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Thermodynamic data as tools for investigation of defect interactions in nonstoichiometric oxides: Application to $YBa_2Cu_3O_{6+2x}$

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Due to the recent availability of accurate measurements, the use of partial molar quantities (free energy, enthalpy, and entropy) has emerged as a tool aimed at evaluating effective pair interactions in nonstoichiometric compounds. In the present paper, this approach has been used to ascertain the validity of inverse methods in a simple academic case and to discuss available thermodynamic data in the most extensively studied system, i.e., $YBa_2Cu_3O_{6+2x}$, in the framework of asymmetric two-dimensional lattice-gas models proposed for this system.

I. INTRODUCTION

The physicochemical properties of nonstoichiometric compounds are strongly dependent on the interactions between defects. The determination of these interactions is therefore a prerequisite to the understanding of the behavior of these compounds. In this paper, we are specifically interested in nonstoichiometric oxides, for which accurate thermodynamic data are available. More precisely, the relative partial molar Gibbs free energy and enthalpy of oxygen, $\Delta G(O_2)$ and $\Delta H(O_2)$, have been measured as functions of both composition and temperature for a large number of oxides.[1] $\Delta S(O_2)$ may be obviously deduced from the well-known relationship: $\Delta G(O_2)=\Delta H(O_2)-T\Delta S(O_2)$. The usefulness of the partial molar quantities to test the validity of defect formation energies calculated by simulation has been shown by Tétot and Gerdanian.[2] On the other hand, Boureau[3,4] has shown that they provide insight on quantities such as the environment of a defect, interaction energies and tracer correlation coefficients. As a consequence of the defect interactions, the partial molar quantities are heavily composition dependent. Therefore, provided that an appropriate statistical model is available, it is in principle possible to evaluate defect-defect interactions from the knowledge of $\Delta G(O_2)$ and $\Delta H(O_2)$ by an inverse method.[5,6] Of course, it is also possible to test the validity of interactions obtained by other ways by comparing calculated and experimental functions. Let us emphasize the following fact: as developed elsewhere,[4] in order to be credible, a microscopic model should be consistent with both partial molar enthalpy and entropy which convey information which are lost when the sole free energy is considered. As a matter of fact, it is very common that models are consistent with free energy but not with enthalpy and entropy separately.[3,7]

In this paper, we present a general thermodynamic formalism aimed to connect pair interactions and partial molar quantities, as well as the way to calculate these quantities by means of Monte Carlo simulations and the cluster variation method[8] (Sec. II). In Sec. III, in the framework of a simple academic case, we compare the results obtained by the two methods of calculation. The reliability of inverse methods aimed to extract pair interactions from experimental data is discussed. Finally, in Sec. IV, the predictions of the asymmetric lattice gas model assuming three effective pair interactions between oxygen sites in the basal plane of $YBa_2Cu_3O_{6+2x}$, proposed first by de Fontaine, Wille, and Moss,[9] have been compared with experimental data.[10]

II. THERMODYNAMIC FORMALISM

A. General considerations

For the sake of simplicity, let us consider as an example a nonstoichiometric oxide containing only oxygen interstitials as point defects. All the other cases may be derived easily. In this example, the sole oxygen sublattice (interstitial sublattice with respect to the metal sublattice) needs to be considered. Every site of this sublattice is occupied either by an oxygen atom (○) or by a vacancy (□). The system of interest is therefore equivalent to a classical lattice gas system. We assume that the Hamiltonian of this system may be separated into a purely configurational part $\mathcal{H}(\mathcal{C})$, and another part, $\mathcal{H}(\text{vib})$, containing all other effects (vibrational, volume, . . .):

$$\mathcal{H}=\mathcal{H}(\mathcal{C})+\mathcal{H}(\text{vib}) .$$

The first term is an Ising Hamiltonian, which may be written the most generally as:[11]

$$\mathcal{H}(\mathcal{C})=\sum_{\substack{n,m\\ i,j}}{}' V^{ij}_{nm}p^{i}_{n}p^{j}_{m}-\sum_{\substack{n\\ i}}\mu(i)p^{i}_{n} \; . \qquad (1)$$

Only pair interactions have been considered here. p^{i}_{n} is the occupation variable of the site n: $p^{i}_{n}=1$ if the site n is occupied by the species i and $p^{i}_{n}=0$ otherwise. V^{ij}_{nm} is the pair interaction between a site n occupied by the species i and a site m occupied by the species j. The prime on the first sum means that each pair is counted only once. $\mu(i)$ is the chemical potential of the species i (in the present example, only $\mu(\mathrm{O})$ has to be considered, oxygen being the sole chemical species). The variables p^{i}_{n} are not independent: $p^{\circ}_{n}+p^{\square}_{n}=1$. Therefore, let us note: $p^{\circ}_{n}=p_n$ and $p^{\square}_{n}=1-p_n$. With these notations, relation (1) may be written:

$$\mathcal{H}(\mathcal{C})=\mathcal{H}_0+\sum_{n}\sum_{m\neq n}(V^{\circ\square}_{nm}-V^{\square\square}_{nm})p_n+\sum_{n,m}{}' V_{nm}p_n p_m -\sum_{n}\mu(\mathrm{O})p_n \qquad (2)$$

$\mathcal{H}_0=\sum_n \sum'_{m\neq n} V^{\square\square}_{nm}$ is constant, as long as the pair interactions are composition independent. This will be assumed in the following and, consequently, $\mathcal{H}_0$ will be omitted. $V_{nm}=V^{\circ\circ}_{nm}+V^{\square\square}_{nm}-2V^{\circ\square}_{nm}$ are effective pair interactions (EPI). In the case of equivalent sites, V_{nm} depends only on the distance between the sites n and m, which allows us to write $V_{nm}=V_k$, where k extends over all pairs of sites compatible with the limited range of interactions considered. Hence, Eq. (2) may be written as

$$\mathcal{H}(\mathcal{C})=\mathcal{H}_0+N_{\circ}\sum_{k}z_k(V^{\circ\square}_{k}-V^{\square\square}_{k}) +\sum_{k}N^{\circ\circ}_{k}V_k-N_{\circ}\mu(\mathrm{O}) \; , \qquad (3)$$

where $N_{\circ}$ is the number of occupied oxygen sites, $N^{\circ\circ}_{k}$ is the number of oxygen-oxygen pairs k and z_k is the number of neighbors in the kth coordination shell. $z_k(V^{\circ\square}_{k}-V^{\square\square}_{k})$ represents the configurational formation energy of one isolated oxygen interstitial.

The second part of the Hamiltonian, $\mathcal{H}(\mathrm{vib})$, is assumed to be proportional to the number of oxygen atoms and may be written as

$$\mathcal{H}(\mathrm{vib})=N_{\circ}(E_{\mathrm{vib}}-TS_{\mathrm{vib}}+P\delta V) \; . \qquad (4)$$

E_{vib} is the part of the formation energy of an oxygen interstitial which is temperature dependent and is essentially vibrational. S_{vib} and δV are, respectively, the change of nonconfigurational entropy and the change of the volume induced by the addition of one oxygen atom into the crystal. P is the external pressure. The summation of Eqs. (3) and (4) yields

$$\mathcal{H}=\sum_{k}N^{\circ\circ}_{k}V_k-N_{\circ}\left[\mu(\mathrm{O})-\sum_{k}z_k(V^{\circ\square}_{k}-V^{\square\square}_{k}) +H_{\mathrm{vib}}-TS_{\mathrm{vib}}\right] \; , \qquad (5)$$

where the terms proportional to $N_{\circ}$ have been gathered and $H_{\mathrm{vib}}=E_{\mathrm{vib}}+P\delta V$. The occupation of one oxygen site by reaction with oxygen gas at the temperature T may be written symbolically as:

$$\tfrac{1}{2}\,\mathrm{O}_{2(g)}\rightarrow \mathrm{O} \; .$$

In terms of chemical potentials, the thermodynamic equilibrium corresponds to:

$$\tfrac{1}{2}\mu(\mathrm{O}_{2(g)})=\mu(\mathrm{O}) \; .$$

If the experimental temperature T is chosen as reference temperature and the reference pressure is 1 bar, we have

$$\tfrac{1}{2}\mu(\mathrm{O}_{2(g)})=H^{0}_{g}-TS^{0}_{g}+\Delta G(\mathrm{O}_2)/2 \; , \qquad (6)$$

where H^{0}_{g} and S^{0}_{g} are standard quantities related to gaseous oxygen. Equation (5) may thus be written as

$$\mathcal{H}=\sum_{k}N^{\circ\circ}_{k}V_k-N_{\circ}[(H^{0}_{g}-H_{\circ})-T(S^{0}_{g}-TS_{\mathrm{vib}}) +\Delta G(\mathrm{O}_2)/2] \; , \qquad (7)$$

where

$$H_{\circ}=\sum_{k}z_k(V^{\circ\square}_{k}-V^{\square\square}_{k})+H_{\mathrm{vib}}$$

is the total formation enthalpy of one isolated oxygen interstitial. In order to lighten the writing, let us note

$$\mu=(H^{0}_{g}-H_{\circ})-T(S^{0}_{g}-S_{\mathrm{vib}})+\Delta G(\mathrm{O}_2)/2 \; . \qquad (8)$$

From experimental values of $\Delta G(\mathrm{O}_2)$, the Hamiltonian (7) allows us to compute, for a set of parameters $H_{\circ}$, S_{vib}, and V_k, the departure from stoichiometry and $\Delta H(\mathrm{O}_2)$. In the two following paragraphs, the methods of calculation of these quantities by the Monte Carlo method and by the cluster variation method (CVM) are exposed.

B. Monte Carlo calculations

The average of any quantity A is defined as

$$\langle A\rangle=\frac{1}{\xi}\sum A\exp(-\beta\mathcal{H}) \; , \qquad (9)$$

where ξ is the grand-canonical partition function. The calculated averages are first the number of occupied sites $\langle N_{\circ}\rangle$, which yields the deviation from stoichiometry, $x=\langle N_{\circ}\rangle/N_s$, where N_s is the number of lattice sites, and the internal energy:

$$\begin{aligned}\langle E\rangle&=\sum_{k}\langle N^{\circ\circ}_{k}\rangle V_k-\langle N_{\circ}\rangle(H^{0}_{g}-H_{\circ})\\ &=\langle E_I\rangle-\langle N_{\circ}\rangle(H^{0}_{g}-H_{\circ}) \; ,\end{aligned} \qquad (10)$$

where $\langle E_I\rangle$ is the total interaction energy.

From one of its definitions, $\Delta H(\mathrm{O}_2)$ may be written as

$$\begin{aligned}\frac{1}{2}\Delta H(\mathrm{O}_2)&=\left[\frac{\partial\langle E\rangle}{\partial\langle N_{\circ}\rangle}\right]_{T,P,N_M}\\ &=-(H^{0}_{g}-H_{\circ})+\left[\frac{\partial\langle E_I\rangle}{\partial\langle N_{\circ}\rangle}\right]_{T,P,N_M} \; ,\end{aligned} \qquad (11)$$

where N_M is the number of metal atoms. The first term is an ideal term and the second term may be calculated as follows (constraints will be omitted):

$$\frac{\partial\langle E_I\rangle}{\partial\langle N_O\rangle}=\frac{\partial\langle E_I\rangle}{\partial\mu}\times\frac{\partial\mu}{\partial\langle N_O\rangle} .$$

From Eq. (9), easy algebra leads to

$$\frac{\partial\langle E_I\rangle}{\partial\mu}=\beta(\langle E_I N_O\rangle-\langle E_I\rangle\langle N_O\rangle)$$

and

$$\frac{\partial\langle N_O\rangle}{\partial\mu}=\beta(\langle N_O^2\rangle-\langle N_O\rangle^2)$$

This finally yields

$$\frac{1}{2}\Delta H(O_2)=-(H_g^0-H_O)+\frac{\langle E_I N_O\rangle-\langle E_I\rangle\langle N_O\rangle}{\langle N_O^2\rangle-\langle N_O\rangle^2} . \tag{12}$$

Hence, $\Delta H(O_2)$ may be calculated in a single simulation as the ratio of two fluctuations.

C. CVM calculations

The cluster variation method (CVM), introduced first by Kikuchi in 1951,[8] is a powerful technique for studying statistical problems on lattices and calculating phase diagrams. Since this time, many improvements have been brought and many formulations of the method have been proposed. The most useful is the variational formulation in algebraic form that we have used in this work (see Refs. 11 and 12, and references therein). The accuracy of the results obtained depends on the size of the basic cluster upon which a CVM approximation is defined and therefore, on the range of interactions which is possible to handle. Basically, a CVM study consists in minimizing a free energy functional where the exact configurational entropy has been replaced by a linear combination of entropies of finite clusters included in the basic cluster. For the CVM formulation, it is more convenient to describe the occupation states of a lattice site n by the symmetrical variable $\sigma_n(=\pm 1)$, rather than the variable p_n used previously. The two variables are related through

$$\sigma_n=2p_n-1 .$$

The free energy minimization yields the equilibrium correlation functions, $\langle\sigma_\alpha\rangle$, where α denotes any subcluster included in the basic cluster with

$$\sigma_\alpha=\prod_{n\subset\alpha}\sigma_n .$$

In our example, the point correlation function, $\langle\sigma_0\rangle\equiv\langle\sigma_n\rangle$, is related to the departure from stoichiometry, x, through

$$x=\langle p_n\rangle=\frac{1+\langle\sigma_0\rangle}{2} . \tag{13}$$

The pair correlation functions, $\langle\sigma_k\rangle\equiv\langle\sigma_n\sigma_m\rangle^k$, where the sites n and m are kth neighbors, are related to the $\langle N_k^{OO}\rangle$s defined in (10) through

$$\frac{\langle N_k^{OO}\rangle}{N_s}=\frac{z_k}{2}\langle p_n p_m\rangle^k=\frac{z_k}{2}\left[x-\frac{1-\langle\sigma_k\rangle}{4}\right] . \tag{14}$$

From Eqs. (10), (11), (13), and (14), $\Delta H(O_2)$ may be written as

$$\frac{1}{2}\Delta H(O_2)=-(H_g^0-H_O)+\sum_k\left[2+\frac{\partial\langle\sigma_k\rangle}{\partial\langle\sigma_O\rangle}\right]\frac{z_k}{4}V_k \tag{15}$$

and can be calculated analytically. In expressions (12) and (15), the ideal term is equal to $\frac{1}{2}\Delta H(O_2)$ when $x\rightarrow 0$ and can often be obtained experimentally by extrapolation.

III. STUDY OF AN ACADEMIC CASE

In order to ensure that the two methods of calculation are reliable, we have considered, as an example, a model oxide in which the fcc oxygen sublattice is partially occupied. We only consider first and second neighbor interactions between oxygen.

We have first compared $\Delta G(O_2)$ and $\Delta H(O_2)$, as a function of the departure from stoichiometry, obtained by Monte Carlo simulations and by the CVM in the tetrahedron-octahedron approximation. The results shown in Table I have been obtained with the following parameters:

$$T=1300\text{ K} ,\quad V_1=20\text{ kJ/mol} ,\quad V_2/V_1=0.2 ,$$

$$(H_g^0-H_O)=400\text{ kJ/mol and } S_{\text{vib}}=0 ,$$

which are representative of what may be expected in solid solutions of oxygen in transition metals. The agreement between the results obtained by the two methods of calculation is noteworthy in the whole range of composition. This shows that the CVM is well adapted to the calculations of partial molar quantities even for very large departures from stoichiometry. This is very interesting because this technique is very less computer time con-

TABLE I. Comparison between the departure from stoichiometry and $\Delta H(O_2)$ calculated with the CVM (tetrahedron-octahedron approximation) and Monte Carlo simulations (6912 sites and 1000 Monte Carlo steps by site). $\Delta G(O_2)$ and $\Delta H(O_2)$ are in kJ/mol.

$\Delta G(O_2)$	x		$\Delta H(O_2)$	
	CVM	MC	CVM	MC
−510.0	0.0632	0.0632	−789.3	−787.8
−500.0	0.0772	0.0773	−784.8	−786.5
−450.0	0.1505	0.1507	−753.4	−752.5
−400.0	0.2228	0.2232	−712.6	−714.6
−350.0	0.2945	0.2948	−665.4	−664.1
−300.0	0.3666	0.3668	−620.4	−620.8
−250.0	0.4389	0.4390	−575.2	−575.4
−200.0	0.5109	0.5108	−528.9	−531.4

suming than Monte Carlo simulation. However, the limitation of the range of interactions which may be handled may be a great disadvantage. Nevertheless, let it be specified that interactions which are not included in the basic cluster may be taken into account accurately by means of the Bragg-Williams approximation.[13]

In a second stage, we have tried to determine unknown parameters (S_{vib} and the V_ks) from the knowledge of $\Delta G(\text{O}_2)$ and $\Delta H(\text{O}_2)$. The question is: is there only one set of parameters which are consistent with given functions $\Delta G(\text{O}_2)$ and $\Delta H(\text{O}_2)$. We have to minimize the least square function:

$$F(S_{\text{vib}}, V_k) = \sum_l a_l [\Delta H(\text{O}_2)_l^{\text{cal}} - \Delta H(\text{O}_2)_l^{\text{exp}}]^2 + b_l (x_l^{\text{cal}} - x_l^{\text{exp}})^2 \tag{16}$$

with respect to S_{vib} and V_k. The subscripts cal and exp refer to calculated and experimental quantities. The sum runs over the number of experimental couples $\Delta G(\text{O}_2) - x^{\text{exp}}$ considered. a_l and b_l are constants fitted to ensure that the two parts of the function will have close weights. The most efficient minimization algorithms, Newton-Raphson, for example, require the knowledge of the derivatives of F with regards to the adjustable parameters. Such derivatives can be calculated in a single Monte Carlo simulation by means of relations such as

$$\frac{\partial x_l^{\text{cal}}}{\partial V_k} = \frac{\beta}{N_s} (\langle N_\bigcirc \rangle \langle N_k^{\bigcirc\bigcirc} \rangle - \langle N_\bigcirc N_k^{\bigcirc\bigcirc} \rangle) \tag{17}$$

and

$$\frac{\partial \langle E_I N_\bigcirc \rangle}{\partial V_k} = \langle N_k^{\bigcirc\bigcirc} N_\bigcirc \rangle + \beta (\langle N_\bigcirc \rangle \langle E_I N_\bigcirc \rangle - \langle E_I N_\bigcirc N_k^{\bigcirc\bigcirc} \rangle) \tag{18}$$

entering the derivatives of $\Delta H(\text{O}_2)$. With the CVM, the derivatives can be calculated analytically. In Table II, the values of the derivatives of x^{cal} and $\Delta H(\text{O}_2)^{\text{cal}}$ obtained by the two methods have been compared. Those concerning x are in very good agreement, but discrepancies are observed for those concerning $\Delta H(\text{O}_2)$. We have checked by numerical derivatives that the results yielded by the CVM are very accurate. The reason of the breakdown of the Monte Carlo method for these calculations is that the fluctuations such as those of Eq. (18) concern three physical variables and are very difficult to calculate with accuracy. From this point of view, the CVM is more efficient than the Monte Carlo method. Only minimization algorithms that do not need derivatives can therefore be used confidently with Monte Carlo simulations.

TABLE II. An example of derivatives of the departure from stoichiometry and $\Delta H(\text{O}_2)$ calculated with the CVM (tetrahedron-octahedron approximation) and Monte Carlo simulations [(1): 6912 sites, 2000 MCS/site; (2): 32 000 sites, 5000 MCS/site].

	MC		CVM
	(1)	(2)	
x	0.3002	0.3000	0.2997
$\Delta H(\text{O}_2)$	−657.8	−655.9	−656.9
$\partial x/\partial V1$	−0.0349	−0.0327	−0.0316
$\partial \Delta H(\text{O}_2)/\partial V1$	2.71	8.87	0.448
$\partial x/\partial V2$	−0.0190	−0.0173	−0.0159
$\partial \Delta H(\text{O}_2)/\partial V2$	−2.64	−5.83	−0.025

The inverse method has been tested for several sets of parameters by calculating directly "experimental" results by the Monte Carlo method and finding again, from these data the initial parameters by inverse CVM. The method works well and the results are independent from the starting parameters. Of course, we are unable to extend this result to all actual situations. In these cases, in order to limit the risks of error, the parameters must be confronted, if possible, with other experimental properties.

IV. APPLICATION TO $\text{YBa}_2\text{Cu}_3\text{O}_{6+2x}$

It is now well known that the oxygen defects are almost exclusively located at the so-called Cu-O basal planes of $\text{YBa}_2\text{Cu}_3\text{O}_{6+2x}$. Therefore, the study of the nonstoichiometry may be restricted, as a first approximation, to a two-dimensional problem. The oxygen concentration of the basal plane varies from $x = 0$ to $x = 0.5$. It is also well known that various structures can exist, depending on the ordering of the oxygen atoms. Principally, there are a high-temperature disordered phase with tetragonal symmetry (T), for which oxygen sites are occupied at random, and an ordered orthorhombic phase (O_I), for which oxygen sites are separated into two equivalent sublattices; at $x = 0.5$, one of these sublattices is fully empty and the other one is fully occupied, which forms O-Cu-O chains. The T-O_I phase boundary is strongly temperature and composition dependent. Near $x = 0.25$, another ordered orthorhombic phase (O_{II}) is stable under about 500°C. In this phase, one O-Cu-O chain over two is missing. The present paper only considers the T and O_I phases.

Several lattice gas models that consider only EPI's between oxygen atoms have been proposed to describe this system. de Fontaine, Wille, and Moss[9] have proposed an asymmetric model with three interactions: V_1 coupling nearest-neighbor oxygen atoms, V_2 and V_3 coupling next-nearest-neighbor oxygen atoms, V_2 through a copper atom along the O-Cu-O chains and V_3 directly, in the direction normal to the chains (see Fig. 1). Values

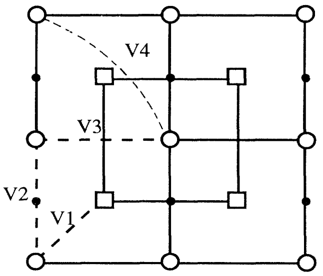

FIG. 1. The ground state structure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ basal plane. Cu ions: black dots, oxygen atoms: open circles, oxygen vacancies: open squares. The EPI's ($V_1 - V_4$) used in this study are indicated.

such as $V_2 < 0 < V_3 < V_1$ accounts for the essential features of the phase diagram and, particularly, predicts the stabilization of the O_{II} phase. Our contribution takes place in the framework of this model which has been extensively applied.[14–18,25,28] Nevertheless, let us describe briefly other models proposed by different groups.

Aligia *et al.*[19–21] propose a model based on screened Coulomb interactions:

$$V(R) = \frac{V}{R} e^{-R/\lambda} ,$$

where R is the distance between oxygen atoms, except for V_2 which remains positive but very small. According to the authors, this model allows them to predict few ground states, in agreement with experimental diffraction patterns, which cannot be predicted by the previous short-range model.

On the other hand, Khachaturyan *et al.*[22,23] put forward long-range interactions (exceeding 20 atomic coordination shells) of elastic origin. These interactions allow these authors to explain the expected microstructure induced by the low-temperature decomposition of $YBa_2Cu_3O_{6+2x}$, consisting of twin and tweedlike structures.

In this paper, illustrating the foregoing, we have compared the predicted functions $\Delta G(O_2)$ and $\Delta H(O_2)$ obtained from the asymmetric V_1-V_3 lattice gas models described above, with the experimental data of Gerdanian, Picard, and Marucco.[10] The more interesting results of these authors are those obtained at 873 K and reported on Fig. 2 because, at this temperature, the range of composition experimentally accessible $(0.23 < x < 0.39)$ includes the transition composition between T and O_I phases which are only present. As expected, $\Delta G(O_2)$ is continuous with a singularity at $x_t \cong 0.31$, showing a second-order transition. $\Delta H(O_2)$ exhibits a λ-type shape with a discontinuity at x_t.

Two sets of V_1-V_3 have been tested by computing partial functions. The first one has been obtained by Sterne and Wille[24] (SW) from first-principle calculations and has been used also by de Fontaine, Ceder, and Asta.[17] to calculate a phase diagram. The second one has been estimated very recently by Hilton *et al.*[25] (HGRN) by a fit to newly available experimental data on phase diagram. We have performed calculations by using Monte Carlo simulations and the CVM in the four- and five-point approximation used by other authors. These two methods yield very close results at the temperature studied here [the discrepancy is always below 3.10^{-3} on x and below 3 kJ/mol on $\Delta H(O_2)$]. Only the ones obtained by the CVM are reported in Fig. 3. For the two sets of EPI's, large discrepancies can be observed between experimental and calculated functions.

(i) Calculated $\Delta G(O_2)$ varies too slowly with x, which may be understood as due to an overestimation of attractive interactions with respect to the repulsive ones. This causes also a decreasing of $\Delta H(O_2)$ for small x which seems to be in disagreement with experimental data at 973 K (see Ref. 10). Due to the lower value of V_2/V_1, these effects are more pronounced with HGRN's EPI's than with SW's EPI's.

(ii) With SW's EPI's, the discrepancies are more pronounced in the O_I phase than in the T phase. Moreover, in the O_I phase, $\Delta H(O_2)$ varies in the wrong direction for the two sets of EPI's. These last observations suggest that the thermodynamic behavior of this system is somewhat different in the two phases.

We have tried to improve the agreement between calculated and experimental functions by varying the EPI's. The conclusion is that there is no way to obtain satisfactory agreement for the T and O_I phases with the same set of EPI's, which confirms the difference of thermodynamic behavior of these two phases. Let us note that only V_2/V_1 and V_3/V_1 are relevant parameters for these calculations. As a matter of fact, for given values of these parameters, the value of V_1 is imposed by the experimental transition point: $x_t = 0.31$, $T_t = 873$ K. A rather good agreement for the T phase (see Fig. 4) can be obtained with $V_3/V_1 = -V_2/V_1 \cong 0.25$ which yields $V_1 \cong 33$ kJ/mol. These values are not very far from SW's. Unfortunately, there is no agreement for the O_I phase.

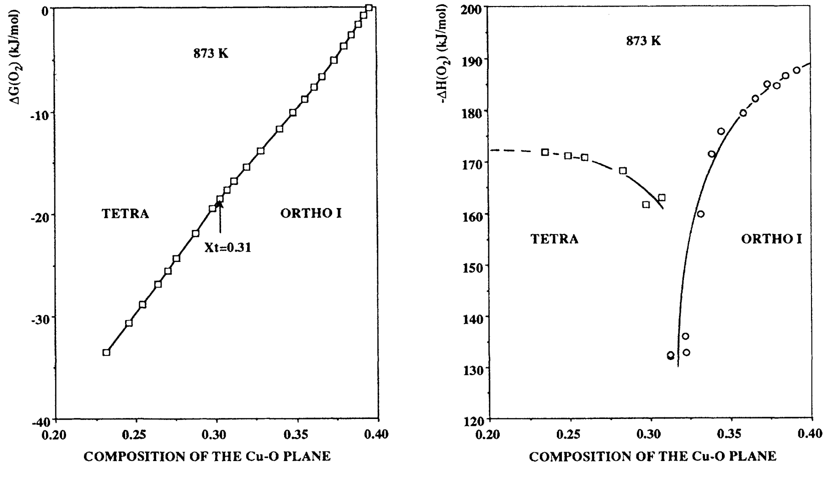

FIG. 2. Experimental $\Delta G(O_2)$ and $\Delta H(O_2)$ vs x for $YBa_2Cu_3O_{6+2x}$ at 873 K [from Gerdanian, Picard, and Marucco (Ref. 10)].

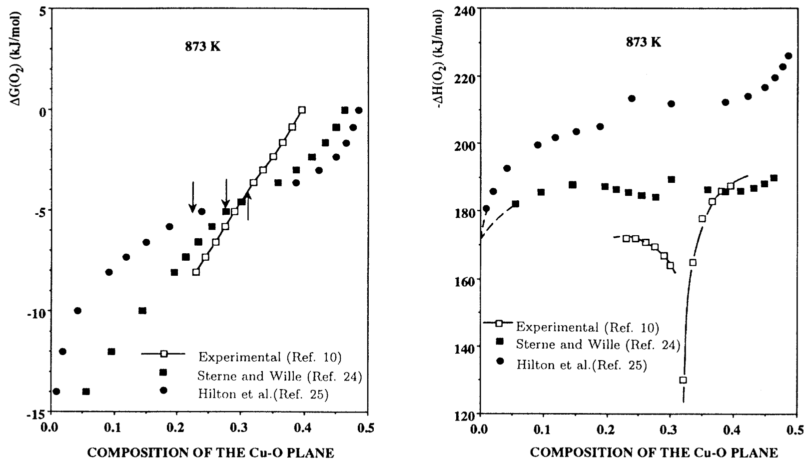

FIG. 3. $\Delta G(O_2)$ and $\Delta H(O_2)$ vs x for $YBa_2Cu_3O_{6+2x}$ at 873 K: comparison between experimental and calculated functions obtained from the parameters of Sterne and Wille (Ref. 24): $V_1=34.2$ kJ/mol, $V_2/V_1=-0.369$, $V_3/V_1=0.169$ and from the parameters of Hilton *et al.* (Ref. 25): $V_1=23.3$ kJ/mol, $V_2/V_1=-0.85$, $V_3/V_1=0.096$. In the calculations we have used $(H_g^0-H_{\mathrm{O}})=86$ kJ/mol and the reference point: $x=0.30$, $\Delta G(O_2)=-4.6$ kJ/mol.

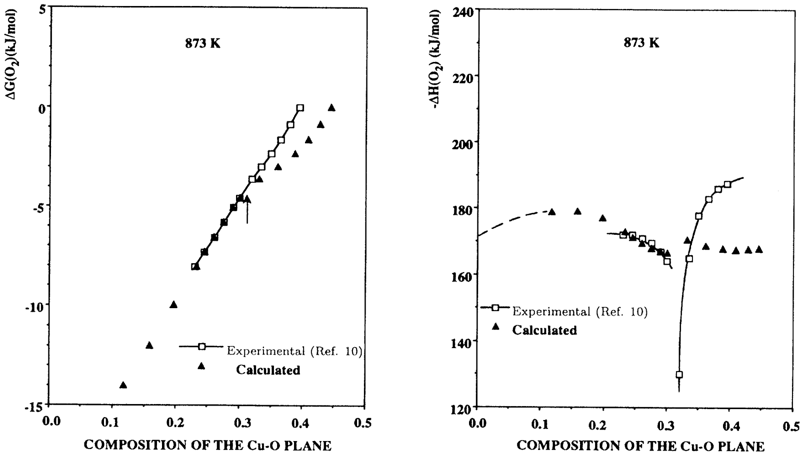

FIG. 4. $\Delta G(O_2)$ and $\Delta H(O_2)$ vs x for $YBa_2Cu_3O_{6+2x}$ at 873 K: Best fit obtained for the T phase.

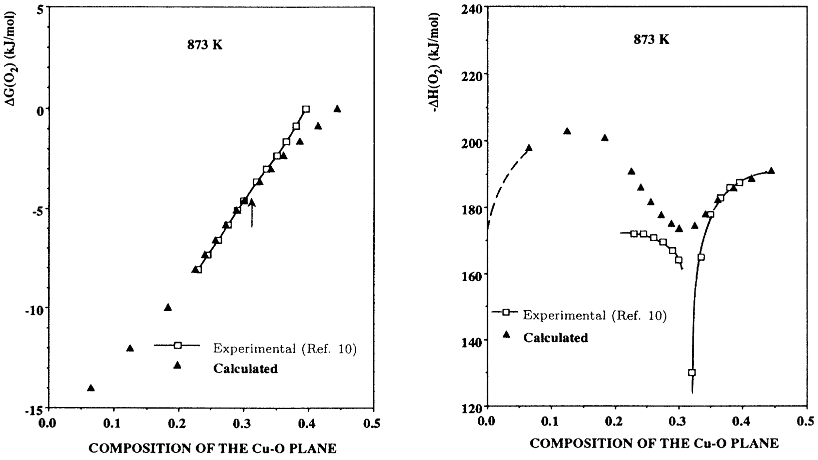

FIG. 5. $\Delta G(O_2)$ and $\Delta H(O_2)$ vs x for $YBa_2Cu_3O_{6+2x}$ at 873 K: Best fit obtained for the O_I phase.

In order to account for the characteristic shape of $\Delta H(O_2)$ in the O_I phase (see Fig. 5), we must use $V_2/V_1 \cong -1.8$ and $V_3/V_1 \geq 0.9$, which yield $V_1 \cong 11.5$ kJ/mol. As far as $\Delta G(O_2)$ is concerned, the agreement is never completely satisfactory. These values yield a rather good agreement for $\Delta G(O_2)$ in the T phase for x not too small but lead to a largely composition dependent $\Delta H(O_2)$. The problem set by the high value of V_3/V_1 (which must be $\ll 1$ in the model) may be solved by introducing a new EPI, noted V_4 (see Fig. 1), which couples third neighbor oxygen atoms. This does not change the conclusions. What happens is that a part of the interaction energy due to V_3 is replaced by an interaction energy due to V_4 without changing appreciably the correlation functions. We have observed that very close results can be obtained by taking two sets of values (one with $V_4=0$ and one with $V_4 \neq 0$) provided that they follow the rule: $V_3/V_1=\alpha$ and $V_4/V_1=0$, on the one hand, and $V_3/V_1=\alpha-\beta$ and $V_4/V_1=\beta/2$, on the other hand, whatever the values of α and β may be.

We have also explored the consequences of taking into account a concentration dependent heat of solution, e.g., $(H_g^0-H_{\mathrm{O}})=a+bx>0$, as proposed by Salomons *et al.*[26] As already pointed out by Cai and Mahanti,[27] this can be a way to handle the long-range (beyond V_4) oxygen-oxygen repulsion in a mean field way (note that Salomons *et al.*[26] have only taken explicitly V_1 into account in their model). Unfortunately, the introduction of such a dependence does not modify qualitatively the results presented above. Of course this favorably tends to increase the variation of $\Delta G(O_2)$ vs x, but does not induce any change in the shape of $\Delta H(O_2)$ for a given set of EPI's.

V. CONCLUSION

In this paper, we have shown that the partial molar quantities of oxygen in $YBa_2Cu_3O_{6+2x}$ cannot be described with a single set of short-range EPI's although this model can account for the essential features of the phase diagram. It is noteworthy that such a similar situation has already been met in metal-hydrogen systems.[4] The introduction of a long-range repulsive interaction proportional to x is not sufficient to solve the problem. Let us specify that the case of long-range Coulomb potential used by Aligia *et al.*,[19–21] Semenovskaya and Khachaturyan[28] and de Fontaine, Ceder, and Asta[29] has not been examined. As already noted by Pörschke, Meuffels, and Wenzl[30] in a recent study on $ErBa_2Cu_3O_{6+2x}$, due to structural and electronic structure changes in these compounds when x varies, the major shortcoming of this model is probably to employ concentration independent EPI's. To get an insight into this dependence seems to be obtained by the more important need to understand the discrepancies. More generally, this paper emphasizes the important role, often ignored, of the partial molar quantities in the understanding of the behavior of nonstoichiometric compounds.

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