

Statistical thermodynamic study of nonstoichiometric titanium monoxide: Determination of formation and interaction energies of vacancies

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The energy and entropy of formation of titanium and oxygen vacancies as well as interaction energies between vacancies up to sixth-nearest neighbors have been determined in nonstoichiometric TiO. These values have been extracted from experimental partial molar enthalpy and entropy by means of a numerical method based on an enumeration of configurational states of defects in a small sample. As might be expected, a repulsion between like vacancies has been found. The calculations show that the repulsive interaction between titanium vacancies is very strong and limited to second neighbors (≈ 20 kcal/mol), while the repulsion between oxygen vacancies is weaker (≈ 5 kcal/mol between second neighbors) and is slowly decreasing as the separation between vacancies increases. More surprising are the interactions between unlike vacancies. A strong repulsion between first neighbors and a small attraction between second neighbors have been found. We show that all these interactions may be interpreted in terms of electronic structure and chemical bonding and that they allow one to understand in a qualitative way the low-temperature ordered structure of TiO.

I. INTRODUCTION

The refractory transition-metal compounds MX ($M = \text{Ti, V, Nb}$, $X = \text{C, N, O}$) are of great technological and theoretical interest due to the unusual combination of their physicochemical properties. On the one hand, they have the hardness and refractory properties of typical covalent materials, and on the other hand, they exhibit metallic properties such as electrical conductivity, and, in some cases, superconductivity comparable to those of the transition metals. In addition, their rocksalt structure is sufficiently simple to be attractive for theoretical analysis on electronic structure and chemical bonding. Many studies have been made in this direction.¹⁻¹⁰ It appears from these studies that, in these compounds, the electrons may be divided into two groups: The first group is involved in $M-X$ bonding which is a mixture of covalent binding from the hybridization of the $X 2p$ and $M 3d$ orbitals and ionic binding due to the electron transfer from M to X ; the second group is present in a conduction band mostly made of $M 3d$ orbitals of t_{2g} symmetry and is responsible for the metallic properties. The respective covalent and ionic parts in the $M-X$ bonding change from one compound to another and it has been shown, for example, that the bonding is of more "covalent" type in TiC and of more "ionic" type in TiO.⁴ This result may be generalized by observing that the melting temperature T_m increases from the oxide to the nitride then to the carbide of the same metal [for example, $T_m(\text{TiO}) = 1750^\circ\text{C}$, $T_m(\text{TiN}) = 3220^\circ\text{C}$, $T_m(\text{TiC}) = 3290^\circ\text{C}$, and $T_m(\text{VO}) = 1790^\circ\text{C}$, $T_m(\text{VN}) = 2310^\circ\text{C}$, $T_m(\text{VC}) = 2810^\circ\text{C}$], which can be understood by the increase in the covalent part in the $M-X$ bonding, which is responsible for the refractory properties. The importance of the $M-X$ bond with respect to the $M-M$ bond has also been studied.⁴ The comparison of the melting points are here again in-

teresting. For example, T_m of pure titanium is equal to 1675°C , therefore only 75°C lower than that of TiO, and, in addition, the lattice parameter of Ti is about equal to the first cation-cation separation in TiO. This may be explained by the fact that metallic bonding in TiO plays a major role, and that this role decreases for TiN and then further for TiC.

Another common property of these compounds is their capacity to accommodate high concentrations of atomic vacancies: anionic vacancies only for carbides and nitrides and both cationic and anionic vacancies for oxides. This generally induces large deviations from stoichiometry ($0.5 < x < 0.97$ for TiC_x , $0.5 < x < 1$ for TiN_x , $0.7 < x < 1.25$ for TiO_x and VO_x , . . .), apart from the case for which the vacancies are ordered (NbO, for example). The influence of the anionic vacancies on the properties of these compounds has been studied,^{11,12} and most of the authors have concluded that their presence results essentially in the creation of new "defect"-filled states below the Fermi level, which stabilizes the crystal. In the cases of oxides, the relative position of the various bands and the position of the Fermi level with respect to these defect states make this stabilization possible even at the stoichiometric composition, which explains the presence of the two types of vacancies (15% in $\text{TiO}_{1.0}$ and $\text{VO}_{1.0}$ and 25% in $\text{NbO}_{1.0}$). In addition, it has been shown from augmented plane wave (APW) band-structure calculations¹ that, in the case of TiC, the presence of empty carbon sites leads to the formation of a new type of bond not present in the ideal $\text{TiC}_{1.0}$: weak bonds between second-nearest Ti neighbors across the vacancy sites and stronger Ti-Ti bonds in the Ti octahedra around the vacancies caused by the reduction of the number of C-Ti bonds. The first of these new bonds is sometimes discussed, while the existence of the second type can be easily understood by means of qualitative arguments from

electronic structure in all the MX compounds discussed up to now (see Sec. III).

Simultaneously with the theoretical studies, many structural studies have been carried out on these compounds by x-ray or neutron diffraction.¹³⁻¹⁸ Particular attention has been paid in many papers to the short-range-ordering phenomena of the vacancies. In the case of monoxides, thermodynamic measurements have been carried out. In particular, the three thermodynamic functions $\Delta G(O_2)$, $\Delta H(O_2)$, and $\Delta S(O_2)$, respectively, the partial-molar Gibbs-free energy, enthalpy, and entropy of mixing of oxygen in the oxide, have been determined versus x for TiO_x and VO_x at 1323 K.¹⁹⁻²² The two last functions convey a lot of information on the defect structure, such as formation and interaction energies or order parameters. $\Delta H(O_2)$ and $\Delta S(O_2)$ are directly related, respectively, to the defect energy and to the mode of repartition of the defects in the lattice sites. In order to extract this information, we have recently developed²³ a numerical method for the statistical thermodynamic study of phases with high defect contents. In this paper this method has been applied to TiO , which is a model example owing to the very high concentration of defects and its very large nonstoichiometry domain. In addition, the experimental temperature of 1323 K is only 100 K higher than the transition temperature at which a long-range ordering of vacancies occurs.^{15,17} One may therefore expect that some short-range order of the vacancies remains at 1323 K, which is a favorable situation to study the role of the interactions.

II. STATISTICAL THERMODYNAMICS

A. Formalism

The method has been described elsewhere.²³ Let us recall here the useful features for the following. The oxide is simulated by a small crystal of NaCl-type structure made of $4 \times 4 \times 4 = 64$ sites (32 titanium sites and 32 oxygen sites). The partition function is computed by imposing the temperature, the external pressure, and the oxygen chemical potential. This small crystal, named S (for system) in the following, is in thermal and diffusive contact with a large reservoir R of TiO . It has been shown²³ that the probability of occurrence of a given microscopic site i of S is proportional to the Gibbs factor (see Ref. 24):

$$\exp(-\{N_{V_{Ti}}^i [H_{V_{Ti}}^F - TS_{V_{Ti}}^F + \Delta G(Ti)] - N_{V_{O}}^i [H_{V_{O}}^F - TS_{V_{O}}^F + \frac{1}{2}\Delta G(O_2)] + E_j^i\} / kT). \quad (1)$$

In this expression, $N_{V_{Ti}}^i$ and $N_{V_{O}}^i$ are the numbers of titanium and oxygen vacancies in the state i and $H_{V_{Ti}}^F$ and $H_{V_{O}}^F$ their respective enthalpy of formation. $S_{V_{Ti}}^F$ and $S_{V_{O}}^F$ are nonconfigurational entropy terms representing essentially the variations of the vibration entropy of the system when a vacancy is formed. $\Delta G(Ti)$ and $\Delta G(O_2)$ (partial titanium and oxygen-free energy) are linked to the chemical potentials μ_{Ti} and μ_O by $\Delta G = \mu - \mu^0(T)$. μ_{Ti} and μ_O are not independent and are related by the classical

Gibbs-Duhem relationship:

$$N_{Ti}d\mu_{Ti} + N_{O}d\mu_{O} = 0.$$

E_j^i is the vacancy interaction energy which is supposed to be the sum of pair interaction energies depending only upon the separation between the vacancies.

B. Treatment of interactions

For every accessible state i of the system S , which corresponds to a given configuration of the vacancies in the simulation box, every type of interaction (first, second, . . . neighbor) has been counted. This has been done as follows: Let the box be surrounded by its 26 next-nearest images (see Fig. 1). A vacancy in the box is allowed to interact with another vacancy in the box or with the nearest image of that vacancy in one of the neighboring boxes. This method is known as the "minimum-image (MI) convention." In doing so, the surroundings of every site of the box are treated in the same way, which minimizes the border effects but imposes some constraints to the system. This is shown in Table I, where all the interactions with ranges included inside the limits of the box are reported. In Table I also reported, for each interaction range, are the total number of neighbors per site and the partial numbers of neighbors inside and outside the box. It can be seen that the fifth neighbors belonging to a same sublattice and the fourth neighbors belonging to different sublattices in [300] position become first neighbors. In the same way, the interaction range is limited to sixth neighbors on a same sublattice and to fourth neighbors between the two different sublattices.

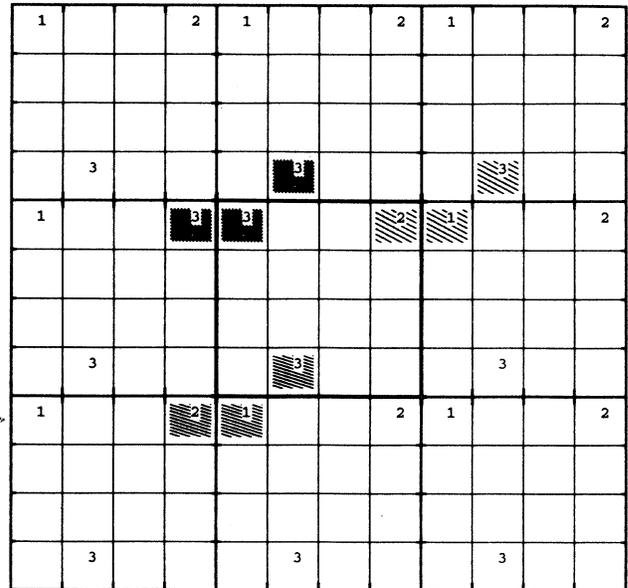


FIG. 1. MI conventions applied to a 4×4 two-dimensional simulation box. The configuration presented here contains three interactions: one nearest neighbor between 1 and 2, one second neighbor between 1 and 3, and one fourth neighbor between 2 and 3.

TABLE I. Interaction ranges taken into account in the calculations: (top) interactions in fcc titanium or oxygen sublattice and (bottom) interactions between titanium and oxygen sublattices.

Type of neighbor	New type given by MI conventions	Position (origin: 000)	R^2	Total number	Number in the box	Number outside the box
1	1	110	2	12	12	0
2	2	200	4	6	3	3
3	3	211	6	24	12	12
4	4	220	8	12	3	9
5	1	310	10			12
6	6	222	12	8	1	7
7	3	321	14			
8	1	330	18			
9	3	332	22			
1	1	100	1	6	6	0
2	2	111	3	8	8	0
3	3	210	5	24	12	12
4	4	221	9	24	6	18
4	1	300	9			3
5	2	311	11	24		12
6	3	320	13			
7	4	322	17			
8	3	331	20			
9	1	333	27			

tices (second column). All the neighbors of a vacancy, the coordinates of which differ by less than $L/2$ (L being the side of the box) from the coordinates of the vacancy are included inside the box; therefore, all the corresponding interactions can be completely enumerated in the box, while some of the others are inside and some are outside the box (see also Fig. 2). When only one coordinate differs by $L/2$, the two parts are equal; when two coordinates differ by $L/2$, $\frac{1}{4}$ of the neighbors are inside and $\frac{3}{4}$ outside the box, and when the three coordinates differ by $L/2$, $\frac{1}{8}$ of the neighbors only are inside the box. This sets the problem of boundary conditions to be used. If usual periodic boundary conditions are applied to the system, this will amount to counts of two, four, or eight times the interactions of ranges equal to or greater than $L/2$ (see Fig. 2). For example, the number of interactions with sixth neighbors on the same sublattice will be allowed to be only 0 or 8. This would impose an artificial short-range order of the vacancies and would lead to erroneous values of interaction energies.

In order to overcome this difficulty, we have developed a treatment which allows us to estimate with good accuracy the number of interactions of a vacancy with its neighbors outside the box. This treatment has been detailed elsewhere²³ and is only briefly summarized in the following: The interactions concerned with this treatment are, on the one hand, the interactions lacking in the box and discussed earlier and, on the other hand, the interactions the ranges of which are not included in the limits of the box, with the exception of any long-range interaction, Coulombic for example, which have to be treated in another way. All these interactions may be visualized as short- or middle-range interactions between

the system S and the reservoir R . Only short-range interactions (up to sixth neighbors) have been taken into account in TiO.

Let the sites of the reservoir be classified into l energy levels according to their interaction energies with the system. It has been shown²³ that the contribution of these interactions system reservoir in the probability of occurrence of a state i may be expressed as

$$p_{\text{ext}}^i = \prod_l [1 - c_n(1 - \delta_l)]^{N_l^i} \quad (2)$$

with

$$\delta_l = \exp(-E_l/kT).$$

In this expression, E_l and N_l^i are, respectively, the energy and the number of sites in level l . c_n is the mean concentration of the n th type of vacancies in the reservoir (oxygen or titanium).

C. Enumeration of configurations

We have supposed that two vacancies of the same kind (two titanium or two oxygen vacancies) are not allowed to be first-nearest neighbors. This treatment is known as a blocking-site model, which has been applied with success in a number of systems to calculate the configurational entropy.²⁵ This assumption will be justified in the discussion section further in the paper. All the configurations consistent with this assumption have been enumerated and gathered into family of states, according to the numbers of each type of vacancy (titanium

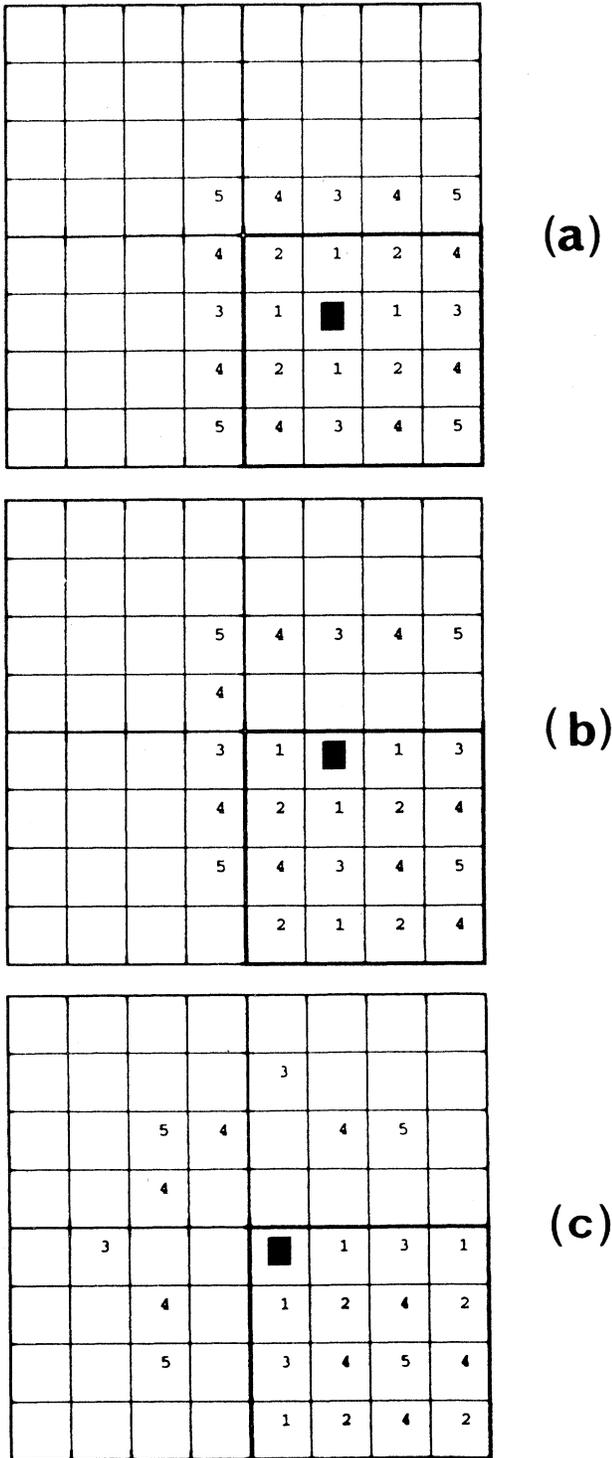


FIG. 2. Positions of neighbors of a vacancy with MI conventions (4×4 two-dimensional simulation box): (a) vacancy on bulk position, (b) vacancy on surface position, and (c) vacancy on corner position. Note that the neighbors of the vacancy for which the interaction ranges are less than $L/2$ are always present in the box. The third and fourth neighbors are half inside and half outside (only one coordinate $=L/2$). One quarter of the fifth neighbors are inside and $\frac{3}{4}$ outside (two coordinates $=L/2$).

um and oxygen) and the numbers of each type of interaction. The above assumption allows to decrease the number of configurations from $2^{64} = 1.84 \ 467 \times 10^{19}$ to only 21 613 201. In order to limit the number of families, we have only considered explicitly the interaction ranges up to third neighbors. This number is then equal to 82 687. A mean energy has been assigned to the set of interactions of larger ranges. This number is the difference between the total number of interactions [equal to $N_V(N_V - 1)/2$ on the same sublattice and to $N_V N_V$, between the two differential sublattices] and the number of interactions up to third neighbors. As shown in Table I, interactions concerned are fourth and sixth neighbors interactions between vacancies on the same sublattice and only fourth neighbors between oxygen and titanium vacancies.

Preliminary calculations have shown the existence of a strong repulsive energy between titanium and oxygen vacancies first neighbors. The physical meaning of this repulsion will be discussed further. This has allowed us to use the blocking-site model for this interaction and still to reduce the number of families of states to 3565.

D. Probability of occurrence of a family of states

The interaction energy in a family of state j in the box may be expressed as

$$E_j^i = \sum_{k=1}^4 N_k^i E_k, \quad (3)$$

where N_k^i is the number of interactions of the k th type and E_k the corresponding interaction energy. The probability of occurrence for the family of states j is now, at given T and μ_0

$$\rho^j = g^j \exp(-\{N_{V_{Ti}}^j [H_{V_{Ti}}^F - TS_{V_{Ti}}^F + \Delta G(Ti)] - N_{V_{O}}^j [H_{V_{O}}^F - TS_{V_{O}}^F + \frac{1}{2} \Delta G(O_2)] + E_j^i\} / kT) \prod_{l=1}^{16} [1 - c_n(1 - \delta_l)]^{N_l^j / \zeta}, \quad (4)$$

where ζ is a generalized partition function. c_n stands for the mean concentration of titanium vacancies ($n=1$ or oxygen vacancies ($n=2$) in the reservoir.

E. Calculation of thermodynamic functions

For a given set of values of the parameters $H_{V_{Ti}}^F$, $H_{V_{O}}^F$, $S_{V_{Ti}}^F$, $S_{V_{O}}^F$, and E_k , any average physical property $\langle A \rangle$ may be calculated as a function of T and μ_0 in a classical way by

$$\langle A \rangle(T, \mu_0) = \sum_j A^j \rho^j / \sum_j \rho^j, \quad (5)$$

where A^j is the value of the property A in the state j . The average numbers of titanium and oxygen vacancies $\langle N_{V_{Ti}} \rangle$ and $\langle N_{V_{O}} \rangle$, as well as the average numbers of each type of interaction are calculated in this way. This has allowed us to obtain the average composition of the oxide by

$$\langle O/Ti \rangle(T, \mu_O) = \langle x \rangle = (32 - \langle N_{V_O} \rangle) / (32 - \langle N_{V_{Ti}} \rangle), \quad (6)$$

and therefore the function $\Delta G(O_2) = f(\langle x \rangle)$.

$\Delta H(O_2)$ and $\Delta S(O_2)$ may be calculated²⁶⁻²⁷ at each composition by

$$\Delta H(O_2) = 2 \left[H_1 \frac{d\langle N_{V_{Ti}} \rangle}{d\langle x \rangle} + H_{V_O}^F \frac{d\langle N_{V_O} \rangle}{d\langle x \rangle} + \sum_k E_k \frac{d\langle N_k^T \rangle}{d\langle x \rangle} \right] - H_T^0(O_2) \quad (7)$$

and

$$\Delta S(O_2) = [\Delta H(O_2) - \Delta G(O_2)] / T. \quad (8)$$

In relation (7),

$$H_1 = H_{V_{Ti}}^F - \Delta H_f^0(Ti_g) + \Delta H_f^0(TiO_s),$$

where $\Delta H_f^0(Ti_g)$ is the standard formation enthalpy of gaseous titanium and $\Delta H_f^0(TiO_s)$ is the standard formation enthalpy of solid TiO at T . $H_T^0(O_2)$ is the standard enthalpy of gaseous oxygen at T . $\langle N_k^T \rangle$ is the total average number of the interaction of type k (including the interactions inner the box plus the system-reservoir interactions).

Experimental determination at 1323 K of the functions $\Delta G(O_2)$, $\Delta H(O_2)$, and $\Delta S(O_2)$ have been carried out in the whole homogeneity range ($0.98 < x < 1.25$) of TiO_x .²⁰⁻²² The values of the parameters, enthalpies, and entropies of formation of the vacancies, and interaction energies, have been fitted in order to obtain the best agreement between experimental functions and the ones calculated by the relations (6)–(8).

III. RESULTS AND DISCUSSION

A. Experimental data

In Figs. 3–5, the continuous lines represent experimental functions.

(i) Oxygen partial pressure P_{O_2} in equilibrium with TiO is very low and varies from 10^{-26} to 10^{-34} atm at 1323 K. These results have been obtained by emf measurements in solid-state galvanic cells.²⁰ The shape of the curve keeps the memory of the order-disorder transition of the vacancies occurring at a lower temperature [≈ 1270 K (Refs. 15 and 17)].

(ii) $\Delta H(O_2)$ has been determined by high-temperature microcalorimetry.²¹ A strong increase in $\Delta H(O_2)$ in the first third of the homogeneity range is observed. Intuitively, this can be partially related to the progressive disappearance of oxygen vacancies in unfavorable second-neighbor position when the composition increases. $\Delta H(O_2)$ is then constant and decreases slightly at the end of the domain, probably interpreting an ordering of the titanium vacancies observed by x-ray diffraction.¹⁵

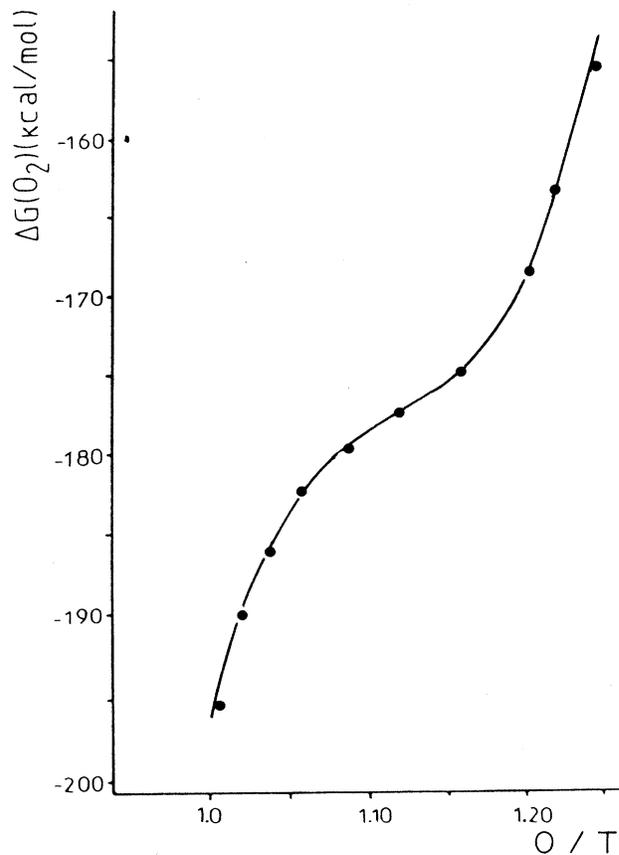


FIG. 3. $\Delta G(O_2)$ vs composition: — experimental (from Ref. 19) and ● calculated.

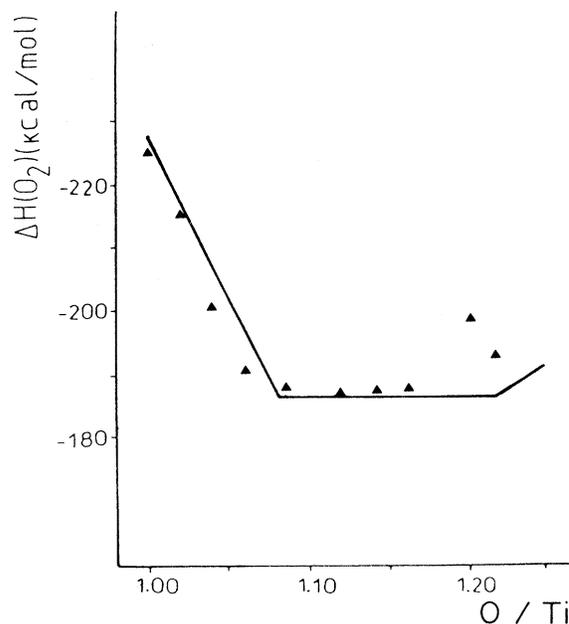


FIG. 4. $\Delta H(O_2)$ vs composition: — experimental (from Ref. 21) and ▲ calculated.

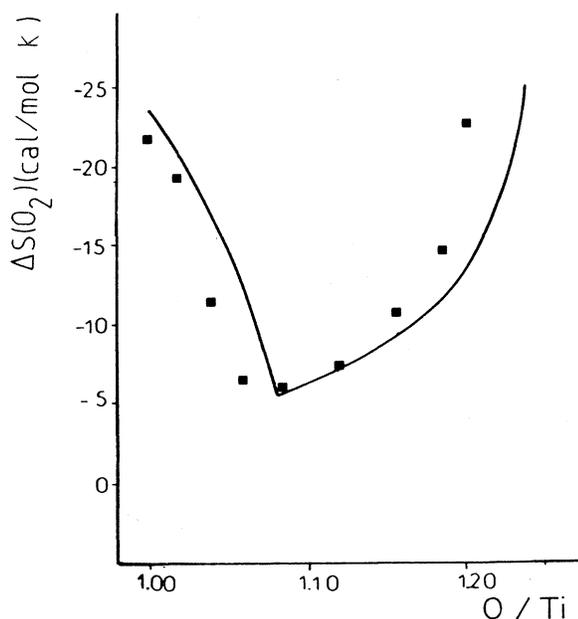


FIG. 5. $\Delta S(O_2)$ vs composition: — experimental (from Ref. 19) and ■ calculated.

(iii) $\Delta S(O_2)$ has been calculated by Eq. (8). Two domains have to be distinguished: a strong decrease in the first third of the domain followed by a strong climb.

B. Calculations

It may be seen in Figs. 3–5 and in Table II that our assumptions and our treatment allow us to obtain a very satisfactory agreement between our calculations and the experimental results. On the whole, the characteristics of the three thermodynamic functions are described by the calculations. Nevertheless, the decreasing of $\Delta H(O_2)$ at the end of the composition range occurs for a too low value of the ratio O/Ti. This is due to the small size of our box in which the titanium vacancies cannot be ar-

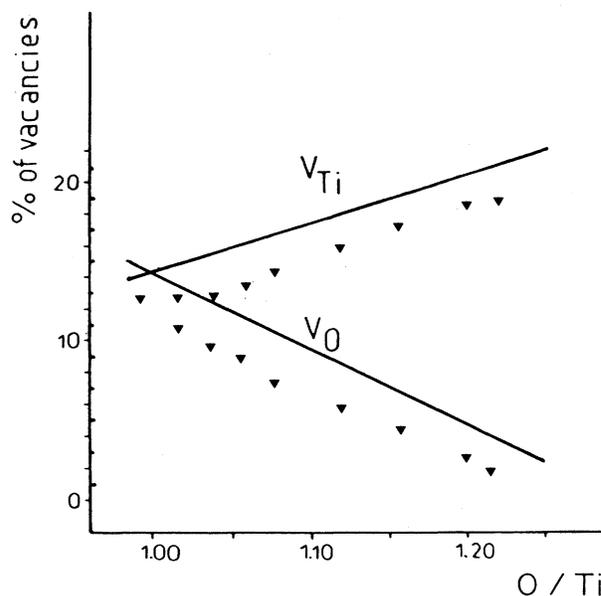


FIG. 6. Percentages of titanium and oxygen vacancies vs composition: — experimental (from Ref. 28) and ▼ calculated.

ranged in a favorable way. As a matter of fact, the ordered structure of $TiO_{1.25}$ presented in Fig. 8 shows that titanium vacancies are either third or fifth neighbors. This last position is not allowed in our system because of the boundary conditions which change fifth neighbors to first ones. This problem may be solved in using a larger cell and a Monte Carlo simulation using energy values calculated here, which will be done in a later paper in which order phenomena will be studied.

In Fig. 6 we show the comparison between calculated and experimental percentages of titanium and oxygen vacancies. These quantities have not been adjusted but are a direct result of our calculations. The good agreement obtained is a strong support of the validity of our ap-

TABLE II. Comparison between experimental and calculated thermodynamic functions. $\Delta G(O_2)$ and $\Delta H(O_2)$ are in kcal/mol. $\Delta S(O_2)$ is in cal/mol/K (e.u.).

$\Delta G(O_2)$ imposed	O/Ti		$\Delta H(O_2)$		$\Delta S(O_2)$	
	expt	calc	expt	calc	expt	calc
-196.6	1.000	1.001	-228.2	-226.4	-23.8	-22.4
-191.3	1.020	1.020	-217.9	-216.9	-20.1	-20.3
-186.8	1.040	1.038	-207.6	-201.7	-15.7	-12.6
-183.4	1.060	1.059	-197.3	-190.8	-10.5	-6.9
-181.3	1.080	1.082	-187.0	-187.5	-4.3	-6.2
-180.1	1.100	1.102	-187.0	-186.7	-5.2	-6.7
-178.9	1.120	1.119	-187.0	-186.7	-6.1	-7.5
-177.7	1.140	1.135	-187.0	-187.0	-7.1	-8.6
-176.2	1.160	1.156	-187.0	-188.1	-8.2	-10.6
-174.1	1.180	1.181	-187.0	-191.7	-9.8	-15.0
-170.1	1.200	1.201	-187.0	-199.0	-12.8	-23.1
-166.2	1.220	1.216	-189.2	-194.3	-17.4	-23.3
-158.9	1.240	1.243	-191.4		-24.5	

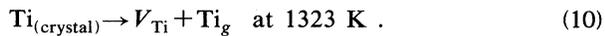
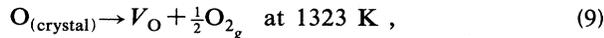
TABLE III. Values of adjustable parameters.

Formation parameters	Enthalpy kcal/mol	Entropy cal/mol K		
V_{Ti}	-127.7	54.6		
V_O	103.4	14.4		
Interaction energies (kcal/mol)				
	first neighbor	second neighbor	third neighbor	> third neighbor
$V_{Ti} - V_{Ti}$	∞	20.34	0.033	0.002
$V_O - V_O$	∞	5.44	5.35	3.45
$V_{Ti} - V_O$	∞	-1.67	-0.0014	-0.0006

proach. All these results have been obtained with the values of parameters given in Table III which are discussed in the following.

1. Formation parameters

$H_{V_i}^F$ and $S_{V_i}^F$ represent the variations of enthalpy and entropy of the following formation processes of an oxygen and a titanium vacancy



Generally, the process which is considered to describe the formation of a vacancy is the motion of an atom from the bulk to the surface. Nevertheless, these are the quantities connected with the processes^{9,10} which enter the partial thermodynamic functions which take place in our calculations [see relation (7)]. The variations of enthalpy and entropy for these two processes are

$$H_{V_O}^F = \frac{1}{2}H_T^0(O_2) - H(O_s) \text{ and } S_{V_O}^F = \frac{1}{2}S(O_2) - S(O_s),$$

$$H_{V_{Ti}}^F = H_T^0(Ti_g) - H(Ti_s) \text{ and } S_{V_{Ti}}^F = S(Ti_g) - S(Ti_s).$$

The suffix *g* and *s* are relevant on quantities in gaseous and solid phase, respectively. If the zero of energy is chosen as the energy of atoms at rest, at infinite separation in their lowest electronic level

$$H_T^0(O_2) = -107.456 \text{ kcal/mol}$$

and

$$H_T^0(Ti_g) = 7.162 \text{ kcal/mol}$$

at 1323 K.²⁹ On the other hand,

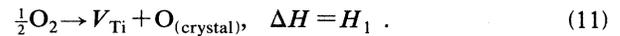
$$\frac{1}{2}S(O_2) = 30.281 \text{ e.u.}$$

and

$$S(Ti_g) = 52.643 \text{ e.u. at } 1323 \text{ K} \text{ (e.u.} \equiv \text{cal/mol/K)}.$$

From values in Table III, we obtain for the nonconfigurational entropy of an atom in the crystal: $S(O_s) = 15.9$ and $S(Ti_s) = -2$ e.u. These values are of the order of magnitude that can be expected for these quantities. Let us point out an important uncertainty on $S(Ti_s)$, estimated to ± 4 e.u., due to the one on the value

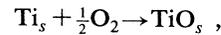
of μ_{Ti} at $TiO_{1.00}$ at 1323 K which is extrapolated from the results obtained over the range 1694–1919 K by Sheldon *et al.*³⁰ From the definition of $\Delta H(O_2)$, the term H_1 present in the relation (7) is related to the formation of a titanium vacancy when an oxygen atom is added to the crystal at constant number of metal:



H_1 is then different from $H_{V_{Ti}}^F$ [process (10)]. Process (11) may be decomposed in the three following processes:

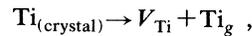


$$= -110.1 \text{ kcal/mol at } 1323 \text{ K}$$



$$\Delta H = H_f^0(TiO_s) = -122.32 \text{ kcal/mol at } 1323 \text{ K}$$

[from Ref. (29)] and



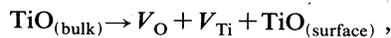
$$\Delta H = H_{V_{Ti}}^F = H^0(Ti_g) - H(Ti_s).$$

So, it appears that

$$H_1 = H_{V_{Ti}}^F - H_f^0(Ti_g) + H_f^0(TiO_s)$$

$$= -115.5 \text{ kcal/mol at } 1323 \text{ K}.$$

The sum of the two processes (9) and (11) gives



$$\Delta H = H_{V_O}^F + H_1 = -12.1 \text{ kcal/mol}.$$

This value, which represents the formation enthalpy of a pair of titanium and oxygen vacancies when no interaction occurs, is indeed in agreement with a stabilization of stoichiometric TiO by spontaneous formation of vacancies.

2. Interaction parameters

First, let us discuss the justification of our assumption, consisting of prohibiting two vacancies of the same species from being first neighbors. This assumption is supported by the study of the ordered structure of stoichiometric TiO [see Fig. 8(a)] which shows that no pair of first-neighbor vacancies exists at only 100 K below

our working temperature. Therefore, we can safely suppose that the formation of such a pair is energetically unfavorable enough to be neglected as long as the working temperature is only slightly higher than the transition temperature. When the ratio O/Ti increases, the concentration of oxygen vacancies decreases, which can only cause a decrease in the number of first-neighbor oxygen vacancy pairs; the number of titanium vacancies increases but no first-neighbor titanium vacancy pair exists in the ordered structure of $\text{TiO}_{1.25}$ (see Fig. 7). The correctness of our assumption is confirmed by the values of interaction energies obtained between second-neighbor vacancies on the same sublattice which remains strongly repulsive. The repulsion between titanium vacancies appears very strong for second neighbors and almost negligible after, which is consistent with the presence of third neighbors in the ordered structure of $\text{TiO}_{1.25}$. The repulsion between oxygen vacancies is smaller but spreads over a higher number of neighbors.

The second point concerns the very strong repulsive interaction between titanium and oxygen vacancy nearest neighbors, which has been observed in preliminary calculations, even though the interaction becomes attractive between second neighbors. To understand this point it is necessary to go back to the electronic structure of TiO. In Fig. 8 the positions of orbitals in TiO and the bonding types between Ti d and O p orbitals are schematized. The

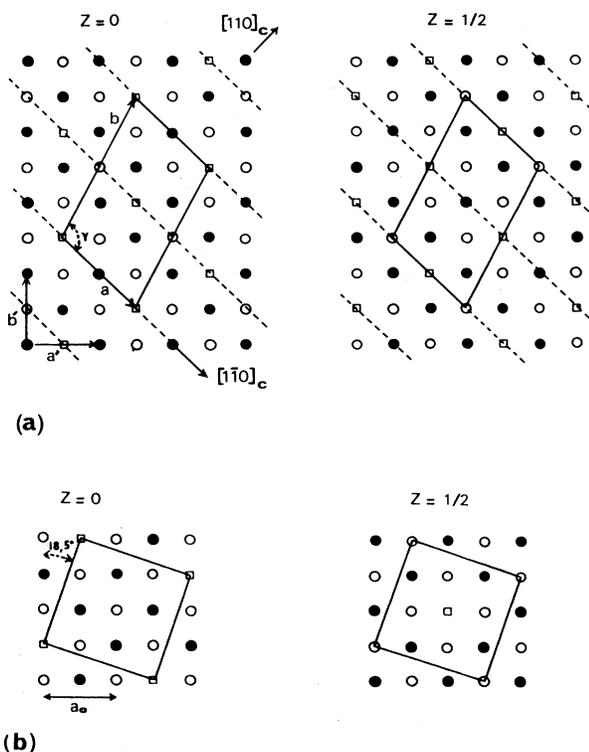


FIG. 7. Ordered structures of TiO (from Ref. 15): ● titanium atoms, ○ oxygen atoms, and □ vacancies. (a) $\text{TiO}_{1.00}$: — monoclinic unit cell and - - - vacant plane. (b) $\text{TiO}_{1.25}$: — tetragonal unit cell.

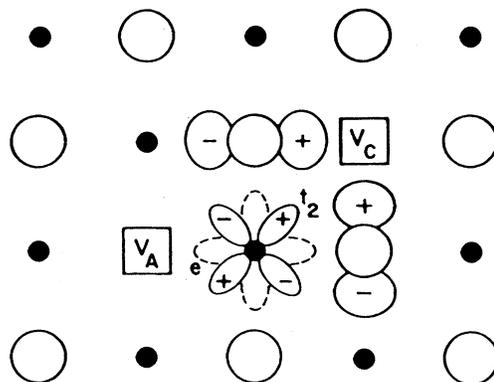


FIG. 8. Relative geometries of atomic orbitals and atomic vacancies in TiO_x (from Ref. 11).

introduction of an oxygen vacancy removes one p - d bonding of the six first-neighbors Ti atoms of the vacant site. The Ti $3d$ orbitals which no longer participate in these bondings are then available to create new Ti-Ti bonds which result in reinforcing the Ti-Ti bonds in the Ti octahedra around the oxygen vacancy. In the following, such an octahedra will be called a stabilized octahedra (SO). In addition, from band calculations some authors deduce the existence of new weak bonds between second-nearest Ti neighbors across the vacancy site which would stabilize the SO a little more.¹ The creation of a titanium vacancy at one of the six sites on an SO is therefore strongly unfavorable because this would result in breaking reinforced Ti-Ti bonds. This explains the strong repulsive interaction observed between two unlike vacancy nearest neighbors.

When a titanium vacancy is formed, the Ti $d(t_{2g})$ orbitals at Ti atoms surrounding the vacancies are no longer stabilized by σ bonding with the Ti $d(t_{2g})$ orbitals normally at the vacancy. In addition, they are more strongly destabilized by π -bond covalent mixing with the anions, since the anions p orbitals do not σ bond with $d(eg)$ orbitals of the vacancy.¹¹ This is, for example, the case for atoms 1, 2, and 3 of Fig. 9 belonging to one of the twelve Ti octahedra surrounding the titanium vacancy. Now, if an oxygen vacancy is present at the center of this octahedra, the Ti atoms 1, 2, and 3 will have their bonds with the other Ti atoms of the octahedra reinforced by formation of a SO, which will limit their destabilization. In other terms, an oxygen vacancy will lower the perturbation due to a titanium vacancy and therefore will be attracted by it. This is in agreement with the attractive interaction deduced from our calculations.

Now, let us assume that the cluster shown in Fig. 9, made of a titanium vacancy and a stabilized octahedra, is the energetic entity stabilizing the stoichiometric crystal. In Figs. 10 and 11, the results obtained by moving such a cluster through the rock salt structure, in such a way that two vacancies of the same type cannot be first neighbors, as already assumed, are shown.

(a) If the move is made in the three $[100]$ directions (Fig. 10), by a distant Ti-Ti second neighbor, each vacan-

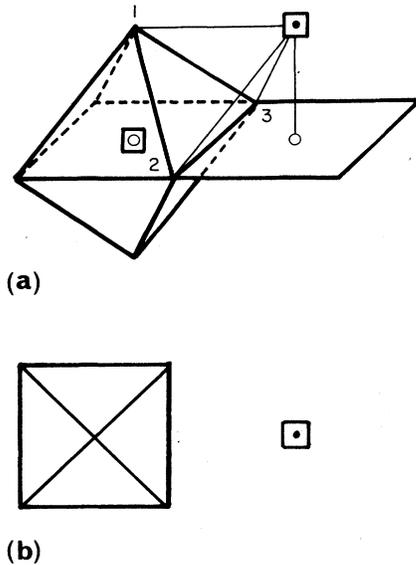


FIG. 9. (a) Stabilized octahedron (titanium octahedron with an oxygen vacancy at the center) associated with a titanium vacancy. (b) Schematic representation of this cluster for use in next figures.

cy has its eight second-neighbor sites of the same sublattice vacant. Every metal vacancy is surrounded by eight stabilized octahedra. The elementary cubic cell so obtained accommodates 25% of metal and oxygen vacancies and describes exactly the ordered structure of NbO. In this case, the attractive energy is maximum (maximum number of pairs of $V_{Ti}-V_O$ second neighbors), but the number of pairs of second neighbors of the same type is

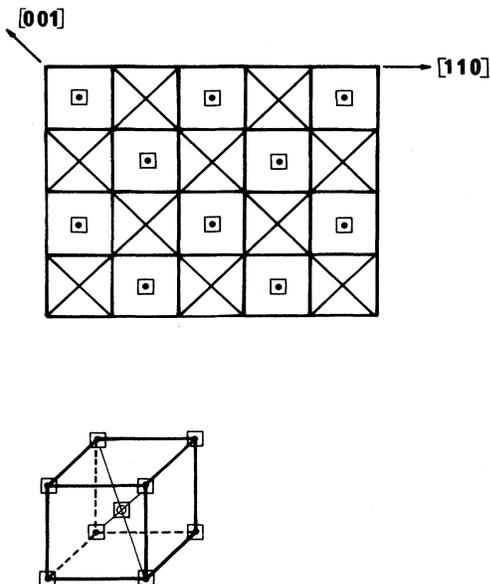


FIG. 10. (a) Ordered structure of NbO obtained by moving the cluster of Fig. 9 in the three $[110]$ directions. (b) Cubic unit cell of NbO.

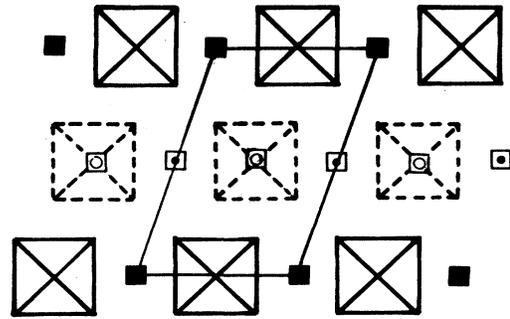


FIG. 11. (a) Ordered structure of $TiO_{1.00}$ obtained by moving the cluster of Fig. 9 to avoid second-neighbor vacancy pair: — $z=0$ and - - - $z=1$.

also maximum and the third neighbors are absent. This situation will be favored by a strong attractive energy between unlike vacancies or/and a small repulsive energy between second neighbors of the same type with regard to the third neighbors.

(b) Now, if the metal vacancies are shifted from second-neighbor occupation of the previous structure, to third-neighbor occupation, we obtain the ordered structure shown in Fig. 11. In this structure, every metal vacancy is surrounded by only four stabilized octahedra in $[111]$ directions in a (110) plane. This structure accommodates $\frac{1}{6}$ (16.6%) of each type of vacancy which are present in every third (110) plane and describes the low-temperature ordered structure of stoichiometric TiO as described by Watanabe *et al.*¹³ from x-ray studies. In this case, some attractive energy is lost with regard to the previous structure, but the repulsive energy due to second-neighbor vacancy pairs, particularly titanium ones, is minimized to a maximum. This is consistent with the calculated interaction energies.

IV. SUMMARY AND CONCLUSIONS

In this paper, a numerical method based on the direct enumeration of the configurations of defects in a small sample has been applied to the statistical thermodynamic study of TiO. This method has allowed us to extract from experimental partial molar quantities the enthalpies and entropies of formation of vacancies as well as their short-range interaction energies up to the sixth-nearest neighbors. The general tendency observed is a repulsion between like vacancies and an attraction between unlike vacancies.

Between titanium vacancies, the repulsion is of very short range: very strong up to the second neighbors and negligible beyond. This is notably consistent with the ordered structure of $TiO_{1.25}$ (the presence, principally, of third-neighbor pairs), although the small size of the sample does not allow one to exactly describe this structure. The repulsions between oxygen vacancies are rather small compared with the preceding one but slowly decrease when the distance increases. More surprising are the in-

teractions between unlike vacancies: very strong repulsion between first neighbors and then small attraction limited to second neighbors. This has been qualitatively understood in terms of chemical bonding and electronic structure. Finally, it has been shown that the set of results concerning the interaction energies allows us to describe qualitatively the ordered structure of stoichiometric TiO.

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