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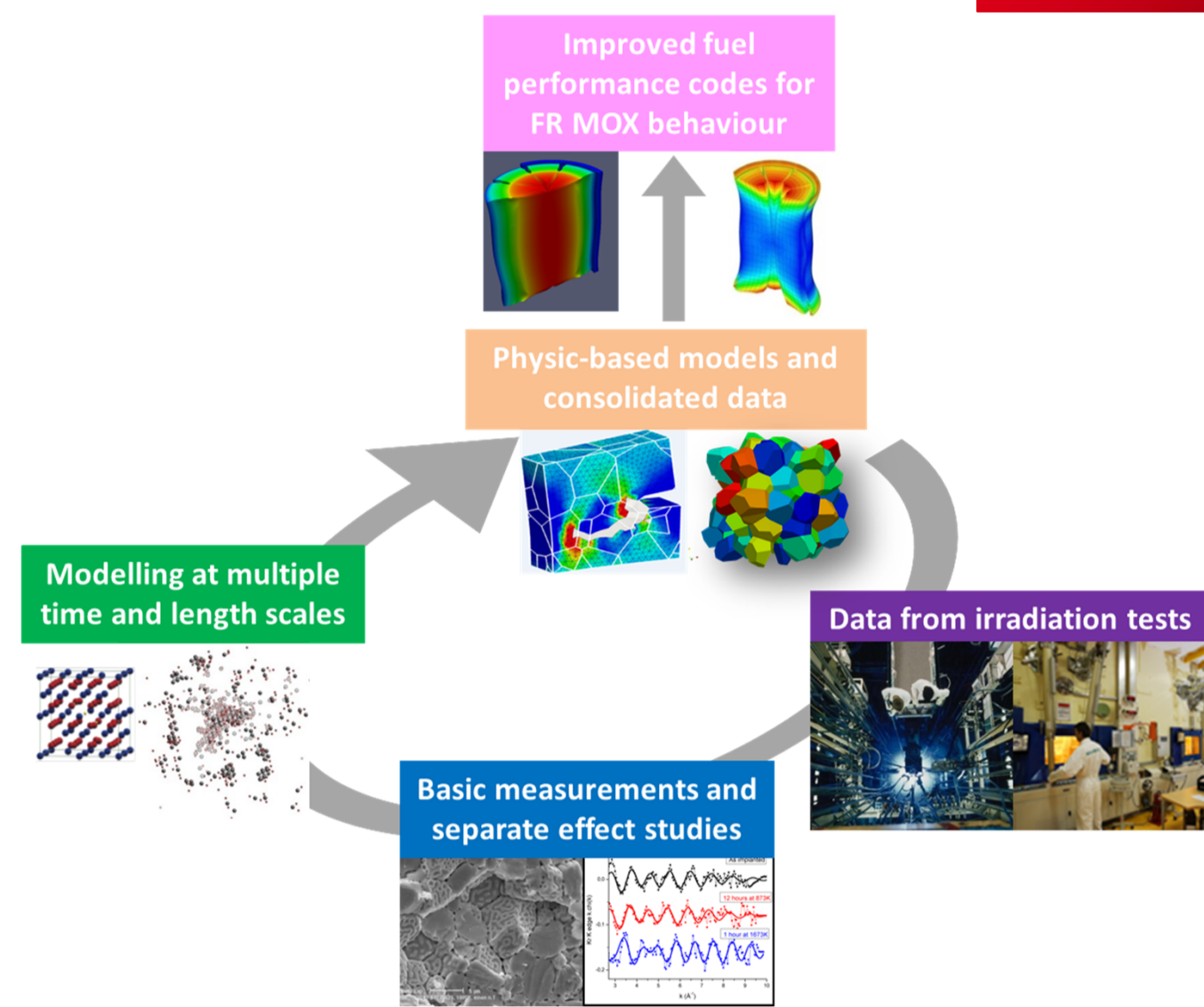
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# Atomic scale investigation of the diffusion of defects and fission gases in uranium dioxide

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## Context



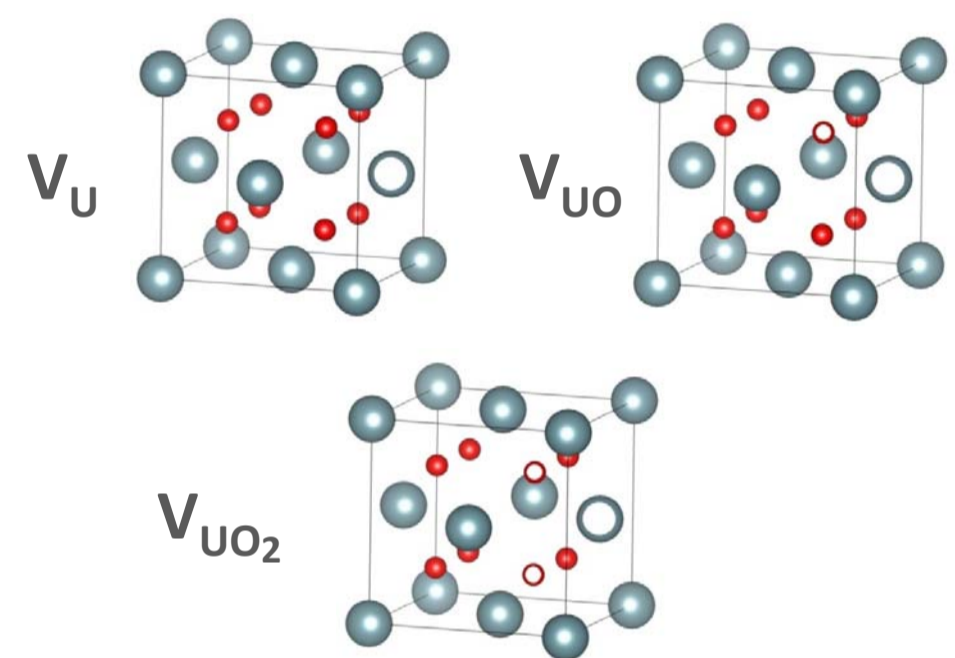
- Basic research approach applied to oxide nuclear fuels
- Actinide fission in reactor produces large quantities of defects and fission products, in particular fission gases (e.g. Xe, Kr), which have low solubility in the material
- Important consequences for fuel behaviour: swelling, decrease of thermal 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]

## Study of Kr diffusion in $UO_2$

- $UO_2$ : binary compound  $\Rightarrow$  Further approximations needed to apply the 5-frequency model
- Kr: large impurity and high incorporation energy on O sublattice
  - $\Rightarrow$  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 2<sup>nd</sup> nearest neighbours in U lattice is large enough so that defect and impurity are non-interacting as 2<sup>nd</sup> 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:  $V_U$



### 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

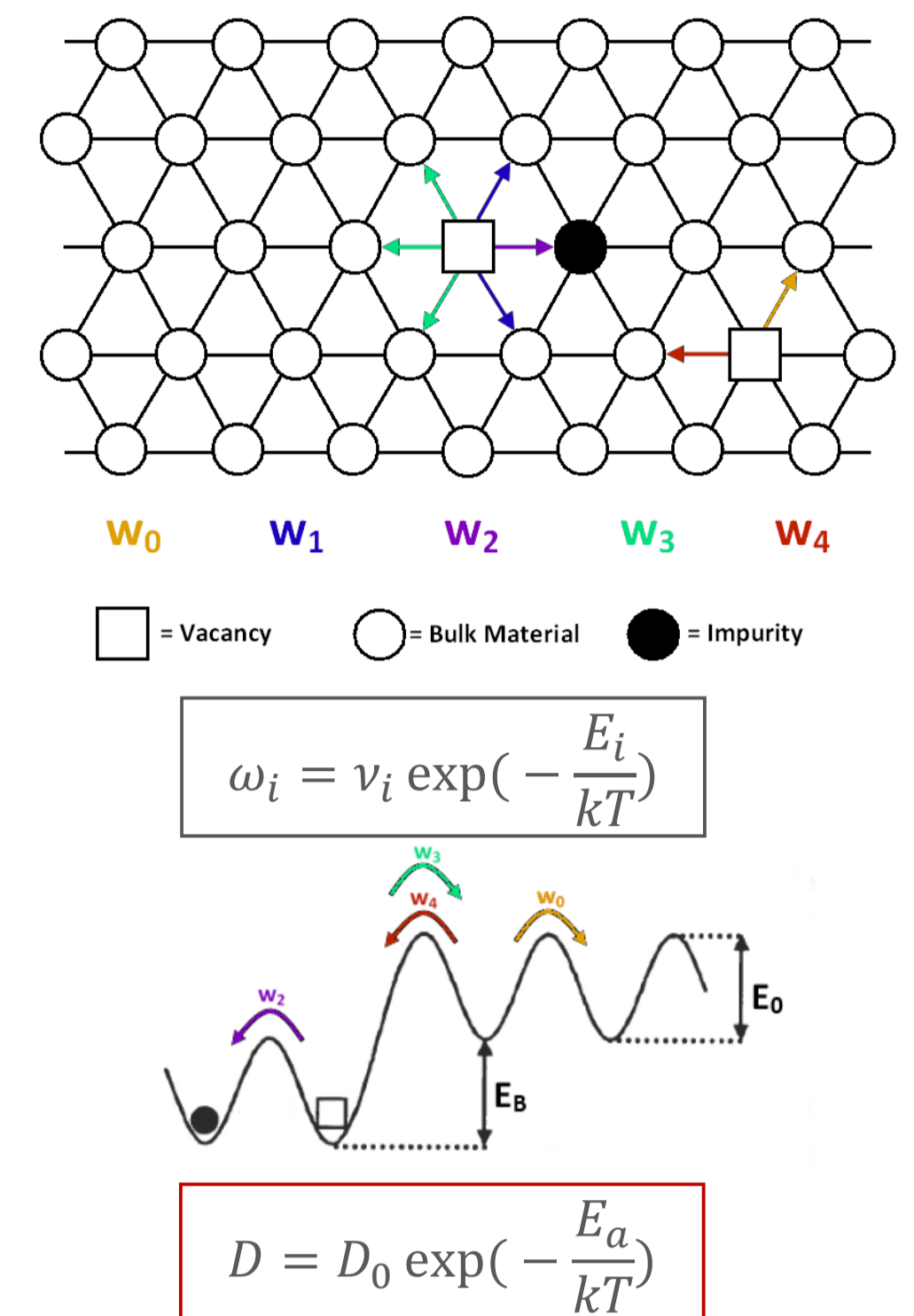
- Defect formation and Kr solution energies
- Elementary migration energies calculated using NEB: static method for pathway and saddle-point determination

Pair empirical potential: Buckingham form  
Attempt frequencies obtained from phonon modes of defect at initial and saddle points

- Interstitial migration also considered

## 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 (Mehrner [5])
- Data needed: theoretically all elementary mechanisms
- Approximation to limit the number of mechanisms: no interaction beyond 2<sup>nd</sup> neighbours  $\Rightarrow$  5-frequency model
- Elementary mechanisms considered
  - $\omega_0 (E_0, v_0)$ : vacancy migration between adjacent lattice positions in absence of impurity
  - $\omega_1 (E_1, v_1)$ : vacancy migration between first neighbour sites of the impurity
  - $\omega_2 (E_2, v_2)$ : vacancy-impurity exchange
  - $\omega_3 (E_3, v_3)$ : transition of the vacancy from a 1<sup>st</sup> neighbour site to a 2<sup>nd</sup> neighbour site (dissociation)
  - $\omega_4 (E_4, v_4)$ : reverse transition of  $\omega_3$  (association)
- Diffusion coefficient  $D$  can be obtained from atomic scale calculations of elementary mechanisms



## 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  $\omega_1, \omega_2, \omega_3$ )

$$D = a^2 v_2 f_2 e^{-\frac{(E_f + E_2 + E_B + E_R)}{kT}}$$

In  $UO_2$ , stable complex between Kr and  $V(U_2O)$  or  $V(U_2O_2)$   
 $\Rightarrow$  no  $\omega_2$  mechanism:  $\omega_1$  drives the diffusion (Catlow)

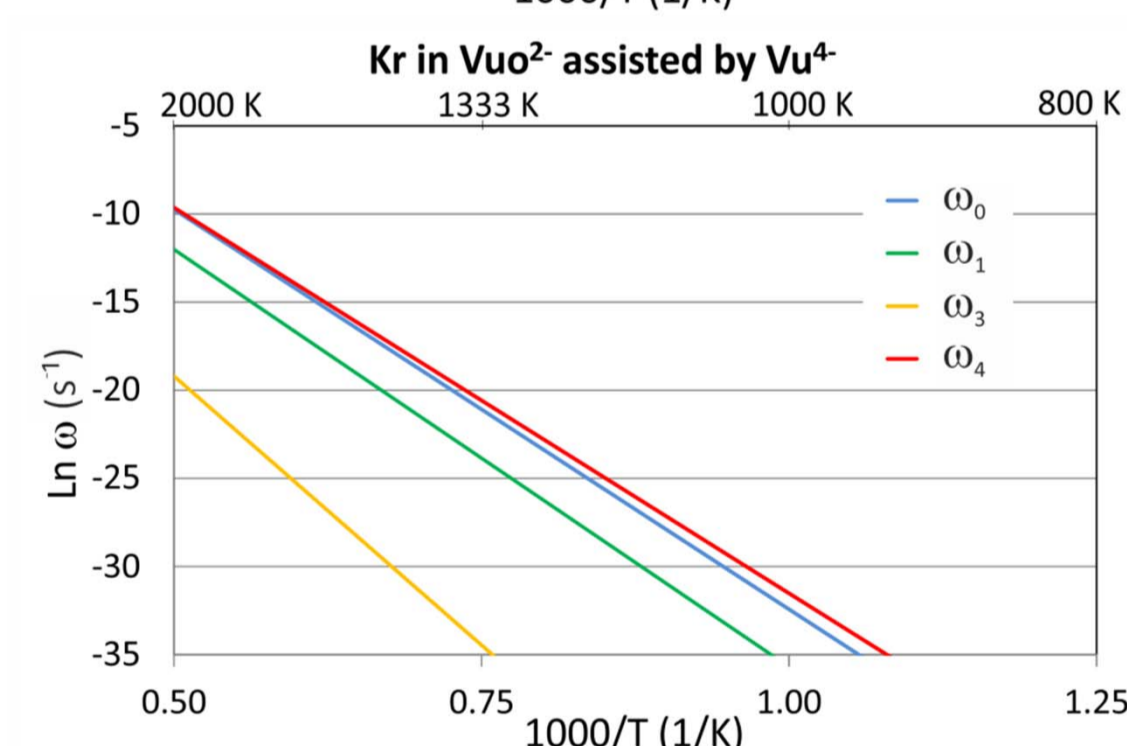
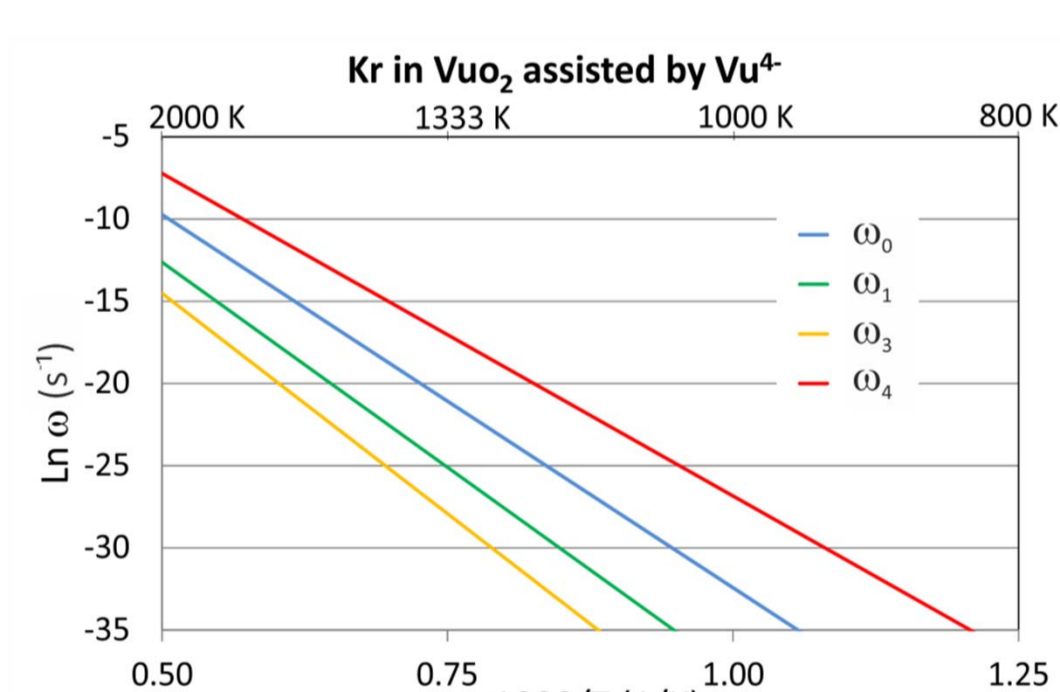
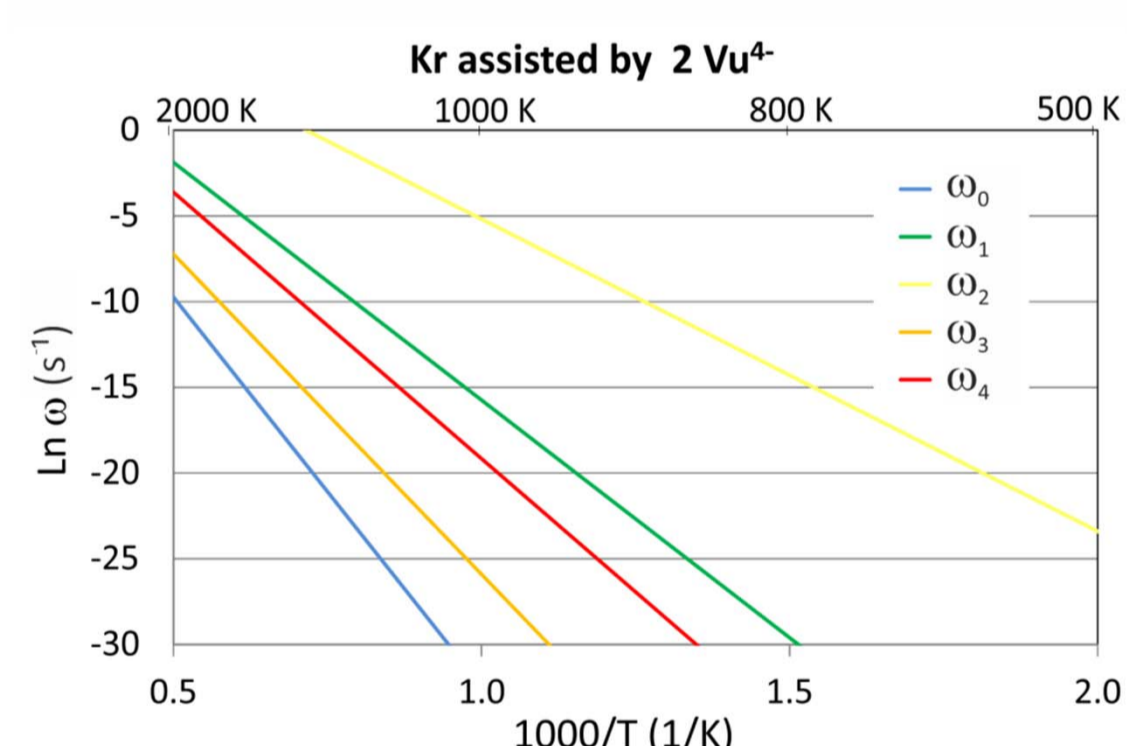
Diffusion model was adapted and expression of  $D$  was derived

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

$$D = \frac{1}{4} a^2 v_1 f_1 e^{-\frac{(E_f + E_1 + E_B + E_R)}{kT}}$$

Not generally Arrhenius since prefactor depends on T  
 $\Rightarrow$  Study of limiting cases which depend on inequalities between  $\omega_1, \omega_2, \omega_3$

## Results on elementary migration mechanisms



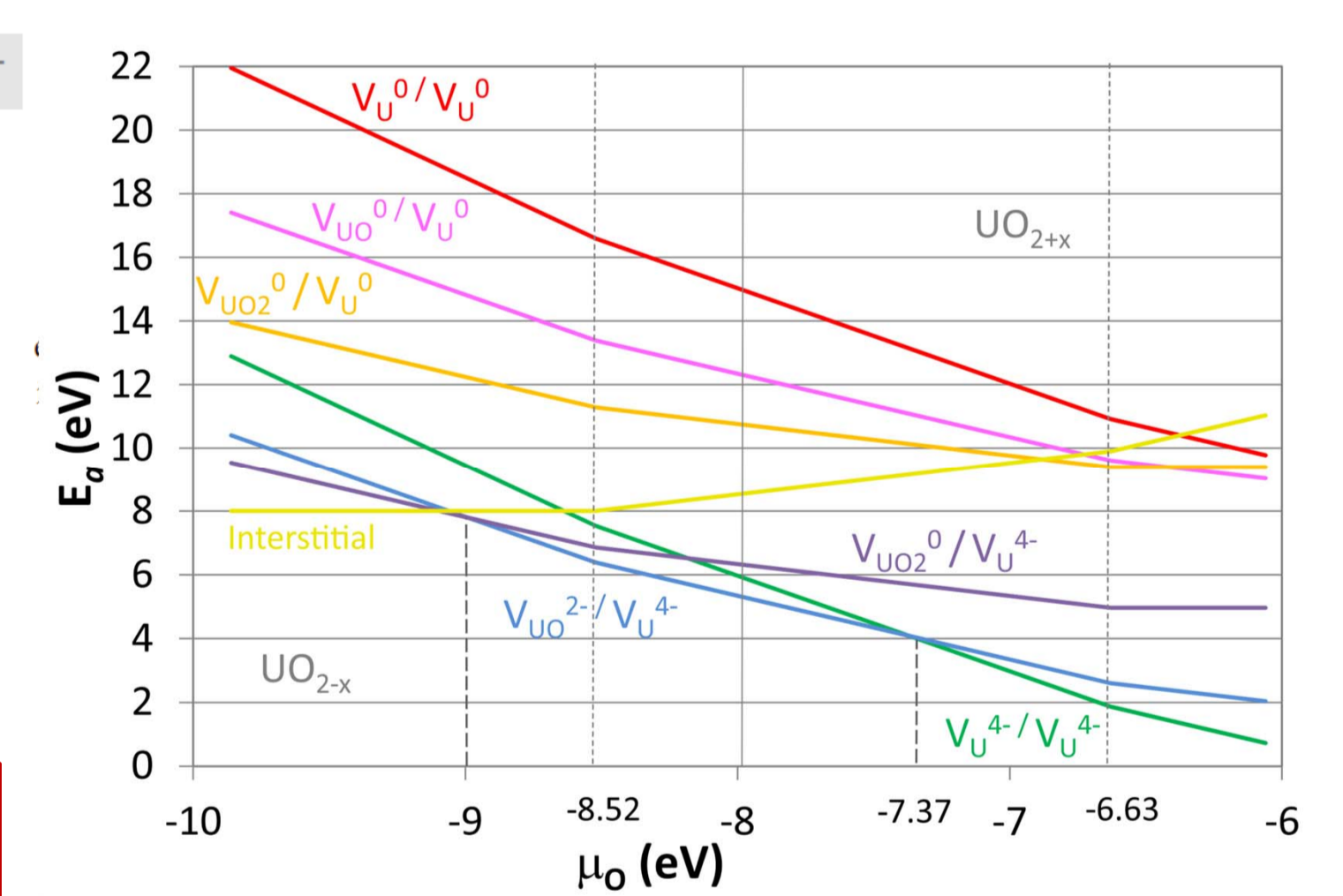
$\omega_0 \ll \omega_4$  for all traps and assisting vacancies, except for the migration of Kr assisted by two  $V_U^0$  for which  $\omega_0 \gg \omega_4$   
 $\Rightarrow$  vacancy moves faster far from impurity than from second to first neighbour of the impurity  
For Kr assisted by two  $V_U^{4-}$ ,  
 $\omega_0 \ll \omega_3 \ll \omega_4 \ll \omega_1 \ll \omega_2$   
For Kr in  $V_{UO_2}^{2-}$  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  $\Rightarrow$  dependence of energies on oxygen and electron chemical potential, i.e. stoichiometry and doping level

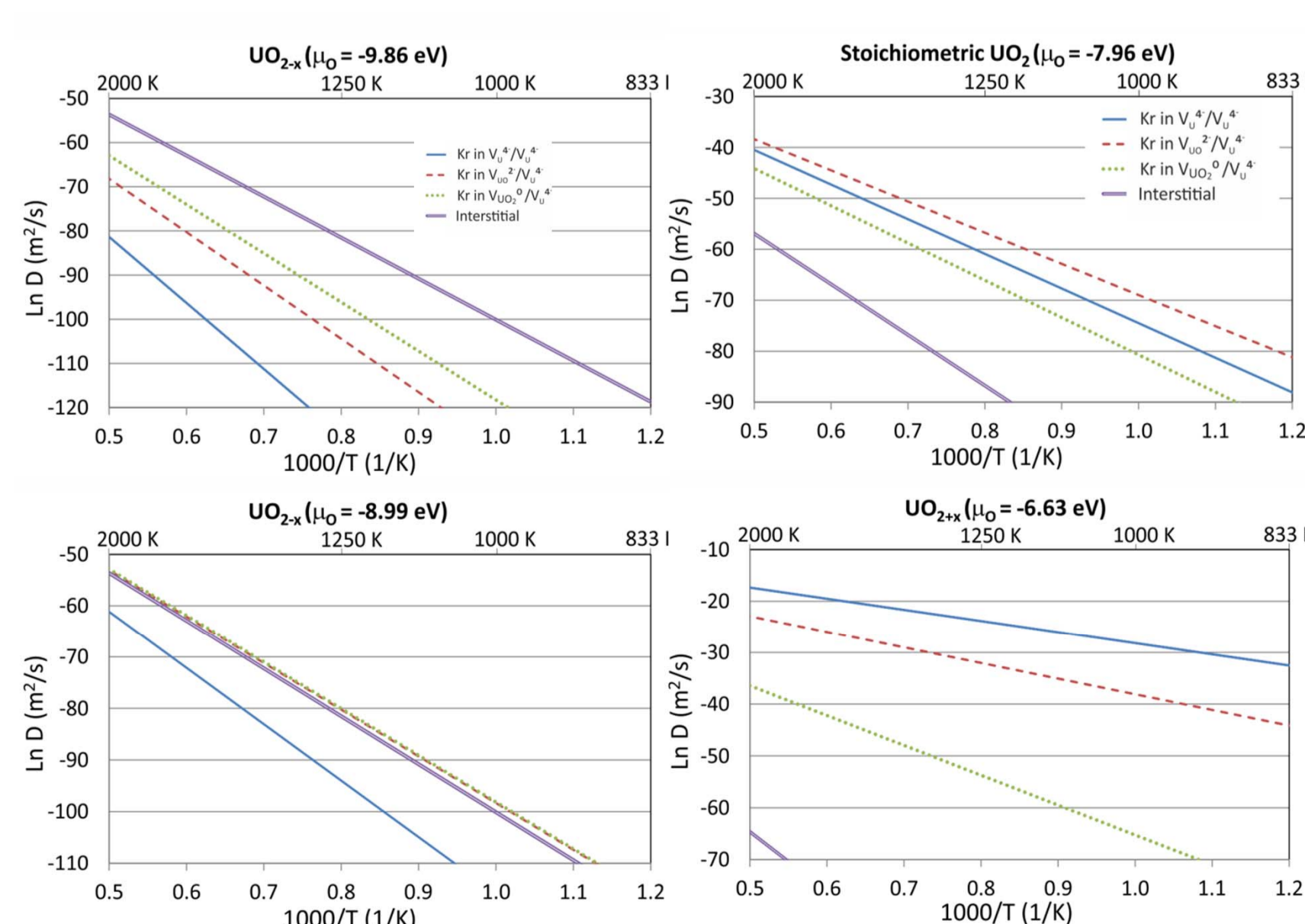
	Kr in $V_U^0/V_U^{4-}$	Kr in $V_{UO_2}^{2-}/V_U^{4-}$	Kr in $V_{UO_2}^0/V_U^{4-}$
model	5-frequency	Catlow	Catlow
rate	$\omega_0 \ll \omega_4$	$\omega_0 < \omega_4$	$\omega_0 \ll \omega_4$
inequalities	$\omega_3 \ll \omega_1 \ll \omega_2$	$\omega_3 \ll \omega_1$	$\omega_1 \ll \omega_3$
equation	17	29	30
$E_i$	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,  $\mu_O = -6.06$  eV  
stoichiometric  $UO_2$ ,  $\mu_O = -7.96$  eV  
U-rich,  $\mu_O = -9.86$  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

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