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

Hj. Matzke

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Hj. MATZKE

European Institute for Transuranium Elements, EURATOM,
D 75 Karlsruhe, Postfach 2266, Deutschland

Résumé. — Les défauts prédominants dans la structure fluorine sont les lacunes et les interstitiels anioniques. Les défauts cationiques apparaissent de manière beaucoup moins prononcée ; leur étude est donc beaucoup plus délicate. Ils sont, toutefois, d'un intérêt crucial, car ils déterminent la cinétique de la plupart des procédés de transport de matière à haute température.

La diffusion cationique a donc été étudiée dans le domaine de température ~ 1 400-2 200 °C. Dans les oxydes stœchiométriques et surstœchiométriques, c'est-à-dire MO_2 et MO_{2+x} (M = U ou U + Pu), un mécanisme de diffusion lacunaire avec des vitesses sensiblement proportionnelles à x^2 a été retenu. Pour MO_{2-x}, les vitesses de diffusion diminuent lorsque x augmente, jusqu'à ce qu'un minimum de diffusion soit observé. Pour une réduction plus prononcée, les vitesses de diffusion augmentent de nouveau. Cet accroissement s'explique par un mécanisme impliquant des interstitiels métalliques, plus probablement même un mécanisme « interstitialcy » de diffusion, quoique l'alternative d'un transport prédominant par triplets de Schottky ne saurait être exclu. Les énergies de formation applicables aux défauts ponctuels de l'UO₂ à structure fluorine et déduites des résultats présentés concordent favorablement avec les prévisions théoriques et des valeurs mesurées pour les halogénures alcalins des terres isostructurales CaF_2 et BaF_2. Les présents paramètres de diffusion sont utiles pour l'interprétation des mesures de fluage effectuées sur des oxydes mixtes sous-stœchiométriques d'uranium-plutonium.

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, MO_2 and MO_{2+x} (M = U or U + Pu), a vacancy mechanism is indicated with diffusion rates increasing roughly proportional to x^2. In MO_{2-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, CaF_2 and BaF_2. 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 defects, 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, CaF_2 and BaF_2, 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 CaF_2 and BaF_2 as well as on hyperstoichiometric oxides by measuring cation self-diffusion in hypo-stoichiometric (U, Pu)O$_{2-x}$. In contrast to the UO₂-system, where hypo-stoichiometric compositions are difficult to obtain due to U^{4+} being the lowest oxidation state, hypo-stoichiometric single phase compositions of (U, Pu)O$_{2-x}$ 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)O$_{2-x}$.

2. **Experimental.** — The diffusion specimens were high density polycrystalline UO₂, UO₂ single crystals

and $(U_{0.85}Pu_{0.15})O_2$. The method of α-energy degradation [1]-[3] was used to determine diffusion profiles employing U-233 and Pu-238 as tracers. Diffusion coefficients were calculated from the measured extended α-spectra with the aid of energy loss data determined particularly for these two oxides [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 [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 NOMINALLY STOICHIOMETRIC « UO₂ ».

— Measurements of uranium diffusion in UO_2 were extended up to a temperature of 2 000 °C. Typical α-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
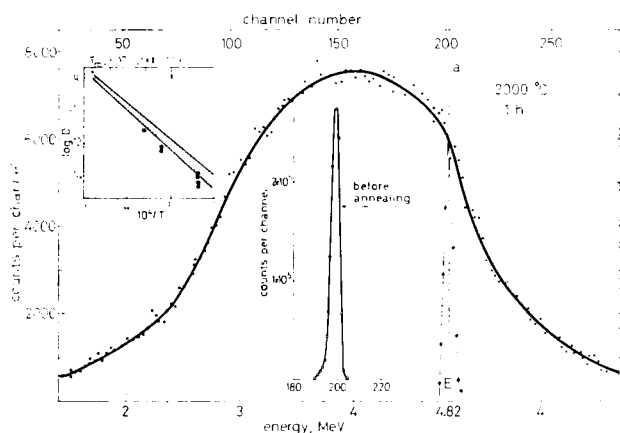

FIG. 1. — Extended α-spectrum of two initially thin layers (see insert in middle) of U-233 in « UO_2 » following annealing at 2 000 °C in vacuum for 1 h. The insert in the left part shows the suggested range of diffusion coefficients for « stoichiometric UO_2 » plus new data points for slightly substoichiometric UO_2.

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 [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

([1]) Note that in this case a spectrometer with low resolution was used which is adequate [3] since big diffusion distances were expected. Therefore, the two α-energies of U-233 were not resolved since at such distances, the existence of two lines does *not* interfere with the evaluation.

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 α-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 [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 $UO_{1.999\pm0.002}$. 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 $UO_{2.000\pm0.002}$, 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_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/UO₂ performed so far, the apparent diffusion coefficient decreased with increasing annealing time. This effect was noted very early [7], and was discussed in more detail in a previous paper [8]. Figure 2 shows

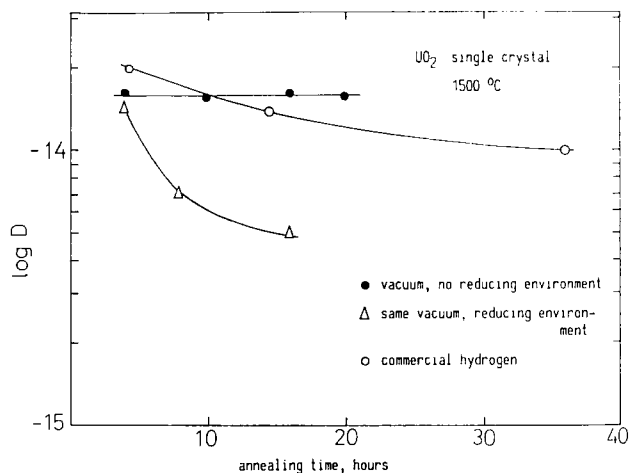FIG. 2. — Decrease of the apparent diffusion coefficient of U in UO_2 single crystals with time under reducing annealing conditions. In the absence of a reducing environment, a time-independent D-value was observed occasionally.

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

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
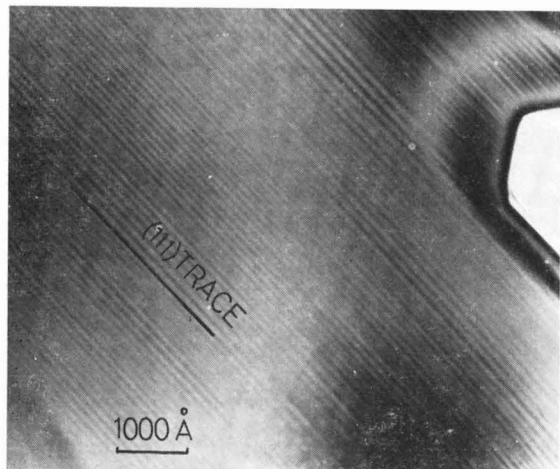

FIG. 3. — Transmission electron micrograph of a UO_2 sinter annealed in commercial H_2 in a reducing environment at 1 500 °C for only 5 min.

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 $UO_{1.98}$ [2]. 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 attemps 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 iso-thermal experiments. It is obvious from the above,

[2] Note, that the overall composition of a typical bulk UO_2 diffusion sample will nevertheless show a practically undetectable deviation ($x \approx 0.00005$) from stoichiometry only which will not be detected by conventional chemical analysis.

that UO_{2+x} can be used for the hyper-stoichiometric region, whereas $(U, Pu)O_{2-x}$ promises more reliable results for the hypostoichiometric 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
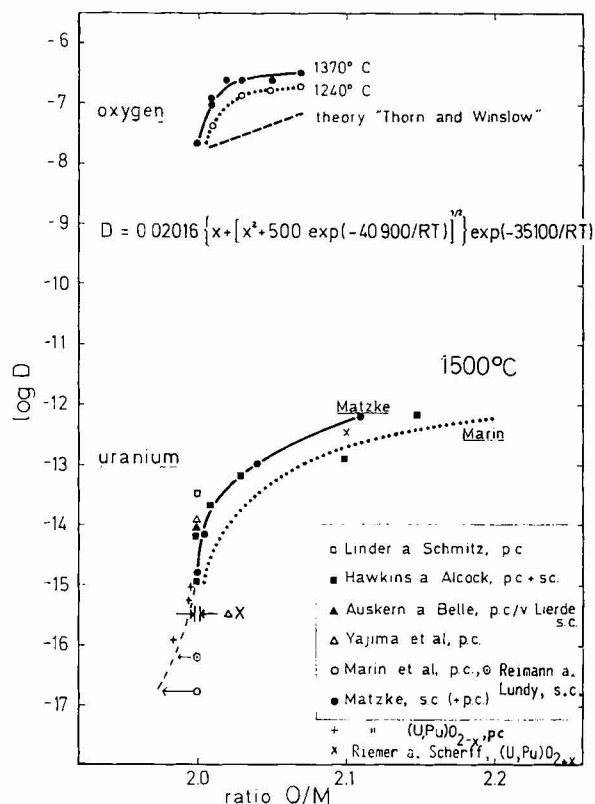

FIG. 4. — Dependence of the diffusion of U in UO_{2+x} on oxygen excess x at 1 500 °C due to data of Hawkins and Alcock [11], Marin *et al.* [12], and Matzke [8], as well as of Pu in (U, Pu)O_{2+x} due to data of Riemer and Scherff [13]. For « nominally stoi-chiometric UO_2 », data of Lindner and Schmitz [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 +. Results for oxygen diffusion [19] together with a theoretical treatment due to Thorn and Winslow [20] are shown for comparison. pc = polycrystal, sc = single crystal.

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 lite-rature 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 substoichio-metric, as indicated by the arrows at the two data

points. The biggest change in D occurs in a small range of O/M ratios marked with Δx 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
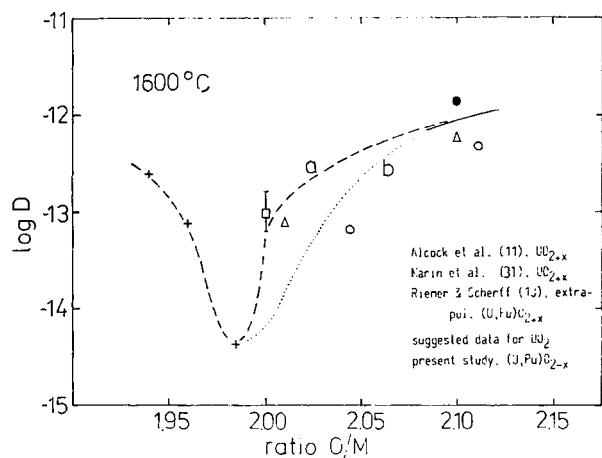

FIG. 5. — Dependence of the diffusion of U in UO_{2+x}, and of the diffusion of Pu in $(U, Pu)O_{2+x}$, on the O/M ratio. The scatter of the data for UO_{2+x} is such that different curves (dashed or dotted ones, etc.) seem motivated.

shows this phenomenon for a temperature of 1 600 °C. The scatter in the data for UO_{2+x} is such that any curve between, say, the dashed and the dotted one would seem plausible. The present author would, however, like to suggest that the dashed line represents best the dependence of D on the O/M ratio. In any case, the decrease of D with decreasing positive x, and an increase in D with the negative x-values increasing beyond $x \approx -0.02$ seem to be proven beyond doubt. This implies the existence of a minimum in diffusion rates for $x \approx -0.02$ (hence $O/M \approx 1.98$) [3].

4. Discussion. — The present study allows to deduce qualitatively the diffusion mechanism of metal ions

[3] Whether or not the exact position of the minimum, or the minimal value of D were found, will have to be investigated in further work. Note also that due to recently discovered uncertainties in the thermodynamical data, and due to discrepancies between different laboratories on the kinetics of achieving equilibrium compositions of $(U, Pu)O_{2\pm x}$, the accuracy in O/M determinations and the scatter between analytical results of different laboratories is at least of the order of ± 0.01.

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
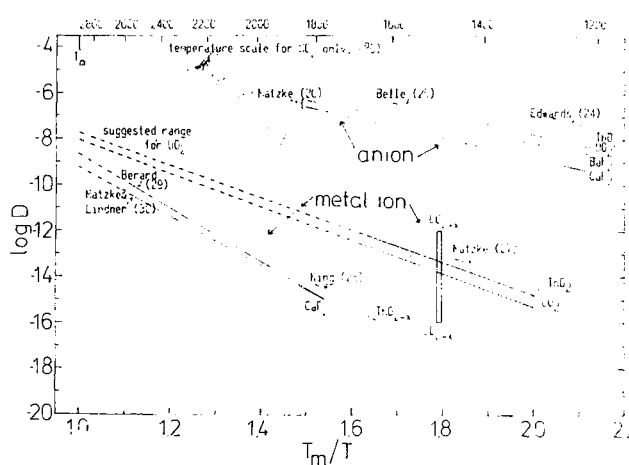

FIG. 6. — Summary of diffusion measurements for both anion and metal diffusion in materials of the fluorite structure. For ease of comparison, a normalized temperature scale has been used.

diffusion results for both the anions and the metal ions in substances of the fluorite structure, the fluorides CaF_2 and BaF_2, and the oxides UO_2 and ThO_2. The data are normalized in a reduced temperature scale, i. e. $\log D$ is plotted versus T_m/T with T_m being the melting point (K).

Anion diffusion is seen to be much faster than metal diffusion in all substances. In addition, an approximate melting point dependence for anion diffusion is indicated, with diffusion in the oxides being slightly faster than diffusion in the fluorides at identical reduced temperatures. The fast anion mobility is in agreement with the now commonly accepted statement that in the fluorite structure, the predominant defects are anion vacancies and anion interstitials.

For the much slower cation diffusion, a melting point rule seems to exist as well, but it is less obvious. Again, diffusion in the oxides is faster than in the fluorides, but this time the difference is appreciable. The data for CaF_2 seem to be well established since they are based on two independent studies on single crystalline samples. The dashed area for UO_2 is what the present author would like to suggest as representing the most probable range for metal diffusion in stoi-

chiometric UO_2. 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 [28] 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, ΔH, 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 $\Delta H/T_m$ = const. For the free energy of formation of anion Frenkel defects,
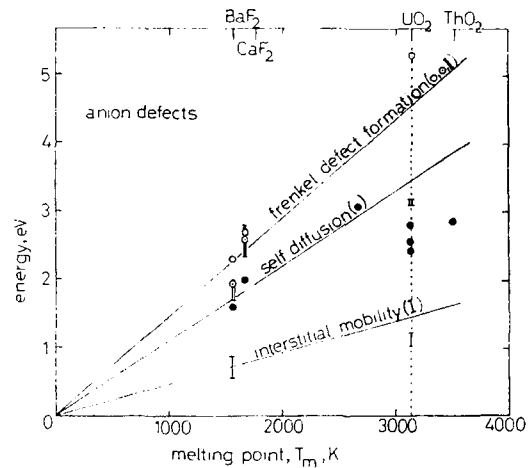

FIG. 7. — Energies for anion defects in fluorides and oxides as function of the melting point. For the experimental data for fluorides, see [26] (bars for interstitial mobility and Frenkel defect formation energy, full dots for self-diffusion). The theoretical values for ΔG_{Fo} and CaF_2 and BaF_2 are from [32]-[34] (open circles). For the data for UO_2, see table I. The result for oxygen self-diffusion in ThO_2 is from [24].

ΔG_{FO}, which is a crucial quantity for a defect model o 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

Measurement	Material	Result (eV)	Suggested interpretation	References
Oxygen diffusion	UO_2	2.8	$\Delta H = \frac{1}{2} \Delta G_{FO} + \Delta H^m_{O,v(i)}$	[35]
« «	«	3.0	«	[19]
« «	«	2.6	«	[31]
Anion transport	«	2.8	«	[36]
Oxidation	«	2.5	«	[37]
Survey	«	2.5	«	[25]
Oxygen diffusion	UO_{2+x}	1.3	$\Delta H^m_{O,i}$	[35]
« «	«	1.0-1.3	«	[19]
« «	«	0.9	«	[38]
Oxidat.-reduct.	«	1.0-1.3	«	e. g. [39], [40]
Quenching	«	0.9	«	[15]
«	«	1.0	«	[42]
Quenching	$UO_{2(+x)}$	1.7	$\Delta H^m_{O,v}$	[43]
Oxygen diffusion (^{a})	PuO_2	1.8	«	[40]
Oxygen diffusion	$UO_{2(+x)}$	3.1	ΔG_{FO}	[35]
Statistic. model	«	2.6	«	[44]
Thermodyn. study	UO_{2-x}	3.2	«	[45]
Calculation	UO_2	5.3	«	[34]
Conductivity	PuO_2	3.0	«	[46]

(^{a}) 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 ΔG_{FO} = 3.0 eV ; migration energy for oxygen interstitials $\Delta H^m_{O,i}$ = 1.2 eV ; migration energy for oxygen vacancies $\Delta H^m_{O,v}$ = 1.7 eV.

succeeded in calculating defect energies for UO_2 as well. Their value of $\Delta G_{FO} = 5.3$ 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 ΔG_{FO} 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 $\Delta G_{FO} = 3.1$ eV of Auskern and Belle [35] should be revised since anion diffusion in UO_2 probably proceeds via a vacancy mechanism. They use their calculated value of $\Delta H_{O,v}^m$ of only 0.25 eV to revise the Auskern and Belle result to 5.1 eV. However, some available experimental evidence (Table I) seems to show that 0.25 eV is low for $\Delta H_{O,v}^m$ — the experimental data being around 1.7 eV ($^+$). A final answer on the best value of ΔG_{FO} will obviously necessitate further information. An attempt to consistently interpret the available literature on oxygen defect energies in UO_2 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 CaF_2, theoretical figures for defect formation energies together with self-diffusion data as well as estimates on the energy for metal vacancy migration. For UO_2, 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 CaF_2 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, ΔG_{FO}, 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 ΔG_{FO}, when going from UO_2 to UO_{2-x}, or UO_{2+x}, respectively (see also Table III).

TABLE II

Defect energies for metal defects in CaF_2 and UO_2

Quantity	theor.	CaF$_2$ experim.	UO$_2$ expected (^{a})	experim.
$\Delta H_{M,v}^m$		1.5 [26] 1.75 [29]	2.2	2.3 [15] 2.2 [43]
$\Delta H_{self\ diff.}$		3.8 [30] 4.1 [29]	5.3	4.8 (^{b})
ΔG_S	5.8 [32] 7.0 [34]		~ 7.8	6.4 (^{c})
ΔG_{FM}	7.1 [32]		9.6	9.5 (^{d})

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

(^{a}) Expected for UO_2 on basis of an extrapolation from CaF_2 as explained in the text for figure 7.

(^{b}) Suggested in the present study (see below). First reported in [53].

(^{c}) Suggested in the present study (see below). First reported in [23].

(^{d}) Suggested in the present study (see below).

($^+$) Note that the calculated value for the mobility of oxygen interstitials ($\Delta H_{O,i}^m = 0.6$ eV) is lower than experimental results as well. Both energies are lower than the corresponding results for CaF_2 and BaF_2. On the other hand, the experimental evidence is not consistent either as is particularly obvious with the data for PuO_2 [41], [46]. Note also that different studies [47]-[51] on CaO- or Y_2O_3-stabilized ZrO_2 (diffusion, oxidation, permeation, conductivity) have revealed a $\Delta H_{O,v}^m$ of 1.3 eV which seems to confirm the experimental value of 1.7 eV for UO_2, the melting point of ZrO_2 being somewhat smaller than that of UO_2. In addition, there is evidence [52] that the mobility of interstitial oxygen in ZrO_2 is bigger than that of oxygen vacancies.

TABLE III

Activation energies for diffusion processes in stoichiometric and off-stoichiometric materials of the fluorite structure, based on a simple thermodynamical model [23]

	Metal	Oxygen
MO_{2+x}	$\Delta G_S - 2\,\Delta G_{FO} + \Delta H_{M,v}^m$	$\Delta H_{O,i}^m$
MO_2	$\Delta G_S - \Delta G_{FO} + \Delta H_{M,v}^m$	$\frac{1}{2}\Delta G_{FO} + \Delta H_{O,v}^m$
MO_{2-x}	$\Delta G_S + \Delta H_{M,v}^m$, or $\Delta G_{FM} - \Delta G_S + \Delta H_{M,i}^m$	$\Delta H_{O,v}^m$

Where ΔG = free energy of formation of
  S = Schottky defects.
  FO = oxygen Frenkel defects.
  FM = metal Frenkel defects.
  ΔH^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 (U_4O_9 in UO_{2+x}, U-metal in UO_{2-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 UO_{2+x} [55], [56], and for effects due to valence changes of uranium. Therefore, while it could be expected to be strictly 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 $x \geqslant -0.02$ ($O/M > 1.98$), are compatible

only with a *vacancy mechanism* for metal diffusion within this range of compositions. The predicted parabolic increase of D^U with x is approximately verified experimentally. A diffusion via interstitials which is operative for oxygen diffusion in UO_{2+x}, would in contrast lead to a decrease of D^U with increasing x. For $O/M \lesssim 1.98$ ($x \lesssim -0.02$), an increase in D^U 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 UO_{2+x} to 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 UO_2 doped with TiO_2. Whether the exact location and depth of the minimum were found, awaits further experimental clarification. In principle, the existence of a minimum could also be explained with an increased contribution of Schottky trios to mass transport at small values of O/M, though the observed minimum seems to be too pronounced for such an explanation.

Based on the above, the predicted activation enthalpies for diffusion processes in UO_2, UO_{2+x}, and UO_{2-x} are given in table III, expressed in terms of the different defect formation energies. These can be estimated if a few more simplifying assumptions are incorporated into the model, i. e. assuming that

— the migration energies are independent of the O/M ratio,

— the formation energies are independent of the O/M ratio,

— the effect of substituting 15 % of the U-atoms with Pu is negligible,

— the observed minimum in metal self-diffusion rates is definitely due to a change in mechanism from vacancies to interstitials.

The Schottky defect energy $\Delta G_S \approx 6.4$ eV, can then be deduced by comparing matter transport in e. g. UO_2 and UO_{2+x}, as shown already in [23]. The formation energy of metal Frenkel defects, ΔG_{FU}, can be estimated from the observed minimum in diffusion. A value of about 9.5 eV is thus obtained.

Using these formation energies, the dependence of defect concentrations on the O/M ratio can be calculated. This is shown in figure 8 for 1 600 °C. Drastic changes in defect concentrations are seen to occur at the stoichiometric composition for both oxygen and uranium defects. Similarly, the dependence of the activation enthalpies ΔH, of oxygen and uranium diffusion on the O/M ratio can qualitatively be given as shown in figure 9. The predominant mechanism is indicated along the curves. A maximum in ΔH is predicted for oxygen diffusion in stoichiometric UO_2,
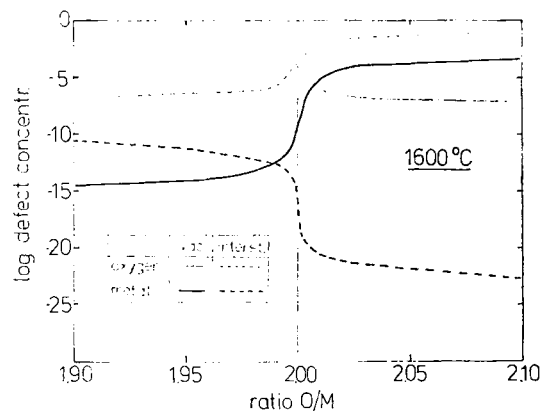

FIG. 8. — Predicted defect concentrations in UO_2 at 1 600 °C for different deviations from stoichiometry. The set of formation energies $\Delta G_{FO} = 3.0$ eV, $\Delta G_S = 6.4$ eV and $\Delta G_{FM} = 9.5$ eV was used for the calculations.

and for metal diffusion in $MO_{1.98}$. The energy scale in figure 9 depends on the chosen starting values (here $\Delta G_{FO} = 3.0$ eV and the migration energies of Table I and II).
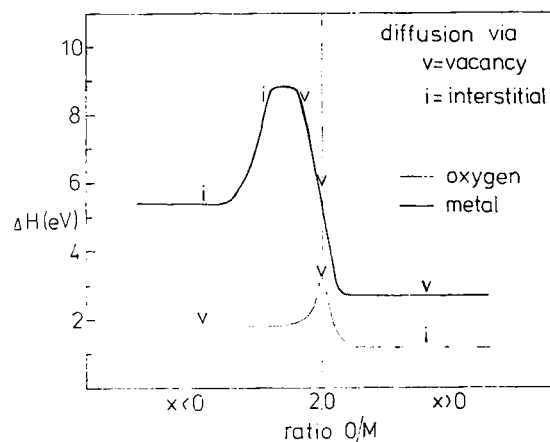

FIG. 9. — Predicted qualitative dependence on deviations from stoichiometry of the activation enthalpy, ΔH, of anion and metal self-diffusion in UO_2. The shape of the curves is thought to be reliable ; the energy scale on the ordinate shows *suggested* values based on $\Delta G_{FO} = 3.0$ eV, and the simplified assumption of defect migration energies being independent of the O/M ratio.

4.3 COMPARISON WITH RELATED KINETIC MEASUREMENTS. — A comparison with results of kinetic measurements, that can be related with metal self-diffusion, serves a two-fold purpose. First, it can yield additional support to the deductions on the defect structure drawn from the diffusion data. Secondly, it can be used to confirm the suggested activation enthalpy for uranium diffusion in stoichiometric « UO_2 » since measurements on bulk samples, like creep measurements, are not affected by the type of surface effects discussed in Section 3.1.

Relevant data on sintering, grain growth, and creep in UO_2 and UO_{2+x} have been shown already in [23] to yield ΔH's of 4.0 to 4.7 eV for « UO_2 ». Since then,

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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 « UO$_2$ » indicated in figures 1 and 6 and described by the equation

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

seems to be well confirmed. It finds additional confirmation in experiments on rare gas diffusion which can be shown to be practically independent of the O/M ratio [58].

The drastic increase with x in UO$_{2+x}$ of uranium ion mobility (see Fig. 4, 5) finds confirmation in practically all other kinetic measurements of creep, sintering, plastic deformation, grain growth etc. Recent observations include extensive creep measurements by Seltzer, Clauer, and Wilcox [61] on both polycrystalline and single crystalline UO$_2$ and UO$_{2+x}$. At 1 300 °C, for instance, creep rates increase by about a factor of 1 000 between « UO$_2$ » and UO$_{2.06}$. Simultaneously, the activation enthalpies decrease from about 5 eV to about 2.6 eV, as would be expected from our model. (The very high value of 5.8 eV reported for the sample with the smallest oxygen content is probably due to some reduction of the specimens below $O/U = 2$.) A further confirming example are the measurements of Lay [59] who showed that D^U as deduced from sintering rates is proportional to x^2 for the range $2.03 < O/U < 2.16$, as would again be expected from the model. Some discrepancies, however, remain, the most severe one of them probably being the high ΔH of 3.7 eV for uranium diffusion in UO$_{2+x}$ reported by Marin and Contamin [31].

The increase in ΔH in definitely substoichiometric samples (Fig. 9) was first indicated in grain growth work by MacEwan and Hayashi [60] on UO$_2$ doped with CaO. These authors observed $\Delta H'$s of 2.8, 4.7 and 5.9 eV for UO$_{2+x}$, UO$_2$, and UO$_2$ + CaO (representing UO$_{2-x}$), respectively. More recent confirmations were obtained from creep studies on (U, Pu) O$_{2-x}$. Routbort, Javed, and Voglewede [63] reported the expected decrease in creep rate with decreasing O/M, with a minimum being indicated at about $O/M = 1.94$. Simultaneously, they observed a maximum in ΔH at $O/M = 1.985$ with 5.8 eV. Vollath [62] has reported an even higher ΔH of 7.6 eV for (U, Pu) O$_{2-x}$, which is more in accord with the suggested values presented in figure 9. Note also that the accuracy in analytically determining O/M ratios at present is only about $\pm$ 0.01, with differences between various laboratories being up to 0.03. Therefore, slight differences in O/M ratios, e. g. for the observed minima in metal ion mobility, do not necessarily imply a discrepancy.

5. Conclusions and Summary. — Metal self-diffusion has been studied in substoichiometric

(U, Pu)O$_{2-x}$ in order to extend previous data on hyperstoichiometric UO$_{2+x}$ and (U, Pu)O$_{2+x}$ 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 extrapolation from both the hypo- and the hyperstoichiometric side (neglecting effects of Pu). Comparison with known data on other materials of the fluorite 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

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

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

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

2) Oxygen diffusion occurs via an interstitialcy mechanism in UO$_{2+x}$ and via a vacancy mechanism in UO$_{2-x}$. 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$_{2+x}$, 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 interstitialcy 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 $\Delta G_S \approx 6.4$ 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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