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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Contribution to the understanding of the point defect influence on some transport properties in UO_{2+x}

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Abstract

A point defect model is developed in hyperstoichiometric uranium dioxide, UO_{2+x},in order to explain some experimental results of deviation from stoichiometry and electrical conductivity existing in the literature. This model takes into account both singly charged uranium vacancy,V_U', and 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 $2(O_i''O_i'V_{\dot{O}})''$ and $2(O_i''O_i'V_{\dot{O}})^{4'}$. The electron holes, $h^{\cdot}$, are also introcued to ensure the crystal global electroneutrality.

An adjustment procedure of the most convincing experimental data of the literature, corresponding to the temperature and oxygen partial pressure dependencies of departure from stoichiometry,x, and electrical conductivity, σ, has been undertaken. The fit model/experience obtained has been found fairly good, justifying, a posteriori, the relevance of the nature of the selected defects in the model.

Keywords: point defect, hyperstoichiometric uranium dioxide, stoichiometry, electrical conductivity

I-Introduction

hyperstoichiometric uranium oxide , UO_{2+x} , is an ionocovalent component with fluorite structure (CaF_2): oxygen anions occupy the tetraedric sites of geometrically compact piling of metallic atoms and the empty octaedric sites constitute preferential positions for interstitial ions[1].

UO_{2+x} has been subject to a considerable amount of research, from a fundamental point of view since it represents a reference material to better understand many transport properties (conductivity, creep, diffusion) in relation to the established presence of high concentration defects, simples and complexes[2], as well as a practical point of view, given its use as a nuclear fuel [3].

The departure from stoichiometry, x, has been extensively studied as a function of temperature, T, and oxygen partial pressure,Po_2, [4-14]. Various research methods have been adopted (thermogravimetry, coulometric titration, EMF, hardening …..) upon study materials subject to specific elaboration and preparation modes.

Most experimental results obtained seem, however, to show qualitative agreement, with the appreciable exception of those related to the so called intermediate oxygen partial pressure domain ($10^{-14} \leq Po_2$ (atm) $< 10^{-12}$ and T ≥1273 °K).

Consequently, the analyses suggested in terms of defects responsible for the evolution of that property are consistent with the presence of $(2O_i^a 2O_i^b 2V_o)'$ Willis clusters at very high Po_2 ($10^{-12} \leq Po_2$ (atm) $< 10^{-7}$ and T ≥1273 °K) and $(2O_i^a 2O_i^b 2V_o)^{4'}$ ones at very low Po_2 ($Po_2 \leq 10^{-16}$atm and 973 ≤ T(°K) ≤1273) but not with intermediate Po_2, where significant divergences can be noticed, that is, where x varies between $10^{-2}$and 10^{-3}.

Electrical conductivity in UO_{2+x} has also been subject to a considerable amount of experimental investigations [10],[14-18]. Nevertheless, the values obtained by the various authors show great discrepancies between themselves (sometimes up to two orders); such differences may be accounted for by the analysis tools used, the thermomechanical history and the crystallographic nature of each study material, together with the possible lack of mastery, on the part of many experimenters, of the specific oxygen partial pressure measure conditions.

However, the overall aspect of the electrical conductivity curves observed in UO_{2+x} supports the idea of a p-type behavior at high T and Po_2.

More specifically, and although the definition of the three Po_2 domains, high, intermediate or low, adopted by the different authors [4] ,[17] is not probably the same, it seems, however, that at very high Po_2, the experimental conditions are such that measures may be characterized by uncertainty[16].

In the domain of Po_2 just inferior to the previous one, the authors agree to say that σ is proportional to $Po_2^{1/2}$, point defect suggested to account for such results being the $(2O_i^a 2O_i^b 2V_O)'$ Willis cluster [1],[4], [16].

The disagreement, experimental as well as theoretical, between the authors becomes noticeable in the third Po_2 domain, just inferior to the previous one.

Indeed, Kang and al[10]found an $Po_2^{1/5}$ dependence of σ due to the influence of $(2O_i^a 2O_i^b 2V_O)^{4'}$ defects, whereas Mastui and Naito[4] identified an $\sigma \alpha Po_2^{1/2}$behavior law, implying the preponderant presence of $(2O_i^a O_i^b 2V_O)^{5'}$ as the defect responsible for this situation.

Finally, at very low Po_2, the results prove a Po_2 non-dependence on conductivity, the influence of ionized impurities being likely to interfere significantly.

The present contribution is in keeping with such a framework and its aim is to develop a model of point defects, simples and complexes, likely to fit and analyses the σ and x results already available in the literature.

The various defect concentrations will thus be determined and carrier mobility specified.

II- Point defects model for UO_{2+x}

In the forthcoming section, our purpose is to explain the most convincing experimental results in the literature concerning electrical conductivity and non-stoichiometry, based on a point defect model that integrates two Willis defect types, $(2O_i''2O_i'2V_O^{=})''$and $(2O_i''2O_i'2V_O^{\cdot\cdot})^{4'}$, referred to as C_{222}'' and $C_{222}^{4'}$ respectively, and singly charged vacancy uranium, V_U'.

The formation equations of the elementary point defects constituting the two complexes, namely the interstitial oxygen and oxygen vacancy , can be written, by adopting the formalism of Kröger and Vink, as follows [16]:

- For the interstitial oxygen charged negatively α times , $O_i^{\alpha'}$,with α=1 or 2 :

$$\frac{1}{2}O_2(g) \Leftrightarrow O_i^{\alpha'} + \alpha\dot{h} \qquad (1)$$

which gives, by applying the mass action law:

$$K_{O_i^{\alpha'}}^f = [O_i^{\alpha'}]p^{\alpha}Po_2^{-1/2} \qquad (2)$$

$K_{O_i^{\alpha'}}^f$ stands for the formation constant of the interstitial oxygen ion, $[O_i^{\alpha'}]$ its concentration, p, the hole concentration $([h^{\cdot}] = p)$ and Po_2, the oxygen partial pressure.

- For the oxygen vacancy charged positively β times , $V_O^{\beta\cdot}$, with β=1 or 2 :

$$O_o \Leftrightarrow V_O^{\beta\cdot} + \beta e^- + \frac{1}{2}O_2(g) \qquad (3)$$

The law of mass action is written this time:

$$K_{V_O^{\beta\cdot}}^f = [V_O^{\beta\cdot}]n^{\beta}Po_2^{1/2} \qquad (4)$$

where $K_{V_O^{\beta\cdot}}^f$ represents the formation constant the oxygen vacancy, $V_O^{\beta\cdot}$, $[V_O^{\beta\cdot}]$ its concentration, and n the electron concentration, $([e^-] = n)$.

Concerning the defects of Willis, $C_{222}^{''}$ and $C_{222}^{4'}$, the formation equations are the following:

$$2O_i^{''} + 2O_i^{'} + 2V_O^{\cdot\cdot} \Leftrightarrow \left(2O_i^{''}2O_i^{'}2V_O^{\cdot\cdot}\right)^{''} \qquad (5)$$

and

$$2O_i^{''} + 2O_i^{'} + 2V_O^{\cdot\cdot} \Leftrightarrow \left(2O_i^{''}2O_i^{'}2V_O^{\cdot\cdot}\right)^{4'} \qquad (6)$$

with the mass action laws, respectively:

$$K_{C_{222}^{''}}^{f} = [C_{222}^{''}][O_i^{'}]^{-2}\left[V_O^{\cdot\cdot}\right]^{-2}[O_i^{''}]^{-2} = [C_{222}^{''}]\left(K_{O_i^{'}}^{f}K_{O_i^{''}}^{f}K_{V_O}^{f}\right)^{-2}(K_G)^{-4}\ \ Po_2^{-1}p^{2} \qquad (7)$$

and

$$K_{C_{222}^{4'}}^{f} = [C_{222}^{4'}][O_i^{'}]^{-2}\left[V_O^{\cdot\cdot}\right]^{-2}[O_i^{''}]^{-2} = [C_{222}^{4'}]\left(K_{O_i^{'}}^{f}K_{O_i^{''}}^{f}K_{V_O}^{f}\right)^{-2}K_G^{-2}Po_2^{-1}p^{4} \qquad (8)$$

$K_{C_{222}^{''}}^{f}$ and $K_{C_{222}^{4'}}^{f}$ are the formation constants of the complexes $C_{222}^{''}$ and $C_{222}^{4'}$,respectively; K_G which represents the intrinsic ionization constant of electronic carriers, is determined according to the relation:

$$e' + h^{\cdot} \Leftrightarrow \emptyset \qquad (9)$$

the mass action law concerning this relation is written as:

$$[e']\left[h^{\cdot}\right] = np = K_G \qquad (10)$$

As far as the cation defect sublattice is concerned, which is less defective than the anion-sublattice, the formation of the vacancy uranium singly charged, $V_U^{'}$, whose presence many authors recognize at the highest concentration [18],[19], is characterized by the following equation:

$$O_2(g) \Leftrightarrow 2O_o + V_U' + \dot{h} \qquad (11)$$

By applying the mass action law, we get:

$$K^f_{V_U'} = [V_U']\,p\,Po_2^{-1} \qquad (12)$$

where $K^f_{V_U'}$ represents the vacancy uranium formation constant, and $[V_U']$, its concentration.

As for the crystal global equation of electroneutrality, it is written, in this case, as follows:

$$2\left[\left(2O_i''2O_i'2V_O^{\bullet\bullet}\right)''\right] + 4\left[\left(2O_i''2O_i'2V_O^{\bullet\bullet}\right)^{4'}\right] + [V_U'] = [\dot{h}] = p \qquad (13)$$

Taking into account relations (1-12), this relation becomes:

$$4K_{cls4}P_{O_2}[\dot{h}]^{-4} + 2K_{cls2}P_{O_2}[\dot{h}]^{-2} + K^f_{V_U'}[\dot{h}]^{-1}P_{O_2} = p \qquad (14)$$

The K_{cls4} and K_{cls2} constants can be defined as:

$$K_{cls4} = K^f_{C_{222}^{4'}}\left(K^f_{O_i'}K^f_{O_i''}K^f_{V_O}\right)^2(K_G)^{-2}$$

and (15)

$$K_{cls2} = K^f_{C_{222}''}\left(K^f_{O_i'}K^f_{O_i''}K^f_{V_O}\right)^2(K_G)^{-4}$$

Relation (14) constitutes the basic equation of our approach, every single step of which is now being accounted for.

III-Electrical conductivity in UO_{2+x}

It is now acknowledged that hyperstochiometric uranium dioxide, UO_{2+x}, has a p-type semi-conductor character over a wide domain of Po_2[5].

Electrical conductivity can thus be expressed as:

$$\sigma = \mu_p q\, p \tag{16}$$

Where $\mu_p$represents the electronic hole mobility and q the elementary charge.

By combining equations (14) and (16), we get a relation of the type:

$$\sigma^5 - 4K_{cls4}(\mu_p q)^4 P_{O_2} - 2K_{cls2}(\mu_p q)^2 P_{O_2}\sigma^2 - K^f_{V'_U}(\mu_p q)P_{O_2}\sigma^3 = 0 \tag{17}$$

Let us introduce the following parameters:

$$\begin{cases} A(T) = 4K_{cls4}(q\mu_p)^5 \\ B(T) = 2K_{cls2}(q\mu_p)^3 \\ C(T) = K^f_{V'_U}(q\mu_p)^2 \end{cases} \tag{18}$$

Relation (17) can then be simplified as:

$$\sigma^5 = A(T)P_{O_2} + B(T)P_{O_2}\sigma^2 + C(T)P_{O_2}\sigma^3 \tag{19}$$

An adjustment procedure of the most convincing experimental results in the literature concerning conductivity as a function of Po_2 with theoretical equation (19), and A, B and C used as adjustment parameters, has been undertaken.

In figure1, which represents this operation, a satisfactory theory/experience agreement can clearly be noticed and this, for the three different temperatures.

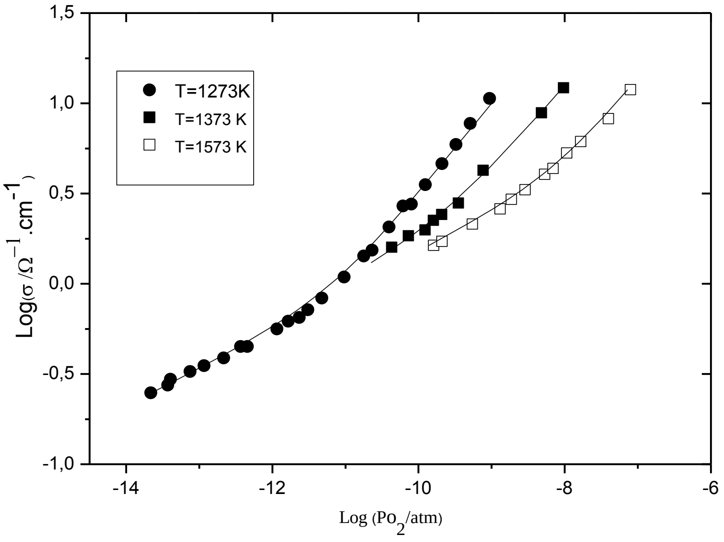

Fig.1: Adjustment procedure theory/experimental results of $\sigma = f(Po_2)$ obtained by [15], for three temperatures.

The determination of A, B and C the parameters for each adjustment has enable us to express them in an Arrhenius form, of the $Y=Y_0\exp(-Q/RT)$ type.

	Q(Kcal/mol)	Y_0
A	34.7±0.4	(3.4±0. 4)E16
B	6. 1±0.1	(2.1±0.1)E+11
C	67. 8±0.6	0.2±0.1

Table1: Results obtained for A, B and C parameters.

IV- Non-stoichiometry

The second step of our operation consists in expressing the oxygen non-stoichiometry ,x, as a function of the various defects retained in our model:

$$x = 2[C_{222}^{''}] + 2[C_{222}^{4'}] + [V_U'] \qquad (20)$$

By taking into account the different mass action laws associated with these defects, we get:

$$x = A_1(T)\frac{P_{O_2}}{\sigma^4} + B_1(T)\frac{P_{O_2}}{\sigma^2} + C_1(T)\frac{P_{O_2}}{\sigma} \qquad (21)$$

where A_1, B_1 and C_1 represent new adjustment parameters, equal to, respectively:

$$\begin{cases} A_1(T) = 2K_{cls4}\left(q\mu_p\right)^4 \\ B_1(T) = 2K_{cls2}\left(q\mu_p\right)^2 \\ C_1(T) = K_{V_U'}^{f}\left(q\mu_p\right) \end{cases} \qquad (22)$$

Figure 2 characterizes the product of the adjustment process between theory, represented by the relation (21) and the experimental results found in the literature. A satisfactory agreement between the two can be noticed.

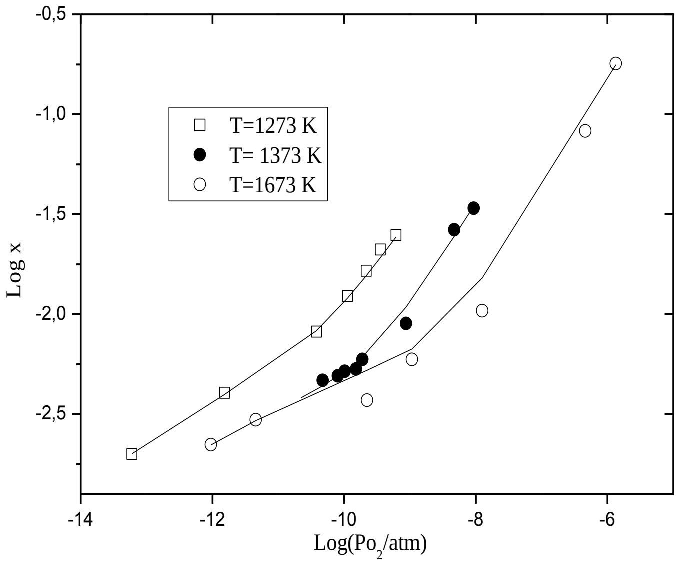

Fig. 2: Adjustment procedure theory/experimental results of x = f (Po_2) obtained by [15] and [16], for three different temperatures.

As with electrical conductivity, it has possible to confer an Arrhenusian behavior, $Y=Y_0\exp(-Q/RT)$ type, to adjustment parameters A_1, B_1 and C_1.

	Q(Kcal/mol)	Y_0
A_1	34.6±2.0	(1.1±0.9)E13
B_1	24.0 ± 1.0	(4.0 ±1.0)E4
C_1	63.9±0.6	(2.9 ± 0.7)E-3

Table2: Results obtained for A_1, B_1 and C_1 parameters.

V- Defect concentrations

The first consequence inherent in the adjustment procedure, with our theoretical model, of the experimental results of electrical conductivity and non-stoichiometry, consists in the indirect determination of the defect concentrations present in the model; indeed, the product of these operations can be related to the knowledge of A_i , B_i and C_i parameters, defined by relations (18) and (23), which integrate with the various defect formation constants shown and thus, their concentrations.

Prior knowledge of electronic holes mobility is, however necessary. Several studies on the subject have been conducted, [15] [17] [20], and the most convincing ones recognize a mechanism of small polaron thermically activated for electronic transport, of the form:

$$\mu_p = \mu_0 exp\left(-\frac{\Delta H_m^p}{RT}\right) \qquad (23)$$

ΔH_m^p, the hole mobility enthalpy, has been calculated and found equal to 0.17eV [15] and 0.20 eV [20] by the authors mentioned above.

At high temperature, the intrinsic nature of the electronic transport has led to the determination of the gap energy, E_G, which comes into play in constant K_G. It has found equal to 2.0eV [13], a result confirmed by other authors [5].

As far as we are concerned, the procedure adopted has made it possible to determine the relation expressing the electronic carriers mobility evolution, in the sense that the evolution of the relationships between the parameters A and A_1 defined by the relations (18) and (22), reflects a behavior well materialized by equation (23), which is confirmed in figure (3).

The mobility enthalpy, which has been obtained from the curve, is equal to 0.20 eV, that is to say, a value in very good agreement with those found in the literature.

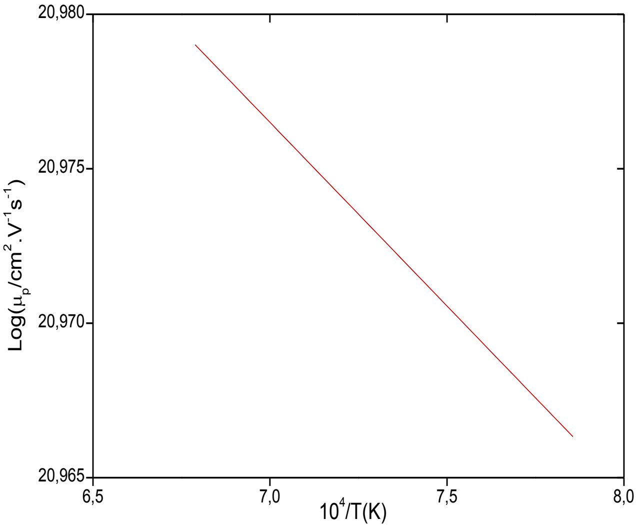

Fig. 3: Evolution of the electronic carrier mobility as a function of T.

It is now possible to determine the model defect concentrations and this, by solving an equation system defined by the relations (7-24).

This operation enable us to appreciate the concentration evolution of the two Willis complexes, C''_{222} and $C^{4'}_{222}$, the vacancy uranium, V'_U, and the holes, h , as a function of temperature.

Figure 4 represents this situation.

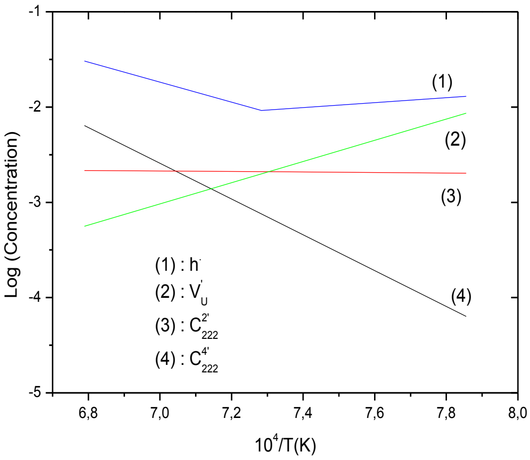

Fig. 4: Evolution of the various defect concentrations as a function of temperature, at $Po_2=10^{-10}$atm.

At low temperature, Figure 4 shows that the uranium vacancy concentration is higher than the Willis defect ones, but not than their sum; this situation is logical since the formation of these clusters is much likely at high temperature , particularly when they are partially constituted with interstitials.

Furthermore, it appears that the concentration of the C''_{222} Willis defect type is quasi-constant on the overall investigated temperature range.

It is to be noticed that the Willis defect concentration that admits the much higher ionization degree becomes predominant at T greater than or equal to 1400° K.

IV- *Conclusion*

A defect model, simples and complexes, has been developed to account for, in a self-consistent way, the most convincing experimental results found in the literature regarding electrical conductivity and deviation from stoichiometry in hyperstoichiometric uranium oxide, UO_{2+x}.

Two defect Willis of the type $2(O_i''O_i'V_O^{\bullet\bullet})''$and $2(O_i''O_i'V_O^{\bullet})^{4'}$belonging to the most deficient sublattice oxygen, the uranium vacancy once charged negatively, V_U', positioned on the cation sublattice, as well as the electronic holes, have been taken into consideration.

The theory/experience adjustment procedures undertaken have revealed a satisfactory agreement, justifying a posteriori, the relevance of the defects identified.

The most important outcomes of this operation are the determination of the various defect concentrations, as well as the hole mobility.

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.

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