Diffusion of Zr, Ru, Ce, Y, La, Sr and Ba fission products in UO₂

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Abstract

The diffusivity of the solid fission products (FP) Zr (Zr⁴⁺), Ru (Ru⁴⁺, Ru³⁺), Ce (Ce⁴⁺), Y (Y³⁺), La (La³⁺), Sr (Sr²⁺) and Ba (Ba²⁺) by a vacancy mechanism has been calculated, using a combination of density functional theory (DFT) and empirical potential (EP) calculations. The activation energies for the solid fission products are compared to the activation energies for Xe fission gas atoms calculated previously. Apart from Ru, the solid fission products all exhibit higher activation energies than Xe. For all solid FPs except Y³⁺, the migration of the FP has lower barrier than the migration of a neighboring U atom, making the latter the rate limiting step for direct migration. An indirect mechanism, consisting of two successive migrations around the FP, is also investigated. The calculated diffusivities show that most solid fission products diffuse with rates similar to U self-diffusion. However, Ru, Ba and Sr exhibit faster diffusion than the other solid FPs, with Ru³⁺ and Ru⁴⁺ diffusing even faster than Xe for T < 1200 K. The diffusivities correlate with the observed fission product solubility in UO₂, and the tendency to form metallic and oxide second phase inclusions.

1. Introduction

In nuclear reactors, the ²³⁵U ions in the UO₂ fuel fission, thus yielding a number of different fission products. The presence of these fission products impacts fuel performance by, for example, changing the fuel thermal conductivity and contributing to swelling that leads to mechanical interaction with the clad [1]. The fission products can be categorized according to their chemistry and interaction with the UO₂ matrix [2], i.e. noble gas atoms (He, Xe, Kr) that are insoluble and form fission gas bubbles, other volatile elements (halogens, e.g., Br and I), elements that form metallic inclusions (noble metals, e.g., Ru), elements that form oxide inclusions (alkaline earths and transition metals, e.g., Ba, Sr, Mo and Zr), and elements that exist in solid solution (rare earths, e.g., Y, Ce and La). Among the fission products, the noble gases, followed by other volatiles, have received the most attention [3–7], due to their high impact on fuel performance. Furthermore, both of these groups are critical during accident scenarios, since they are easily spread through the air. Even though the solid fission products are not as critical as the previously mentioned groups, they have a significant impact on fuel behavior.

The solubility and trap site preference of solid fission products in UO_{2±x} has been studied using molecular statics and DFT calculations by several authors [8–21], and the preferred trap site is the starting point for analyzing diffusion. Existing studies generally agree that the solid fission products occupy uranium vacancy trap sites for all UO_{2±x} non-stoichiometries. We will see that for the fission products considered in this study, the preferred trap site in stoichiometric UO₂ is also a single uranium vacancy. This is in contrast with large fission gas atoms such as Xe, which occupy divacancy trap sites (one uranium vacancy and one oxygen vacancy) in stoichiometric UO₂ [22].

The kinetic properties of fission products have received much less attention than their solution thermodynamics. Among the references above, only Busker *et al.* attempted to calculate the activation energy for

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Table 1: Description of the migration (G_m) and binding (G_b) free energy for the calculation of the activation energy (Eq. 1).

Mechanism	G_m		G_b
U self-diffusion	$G_m^{V_U}$	migration $U \rightarrow V_U$ (no FP)	NA
Direct FP	G_m^{FP}	migration $FP_U \rightarrow V_U$	binding of V_U to FP_U
Direct U	$G_m^{V_U^B}$	migration $U_{FP} \rightarrow V_U$	binding of V_U to FP_U
Indirect U	$G_m^{V_U^{ind}}$	migration $U_{2nn} \rightarrow V_U$	binding of V_U to FP_U

Table 2: Thermodynamic parameters describing fission product diffusion in $UO_{2\pm x}$ derived from DFT [6]. Data entries that were not calculated from DFT are labeled by “*” and the corresponding references are listed.

Energy (eV)		Entropy (kB)		Defect description
E_{O_I}	-0.50	S_{O_I}	-5.20	Oxygen interstitial
E_S	7.88	S_S	14.78	Schottky defect
E_{eh}	1.75	S_{eh}	0.73	Electron-hole pair
E_{FP_O}	4.34	S_{FP_O}	10.55	Frenkel pair
$E_{pO_2}^{H_2}$	5.1* [23]	$S_{pO_2}^{H_2}$	10.68* [23]	Oxygen buffering reaction

diffusion of Ru [14], using empirical potentials. In the present study, the diffusion rates of the Zr (Zr^{4+}), Ru (Ru^{4+}), Ce (Ce^{4+}), Y (Y^{3+}), La (La^{3+}), Sr (Sr^{2+}), and Ba (Ba^{2+}), solid fission products (FP) are determined. Although most of these species conserve their charge when introduced in UO_2 , previous work reported that Ru^{3+} , and not Ru^{4+} , is the stable form for Ru ions in UO_2 [14]. For this reason, both species were investigated. A combination of density functional theory (DFT), and empirical potentials (EP), calculations was used to calculate the diffusion activation energy and the diffusion pre-exponential factor. The diffusion coefficients are compared to recently published results for Xe diffusion in stoichiometric UO_2 [6]. Although not exhaustive, the present selection of solid FPs spans a representative range of positive charge states (2+, 3+, 4+), and ionic radii (0.62 to 1.42 Å).

The following section (Sec. 2) presents the methods used to calculate diffusivity, including the point defect model used to determine the activation energy and the diffusion coefficient (2.1), the DFT calculations (2.2), and the EP calculations (2.3). Sec. 3 discusses the migration barriers and activation energy (3.1), and the diffusivity of the solid FPs (3.2). Finally, conclusions are presented in Sec. 4.

2. Methods

2.1. Point defect model of the activation energy for fission product diffusion

Diffusion of solid fission products occurs by a vacancy mechanism, similar to that recently elucidated for the Xe fission gas [6]. However, as opposed to fission gas atoms, which prefer divacancy trap sites (one uranium vacancy and one oxygen vacancy) [6, 9, 15, 22, 24], solid fission products usually favor the uranium vacancy trap site (FP_U , where FP is the fission product) in stoichiometric UO_2 . This was shown for Zr [24], Ru [9], Ce [9, 24], Y [24], La [24], Sr [9, 15, 24], and Ba [24]. We also independently verified this conclusion for three FPs: Ru^{4+} , La^{3+} , and Sr^{2+} . In agreement with the previous studies, we found that all three FPs prefer the single uranium vacancy trap site over the divacancy, by 1.9, 1.0, and 0.8 eV, respectively. This motivates us to limit the study of fission product diffusion mechanisms to uranium vacancy trap sites only.

Diffusion is enabled by first binding a vacancy to the trap site. Charge compensation for aliovalent ions occurs by holes ($h^\bullet$), however for stoichiometric UO_2 all trap sites are fully charged (no bound holes), which implies that the trap sites are $FP_U^\times$ for tetravalent, FP_U' for trivalent and FP_U'' for divalent fission products (the Kröger-Vink notation [25] was used to label the trap sites). Since the vacancy is also assumed to be

Figure 1: Migration mechanisms involving a solid FP in UO_2 . a: direct migration of the FP to V_U . b: direct migration of U_{FP} (U atom neighboring FP) to V_U . c: indirect migration. A two-step process allows the FP to remain near V_U . Oxygen atoms on the migration path were shaded in a and c to facilitate the visualization.

fully charged, the mobile clusters are thus FP_{U_2}'''' for tetravalent, FP_{U_2}''''' for trivalent and FP_{U_2}'''''' for divalent fission products. The binding of the vacancy then allows for the next step, which is for the fission product atom to migrate from its initial trap site to the neighboring vacancy. In order for net diffusion to occur, after the fission product migration step, the vacancy must move to a new position neighboring the fission product. This may occur either by detaching the vacancy completely from the trap site (U self-diffusion), by partial detachment (indirect U migration), or by intra-cluster vacancy migration (direct FP / direct U migration). The last two migration paths are illustrated in Fig. 1: the direct migration consist of the direct migration of the FP (FP_U), and a neighboring U atom (U_{FP}), to the vacancy (V_U), Figs. 1-a and 1-b. The diffusion rate of this direct mechanism is dictated by the slowest of these two steps. The indirect migration mechanism was described by Thompson and Wolverton [26], and corresponds to the consecutive migrations of a second-neighbor uranium atom (U_{2nn}) to the vacancy, followed by the migration of a neighboring U to the new vacancy site, as shown in Fig. 1-c.

The activation energy for these distinct mechanisms is:

$$G_a = G_m + G_b + G_f^{V_U}. \quad (1)$$

G_m is the migration free energy, and G_b is the vacancy binding free energy. For each mechanism (i.e. U self-diffusion, direct FP / direct U, and indirect U), the details of these energies are described in Table 1. For Xe, the binding energy of the vacancy to the trap site is always high and negative enough to favor the direct migration of the FP cluster. However, because the vacancy binding energy for the solid fission products is expected to be less negative (less attractive), alternative mechanisms must be taken into account. For the indirect mechanism, since the second part of the mechanism typically shows a much smaller migration barrier, only the first step will be used to compute the diffusion coefficient. In Eq. 1, $G_f^{V_U}$ is the effective vacancy formation free energy. For intrinsic conditions in stoichiometric UO_2 (no irradiation), it is given by [27]:

$$G_f^{V_U} = 2G_{O_I} + G_S - 2G_{e_h} - G_{FP_O} + G_{p_{O_2}}. \quad (2)$$

Each of these contributions has already been estimated from DFT [6], following the work of Jackson *et al.* for the calculation of the defect entropies [28]. The same parameters will be used in this study, see Table 2.

The uranium vacancy is fully charged (no bound holes) in this model. The electron and hole concentrations are assumed to be governed by excitations across the band gap, which implies that the temperature must be high enough for this process to dominate over contributions from extrinsic defects (e.g., impurities). Moreover, the analytical expression assumes that $[e'] \approx [h^\bullet]$ (approximately equal concentrations of electrons and holes). This assumption pins the Fermi level close to the mid-gap position. The value of the $G_{p_{O_2}}$ term is determined by the prevailing chemical boundary conditions [6]. In this study the oxygen partial pressure is assumed to be controlled by the H_2O buffering reaction:

The methodology to calculate the diffusion coefficient was discussed in Ref. [6], expanding on the model described by Dorado *et al.* for uranium diffusion [27]. The general form of the diffusivity is given by:

$$D = D_0 \times \exp\left(-\frac{E_a}{k_B T}\right), \quad (4)$$

where E_a is the defect activation energy, obtained similarly to G_a (Eq. 1); k_B is the Boltzmann constant, T the temperature, and D_0 is the temperature independent pre-exponential factor. The diffusivity can be rewritten as:

$$D = \beta \times \exp\left(\frac{S_b}{k_B}\right) \times \nu_0 \exp\left(\frac{S_m}{k_B}\right) \times C_{V_U} \times \exp\left(-\frac{E_m + E_b}{k_B T}\right), \quad (5)$$

where C_{V_U} is the concentration of uranium vacancies:

$$C_{V_U} = \alpha \times \exp\left(-\frac{G_f^{V_U}}{k_B T}\right). \quad (6)$$

The coefficient $\alpha = 1.44 \cdot 10^{-13}$ is a multiplication factor associated with the O_2 partial pressure, and is introduced in order to allow direct comparison with Xe results [6]. In Eq. 5, ν_0 is the characteristic vibrational frequency, and forms the attempt frequency $\nu_m = \nu_0 \exp(S_m/k_B)$, with S_m , the binding entropy of the vacancy to the trap site. The β pre-factor:

$$\beta = \frac{1}{6} \times 4 \times f \times Z \times S^2, \quad (7)$$

contains the jump distance S , taken here as the nearest neighbor distance in UO_2 , $S = 3.87 \text{ \AA}$ with the Buckingham potential, Z , the number of neighboring jump sites (12 for the cation sublattice), and f , the correlation factor (here approximated as 1). The “4” multiplicative factor is due to the ratio of oxygen to uranium sites in UO_2 ($2^2 = 4$) [29].

Finally, the pre-exponential factor D_0 is:

$$D_0 = \frac{2\alpha}{3} \times f \times Z \times S^2 \times \nu_m \times \exp\left(\frac{S_f^{V_U} + S_b}{k_B}\right) \quad (8)$$

In order to complete the calculation of the fission product activation energy and diffusivity, the binding and migration parameters remain to be determined. All free energy terms can be decomposed into energy and entropy contribution, $G = E - T \cdot S$, which will be calculated by DFT or EP. The migration energy and vacancy binding energy, Eqs. 1 and 8, and Table 1, are obtained by DFT. However, the more costly calculations of the binding entropy, as well as the calculation of the attempt frequency ν_m , Eq. 8, are performed using empirical potentials.

2.2. Density functional theory calculations

The DFT calculations were performed according to the same methodology as in Ref. [6], which applied the Vienna Ab Initio Simulation Package (VASP) [30–32] to study the diffusion of Xe in $UO_{2\pm x}$. The electron exchange and correlation potential was described by the local density approximation (LDA) and the rotationally invariant version of the LDA+ U functional due to Lichtenstein *et al.* was used for the correlated U $5f$ electrons [33]. The electron wave function was calculated with the projected-augmented-wave (PAW) method, and core states were taken into account within the frozen core approximation [34, 35]. In accordance with earlier LDA+ U studies of UO_2 , the U and J values were set to $U = 4.5 \text{ eV}$ and $J = 0.5 \text{ eV}$ [36]. Spin-polarization was included by assuming $1k$ antiferromagnetic ordering of the localized U spins.

Defect properties and migration barriers were calculated for a $2 \times 2 \times 3$ supercell expansion of the cubic fluorite unit cell (144 atoms for stoichiometric UO_2). The supercells were allowed to fully relax (both volume and atomic coordinates), and the internal structural parameters were relaxed until the total energy converged, or the Hellmann-Feynman forces on each ion were less than $0.02 \text{ eV/\AA}$. k space integration was performed on a $2 \times 2 \times 1$ Monkhorst-Pack k -point mesh [37] with a Gaussian smearing of 0.05 eV , and the plane-wave cut-off energy was set to 500 eV . The migration barriers were calculated using the climbing-image nudged elastic band (NEB) methodology [38].

The issue of metastable electronic solutions was addressed by using the occupation matrix control and U ramping methodology [39, 40], and all simulations were performed without any assumption regarding the crystal symmetry. We always report data that corresponds to the lowest energy solution obtained, which corresponds to the phase with (very) small Jahn-Teller distortions of the oxygen sublattice.

Charged defects were accounted for by either adding or removing electrons from the supercells. This methodology, following the work of Lany and Zunger [41], was previously applied to U and Xe diffusion calculations in $UO_{2\pm x}$ [6, 22, 27]. Binding energies between fission product trap sites and uranium vacancies

Table 3: Parameterization of the Buckingham potential used in this study.

Interaction	A (eV)	ρ (Å)	C (eV/Å ⁶)	Ref
O ²⁻ -O ²⁻	9547.96	0.2192	32.0	[44]
U ⁴⁺ -O ²⁻	1761.78	0.3582	12.3	[45]
Zr ⁴⁺ -O ²⁻	1502.11	0.3477	5.1	[46]
Ru ⁴⁺ -O ²⁻	1215.78	0.3441	0.0	[46]
Ce ⁴⁺ -O ²⁻	1809.68	0.3547	20.4	[47]
Ru ³⁺ -O ²⁻	2988.58	0.29821	0.0	[14]
Y ³⁺ -O ²⁻	1766.40	0.33849	19.43	[48]
La ³⁺ -O ²⁻	2088.89	0.3460	23.25	[46]
Sr ²⁺ -O ²⁻	682.17	0.3945	0.0	[49]
Ba ²⁺ -O ²⁻	905.70	0.3976	5.43	[50]

were evaluated for the most relevant charge states of the defects [42, 43]. For stoichiometric UO₂ all defects are assumed to be fully charged. The migration barriers were also estimated for the fully charged defects. The volume of the supercell was fixed at the volume of the initial state for the migration process.

2.3. Empirical potentials calculations

As was mentioned earlier (Sec 2.1), the costly calculation of the binding entropy of the uranium vacancy to the fission product, and the attempt migration frequency, see Eq. 8, were performed with empirical classical potentials. The Buckingham potential [51], was chosen to model the FP-O, U-O, and O-O pairwise interactions:

$$V(r) = A \times \exp\left(-\frac{r}{\rho}\right) + \frac{C}{r^6}, \quad (9)$$

where A, ρ , and C are constants, parameterized for the different elements, see Table 3. Although a number of empirical potentials exists for the calculation of pre-exponentials in UO₂ [52–55], we have chosen the parameters in Table 3 since they are a consistent set that includes a wide range of fission product cations. A cutoff $r_c=8$ Å was used for the pairwise interactions, while the U-U and FP-U long-range Coulombic interactions were calculated by the Ewald summation technique.

A $4 \times 4 \times 4$ supercell (768 atoms for stoichiometric UO₂) was used in our calculations. The lateral dimensions (~ 20 Å, more than twice r_c) were chosen big enough to avoid the influence of the image cells under periodic boundary conditions (PBC). The samples contain two neighboring uranium vacancies V_U , one being occupied by the fission product (FP_U). The cell size was first optimized for stoichiometric UO₂, and the atomic positions were then relaxed around the defect, while the cell volume was kept constant.

In order to calculate the quantities associated with the different migrations (see Table 1), NEB calculations with nine images were performed. The defect binding entropy calculation is based on the calculation of the normal modes of vibration [57]:

$$S = -k_B \sum_{n=1}^{3N-3} \ln\left(\frac{h\nu_n}{k_B T}\right) + (3N-3)k_B, \quad (10)$$

where N is the number of atoms in the system, ν_n the normal mode frequency, h and k_B the Planck and Boltzmann constants, and T the temperature. The vacancy binding entropy is then simply obtained as the difference $S_{unbound} - S_{bound}$, entropies for an unbound and bound vacancy, respectively. The modes themselves are calculated with the CLSMAN code [58], through diagonalization of the dynamical force matrix of the system (Hessian).

Table 4: Migration energy for the direct FP (E_m^{FP}), direct U (E_m^{VB}), and indirect U (E_m^{Vind}) mechanisms (Table 1), vacancy binding energy (E_b) and entropy $((S_b)_V)$, $\beta B \Delta V$ term (Eq. 11), and ionic radius [56] of the fission product ions in UO_2 . As reference, the migration barrier for uranium self-diffusion in UO_2 is also listed. All numbers from DFT refer to charged defects. The highest barrier, obtained from DFT, between the two direct diffusion mechanisms is shown in bold font.

Fission Product	E_m^{VB} (eV)		E_m^{FP} (eV)		E_m^{Vind} (eV)		E_b (eV)		$(S_b)_V$ (k_B)	$\beta B \Delta V$ (k_B)	Ionic rad. ($\text{\AA}$)
	DFT	EP	DFT	EP	DFT	EP	DFT	EP			
U^{4+}	4.73	6.90	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1.00
Zr^{4+}	4.05	5.77	3.72	5.85	4.51	6.95	-0.23	0.01	0.92	0.05	0.84
Ru^{4+}	2.82	5.19	2.26	4.15	5.62	7.20	-0.09	0.43	-1.36	-0.10	0.62
Ce^{4+}	4.87	6.75	4.37	6.89	4.76	6.92	-0.08	-0.02	0.04	0.04	0.97
Ru^{3+}	2.66	5.36	2.05	5.47	3.59	6.36	-0.30	0.43	0.91	-0.85	0.68
Y^{3+}	4.39	5.91	4.99	5.19	4.68	6.32	-0.47	-1.00	0.78	-1.03	1.02
La^{3+}	4.65	6.64	4.29	5.34	4.78	6.17	-0.14	-0.96	0.72	-1.33	1.16
Sr^{2+}	4.18	5.67	3.41	2.64	4.63	5.49	-0.72	-1.92	1.38	-1.63	1.26
Ba^{2+}	4.45	6.27	3.48	2.89	4.71	5.31	-1.06	-1.85	1.74	-2.69	1.42

It is to be noted that the calculated entropy corresponds to a constant-volume entropy, S_V . In order to get the pressure-constant entropy S_P , a contribution must be added [59]:

$$S_P = S_V + \beta B \Delta V, \quad (11)$$

where B is the bulk modulus, $\beta = \frac{1}{B} \left(\frac{\partial S}{\partial V} \right)_T$, and ΔV the relative volume change between the perfect and defective structures at zero pressure: $\Delta V = (V - V_0)/V_0$. Based on a previous study [6], $\beta B V_0 = 3888.4 k_B$.

Finally, the attempt frequency for the FP and U migrations is obtained through the Vineyard method [60]:

$$\nu_m = \prod_{n=1}^{3N-3} \nu_n^{defect} \bigg/ \prod_{n=1}^{3N-4} \nu_n^{saddle}. \quad (12)$$

ν^{defect} and ν^{saddle} are the normal modes for the initial configuration, and the migration saddle. The three imaginary translational modes are excluded, as well as one extra negative mode corresponding to the saddle mode.

3. Results

3.1. Barriers and activation energies

The DFT and EP calculated values of the migration energy (for each mechanism, see Table 1), and vacancy binding energy, are listed in Table 4, which also contains the corresponding ionic radius and the binding entropy for each FP. From Table 4, we can also assess the quality of the empirical potentials, by comparing the EP migration, binding and activation energies with DFT values. The migration energies follow almost the same order: $\text{Ce} \sim \text{U} \rightarrow \text{La} \rightarrow \text{Ba} \rightarrow \text{Y} \rightarrow \text{Sr} \rightarrow \text{Zr} \rightarrow \text{Ru}$, only with the exception of switching $\text{Zr} \leftrightarrow \text{Sr}$. Quantitatively, the migration energies obtained from EP calculations are higher, by 1-2 eV, except for the 2+ ions for which the energy is actually smaller. Similar overestimation is observed for U self-diffusion, see Table 4. The main qualitative discrepancies are observed for the defect binding energies, and can be explained by the simple treatment of the charges with empirical potentials. The relative energy difference, observed with DFT calculations, between the U and FP migration energies, is also quite well reproduced by EP. For Ru^{4+} , La, Sr, and Ba, the FP migration energy is lower than that of U. For Ru^{3+} , Ce and Zr, DFT also gives $E_m^{FP} < E_m^{VB}$, while EP gives the opposite relation. However, with both DFT and EP, the energies are close. The main disagreement occurs for Y, for which the difference $E_m^{FP} - E_m^{VB}$

Figure 2: The activation energy for diffusion of a range of solid fission products and the Xe [6] fission gas. The activation energy was calculated for the limiting rate of the direct mechanism, with DFT (see Eq 1 and Tables 1 and 4).

goes from +0.65 eV with DFT to -0.72 eV with EP. Nevertheless, the qualitative agreement between EP and DFT for the migration barriers gives us confidence that the entropy and attempt frequency calculations can be estimated correctly by EP.

The activation energies for the preferred mechanism are compared in Fig. 2, along with that of Xe [6]. Note that Xe occupies a trap site consisting of one uranium and one oxygen vacancy (fully charged) in UO_2 , as opposed to a uranium vacancy for the solid fission products. We are able to draw a couple of qualitative conclusions from these results. The activation energies can be classified according to whether the fission product is soluble in UO_2 (Y, La and Ce), forms metallic inclusion (Ru) or forms oxide inclusions (Ba and Sr). Zr is intermediate between being in solid solution and forming oxide inclusions and the activation energy also falls in-between those two cases. All of these properties are related to the size of the fission product ions and in particular the difference in size compared to the U^{4+} ion (see Table 4). The highest activation energies are obtained for ions with radii close to the uranium ion (Y^{3+} , Ce^{4+} , La^{3+} and to some extent Zr^{4+}), while low activation energies are observed when the difference is large (Sr^{2+} , Ba^{2+} and $\text{Ru}^{3+}/\text{Ru}^{4+}$). With the exception of Ru, all the fission products have higher activation energies than the fission gas atoms and thus are expected to diffuse slower than the latter. Ce^{4+} on the other hand, which has atomic radius and activation energy almost identical to U, is expected to diffuse with similar rate.

Figure 3: Diffusion path for Ba in UO_2 , through a uranium vacancy V_U . a- path calculated from EP calculations. b- path calculated from DFT calculations. c- xz projection, common to a and b. An oxygen atoms was shaded in a and b to facilitate the visualization

3.2. Diffusivity

The pre-exponential factor, attempt frequency, activation energy, and active mechanism are reported in Table 5. In addition, for each FP, the diffusivity for the three mechanisms is plotted in Fig. 4, (4-a to 4-d). As was mentioned earlier, the FP / U direct migrations are part of the same mechanism, so the important step for the direct mechanism is the rate limiting step (i.e. the slowest one). However, the direct and indirect mechanisms are independent, such that the relevant rate (active mechanism) is now the fastest of the two.

The limiting rate for the direct diffusion is in general the direct U migration. Exceptions are: Ru^{4+} and Zr (Fig. 4-a and b), for which the FP migration becomes the limiting direct step above a certain temperature ($T \sim 1500$ K and 1700 K, respectively); Ce (Fig. 4-b), for which all mechanisms are relatively close; and Y (Fig. 4-c), where the direct FP migration is clearly the limiting step. This comes as no surprise, as the direct FP barrier is larger than the direct U barrier for Y, as opposed to all other solid FP (see Table 4). For Ba^{2+} and Sr^{2+} (Fig. 4-d), a qualitative difference was observed in the fission product migration paths (direct FP), between EP and DFT. The direct FP migration path for Ba, obtained from DFT and EP calculations, are shown in Fig. 3 (similar results are observed for Sr^{2+}). With DFT, the FP atom follows

Figure 4: Diffusion coefficient for solid fission products in UO_2 . For each solid FP, the direct FP, direct U, and indirect U migration mechanisms are shown, along with U self-diffusion, and Xe [6] as references. a: Ru^{3+} and Ru^{4+} . b: Zr^{4+} and Ce^{4+} . c: Y^{3+} and La^{3+} . d: Sr^{2+} and Ba^{2+} .

a curved path towards the vacancy site (3-b). The same path is observed for all FPs, as well as uranium self-diffusion. With empirical potentials however, the 2+ ions follow a straight line towards the vacancy (3-a). This disparity was not observed with the other ions, and most likely the charge treatment with the Buckingham potential is the cause. In addition, for Ba, the NEB calculations did not converge to a saddle configuration, such that the direct FP migration path was not available to calculate the diffusion coefficient. However, if Sr, with the same charge and also large ionic radius, is any indication, the limiting rate will be the direct U migration step.

In addition to the direct U or FP mechanism, the indirect U migration mechanism is relevant for three solid FPs: Zr, Ce, and Y. For Zr (Fig. 4-b), all three mechanisms have similar rate at high temperature ($T \sim 2500$ K), however the indirect mechanism is noticeably slower for lower T . For Ce (Fig. 4-b), as discussed just above, the three mechanisms yield similar diffusivity, with the direct U and indirect mechanisms nearly indistinguishable. The fact that Ce and U have similar ionic radius, and the very close activation energy for both mechanisms explains this behavior. Finally, the indirect mechanism is the main active mechanism for Y (Fig. 4-c), with higher diffusion rate than the direct migrations.

Fig. 5 summarizes these results, by showing the diffusion from the active mechanism for each FP. We see that solid FPs can be separated into three groups according to their diffusion rate, and corresponding to the groups described earlier in this paper. The elements that form solid solution in UO_2 , Y, Ce, and La, exhibit slow diffusion, analogous to U self-diffusion. The second group, composed of the elements forming oxide inclusions, Sr and Ba, diffuses at rates between U and the fission gas atom Xe. Zr, which is intermediate between forming a solution and oxide inclusions, exhibits diffusivity in between as well. Finally, the elements forming metallic inclusions, Ru^{3+} and Ru^{4+} , display the fastest diffusion, comparable to that of Xe. Those diffuse even faster than Xe, for temperatures below 1200 K and 1500 K, respectively. A noteworthy phenomena is the switch from a direct U limiting rate to a direct FP limiting rate for Ru^{4+} , at $T \sim 1500$ K. A similar switch is observed for Zr as well, at $T \sim 1700$ K.

The observation of slow diffusion for La can be related to the usage of Nd as a standard fuel burn up indicator. A primary reason that ^{148}Nd is used as a burn up indicator is that it has been assumed to not migrate in UO_2 [61, 62]. Although operational experience has shown that Nd diffusion in UO_2 is likely to be negligible, there are no explicit studies of Nd diffusion. In the present study, we were not able to perform calculations for Nd diffusion, as an LDA PAW potential does not exist. However, given their similar ionic radii (1.109 vs 1.16 Å [56]), we can assume that Nd diffuses in a similar manner to La. From Fig. 5, it is clear that the diffusivity of Nd in UO_2 is correctly assumed to be small.

There is rather limited experimental data on fission product diffusion and activation energies for comparison against our predictions. Mansouri and Olander [63] measured the diffusivity of Xe and Ru as well as of a few other fission products by annealing experiments and earlier closely related studies were performed

by Prussin *et al.* [64]. The activation energies for Xe and Ru in stoichiometric UO_2 are much higher than calculated from DFT, however both theory and experiments predict Ru to have lower activation energy than Xe. The scarcity of the results, as well as the variety of experimental conditions (release *vs* diffusion, before or after irradiation), make direct comparison between theory and experiments difficult. Nonetheless, the results obtained by similar methods on Xe [6], for which more experimental data is available, suggest that the present results can be used with confidence, and that the exposed trends are physical.

4. Conclusions

The diffusivity of Zr (Zr^{4+}), Ru (Ru^{4+} , Ru^{3+}), Ce (Ce^{4+}), Y (Y^{3+}), La (La^{3+}), Sr (Sr^{2+}) and Ba (Ba^{2+}) solid fission products was determined, using a combination of DFT and EP calculations. The solid FPs occupy uranium vacancy trap sites, and migrate by a direct or indirect vacancy mechanism in stoichiometric UO_2 . The rate limiting step for the direct mechanism is in general the migration of U_{FP} , Y being an exception. For Zr and Ce, the indirect mechanism is relevant or even faster than the direct one. The diffusivities correlate with the fission product solubility in UO_2 , and the tendency to form metallic and oxide second phase inclusions, which are properties that can be directly related to the ionic radius of these species. Soluble elements with ionic radius similar to U (Y, La, Ce) diffuse with the slowest rate, comparable to U self-diffusion. Following are the elements with larger ionic radius that form oxide inclusion (Ba, Sr), with Zr as an intermediate between these two categories. Finally, elements that form metallic inclusions (Ru^{3+} and Ru^{4+} , small ionic radius) exhibit the fastest diffusivity, with rates even higher than the inert gas Xe at low temperature ($T < 1200$ K).

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Figure 5: Diffusion coefficient for solid fission products, U self-diffusion, and Xe [6] in UO_2 . For each solid FP, only the active mechanism (i.e. limiting rate) is shown.

Table 5: Pre-exponential factor (D_0) and active mechanism for diffusion of a range of solid fission products. For comparison, uranium self-diffusion and the previously reported Xe results [6] are listed. For the three migration mechanism, the activation energy E_a (calculated with DFT) and the attempt frequency ν_m (calculated with EP) are shown. The limiting step for direct migration is shown in bold font. and the active mechanisms is determined from the diffusivity plot (Fig. 4) . *: the direct FP path obtained with EP differs from DFT results (see Fig. 3). For Ba, a multidimensional saddle prevented the calculation of ν_m . **: the diffusion of Xe involves a divacancy, rather than a single U vacancy for solid FPs.

FP	E_a (eV)	ν_m (Hz)	D_0 (m/s ²)	Mechanism	Active mechanism
U ⁴⁺	4.53	9.29×10^{12}	2.20×10^{-13}	Self-diffusion	Self-diffusion
Zr ⁴⁺	3.29	1.84×10^{10}	1.83×10^{-16}	Direct FP	Direct Indirect
	3.62	2.25×10^{11}	2.24×10^{-15}	Direct U	
	4.08	1.82×10^{12}	1.81×10^{-14}	Indirect U	
Ru ⁴⁺	1.97	3.41×10^{10}	2.87×10^{-15}	Direct FP	Direct
	2.53	2.18×10^{12}	1.84×10^{-13}	Direct U	
	5.33	6.94×10^{12}	5.85×10^{-13}	Indirect U	
Ce ⁴⁺	4.09	9.43×10^{12}	2.24×10^{-13}	Direct FP	Direct Indirect
	4.59	8.49×10^{12}	2.01×10^{-13}	Direct U	
	4.48	1.12×10^{13}	2.66×10^{-13}	Indirect U	
Ru ³⁺	1.55	9.43×10^{12}	3.85×10^{-14}	Direct FP	Direct
	2.16	9.89×10^{11}	4.03×10^{-15}	Direct U	
	3.09	8.36×10^{11}	3.41×10^{-15}	Indirect U	
Y ³⁺	4.32	3.37×10^{12}	1.31×10^{-14}	Direct FP	Indirect
	3.72	2.42×10^{12}	9.38×10^{-15}	Direct U	
	4.01	1.29×10^{12}	4.98×10^{-15}	Indirect U	
La ³⁺	3.95	7.34×10^{13}	2.24×10^{-13}	Direct FP	Direct
	4.31	6.90×10^{12}	2.10×10^{-14}	Direct U	
	4.44	2.11×10^{12}	6.43×10^{-15}	Indirect U	
Sr ²⁺	2.49	5.25×10^{13}	6.13×10^{-14}	Direct FP*	Direct
	3.26	4.86×10^{12}	5.67×10^{-15}	Direct U	
	3.71	7.23×10^{11}	8.44×10^{-16}	Indirect U	
Ba ²⁺	2.22	N/A	N/A	Direct FP*	Direct
	3.19	3.75×10^{12}	1.06×10^{-15}	Direct U	
	3.45	7.22×10^{11}	2.05×10^{-16}	Indirect U	
Xe ⁰ [6]	2.94	4.93×10^{13}	8.26×10^{-12}	Direct**	Direct**