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LATTICE DISORDER
AND METAL SELF-DIFFUSION IN NON-STOICHIOMETRIC UO₂
AND (U, Pu)O₂

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Abstract. — The predominant defects in the fluorite structure are anion vacancies and interstitials. Cation defects occur at a much smaller rate and are therefore more difficult to study. They are, however, of crucial interest since they are rate-determining for many high temperature matter transport processes. Cation diffusion was therefore investigated in the temperature range ~ 1 400 to 2 200 °C. In stoichiometric and hyperstoichiometric oxides, MO₂ and MO₂₋ₓ (M = U or U + Pu), a vacancy mechanism is indicated with diffusion rates increasing roughly proportional to x². In MO₂₋ₓ, a decrease in diffusion rates with x is observed for small values of x until a minimum is indicated. On further reduction, diffusion rates increase again. It is argued that this increase reflects a mechanism involving metal interstitials, hence most probably an interstitialcy mechanism of diffusion, though the alternative of a predominant transport via Schottky trios cannot be excluded. The relevant formation energies of point defects in the UO₂ fluorite structure, as deduced from the diffusion data, compare favorably with theoretical predictions and measured values for the isostructural earth alkali halides, CaF₂ and BaF₂. The present diffusion data serve in addition to explain creep measurements on substoichiometric mixed uranium-plutonium oxides.

1. Introduction. — Though the predominant defects in the fluorite structure are anion vacancies, the less mobile cation defects, that occur at much smaller concentrations, are frequently rate determining for technologically important high temperature mass transport processes, as grain growth, sintering, plastic deformation, creep etc. Much work has been performed in the past on the earth alkaline halides, CaF₂ and BaF₂, as well as on the fluorite-type oxides, UO₂, and to a smaller extent on ThO₂ and on mixed (U, Pu)O₂. The latter substance recently gained in importance since it will be the fuel material for the first generation of fast breeder reactors. Despite all these efforts, the mechanism of cation diffusion and the effects of deviations from stoichiometry into the hypo-stoichiometric regime have not been uniquely determined so far. In addition, reliable diffusion coefficients for the stoichiometric oxides present still an unsettled problem.

We have therefore extended previous investigations on CaF₂ and BaF₂ as well as on hyperstoichiometric oxides by measuring cation self-diffusion in hypo-stoichiometric (U, Pu)O₂₋ₓ. In contrast to the UO₂ system, where hypo-stoichiometric compositions are difficult to obtain due to U⁴⁺ being the lowest oxidation state, hypo-stoichiometric single phase compositions of (U, Pu)O₂₋ₓ are relatively easy to achieve due to the ease of reduction of the plutonium ion to the tri-valent state.

The data thus obtained can be used to suggest consistent sets of defect formation energies as well as to explain other measurements of mass transport, in particular creep measurements on (U, Pu)O₂ and (U, Pu)O₂₋ₓ.

2. Experimental. — The diffusion specimens were high density polycrystalline UO₂, UO₂ single crystals
and (U\textsubscript{0.85}Pu\textsubscript{0.15})O\textsubscript{2}. The method of z-energy degradation \cite{1-3} was used to determine diffusion profiles employing U-233 and Pu-238 as tracers. Diffusion coefficients were calculated from the measured extended z-spectra with the aid of energy loss data determined particularly for these two oxides \cite{4}. Since very low diffusion coefficients were expected, great care was taken in employing high resolution solid-state detectors and stable multi-channel analyzers. In addition, the mathematics to determine small diffusion coefficients in the range of \(10^{-17}\) cm\(^2\) s\(^{-1}\) were developed \cite{3}, and special emphasis was put on achieving thin tracer layers of the order of 10 to 20 Å thickness only by employing an electron beam evaporation device. Channeling techniques (e. g. 5) were used to ensure that any surface damage due to polishing and subsequent surface contamination due to handling of the samples extended to only about 20 atom layers following the final polishing state, and to less than 10 atom layers following a pre-annealing treatment.

3. Results. — 3.1 Uranium Diffusion in Nominal Stoichiometric «U\textsubscript{O}\textsubscript{2}». Measurements of uranium diffusion in UO\textsubscript{2} were extended up to a temperature of 2 000 °C. Typical z-spectra of the two samples of the diffusion couple following annealing for 1 h at 2 000 °C are shown in figure 1. The original line spectra measured before annealing (1) are seen to be greatly extended over an energy range of more than 3 MeV corresponding to a distance scale \cite{4} of more than 7 μm. The center of the curve has migrated to a depth of about 2.3 μm into one of the two pellets due to mass transport by evaporation-condensation from one pellet to the other. The mirror image of the spectrum of the pellet with the smaller peak, as obtained by plotting this second spectrum from the original z-energy of 4.82 MeV to the right rather than to the left, extends the bigger peak to a complete Gaussian. The phenomenon of peak shift due to a surface migration caused by an evaporation-condensation mechanism was observed previously \cite{6} in high temperature diffusion work in the system U/UC and was found to not influence the diffusion results to any appreciable degree. This is confirmed by the fact, that the completed penetration profile is symmetrical and Gaussian. Since the anneal was performed in a good vacuum (\(\approx 1 \times 10^{-6}\) torr), chemical analysis of the diffusion samples following annealing showed a slight reduction with a composition of UO\textsubscript{1.999±0.002}. In the insert of figure 1, the obtained diffusion coefficient is shown together with other data for 1 800 and 1 500 °C, measured in the same way. For these two latter temperatures, chemical analysis yielded compositions of UO\textsubscript{2.000±0.002}, though the surface near layers were probably substoichiometric (see below). The dashed area in the insert of figure 1 indicates the most probable range of diffusion coefficients for nominally stoichiometric UO\textsubscript{2}, as discussed in the following.

For the temperature of 1 500 °C, four data points are given in figure 1 which were obtained with identical samples, but using different furnaces and annealing atmospheres. In most diffusion experiments in the system U/UO\textsubscript{2} performed so far, the apparent diffusion coefficient decreased with increasing annealing time. This effect was noted very early \cite{7}, and was discussed in more detail in a previous paper \cite{8}. Figure 2 shows some typical results. In selected cases, e. g., by using a furnace consisting entirely of ceramic, inert material (and hence not containing any tungsten or graphite

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Extended z-spectrum of two initially thin layers (see insert in middle) of U-233 in « U\textsubscript{O}\textsubscript{2} » following annealing at 2 000 °C in vacuum for 1 h. The inset in the left part shows the suggested range of diffusion coefficients for « stoichiometric UO\textsubscript{2} » plus new data points for slightly substoichiometric UO\textsubscript{2}.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{Decrease of the apparent diffusion coefficient of U in UO\textsubscript{2} single crystals with time under reducing annealing conditions. In the absence of a reducing environment, a time-independent D-value was observed occasionally.}
\end{figure}

\footnote{(1) Note that in this case a spectrometer with low resolution was used which is adequate \cite{3} since big diffusion distances were expected. Therefore, the two z-energies of U-233 were not resolved at such distances, the existence of two lines does not interfere with the evaluation.}
parts, etc.), the expected time-independent diffusion coefficients were observed (see full dots in Fig. 2).

An attempt to explain the decrease in $D$ under reducing conditions can be based on an electron microscope study. As shown in figure 3, parallel striations are observed in UO$_2$ annealed under conditions equivalent to those leading to a decrease with time in $D$. These striations can be explained [9] to represent parallel planar faults caused by an ordered reduction of the surface near layers to about UO$_{1.98}$. The resulting shear structure consists of layers of UO$_2$ separated by lamellae of very low $O/M$ ratio ($O/M \approx 1$). Hence, the suggested composition of UO$_{1.98}$ of surface near layers (the thickness of which is comparable to the diffusion distances) would be an average value for these layers only. The description of diffusion processes and lattice disorder in such samples with the aid of a point defect model alone is obviously not satisfactory; though attempts towards explaining possible diffusion mechanisms in shear structures are being made (e. g. 10), the present state of knowledge is still far from providing a clear understanding.

If thus measurements on «nominally stoichiometric UO$_2$» lead to an unacceptable scatter, an alternative means of determining reliable values of $D$ should be searched for. Such alternatives would, for instance, exist in deducing diffusion coefficients from related kinetic measurements which are less influenced by surface conditions, in trying to find analogies with related substances of the fluorite structure, or else in approaching the stoichiometric composition from both the hyper- and the hypo-stoichiometric side in isothermal experiments. It is obvious from the above, that UO$_{2+x}$ can be used for the hyper-stoichiometric region, whereas (U, Pu)O$_{2-x}$ promises more reliable results for the hypo-stoichiometric region. All three approaches are discussed below.

3.2 Uranium diffusion in UO$_{2+x}$ and Plutonium diffusion in (U, Pu)O$_{2-x}$. — Figure 4 shows that uranium diffusion is essentially enhanced in UO$_{2+x}$ as compared to UO$_2$. This general trend is confirmed by various authors, and it has been observed [13] for the diffusion of Pu in (U, Pu)O$_{2-x}$ as well. The increase in $D$ with $x$, at 1 500 °C, is roughly proportional to $x^2$. For «nominally stoichiometric UO$_2$», different literature data show the scatter which would be expected on basis of the arguments of the preceding Section. We would like to suggest, that the very low value of Marin and Michaud [17], as well as that of Reimann and Lundy [18], represented in figure 4 by open circles, are affected by the type of reduction described above, and that therefore the diffusion layer was substoichiometric, as indicated by the arrows at the two data

![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.](image)

![Fig. 4. — Dependence of the diffusion of U in UO$_{2+x}$ on oxygen excess $x$ at 1 500 °C due to data of Hawkins and Alcock [11], Marin et al. [12], and Matzke [8], as well as of Pu in (U, Pu)O$_{2-x}$ due to data of Riemer and Scherff [13]. For «nominally stoichiometric UO$_2$», data of Lindner and Schmitz [14], Hawkins and Alcock [11], Auskern and Belle [7], van Lierde et al. [15], Yajima et al. [16], Marin and Michaud [17], and Reimann and Lundy [18] are shown. New data for (U, Pu)O$_{2-x}$ are included as well. Results for oxygen diffusion [19] together with a theoretical treatment due to Thorn and Winslow [20] are shown for comparison.](image)
points. The biggest change in \( D \) occurs in a small range of \( O/M \) ratios marked with \( \Delta x \) in figure 4. The corresponding deviations from stoichiometry are probably small enough to escape detection in chemical analysis, especially if the deviation from stoichiometry occurs near the surface only. New data points on definitely substoichiometric \( (U, Pu)O_2-x \) confirm the trend of the dashed line, i.e. a decrease of \( D \) with small negative \( x \)-values, as was already indicated in previous studies [21], [22] on doped \( UO_2 \) and \( ThO_2 \). Since at 1 500 °C no bigger negative \( x \)-values could be reached with the present experimental set-up, the shape of the curve for \( O/M < 1.98 \) at 1 500 °C could not be measured.

However, at higher temperatures, more negative \( x \)-values could be achieved and a minimum in diffusion rates was indicated at \( x \approx 0.02 \) to 0.03. Figure 5 shows this phenomenon for a temperature of 1 600 °C. The scatter of the data for \( UO_2-x \) is such that different curves (dashed or dotted ones, etc.) seem motivated.

The scatter in the data for \( UO_2-x \), as was already indicated in previous studies [21], [22] on doped \( UO_2 \) and \( ThO_2 \), is such that any curve between, say, the dashed and the dotted one scale, i.e. \( \log D \) is plotted versus \( x \), has a trend of the dashed line, which is such that any The data are normalized in a reduced scale has a shape like the dependence of \( D \) on the ratio \( O/M \). The scatter between analytical determinations and the scatter between analytical results of different laboratories is at least of the order of \( \pm 0.01 \).

4. Discussion. — The present study allows to deduce qualitatively the diffusion mechanism of metal ions in the U-O and in the \((U, Pu)-O\) systems. Due to their importance in nuclear technology, these systems have been studied more extensively than any other oxide system. Nevertheless, as will be indicated below, there are still essential discrepancies between results of different authors. A quantitative model of diffusion processes that incorporates all observations is therefore still not feasible. A possible approach in selecting reliable results is a comparison with other materials of the same structure. This will be attempted in the following Section.

4.1 Comparison of diffusion processes in materials of the fluorite structure. — Figure 6 shows the data for \( UO_2-x \) that in the fluorides, but this occurrence near the surface only.

Fig. 6. — Summary of diffusion measurements for both anion and metal diffusion in materials of the fluorite structure. For ease of comparison, a normalized temperature scale has been used.
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The vertical dashed area at $T_m/T \approx 1.8$ (corresponding to 1 500 °C for UO$_2$) indicates the effect of deviations from stoichiometry in UO$_2$, as discussed in Section 3. The data for ThO$_2$ seem to confirm the suggested explanation of the UO$_2$ data, provided one accepts the premise that King's data were affected by the type of reduction described in Section 3.1.

The alternative of King's data representing stoichiometric ThO$_2$, as well as the low values of figure 4 for UO$_2$ representing the stoichiometric composition (and any higher values being due to grain boundary diffusion or slight oxidation), would diminish the differences between oxides and fluorides. However, such an assumption would imply a high activation enthalpy, $\Delta H$, of about 6 eV for cation diffusion. As argued in Section 4.3, such a high value was not observed for stoichiometric UO$_2$ in kinetic measurements of transport processes that can be related to metal self-diffusion.

A comparison of different defect energies for anion diffusion in the fluorite structure is shown in figure 7. For both the migration energy of interstitials and for anion self-diffusion, the results for the oxides are about 20% lower than what would be expected from an extrapolation of the fluoride data based on a simple melting point rule of the type $\Delta H/T_m = \text{const.}$ For the free energy of formation of anion Frenkel defects, $\Delta G_{\text{fo}}$, which is a crucial quantity for a defect model of the fluorite structure (see Section 4.2), approximate agreement exists between different sets of calculations [32]-[34] and of experimental determinations (see e. g. [26]). Recently, Catlow and Norgett [34]

**TABLE I**

Defect energies for oxygen defects in UO$_2$

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Material</th>
<th>Result (eV)</th>
<th>Suggested interpretation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen diffusion</td>
<td>UO$_2$</td>
<td>2.8</td>
<td>$\Delta H = \frac{1}{2} \Delta G_{\text{fo}} + \Delta H_{\text{O}_2}^{m}$</td>
<td>[35]</td>
</tr>
<tr>
<td>Anion transport</td>
<td>UO$_2$</td>
<td>2.6</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[31]</td>
</tr>
<tr>
<td>Oxidation</td>
<td>UO$_2$</td>
<td>2.3</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[36]</td>
</tr>
<tr>
<td>Survey</td>
<td>UO$_2$</td>
<td>2.5</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[37]</td>
</tr>
<tr>
<td>Oxygen diffusion</td>
<td>UO$_2$</td>
<td>1.0-1.3</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[38]</td>
</tr>
<tr>
<td>Oxid.-reduct.</td>
<td>UO$_2$</td>
<td>1.0-1.3</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[39], [40]</td>
</tr>
<tr>
<td>Quenching</td>
<td>UO$_2$</td>
<td>0.9</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[15]</td>
</tr>
<tr>
<td>Quenching</td>
<td>UO$_2$</td>
<td>1.0</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[42]</td>
</tr>
<tr>
<td>Oxygen diffusion (*)</td>
<td>PuO$_2$</td>
<td>1.7</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[43]</td>
</tr>
<tr>
<td>Oxygen diffusion (*)</td>
<td>PuO$_2$</td>
<td>2.6</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[40]</td>
</tr>
<tr>
<td>Oxidation</td>
<td>PuO$_2$</td>
<td>3.1</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[35]</td>
</tr>
<tr>
<td>Statistic. model</td>
<td>PuO$_2$</td>
<td>3.2</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[44]</td>
</tr>
<tr>
<td>Thermodyn. study</td>
<td>PuO$_2$</td>
<td>5.3</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[45]</td>
</tr>
<tr>
<td>Calculation</td>
<td>PuO$_2$</td>
<td>3.0</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[34]</td>
</tr>
<tr>
<td>Conductivity</td>
<td>PuO$_2$</td>
<td>3.0</td>
<td>$\Delta H_{\text{O}_2}^{m}$</td>
<td>[46]</td>
</tr>
</tbody>
</table>

(*) Assuming slight reduction of PuO$_2$.

Because of the scatter in the data, different sets of energies are acceptable. A possible set of data is suggested here: free energy of formation of Frenkel defects $\Delta G_{\text{fo}} = 3.0$ eV; migration energy for oxygen interstitials $\Delta H_{\text{O}_2}^{m} = 1.2$ eV; migration energy for oxygen vacancies $\Delta H_{\text{O}_2}^{m} = 1.7$ eV.
succeeded in calculating defect energies for UO₂ as well. Their value of $\Delta G_{\text{F}}} = 5.3 \text{ eV}$, however, is higher than previous results (see Table I), and it is also above the extrapolation from the fluorides (Fig. 7). If the 20% reduction mentioned above would hold for $\Delta G_{\text{F}}} \text{ as well, we would expect a value of about 3.6 eV which is nearer to previous data (see Table I).}

Catlow and Norgett [34] have also pointed out that the old value of $\Delta G_{\text{F}}} = 3.1 \text{ eV} of Auskern and Belle [35] should be revised since anion diffusion in UO₂ probably proceeds via a vacancy mechanism. They use their calculated value of $\Delta H_{\text{v}}^{m} - 2$ of only 0.25 \text{ eV} to revise the Auskern and Belle result to 5.1 \text{ eV}. However, some available experimental evidence (Table I) seems to show that 0.25 \text{ eV} is low for $\Delta H_{\text{v}}^{m} = \text{ the experimental data being around 1.7 eV (4). A final answer on the best value of $\Delta G_{\text{F}}} \text{ will obviously necessitate further information. An attempt to consistently interpret the available literature on oxygen defect energies in UO₂ is included in table I together with suggested values for those energies.}

A similar comparison for defects in the cation lattice is less satisfactory due to lack of data. The few available results are summarized in table II. This table contains, for CaF₂, theoretical figures for defect formation energies together with self-diffusion data as well as estimates on the energy for metal vacancy migration. For UO₂, data from recovery work [15], [43] on uranium point defects, which most probably are uranium vacancies (see below), are given. The corresponding energies have therefore been attributed to uranium vacancy mobility. The values in the column «expected» are extrapolated from CaF₂ in the way described above for anion defects. The defect formation energies are discussed in the next Section 4.2.

4.2 The defect structure of fluorite-type substances. — A simple thermodynamical model for the defect structure of fluorite-type substances has been given before [8], [23], [54]. The model predicts an interrelation between the various defect formation energies. For instance, the free energy, $\Delta G_{\text{F}}} \text{ for formation of anti-Frenkel defects, hence anion vacancies and interstitials, can be shown to be a crucial quantity for metal diffusion, since the activation enthalpy for metal diffusion should increase, or decrease, respectively, by $\Delta G_{\text{F}}} \text{ when going from UO₂ to UO₂-x, or UO₂+x, respectively (see also Table III).}

<table>
<thead>
<tr>
<th>Table II</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Defect energies for metal defects in CaF₂ and UO₂</strong></td>
</tr>
<tr>
<td><strong>Quantity</strong></td>
</tr>
<tr>
<td><strong>theor.</strong></td>
</tr>
<tr>
<td>$\Delta H_{\text{M,V}}^{m}$</td>
</tr>
<tr>
<td>$\Delta H_{\text{M,SI}}^{m}$</td>
</tr>
<tr>
<td>$\Delta H_{\text{M,SI}}^{m}$</td>
</tr>
<tr>
<td>$\Delta G_{\text{s}}$</td>
</tr>
<tr>
<td>$\Delta G_{\text{FM}}$</td>
</tr>
</tbody>
</table>

$\Delta H_{\text{M,V}}^{m}$ = migration enthalpy for metal vacancies. $\Delta G_{\text{s}}$ = free energy of formation for Schottky defects. $\Delta G_{\text{FM}}$ = free energy of formation for metal Frenkel defects all energies in eV.

(*) Expected for UO₂ on basis of an extrapolation from CaF₂ as explained in the text for figure 7.

(*) Suggested in the present study (see below). First reported in [53].

(*) Suggested in the present study (see below). First reported in [23].

(*) Suggested in the present study (see below).

Note that the calculated value for the mobility of oxygen interstitials ($\Delta H_{\text{O,V}}^{m}$ = 0.6 eV) is lower than experimental results as well. Both energies are lower than the corresponding results for CaF₂ and BaF₂. On the other hand, the experimental evidence is not consistent either as is particularly obvious with the data for PuO₂ [41], [46]. Note also that on different studies [47]-[51] on O₂- stabilized Zr₂ (diffusion, oxidation, permeation, conductivity) have revealed a $\Delta H_{\text{O,V}}^{m}$ of 1.3 eV which seems to confirm the experimental value of 1.7 eV for UO₂, the melting point of Zr₂ being somewhat smaller than that of UO₂. In addition, there is evidence [52] that the mobility of interstitial oxygen in Zr₂ is bigger than that of oxygen vacancies.

<table>
<thead>
<tr>
<th>Table III</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activation energies for diffusion processes in stoichiometric and off-stoichiometric materials of the fluorite structure, based on a simple thermodynamical model [23]</strong></td>
</tr>
<tr>
<td><strong>Metal</strong></td>
</tr>
<tr>
<td><strong>MO₂-x</strong></td>
</tr>
<tr>
<td><strong>MO₂</strong></td>
</tr>
<tr>
<td><strong>MO₂-x</strong></td>
</tr>
</tbody>
</table>

Where $\Delta G$ = free energy of formation of S = Schottky defects. FO = oxygen Frenkel defects. FM = metal Frenkel defects. $\Delta H_{\text{M}}^{m}$ = migration energy for. M = metal, O = oxygen. v = vacancy, i = interstitial.

if the metal ion is diffusing via a vacancy mechanism. The reverse would be true for a diffusion via metal interstitials, etc.

The model is based on simple mass action laws, and it neglects interaction between defects and second phase precipitates (U₂O₅ in UO₂-x, U-metal in UO₂-x, etc.). It does not allow for the formation of shear structures (see Section 3.1), for the formation of complexes of oxygen defects in UO₂-x, and for effects due to valence changes of uranium. Therefore, while it could be expected that purely applicable for small deviations from stoichiometry, it will at most show the qualitative behaviour for bigger deviations. The experimental data discussed above, especially the increase in metal self-diffusion rates with x for x \( \geq 0.02 \) (O/M > 1.98), are compatible
only with a partition mechanism for metal diffusion within this range of compositions. The predicted parabolic increase of $D^0$ with $x$ is approximately verified experimentally. A diffusion via interstitials which is operative for oxygen diffusion in $\text{UO}_2^{x+}$ would in contrast lead to a decrease of $D^0$ with increasing $x$. For $O/M \leq 1.98$ ($x \leq -0.02$), an increase in $D^0$ was observed upon further reduction. The predictions of the model show that this is most probably due to a change in diffusion mechanism from vacancies to interstitials. Since the concentration of uranium vacancies decreases while going from $\text{UO}_2^{x+}$ to $\text{UO}_2^{-x}$, eventually a value must be reached where the concentration of uranium interstitials is greater than that of vacancies. Depending on the migration energies, diffusion must then eventually occur with interstitials acting as diffusion carriers, most probably via the type of interstitialcy mechanism suggested previously [23] for $\text{UO}_2$ doped with $\text{TiO}_2$. Whether the exact location and depth of the minimum would in contrast lead to a decrease of migration energies, diffusion must then eventually occur with interstitials acting as diffusion carriers, most probably via the type of interstitialcy mechanism...
this range of values has been confirmed, e. g. by
Vollath [62] with 4.8 eV for creep and by Lay and
Carter [57] with 4.7 eV for sintering. Therefore, the
suggestion of the most reliable self-diffusion data for
(U, Pu)O$_{2-x}$ in order to extend previous data on
hyperstoichiometric UO$_2$ and (U, Pu)O$_2$ as
well as on nominally « stoichiometric UO$_2$ ». For
the latter, literature data show a substantial scatter.
This is explained as being due to a drastic change in
$D^U$ with small changes in $x$ around the stoichiometric
composition, and with unnoticed surface reductions
connected to the formation of a shear structure
near the surface.

Data on (U, Pu)O$_{2-x}$ are not thought to be disturbed
by these phenomena due to the ease of reducing
plutonium to the three-valent state. Therefore, a
reliable value for « UO$_2$ » can be obtained by extra-
polation from both the hypo- and the hyperstoichi-
ometric side (neglecting effects of Pu). Comparison
with known data on other materials of the fluoride
structure, mainly CaF$_2$ and BaF$_2$, and parallels
with kinetic measurements that can be related to
metal self-diffusion, mainly creep studies, provided
further arguments. On basis of these results and
considerations, it is confirmed that the most reliable
data for uranium diffusion in stoichiometric UO$_2$
are best represented by the equation

$$D^U = 0.5 \exp(- 4.8 \, eV/kT) \, cm^2/s^{-1}$$

The experimental results permit also to describe the
defect structure of fluoride-type materials. The following
statements are for uranium oxide, but equivalent
deductions can be made for the related substance
(U, Pu)O$_2$, ThO$_2$, CaF$_2$, BaF$_2$, CaO-stabilized ZrO$_2$
:  

1) The predominant defects are of the anti-Frenke
type, i. e. oxygen vacancies and interstitials.

2) Oxygen diffusion occurs via an interstitialc:
mechanism in UO$_2$ and via a vacancy mechanism in
UO$_2$. Whether vacancies or interstitials are
more mobile in stoichiometric UO$_2$ is still an open
question.

3) The free energy of formation of oxygen Frenkel
defects is likely to be in the range 3.0 to 3.6 eV.

4) Uranium diffusion proceeds via a vacancy
mechanism in UO$_2$, UO$_2$ and UO$_{2-x}$ (provided $x > - 0.02$). The predicted parabolic dependence of
$D^U$ on $x$ is approximately verified experimentally.

5) On reduction, a minimum in uranium diffusion
rates is passed at about $x = - 0.02$. The subsequent
increase in $D$ can best be explained by an increase
in the concentration of uranium interstitials and an
interstitialc mechanism of diffusion. However, the
alternative of an increased contribution to mass
transport of Schottky trios cannot be excluded.

6) Though there is still considerable scatter in the
experimental data, the free energies of formation
of uranium defects as either Schottky or Frenkel
defects can be estimated to be $\Delta G_F \approx 6.4 \, eV$ and
$\Delta G_{FM} \approx 9.5 \, eV$. 

These results allow to calculate the defect concen-
trations and the diffusion activation enthalpies as function of the $O/M$ ratio for both oxygen and uranium point defects. For instance, the activation enthalpies for self-diffusion have a maximum at $O/M = 2.00$ for oxygen diffusion, and at $O/M = 1.98$ for metal ion diffusion. The results serve in addition to explain creep data on $UO_2$, $UO_{2+x}$, and $(U, Pu)O_{2-x}$ that have been reported recently.

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