between impurity and vacancy
E_R reconfiguration energy

- f_2: solute correlation factor, related to direction impurity is likely to jump next (function of ω_1, ω_2, ω_3)

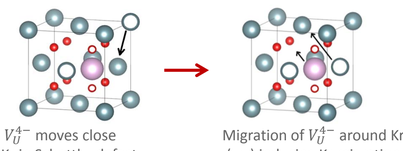
$$D = a^2 \nu_2 f_2 \, e^{-\frac{(E_f + E_2 + E_B + E_R)}{kT}}$$

In UO_2, stable complex between Kr and $V(U_2O)$ or $V(U_2O_2)$
⇨ no ω_2 mechanism: ω_1 drives the diffusion (Catlow)

Diffusion model was adapted and expression of D was derived

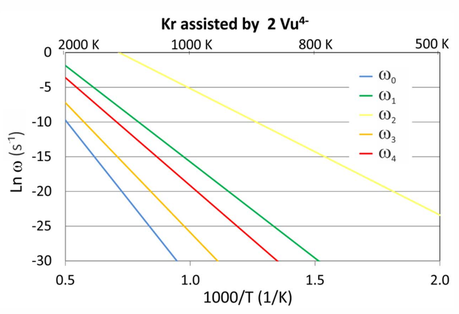
$$D = \frac{1}{6} * {d_1}^2 * f_1 * p' * \omega_1$$

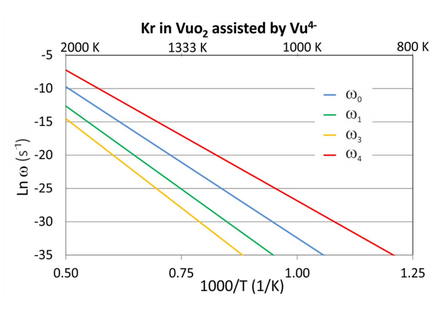
$$D = \frac{1}{4} a^2 \nu_1 f_1 \, e^{-\frac{(E_f + E_1 + E_B + E_R)}{kT}}$$

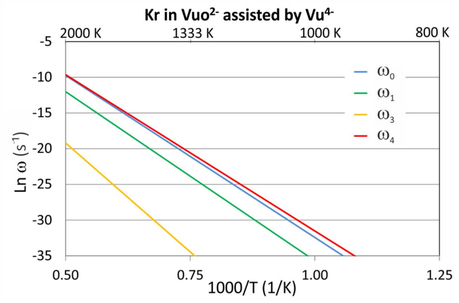


Not generally Arrhenius since prefactor depends on T
⇨ Study of limiting cases which depend on inequalities between ω_1, ω_2, ω_3

Results on elementary migration mechanisms







$\omega_0 \ll \omega_4$ for all traps and assisting vacancies, except for the migration of Kr assisted by two V_U^0 for which $\omega_0 \gg \omega_4$

⇨ vacancy moves faster far from impurity than from second to first neighbour of the impurity

For Kr assisted by two V_U^{4-},
$\omega_0 \ll \omega_3 \ll \omega_4 \ll \omega_1 \ll \omega_2$

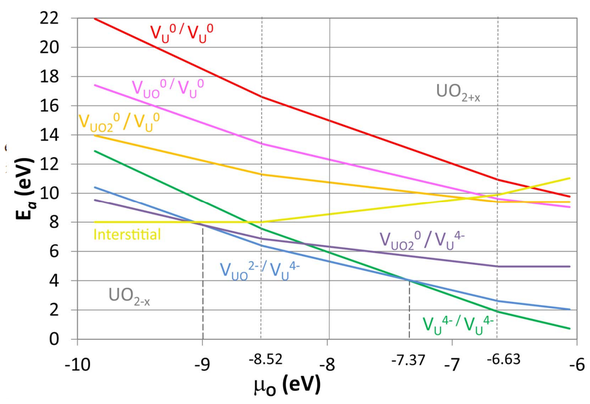
For Kr in V_{UO}^{2-} and $V_{UO_2}^0$ assisted by V_U^{4-},
$\omega_3 \ll \omega_1 \ll \omega_0 \ll \omega_4$

Activation energies to Kr diffusion vs. oxygen potential

Traps and assisting defects are charged ⇨ dependence of energies on oxygen and electron chemical potential, i.e. stoichiometry and doping level

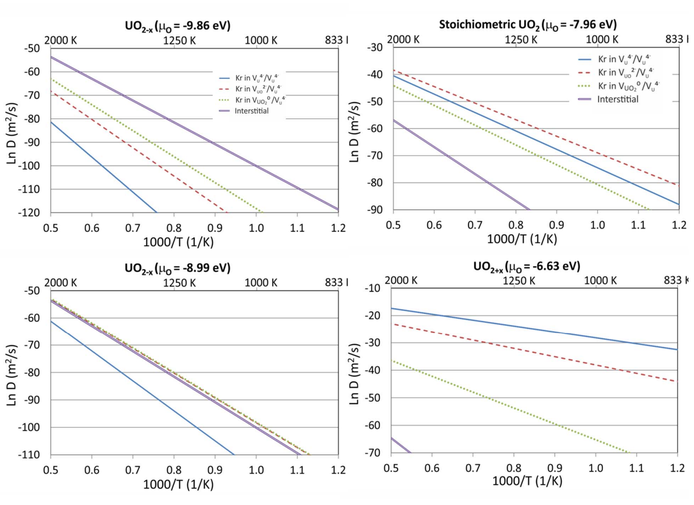
	Kr in V_U^{4-}/V_U^{4-}	Kr in V_{UO}^{2-}/V_U^{4-}	Kr in $V_{UO_2}^{0}/V_U^{4-}$
model	5-frequency	Catlow	Catlow
rate	$\omega_0 \ll \omega_4$	$\omega_0 < \omega_4$	$\omega_0 \ll \omega_4$
inequalities	$\omega_3 \ll \omega_1 \ll \omega_2$	$\omega_3 \ll \omega_1$	$\omega_1 \ll \omega_3$
equation	17	29	30
E_1	2.39	4.08	4.30
E_B	−0.54	−1.49	−1.24
E_f O-rich	−1.12	−1.12	−1.12
E_f stoich.	2.68	2.68	2.68
E_f U-rich	6.48	6.48	6.48
E_R O-rich	0.00	0.57	3.03
E_R stoich.	1.33	0.00	0.56
E_R U-rich	4.57	1.34	0.00
E_a O-rich	0.73	2.04	4.97
E_a stoich.	5.86	5.27	6.30
E_a U-rich	12.90	10.41	9.54

O-rich, μ_O : −6.06 eV
stoichiometric UO_2, μ_O = −7.96 eV
U-rich, μ_O = −9.86 eV



Assisting defect and activation energy depend on O potential

Diffusion coefficients of Kr in UO_2 vs. oxygen potential



Diffusion mechanism depends on O potential

- UO_{2-x} (-9.86 < μ_O < -9.06 eV)
  Kr diffusion by interstitial mechanism
  $D = 6.40 \times 10^{-8} \times e^{-\frac{E_a}{kT}}$ m²/s with E_a = 8.01 eV
- UO_{2-x} (-9.06 < μ_O < -8.99 eV)
  Kr diffusion assisted by Bound Schottky defect and V_U^{4-}
  $D = 5.35 \times 10^{-8} \times e^{-\frac{E_a}{kT}}$ m²/s with 7.80 < E_a < 8.01 eV
- UO_2 (-8.99 < μ_O < -7.37 eV)
  Kr diffusion assisted by V_{UO}^{2-} and V_U^{4-}
  $D = 7.08 \times 10^{-9} \times e^{-\frac{E_a}{kT}}$ m²/s with 4.09 < E_a < 7.80 eV
- UO_{2+x} (-7.37 < μ_O < -6.06 eV)
  Kr diffusion assisted by 2 V_U^{4-}
  $D = 3.07 \times 10^{-7} \times e^{-\frac{E_a}{kT}}$ m²/s with 0.73 < E_a < 4.09 eV

- Mechanisms and trends with non-stoichiometry similar to previous study of Xe by Andersson [7]
- For UO_{2+x}: migration assisted by two V_U^{4-} dominates and 0.73 < E_a < 4.09 eV
- Available experimental E_a (very probably obtained for hyperstoichiometric UO_2) are in this interval

Conclusions

- Determination of diffusion coefficient and corresponding mechanism as a function of non-stoichiometry
- Necessary data for higher scale models and for the interpretation of experimental results on defects and fission gas behaviour

Perspectives

- Calculation of concerted mechanisms involving O sublattice
- Calculation of entropic contribution
- Combination with literature results and new experimental results as a function of non-stoichiometry
- Application to more complex fuel materials for next generation reactors, in particular mixed oxide $(U,Pu)O_2$
- Need of better empirical potentials: not all calculations needed can be done in DFT+U

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