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Influence of defect clusters on diffusion processes in UO_{2+x}

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Abstract

Thermodynamic and transport properties of hyperstoichiometric uranium dioxide,UO_{2+x}, constitute a key issue in the application of this material for nuclear fuel since they are closely related to many chemical and physical processes, e.g., diffusion or creep.
Starting from a point defect model for UO_{2+x} developed by the authors in a preceding work[1] and quantitatively consistent with some literature experimental measurements of deviation from stoichiometry [2] and electrical conductivity[3],the oxygen and uranium self diffusion processes have been studied in order to appreciate the influence of defects involved in the model and particularly, the two Willis complexes i.e., $2\left(O_i'' O_i' V_O^{\bullet}\right)''$ and $2\left(O_i'' O_i' V_O^{\bullet}\right)^{4'}$.
Such a result leads the way to a better understanding of the mechanisms involved in diffusion processes and also helps to define more accurately the nature, as well as the type of the preferential interactions between diffusing impurities and the defects responsible for these transport properties.

Keywords: self diffusion,UO_{2+x} diffusion mechanisms, point defects.

I- Introduction

In a preceding paper [1], a defect model has been presented that is quantitatively consistent with UO_{2+x} electrical conductivity and deviation from stoichiometry experimental measurements [2-3]. This model takes into account both singly charged uranium vacancy, V_U', two types of Willis clusters, characterized by two kinds of interstitial oxygen atoms that are located on two different sites and two oxygen vacancies, namely $2\left(O_i''O_i'V_O^{\bullet\bullet}\right)''$ and $2\left(O_i''O_i'V_O^{\bullet\bullet}\right)^{4'}$. The electron holes, $h^{\bullet}$, are also introduced to ensure the crystal global electroneutrality.

One can briefly recall that this oxide adopts the fluorite structure[4], where the uranium and oxygen atoms define a face centered cubic sublattice and a simple cubic one respectively; this structure has the property to accommodate a very high concentration of defects via small perturbations of anionic sublattice. The mixed valence nature of uranium also helps these structural changes.

A departure from stoichiometry, up to $UO_{2,33}$, is observed without drastic change in the fluorite structure; near the stoichiometry (x~0),the prevailing point defects are assumed to be oxygen Frenkel defects[5], while for a stoichiometry departure $x>10^{-2}$,the oxygen interstitials gather into (2:2:2) clusters consisting in an assembly of oxygen interstitials and vacancies as described by Willis [6].

Several authors have published results for uranium self diffusion in UO_{2+x} as a function of temperature, oxygen partial pressure and deviation from stoichiometry [7-12].

However, the agreements among the sets of data is not good. Some of these differences can be ascribed to experimental limitations of the method used and to possible grain boundary diffusion effects; indeed, the transport mechanism of cations is quite poorly understood.

Generally, one consider that the Frenkel defects greatly contribute to the uranium self diffusion i.e., uranium vacancies at high Po_2 and interstitials ones at low Po_2[8].

Concerning the oxygen self diffusion a great number of authors studied its temperature and defect concentration dependencies and thought that it occurs mainly by oxygen interstitials, probably in clusters in UO_{2+x}[7, 11,13-16] but their structure and movement through the crystal are not clear.

The purpose of the present work is first to appreciate the evolution of some experimental oxygen and uranium self diffusion measurements as a function of temperature and oxygen partial pressure, on the base of the above mentioned model and second, to analyze their transport mechanism whom the knowledge forms an important link in the understanding of diffusive related phenomena of technological interest such as sintering creep and oxidation [17-20] .

II- Oxygen self diffusion in UO_{2+x}

The defect model developed in [1] may be applied to oxygen self diffusion results, whom the Po_2 dependence suggests that diffusion by two types of Willis clusters, namely $2\left(O_i^{\prime\prime}O_i^{\prime}V_O^{\bullet\bullet}\right)^{\prime\prime} \equiv (222)^{2'}$ and $2\left(O_i^{\prime\prime}O_i^{\prime}V_O^{\bullet\bullet}\right)^{4'} \equiv (222)^{4'}$, are both important.

Hence, we may write:

$$D_{Oxy} = D_{Oxy_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{\prime\prime}}} + D_{Oxy_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{4'}}} \qquad (1)$$

where

$$D_{Oxy_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{\prime\prime}}} = D_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O^{\bullet\bullet}\right)^{\prime\prime}} f_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O^{\bullet\bullet}\right)^{\prime\prime}} \left[\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O^{\bullet\bullet}\right)^{\prime\prime}\right] = d_{(222)^{2'}} \left[(222)^{2'}\right] \qquad (2)$$

and

$$D_{Oxy_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{4'}}} = D_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{4'}} f_{\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O\right)^{4'}} \left[\left(2O_i^{\prime\prime}2O_i^{\prime}2V_O^{\bullet\bullet}\right)^{4'}\right] = d_{(222)^{4'}} \left[(222)^{4'}\right] \qquad (3)$$

f_{def} and D_{def} are respectively the correlation factor and the diffusion coefficient of the defect "def ", while [def] is the defect concentration.

The "d_{def}" terms represent the products "correlation factor" by "defect diffusion coefficient".

By using the different mass action laws, associated with the concerned defects, we obtain:

$$D_O = A(T)\frac{P_{O_2}}{\sigma^4} + B(T)\frac{P_{O_2}}{\sigma^2} \tag{4}$$

where σ is the electrical conductivity.

A(T) and B(T) are adjustment parameters, respectively equals to:

$$A(T) = K_{cls4}(e\mu)^4 D_{(2O_i'' 2O_i' 2V_O)^{4'}} f_{(2O_i'' 2O_i' 2V_O)^{4'}}$$

and (5)

$$B(T) = K_{cls2}(e\mu)^2 D_{(2O_i'' 2O_i' 2V_O)''} f_{(2O_i'' 2O_i' 2V_O)''}$$

K_{cls4} and K_{cls2} represent the “normalized” constants of the two defect formation equations, characterized by the adequate laws of mass action[1].

μ is the hole mobility and e the elementary charge.

A fitting procedure of some experimental oxygen self diffusion data [4-5], by the relation (4) , has been made, leading to the knowledge of the temperature dependence of the A(T) and B(T) parameters.

Both A(T) and B(T) have an Arrhenius behavior which is given by:

$$A(T) = (11.0 \pm 3.0)E - 9exp\left(-\frac{(74.9 \pm 0.7)Kcal/mol}{RT}\right) \tag{6}$$

and

$$B(T) = (0.20 \pm 0.02)E - 2exp\left(-\frac{(39.2 \pm 1.8)Kcal/mol}{RT}\right) \tag{7}$$

Figure 1 shows that product of this adjustment is fairly good.

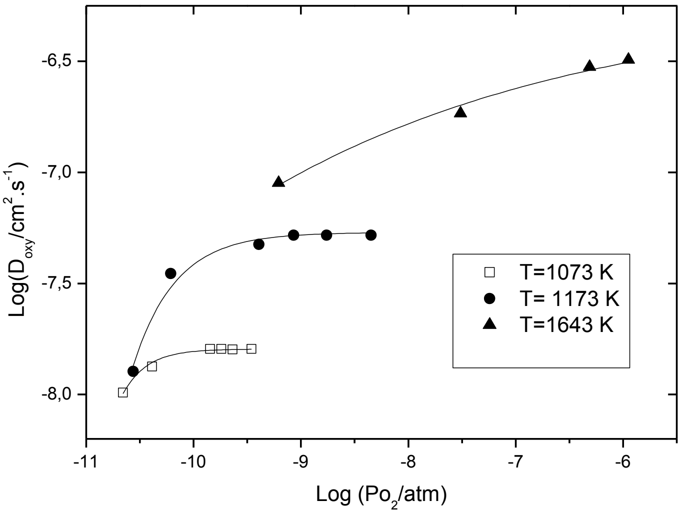

Fig. 1 Fitting of the oxygen partial pressure dependence of D_{oxy} in UO_{2+x} , obtained by [4-5] for three different temperatures (1073˚K,1173˚K and 1643˚K).

Moreover, we have reported in figure 2 the evolution of the oxygen partial diffusion coefficients, $D_{Oxy}{}_{\left(2O_i''2O_i'2V_O\right)''}$ and $D_{Oxy}{}_{\left(2O_i''2O_i'2V_O\right)^{4'}}$ deduced from our defect model, as a function of temperature.

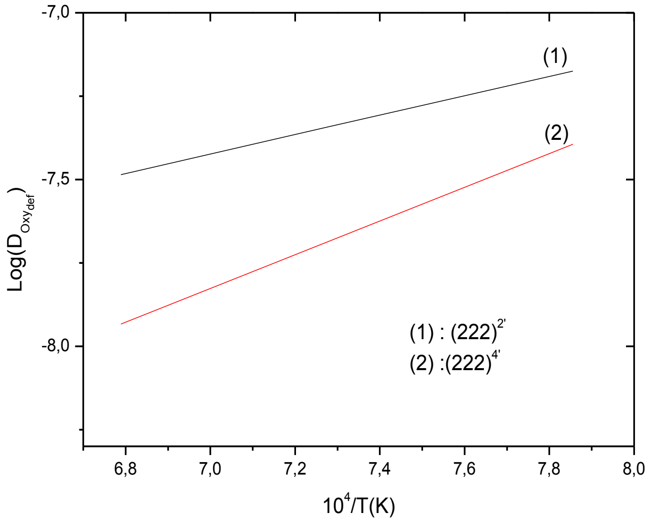

Fig. 2: Evolution of the oxygen partial diffusion coefficients, as a function of T at $Po_2=10^{-10}$atm.

It clearly appears that $D_{Oxy_{(2O_i''2O_i'2V_O)''}}$ is greater than $D_{Oxy_{(2O_i''2O_i'2V_O)^{4'}}}$ on the overall studied temperature domain.

Furthermore, it is known that the slope of these curves permits the obtaining of the defect energy activation, which is equal to:

$$Q_{def}^{Ox} = \Delta H_{def}^{m_{ox}} + \Delta H_{def}^{f_{ox}} \tag{8}$$

$\Delta H_{def}^{m_{ox}}$ and $\Delta H_{def}^{f_{ox}}$ are the defect migration and formation enthalpies , respectively.

Here, the correlation factor $f_{\mathrm{def}}$is assumed to be independent of the defect charge state and of T and this, after Compaan and al works [21-22]; hence, we write:

$$f_{(2O_i''2O_i'2V_O^{\cdot\cdot})''} = f_{(2O_i''2O_i'2V_O^{\cdot\cdot})^{4'}} = 0.986 \tag{9}$$

A least-squares fit of the figure 2 data gives:

$$Q^{ox}_{C^{2'}_{222}} = 13.3 Kcal/mol \quad \text{and} \quad Q^{ox}_{C^{4'}_{222}} = 23.1 Kcal/mol \qquad (10)$$

On the other hand, we have reported the T dependence of the "d_{def}" terms.

Figure3 characterizes the $d_{(222)^{2'}}$ and $d_{(222)^{4'}}$ respective evolutions.

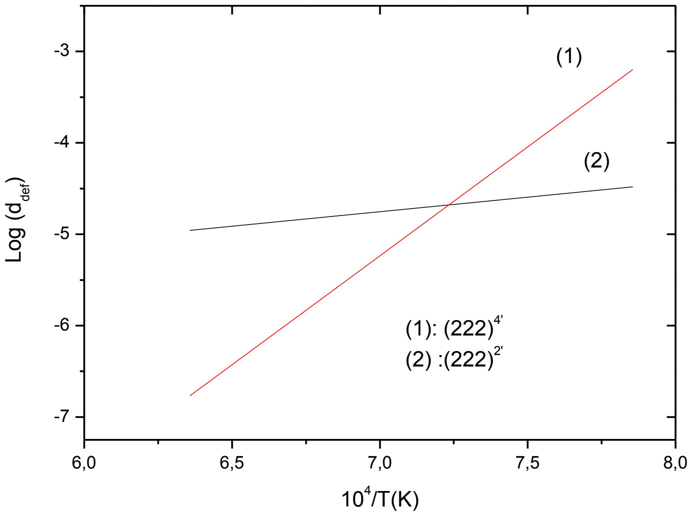

Fig. 3 : Variations of $d_{(222)^{2'}}$ and $d_{(222)^{4'}}$ as a function of temperature.

It appears that the $(222)^{2'}$ cluster diffusion coefficient becomes more important than the $(222)^{4'}$ one at about 1380°K, suggesting the idea that the complex defect mobility associated with the less charge increases according to temperature.

The determination of the slope curves permits the immediate knowledge of the two migration enthalpies. We obtain:

$$\Delta H^{m_{ox}}_{C^{2'}_{222}} = 14.5 Kcal/mol \qquad \text{and} \qquad \Delta H^{m_{ox}}_{C^{4'}_{222}} = 108.7 Kcal.mol^{-1} \qquad (11)$$

From equations (8),(10) and (11), it is possible to determine the formation enthalpies of

$(222)^{2'}$ and$(222)^{4'}$ defects , respectively.

We get:

$$\Delta H^{f_{ox}}_{(222)^{2'}} = -1.24 Kcal.mol^{-1} \quad and \quad \Delta H^{f_{ox}}_{(222)^{4'}} = -\,85.6 Kcal.mol^{-1} \qquad (12)$$

The two values are negative, implying for $(222)^{2'}$ and$(222)^{4'}$ a tendency to separation into isolated defects. It seems that the increasing concentration of oxygen interstitials is not stabilized by defect clusters, in this situation.

III- Uranium self diffusion in UO_{2+x}

We suggest the idea that the Po_2 dependence of uranium self diffusion in UO_{2+x} requires contributions to D_u by V_U^{r}, $(222)^{2'}$ and$(222)^{4'}$.

The reason for this assumption is due to the fact that the uranium sublattice, which should be the natural ground for the uranium ion transport, admits, within itself, weak point defect concentrations, among which, V_U^{r}, especially at high temperature, in comparison with those existing in the oxygen sublattice, that is much more deficient.

We can therefore consider that the uranium ion transport is achieved without distinction in both sublattices, hence the taking into account of the above mentioned Willis defects within the diffusion process.

Such a situation is partially comparable to the impurity diffusion case, where an A atom moves inside an unexpected sublattice.

It therefore seems relevant to consider that the three terms constituting the partial diffusion coefficients, namely, the correlation factor, the defect diffusion coefficient and concentration prove to be different from those which would interfere in a normal context, that is , an oxygen diffusion within its sublattice, due to the defects inherent in the same sublattice (here ,the Willis defects).

We hence write the uranium self diffusion coefficient as the sum of three contributions, the first due to uranium vacancies and the others to Willis defects:

$$D_U = D_{U_{V'_U}} + D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)''}} + D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)^{4'}}} \tag{13}$$

where $D_{U_{V'_U}}$ is equal to:

$$D_{U_{V'_U}} = D_{V'_U} f_{V'_U} [V'_U] \tag{14}$$

$f_{V'_U}$ *and* $D_{V'_U}$ are the uranium vacancy correlation factor and partial diffusion coefficient, respectively.

Concerning $D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)''}}$ and $D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)^{4'}}}$, they have been expressed as:

$$\begin{cases} D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)''}} = D^{(2)}_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)''} f^{(2)}_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)''} [(2O''_i 2O'_i 2V_O^{\cdot\cdot})'']^{(2)} \\ D_{U_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)^{4'}}} = D^{(2)}_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)^{4'}} f^{(2)}_{\left(2O''_i 2O'_i 2V_O^{\cdot\cdot}\right)^{4'}} [(2O''_i 2O'_i 2V_O^{\cdot\cdot})^{4'}]^{(2)} \end{cases} \tag{15}$$

The subscript «2» characterizes a situation where the uranium ion moves into the oxygen sublattice, which is not its “natural” one, via the Willis defects.

$D^{(2)}_{def}$, $f^{(2)}_{def}$ and $[\mathrm{def}]^{(2)}$ can hence be written as:

$$\begin{cases} f_{déf}^{(2)} = f_{déf}^{o}\, exp\left(-\frac{\varphi}{RT}\right) \\ D_{déf}^{(2)} = D_{déf}^{o}\, exp\left(-\frac{\delta G^{m}}{RT}\right) \\ [déf]^{(2)} = [déf]^{o} exp\left(-\frac{\delta G^{f}}{RT}\right) \end{cases} \tag{16}$$

where the subscript «o» concerns a “normal” case, i.e., an uranium diffusion in its sublattice.

The exponential terms that appear in relation (16) may be explained by the fact that the uranium diffusion process in the oxygen sublattice modifies the probability of defect presence near an uranium ion, as well as their exchanges, in comparison with defects and oxygen ions.

Therefore, the partial self diffusion coefficients can be expressed as:

$$\begin{cases} D_{U_{(2O_i''2O_i'2V_O)''}} = D^{o}_{(2O_i''2O_i'2V_O^{\bullet})''} f^{o}_{(2O_i''2O_i'2V_O)''} [(2O_i''2O_i'2V_O^{\bullet})'']^{o} exp\left(-\frac{\delta Q_{(2O_i''2O_i'2V_O)''}}{RT}\right) \\ D_{U_{(2O_i''2O_i'2V_O)^{4'}}} = D^{o}_{(2O_i''2O_i'2V_O)^{4'}} f^{o}_{(2O_i''2O_i'2V_O)^{4'}} [(2O_i''2O_i'2V_O^{\bullet})^{4'}]^{o} exp\left(-\frac{\delta Q_{(2O_i''2O_i'2V_O)^{4'}}}{RT}\right) \end{cases} \tag{17}$$

with $\delta Q_{defect} = \varphi_{defect} + \delta G^{m}_{defect} + \delta G^{f}_{defect}$

The combination of equations (13-17), associated with the different mass action laws of these defects lead to general relation of D_U:

$$D_U = A_1(T)\frac{P_{O_2}}{\sigma^4} + B_1(T)\frac{P_{O_2}}{\sigma^2} + C_1(T)\frac{P_{O_2}}{\sigma} \tag{18}$$

where $A_1(T)$, $B_1(T)$ and $C_1(T)$ are new adjustment parameters, defined as:

$$\begin{cases} A_1(T) = exp\left(-\frac{\delta Q_{(2O_i'' 2O_i' 2V_O)^{4'}}}{RT}\right) K_{cls4}(e\mu)^4 D_{(2O_i'' 2O_i' 2V_O)^{4'}} f_{(2O_i'' 2O_i' 2V_O)^{4'}} \\ B_1(T) = exp\left(-\frac{\delta Q_{(2O_i'' 2O_i' 2V_{\ddot{O}})''}}{RT}\right) K_{cls2}(e\mu)^2 D_{(2O_i'' 2O_i' 2V_{\ddot{O}})''} f_{(2O_i'' 2O_i' 2V_{\ddot{O}})''} \\ C_1(T) = K^f_{V_U'}(e\mu) D_{V_U'} f_{V_U'} \end{cases} \quad (19)$$

We have least-squares fit the Po_2 dependence of uranium self diffusion data of Hawkins and al [12] to equation (18). The results of the fitting procedure are show in figure 4.

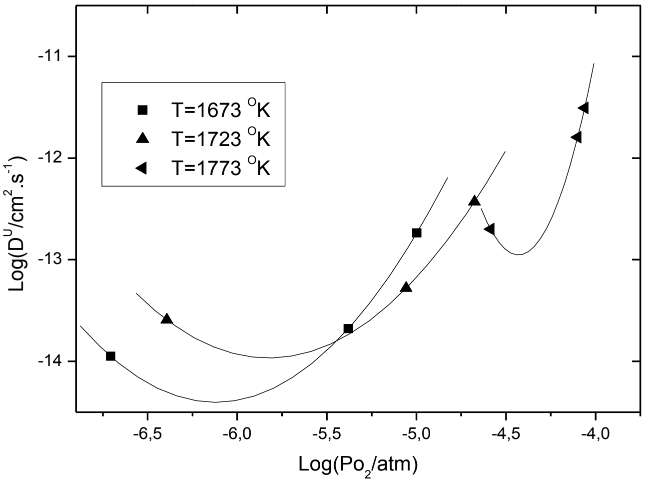

Figure 4: Adjustment procedure theory/experimental results of the cation self-diffusion coefficient in UO_{2+x} obtained by [12], for three different temperatures.

The temperature dependent fitting parameters $A_1(T)$, $B_1(T)$ and $C_1(T)$, have also been found as Arrhenius laws:

$$\begin{cases} A_1 = (5.4 \pm 0.1)\mathrm{E}55\exp\left(-\frac{(435.0 \pm 1.0)\mathrm{Kcal/mol}}{\mathrm{RT}}\right) \\ B_1 = (2.6 \pm 0.3)\mathrm{E}28\exp\left(-\frac{(242.0 \pm 6.0)\mathrm{Kcal/mol}}{\mathrm{RT}}\right) \\ C_1 = (1.7 \pm 0.6)\mathrm{E}41\exp\left(-\frac{(365.0 \pm 34.0)\mathrm{Kcal/mol}}{\mathrm{RT}}\right) \end{cases} \quad (20)$$

Moreover, each of the three partial diffusion coefficients of uranium in UO_{2+x}, namely, $D_{V_U'}$,$D_{U_{(2O_i''2O_i'2V_O)''}}$ and $D_{U_{(2O_i''2O_i'2V_O)^{4'}}}$, have been reported in Figure 5 as a function of temperature.

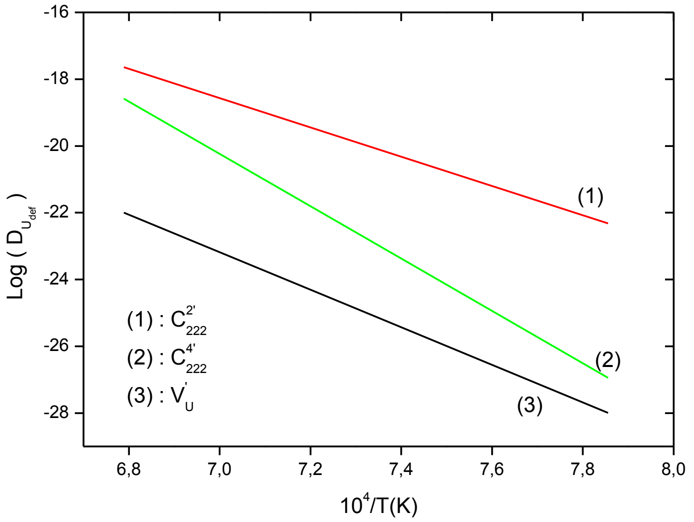

Fig. 5 : Evolution of the uranium partial diffusion coefficients, as a function of T at $Po_2=10^{-10}$atm.

It particularly appears that the uranium transport via the Willis defects is much important that the vacancy one in the overall temperature domain under study.

Indeed, it is known that the activation energy associated which each of three defects is the sum of its migration and formation enthalpies:

$$Q^U_{def} = \Delta H^{m_U}_{def} + \Delta H^{f_U}_{def} \qquad (21)$$

The calculation of the different slopes gives:

$$Q^U_{V_U'} = 172.3\ Kcal.mol^{-1}\ ;\quad Q^U_{(222)^{2'}} = 161.5\ Kcal.mol^{-1}\ ;\quad Q^U_{(222)^{4'}} = 220.0\ Kcal.mol^{-1}\ (22)$$

Concerning the evolution of the product (the defect correlation factor) by (the defect diffusion coefficient),i.e., d_{def}, Figure 6 deals with their temperature dependence.

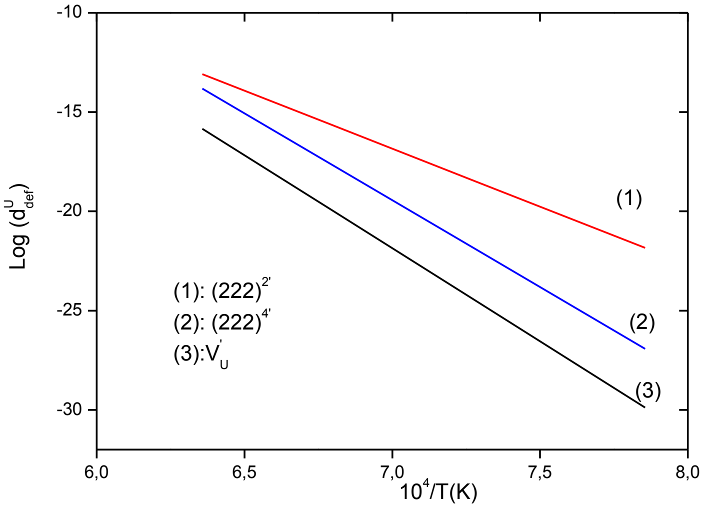

Fig. 6: Variations of $d^U_{V'_U}$, $d^U_{(222)^{2'}}$ and $d^U_{(222)^{4'}}$ as a function of temperature.

We can observe that $d^U_{(222)^{2'}}$ and $d^U_{(222)^{4'}}$ are greater than $d^U_{V'_U}$ and this, for all the studied temperature range.

The evaluation of the different curve slopes gives:

$$\begin{cases} \Delta H^{m_U}_{V'_U} = 186.4K\,cal.mol^{-1} \\ \Delta H^{m_U}_{C^{2'}_{222}} = \Delta H^{m_{ox}}_{C^{2'}_{222}} + \delta H^{m}_{C^{2'}_{222}} + \varphi = 116.1Kcal.mol^{-1} \\ \Delta H^{m_U}_{C^{4'}_{222}} = \Delta H^{m_{ox}}_{C^{4'}_{222}} + \delta H^{m}_{C^{4'}_{222}} + \varphi = 173.9Kcal.mol^{-1} \end{cases} \qquad (23)$$

Here, we have considered that the uranium defect correlation factor, $f_{V_U'}$, is constant and equal to 0.654 [21-22].

From equations (21),(22) and (23), it is possible to determine the formation enthalpies of the defects:

$$\begin{cases} \Delta H_{V_U'}^{f_U} = 14.1\, Kcal/mol \\ \Delta H_{C_{222}^{2'}}^{f_U} = \Delta H_{C_{222}^{2'}}^{f_{ox}} + \delta H_{C_{222}^{2'}}^{f} = 45.4\, Kcal/mol \\ \Delta H_{C_{222}^{4'}}^{f_U} = \Delta H_{C_{222}^{4'}}^{f_{ox}} + \delta H_{C_{222}^{4'}}^{f} = 46.1\, Kcal/mol \end{cases} \qquad (24)$$

It is to be noticed that values $\Delta H_{(222)^{2'}}^{f_{ox}}$ and $\Delta H_{(222)^{4'}}^{f_{ox}}$are known and materialized by equations (12); then, the determination of the excess of defect Willis formation enthalpies is immediate, by taking into consideration equations (24). We get:

$$\delta H_{(222)^{4'}}^{f} = 171.2\, Kcal.mol^{-1} \qquad \text{and} \qquad \delta H_{(222)^{2'}}^{f} = 46.6 Kcal.mol^{-1} \qquad (25)$$

These results highlighted the fact that there is a preferential interaction between uranium ions and the $(222)^{2'}$defects into the diffusion process in UO_{2+x}.

IV- Conclusion

A point defect model, including simple and complex ones, has been elaborated in order to explain, in a self consistent manner, the most convincing results of charge and matter transport in UO_{2+x}.

For this, three point defects have been taken into consideration, i.e., V_U'' , $2\left(O_i''O_i'V_O^{\cdot}\right)''$ and $2\left(O_i''O_i'V_O^{\cdot}\right)^{4'}$.

This model has been used for fitting and suggesting a coherent analysis of cationic and anionic self diffusion data.

The obtained results showed a fairly good adjustment procedure, leading to an appropriate appreciation of the different formation migration and interaction energies of the defects proposed.

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