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THE THERMODYNAMICAL PROPERTIES OF $(U,Pu)O_{2+x}$
DESCRIBED WITH A CLUSTER MODEL

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A simple model is presented which allows to compute easily $\overline{\Delta G}_{O_2}$ and $\overline{\Delta H}_{O_2}$ at any temperature, oxygen and plutonium content for $U(Pu)O_{2+x}$. Some implications on the nature of the defects are drawn, values for their energy of formation are given and their concentration may be computed.

INTRODUCTION

In uranium plutonium mixed oxide fuel, oxygen partial pressure and chemical potential are certainly very important parameters in determining chemical state of fission products, transport mechanisms, elements redistribution, and the stainless steel clad reaction. Many experimental data on UO_{2+x} and a few on $(U,Pu)O_{2+x}$ [1, 2, 3, 4] are available with, unfortunately, some disagreement between results

Oxygen partial pressure p_{O_2} is a function of 3 independent variables: temperature, oxygen and plutonium to metal ratios. So, in order to compare experimental results and to choose a smooth function, some extrapolations have to be performed. To solve this problem, two ways are possible.

a - In a classical manner, oxygen partial enthalpy and entropy $\overline{\Delta H}_{O_2}$ and $\overline{\Delta S}_{O_2}$ are assumed to be independent of temperature T. Following Märkin [1], $\overline{\Delta H}_{O_2}$ and $\overline{\Delta S}_{O_2}$ are calculated as a function of plutonium valency for hypostoichiometric oxide and of uranium valency for hyperstoichiometric oxide. Unfortunately, above 1500°C, this assumption seems to be far from the real case, because uranium dioxide becomes also hypostoichiometric. We must then use the other method.

b - Some authors attempted to apply thermodynamical models to oxide solid solutions. Mainly, Thorn and Winslow [5], and Blackburn [6] tried to reproduce the whole range of non-stoichiometry in uranium dioxide, with very different methods. Their results are very similar. For PuO_{2-x} , Chereau [7] reported an interesting, but complex, application of Atlas's model [8]. Blackburn [9] gave recently a very satisfactory representation of the oxygen potential in mixed oxide $(U,Pu)O_{2+x}$ with an easy method, but it presents some disadvantages :

- For the oxygen partial pressure variation in UO_{2+x} , the agreement with experimental results becomes rather bad for O/M ratios greater than 2.10. In the mixed oxide, there is probably the same deviation, but no experimental data have been reported for this composition range.

- More generally, the agreement is better for $(U,Pu)O_{2+x}$ (8 fitting parameters) than for UO_{2+x} (4 fitting parameters).

- The defects description is completely ionic. The choice of U^{2+} and U^{6+} ions is unsatisfactory.

From these considerations, we tried to achieve a model as easy to use as Blackburn's one, with a better agreement with experimental data. We mainly intended to represent the whole single phase region of $(U,Pu)O_{2+x}$, from UO_{2+x} to PuO_{2-x} , between 800°C and 2500°C,

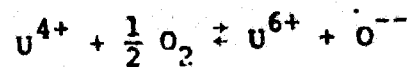
5. International conference on plutonium and other actinides. Baden-Baden, F.R. Germany, 10-13 September 1975
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with, as far as possible, a better physical interpretation.

II - GENERAL FORMULATION OF THE MODEL

1 - Influence of anionic defects on metallic lattice

For UO_{2+x} , Blackburn defined the oxidation of uranium with the following equation :



$$K = \frac{[U^{6+}]}{[U^{4+}] \times [O^{--}]} / P_{O_2}^{1/2} = \exp (A/T + B)$$

Then he describes the UO_2-UO_3 range with only two fitting parameters A and B. If we want to improve the agreement of his model with experiments, we must increase the number of parameters. The partition into 2 steps $U^{4+} \rightarrow U^{5+}$ and $U^{5+} \rightarrow U^{6+}$ is not sufficient. The only description of the $UO_{2.00} - UO_{2.25}$ region requires at least 4 parameters. In ionicity terms, fractional valency states, $U^{4.25+}$ and $U^{4.50+}$ must be used. That means we must renounce in localising on 1 metallic atom the electric charge which occurs in the oxidation. On the contrary, it would be distributed on a group of several cations.

2 - The assumptions of the model

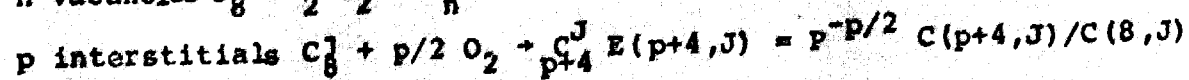
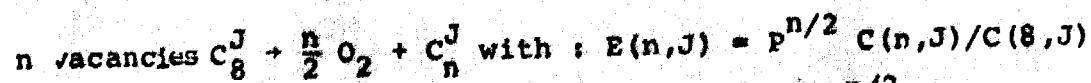
The crystal is formed by a pile of clusters or strings of N metallic atoms, with which 2.N equivalent oxygen sites are associated. The metallic lattice is assumed to be complete. A cluster may contain 0, 1, 2 ... or N uranium atoms, and the complement to N with plutonium.

In a cluster one or several oxygen vacancies or interstitials can exist .

In a preliminary work, we found that in order to get a good fit on experimental data, N should at least equal 8.

So it seems that an oxygen defect would interact with at least eight metal atoms. In this case, taking the lower phase boundary of $(U,Pu)O_{2-x}$ into consideration, we must assume 1, 2, 3 or 4 oxygen vacancies in a cluster, which correspond to $PuO_{1.5}$. For the hyperstoichiometric oxide, we have limited our representation at $UO_{2.275}$ in order to have only 3 types of defects and not too many parameters.

On the basis of these assumptions, the concentrations of defects are determined by the following reactions :



C_I^J symbolize a cluster which contains J plutonium atoms with the I-type defect.

$C(I,J)$ is the C_I^J type cluster concentration.

P is the oxygen partial pressure

$E(I,J)$ is the equilibrium constant of formation of the C_I^J cluster from the C_8^J type.

These equilibrium equations must verify the following balances :
 - oxygen/metal ratio :

$$O/M = \frac{1}{8} \sum_{J=0}^8 [15C(1,J) + 14C(2,J) + 13C(3,J) + 12C(4,J) \\ + 17C(5,J) + 18C(6,J) + 19C(7,J) + 16C(8,J)]$$

- metal lattice

Let $A_1(J)$ the concentration of clusters containing J atoms of plutonium

$$A_1(J) = \sum_{I=1}^8 C(I,J) \quad J = 0 \dots 8$$

$$\sum_{J=0}^8 J/8 A_1(J) = Pu/U+Pu = y$$

$$\sum_{J=0}^8 (8-J)/8 A_1(J) = 1-y$$

To introduce the enthalpy of formation of each defect, we write :

$$E(I,J) = \exp(H(I,J)/T + S(I,J))$$

III - APPLICATION TO UO_{2+x} AND PuO_{2+x}

1 - UO_{2+x}

The equations are greatly simplified because $J=0$.

a-The defects

In the hypostoichiometric region, we assume only 1 or 2 oxygen vacancies in a cluster, which allows to reach the composition $UO_{1.75}$. On the hyperstoichiometric side 1, 2 or 3 oxygen interstitials bound our representation at $UO_{2.375}$, which is commonly high enough. Then we have only 5 types of defects.

b-Results

For $O/M > 2.00$ we fitted the parameters on the references 10 to 19 and for $O/M < 1.99$ on the references [20, 21, 11, 23, 24, 25]. Numerical values are listed in Table I.

Defect	1 vac	2 vac	3 vac	4 vac	1 int	2 int	3 int
H	-86134	-184822	0	0	.6297	35196	45252
S	20.89	42.61	-∞	-∞	-3.37	-10.43	-17.95

Table I

To compare this work with the initial experimental data, we have plotted (fig. 1) the results of Hagemark [10] and Tetenbaum [20], and the curves computed with the model.

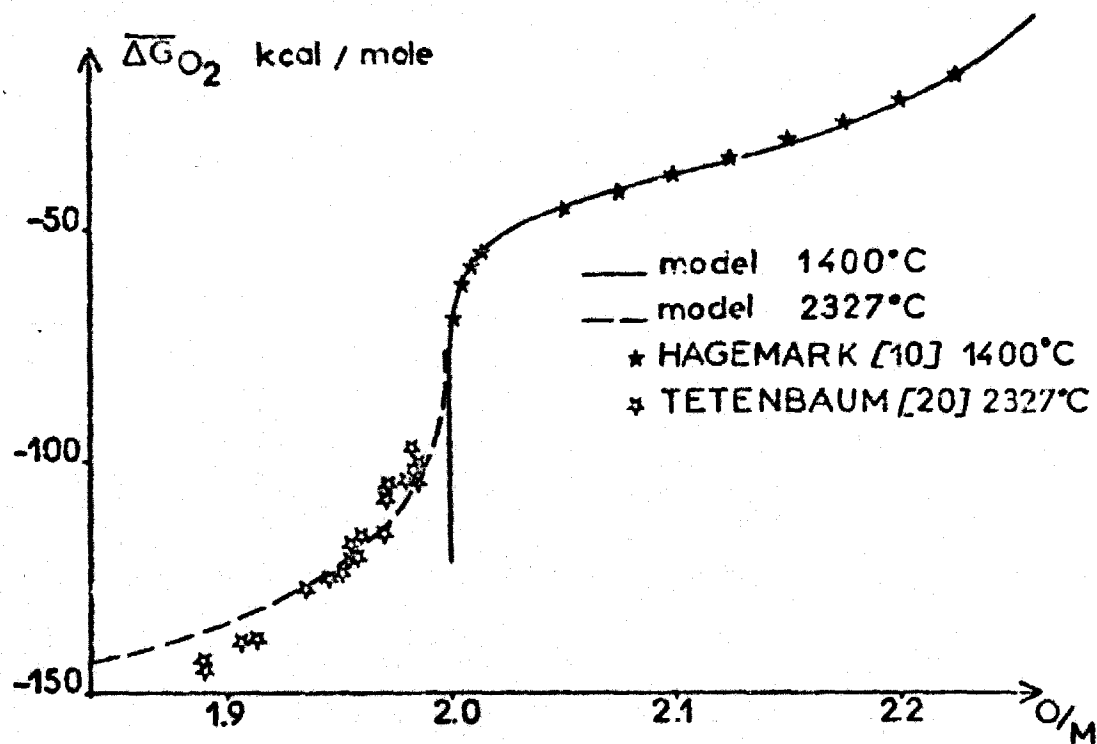


Figure 1

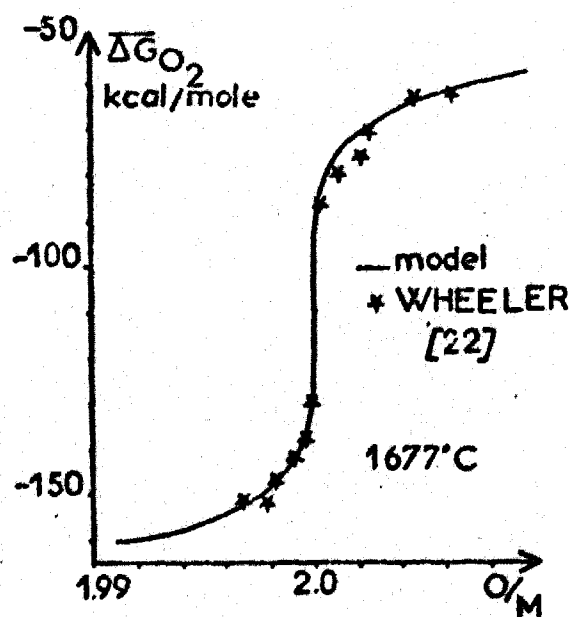


Figure 2

On figure 2, we have plotted our results and those of Wheeler [22], which were not used for the fitting.

In addition, in Table II, we have calculated for each set of reported data, a "standard deviation", according to the formula :

$$\sigma = \left[\frac{\sum (\bar{\Delta G}_{\text{model}} - \bar{\Delta G}_{\text{exp}})^2}{\text{nb of exp. points}} \right]^{1/2}$$

The composition relative to experimental points is assumed to be known accurately. This expression gives an idea of the agreement between our model and the experimental results, but, of course, includes also the scatter of data.

ref.	σ Kcal	ref.	σ	ref.	σ	ref.	σ
10	1.5	14	1.7	18	2.3	22	8
11	5.4	15	1.3	19	12	23	14
12	4.4	16	1.7	20	11	24	15
13	3	17	1.3	21	23	25	16

Table II

2 - PuO_{2-x}

There also, we have a simplification on J, which equals 8 only.

a- The defects

To describe the single phase region from $\text{PuO}_{1.7}$ to PuO_2 , we must consider 1, 2 or 3 oxygen vacancies in a cluster. We will see further that the lower phase boundary of the f.c.c. hypostoichiometric mixed oxide requires the reduction to Pu^{3+} of all the plutonium. That means there is an evidence to have 4 vacancies in a cluster of mixed oxide.

b- Results

The first 6 parameters have been fitted on the $\overline{\Delta G O_2}$ data of Markin [26] and on the $\overline{\Delta H O_2}$ data of Chereau [7]. The calculated curves and experimental points have been plotted on fig. 3. The two last parameters have been fitted on Tetenbaum's results [4] on $(\text{U,Pu})\text{O}_{2-x}$, according to the assumptions defined in part IV. The numerical values of parameters are listed in Table III.

defect	1 vac	2 vac	3 vac	4 vac	1 int	2 int	3 int
H	-62686	-117774	-167163	-208954	0	0	0
S	22.156	35.779	45.75	49.188	$-\infty$	$-\infty$	$-\infty$

Table III

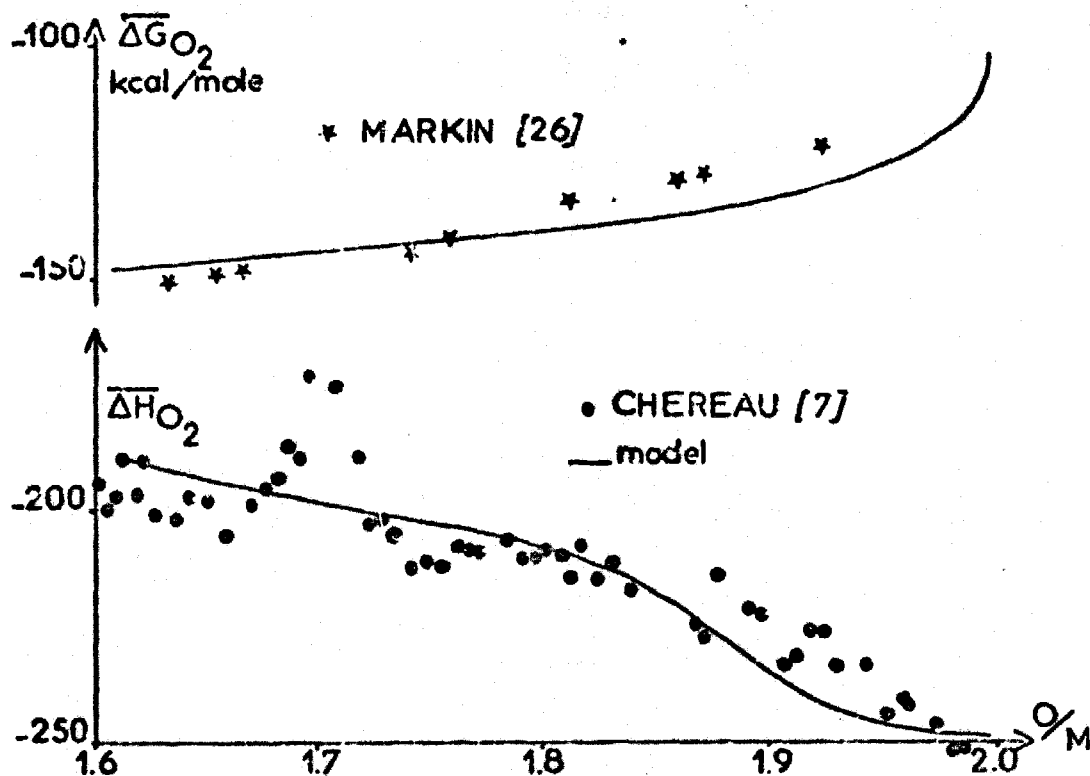


Figure 3

IV - THE MODEL FOR MIXED OXIDE

We need firstly the $AL(J)$ numerical values versus Pu/U+Pu ratio, and, secondly, the corresponding $E(I,J)$. Two cases have been anticipated :

- . Randomly distributed cations, according to a binomial law.
- . Two cluster types, with only 8 Pu atoms or 8 U atoms.

1 - Binomial distribution

The $AL(J)$ values can be calculated according to the expression :

$$AL(J) = \frac{8!}{J!(8-J)!} y^J (1-y)^{8-J}$$

To calculate the equilibrium constant of formation of each type of clusters, we have considered three cases :

a-linear variations from the 8-U cluster to the 8-Pu cluster.

$$E(I,J) = J/8 E(I,8) + (8-J)/8 E(I,0) \quad i = 1 \dots 7$$

b-linear change of H and S parameters.

$$E(I,J) = \exp (H(I,J)/T + S(I,J))$$

$$H(I,J) = J/8 H(I,8) + (8-J)/8 H(I,0)$$

$$S(I,J) = J/8 S(I,8) + (8-J)/8 S(I,C)$$

c-In the two cases, we have introduced some negative or positive deviation to the linear law.

In all the cases, on the hypostoichiometric side, we obtained successive oxidations of clusters, which gave rise to waves on the isothermal curves $\Delta\bar{G}_{O_2} = f(O/M)$, as it can be seen on a titration curve in aqueous solution. Actually, such a curve happens only at $O/M=2.0$. Then we have rejected these assumptions.

2 - If we forgot localizing physically clusters on the lattice, we can keep only the two types of clusters (or strings). "U" clusters and "Pu" clusters.

This assumption leads to the best agreement with experimental results (fig. 4).

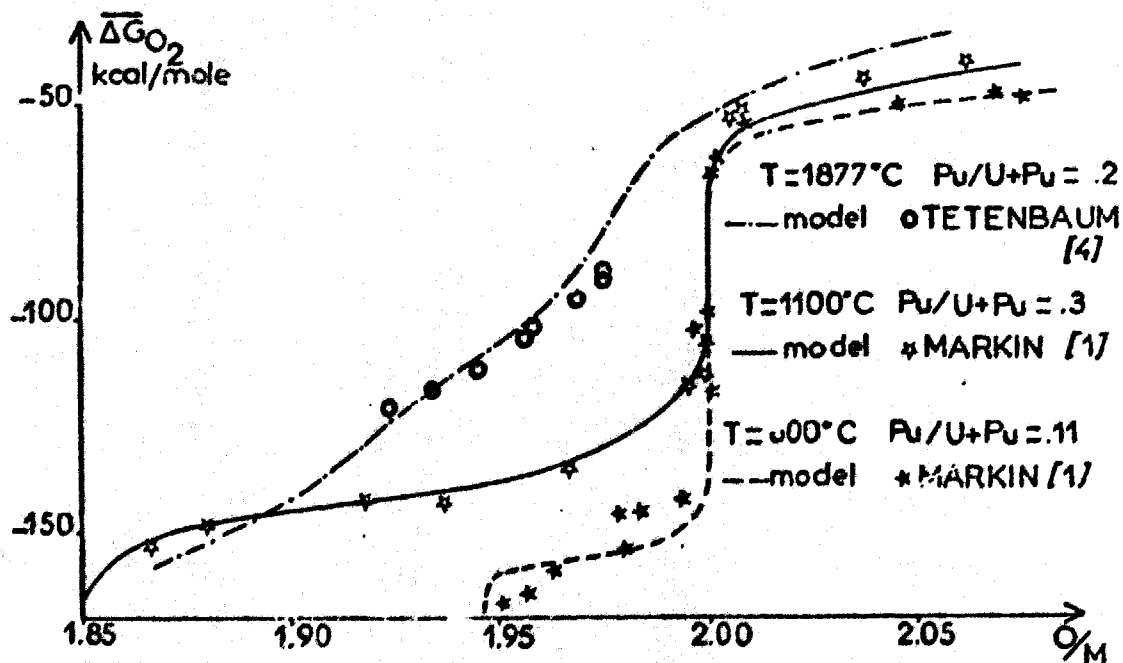


Figure 4

In Table IV, we have listed, as previously, with the same reservation, the standard deviation which gives this agreement.

Ref	1	2	3	4
σ Kcal	11.8	5.5	16.0	3.7

Table IV

Finally, we have computed at 1100°C the partial molar enthalpy $\overline{\Delta H}_{O_2}$ for Pu/U+Pu ratios equal to 0.1, 0.3, 0.5, 0.8, and have compared on fig. 5 our results with those obtained directly with a microcalorimeter by Chereau [7].

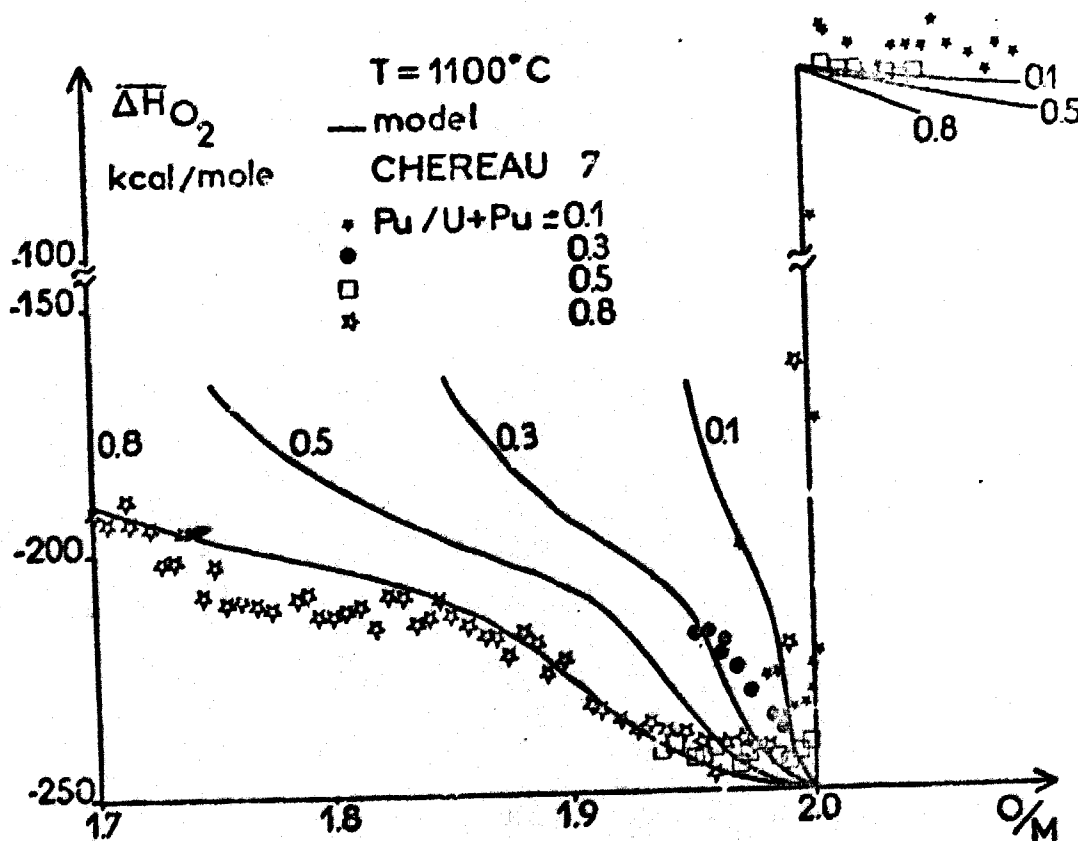


Figure 5

CONCLUSION

We have entered upon this study with a technological purpose. Firstly our model is a smoothing method for the scattered experimental data, with which the agreement seems good enough to allow the use of the so calculated $\overline{\Delta O_2}$ and $\overline{\Delta H O_2}$, without a large risk of deviation.

Secondly, we have pointed out the extent to which our model was sensitive to the basic assumptions. This sensitiveness brings so many difficulties in the fitting that the choice of any model is not free. So we can propose the following assumptions :

- There is an important covalency part in the bounding in both the hypostoichiometric and the hyperstoichiometric regions.
- Defects are either oxygen vacancies or interstitials, but not point defects : they occur in defect strings or clusters, which contain several metallic atoms, either Pu or U, and one or several oxygen defects (either vacancies or interstitials).
- All these defects are present in the lattice, but for a given temperature range Pu/U+Pu ratio and O/M ratio, only some of them are predominant.
- Crossing through the stoichiometric composition corresponds to a minimum of defects, that can be computed, but not to a non-defect state, especially at high temperature. There is an equilibrium between oxygen vacancies and interstitials, but not a discontinuity.

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