

A New Defect Model to Describe the Oxygen Deficiency in Perovskite-Type Oxides

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The defect chemistry of $\text{LaMO}_{3-\delta}$ ($M = \text{Mn, Fe, Co}$) perovskite-type oxides has been studied in order to describe the composition versus oxygen partial pressure phase diagrams in these systems. It is proposed that these systems can be described with extended defects. Literature data on $\text{LaMnO}_{3-\delta}$ and $\text{LaCoO}_{3-\delta}$ indicate that the phase diagrams can be described by a simple cluster model. The simple cluster model is suggested to be the building block for a number of highly defective perovskite-type phases that are known from the literature, like $\text{La}_4\text{Mn}_4\text{O}_{11}$ and $\text{La}_4\text{Ni}_4\text{O}_{11}$, that have different coordination sites for the transition metal ions (tetragonal and square planar, respectively). Other oxygen-deficient perovskite-type oxides probably can be described by similar, but more complicated cluster models, as will be discussed. © 1991 Academic Press, Inc.

1. Introduction

During the past few years there has been a renewed interest in solid oxide fuel cell (SOFC) technology, especially in Europe. This has focused new attention on transition metal, perovskite-type oxides, especially on the La-rich side of the $(\text{La}_{1-x}\text{A}_x)\text{MO}_3$ solid solutions ($A = \text{Sr, Ca, Ba}$; $M = \text{Cr, Mn, Fe, Co, Ni}$), which are of potential interest as cathode materials (1, 2). It is recognized that their physical properties (e.g., electrical conductivity, catalytic activity) are largely dependent on the defect chemistry. A number of studies have been undertaken to elucidate the defect chemistry of these compounds (3-8). So far this has not led to a complete understanding of the nonstoichiometric behavior of these systems.

A wide range of nonstoichiometric ox-

ides, with various structures, have been studied in the past 30 years. As a result of the investigations on many different systems, and the development of new experimental techniques, the knowledge of nonstoichiometric behavior has increased during the years. On the basis of this knowledge three types of nonstoichiometric behavior will be distinguished here.

The first progress was made by Frenkel, Schottky, and Wagner in systems belonging to the first type; the (near) stoichiometric region. In this region the defect concentrations are very small, only point defects occur. A notation for these defects was developed by Kröger and Vink (9), which is used throughout the article. The second type is the region of extended defects and microdomains. It was pointed out by Mrowec (10) that, in general, at defect concentrations ex-

ceeding 0.1 at% there will be interaction between the point defects. Dependent on the nature of the system this interaction may lead to the formation of extended defects and microdomains. The temperature influences the transition from the first type to the second type, since the entropy term increases with increasing temperature, shifting the transition to higher defect concentrations. Examples of systems with extended defects (type 2) are, among others, $\text{Fe}_{1-\delta}\text{O}$ (11) and $\text{UO}_{2+\delta}$ (12).

Depending on the nature of the extended defects, at a particular concentration the extended defects themselves will interact, in the end leading to the formation of new (highly defective) ordered phases, forming the third type of nonstoichiometric behavior. This order/disorder transition is influenced by temperature and defect concentration in a way similar to that discussed above for the point defect/extended defects transition. In $\text{UO}_{2+\delta}$ new phases (for instance U_4O_9 , type 3) occur, when the defect concentrations become too high.

The nonstoichiometric behavior of a number of oxygen-deficient perovskite-type oxides has been investigated (13–17). A large number of phases belonging to the third type were discovered, using techniques such as X-ray and neutron diffraction. More recently, due to the development of other techniques such as electron microscopy, it became also possible to study the defect chemistry of compounds belonging to the second type. The deviation from stoichiometry δ in $\text{AMO}_{3-\delta}$ can be as large as 0.5, without really changing the building blocks of the perovskite-structure. In more complicated systems δ can even become higher. For instance, in $\text{YBa}_2\text{Cu}_3\text{O}_{6.75}$ δ is 0.75 ($\text{Y}_{1/3}\text{Ba}_{2/3}\text{CuO}_{2.25}$). Therefore, it is to be expected that in nonstoichiometric perovskite-type oxides extended defects will play an important role, as has also been pointed out by Eror *et al.* (18) and Hagenmuller *et al.* (19). Nevertheless, the nonstoichiometry of

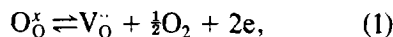
oxygen-deficient perovskite-type oxides has not yet been described by an extended defect model.

It is the scope of this article to show that in many perovskite-type oxides extended defects do occur. A simple defect model is proposed to describe the phase diagrams (defect concentration versus oxygen partial pressure) in a number of these systems. It is also pointed out that this model is intermediary between the near-stoichiometric oxides (first type) and the highly defective, ordered phases that can be formed (third type).

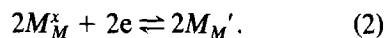
2. Defect Formation in Perovskites

In the perovskites under consideration (mainly $\text{LaMO}_{3-\delta}$, with $M = \text{Cr, Mn, Fe, Co, Ni}$) the ionic bonding is dominant over the covalent bonding. This means that it is a good approximation that the ions are more or less spherical particles with most of their charge on the ion itself. Moreover, for simplicity, every ion will be considered to be fully ionized in this article.

The defects in $\text{LaMO}_{3-\delta}$ can be described by a defect model in which the oxygen loss is accompanied by the reduction of two M^{3+} -ions to two M^{2+} -ions. When an oxygen vacancy is formed, according to the reaction



two electrons are left, and will reduce M^{3+} to M^{2+} , according to the reaction



The oxygen atom, removed from the lattice, leaves a net positive charge of 2+.

It is expected that extended defects exist in perovskites. This implies that interaction between the so-called point defects will occur. Since the perovskites can be described as merely ionic, the most logical interaction is that of a charge interaction. In the perovskites under consideration, $\text{LaMO}_{3-\delta}$, ev-

ery oxygen ion is bound to two M -ions and to four La-ions. The reduction of M^{3+} to M^{2+} will not dramatically change the La–O interaction. The only other interaction is the Mn–O interaction. The electrostatic repulsion will be the smallest if the oxygen vacancy is “bound” to two M^{2+} -ions, forming the defect cluster, $M^{2+}-V_O-M^{2+}$. This cluster formation causes the smallest deviation in charge distribution with respect to the original $LaMO_3$ structure. A similar situation has been suggested by Negas and Roth (13) for Mn^{3+} in $SrMnO_{3-\delta}$. To visualize the cluster formation the perovskite lattice (Fig. 1a, stoichiometric $LaMO_3$) is idealized in that only the (undistorted) MO_6 octahedra are drawn. Figure 1b represents nonstoichiometric $LaMO_{3-\delta}$, with one $M^{2+}-V_O-M^{2+}$ cluster. As can be seen from the picture the M^{2+} -ion is in a square pyramidal coordination. This distortion from octahedral symmetry can also be different from square pyramidal. This will depend on the electronic configuration of the metal-ion and will be discussed in Section 3.

3. From Extended Defects to New Phases

If the concentration of the $M^{2+}-V_O-M^{2+}$ clusters (extended defects) becomes too high it is likely that the clusters themselves will interact, forming larger clusters (microdomains) and in the end new ordered phases (depending on the temperature). In the case of perovskite-type oxides $AMO_{3-\delta}$ there are two ways in which the clusters can interact. Starting with the single cluster, the next cluster can interact either linearly or stepwise. The first possibility, “linear” clustering, is shown in Fig. 1c. In this case the oxygen ions in a $M-O-M-O-M-O-M$ row are removed in one dimension. The coordination of the M -ion will change from octahedral to square planar by the removal of two oxygen ions in one dimension. An example of the result of linear cluster interaction is

the $La_4Ni_4O_{11}$ phase ($LaNiO_{3-\delta}$, $\delta = 0.25$) (20).

The second possibility is “stepwise” cluster interaction (Fig. 1d). In the MO_6 octahedron two oxygen ions next to each other are removed. This will result in a tetragonal coordination; the M -ion will shift to the center of the tetrahedron. Examples of phases that are the result of stepwise cluster interaction are $La_8Mn_8O_{11}$ and $La_4Mn_4O_{11}$ ($LaMnO_{3-\delta}$, $\delta = 0.125$ and 0.25 , respectively) (21). In general the way in which the defects order will depend on the electronic configuration of the metal ion. In the case of Ni^{2+} there is a strong tendency to form a square planar coordination, since it is a d^8 system. This might even result in the effect that extended defects in $LaNiO_3$ are not present at all. Dependent on the temperature and oxygen partial pressure it will either decompose, or form the $La_4Ni_4O_{11}$ phase where the Ni^{2+} can be in a square planar coordination (or another similar phase). Cu^{2+} is known to have different coordinations: tetrahedral, square planar, square pyramidal, trigonal bipyramidal. Like Ni^{2+} , Cu^{3+} is a d^8 system. The structure of $YBa_2Cu_3O_{7-\delta}$ can also be thought of as the result of interaction between the simple clusters, although the actual charge distribution will be more complicated. In $SrMnO_{3-\delta}$ (13) (a structure close to perovskite) the Mn^{3+} ion is thought to be trigonal bipyramidal coordinated, while the structures for $SrFeO_{3-\delta}$ (14) probably consist of tetragonal and octahedral coordinated ions (with the Fe^{3+} ion probably in the tetragonal surrounding).

It is thus proposed that the cluster model appears differently in the various systems, depending on the electronic configuration of the ions, but the phases can always be thought of as being constructed of the same simple cluster building blocks. The structures of oxygen-deficient perovskite-type oxides can thus be described in a very simple manner.

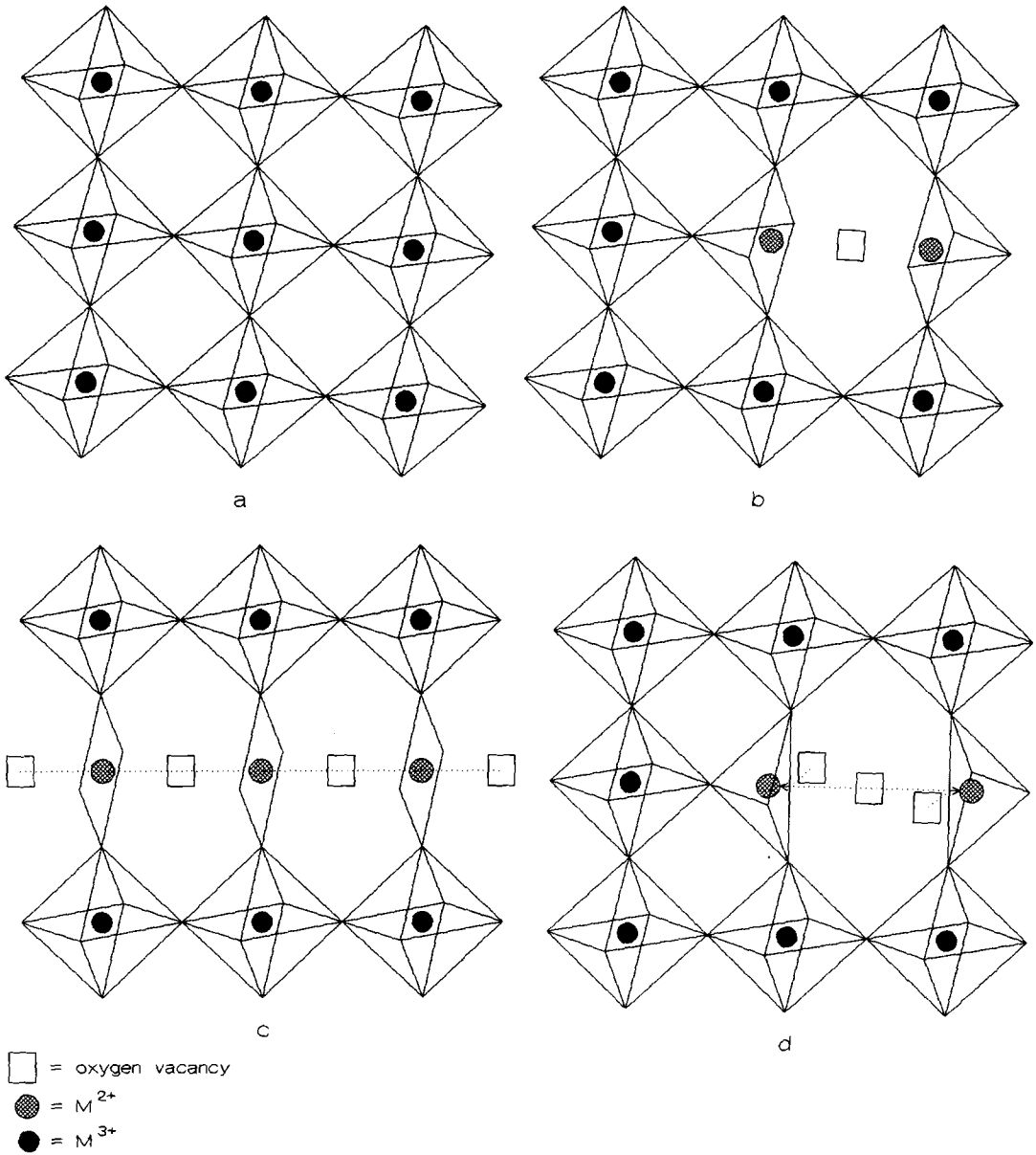
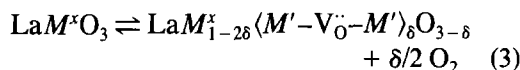


FIG. 1. (a) Idealized $LaMO_3$ structure; only the MnO_6 octahedra are shown. (b) The cluster model, two M^{2+} ions are "bound" to the oxygen vacancy. (c) Linear interaction between the clusters. (d) Stepwise interaction between the clusters.

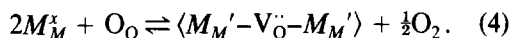
4. Experimental Evidence for the Cluster Formation

Most LaMO_3 systems show large deviations from stoichiometry. In particular the $\text{LaMnO}_{3-\delta}$ and $\text{LaCoO}_{3-\delta}$ systems have been investigated extensively (2, 3, 5, 6, 22). To verify the cluster model for LaMnO_3 only the experimental values of Kamata *et al.* (22) will be used, since other data (2, 3) have to be obtained from the authors' graph. To evaluate the cluster model for LaCoO_3 , data by Seppänen *et al.* (5) will be used, since these are easily obtained from the graph. It is not the scope of this article to discuss the absolute values of the measurements by the various authors, but only to verify the cluster model.

The equilibrium reaction in the case of $M^{2+}-V_O-M^{2+}$ defect clusters can be represented by



or in terms of species participating in the reaction



The equilibrium constant for this reaction is represented by

$$K_I = \frac{\langle M_M' - V_O - M_M' \rangle \cdot p_{\text{O}_2}^{1/2}}{[M_M^x]^2 \cdot [\text{O}_O]} \quad (5)$$

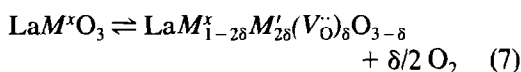
using the defect concentrations in Eq. (3).

$$K_I = \frac{\delta \cdot p_{\text{O}_2}^{1/2}}{(1 - 2\delta)^2 \cdot (3 - \delta)} \quad (6)$$

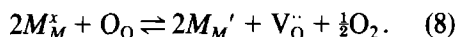
For comparison it is also necessary to describe the defect equilibrium if mainly point defects are present. In that case there will be no interaction between the defects; the oxygen vacancies and M^{2+} -ions will be randomly distributed over the available lattice sites. This defect model will be referred to as the "random" model.

The equilibrium reaction for the loss of

oxygen by LaMO_3 for the random model is represented by



or



The equilibrium constant for this reaction is represented by

$$K_{II} = \frac{[M_M']^2 \cdot [V_O] \cdot p_{\text{O}_2}^{1/2}}{[M_M^x]^2 \cdot [\text{O}_O]} \quad (9)$$

or

$$K_{II} = \frac{4\delta^3 \cdot p_{\text{O}_2}^{1/2}}{(1 - 2\delta)^2 \cdot (3 - \delta)}. \quad (10)$$

The values of K_I and K_{II} are obtained by a nonlinear least squares analysis of the data. Calculated values of p_{O_2} for the cluster model and the random model are listed in Table I (p_{O_2} is represented as $\log p_{\text{O}_2}$). The calculated functions are plotted in Figs. 2a and 2b. It is clear that the data nicely fit the cluster model and cannot be described by the random model.

An easy way to estimate if the model is valid in a particular system is the slope of $\log |\delta|$ versus $\log p_{\text{O}_2}$. Equation (6) can be approximated by

$$K_I' \approx \delta \cdot p_{\text{O}_2}^{1/2} \text{ or } \delta \approx p_{\text{O}_2}^{-1/2}. \quad (11)$$

In the same way Eq. (10) can be approximated by

$$K_{II}' \approx \delta^3 \cdot p_{\text{O}_2}^{1/2} \text{ or } \delta \approx p_{\text{O}_2}^{-1/6}. \quad (12)$$

Although an approximation, it is an indication that the cluster model is valid if the slope of $\log |\delta|$ versus $\log p_{\text{O}_2} = -\frac{1}{2}$. This is the case for $\text{LaMnO}_{3-\delta}$ and for $\text{LaCoO}_{3-\delta}$. For the random model the slope will have to be approximately $-\frac{1}{6}$. In the case of $\text{LaFeO}_{3-\delta}$ the slope of measurements of conductivity (23) and oxygen diffusion (24) is $-\frac{1}{2}$, indicating the cluster

TABLE I

EXPERIMENTAL AND CALCULATED OXYGEN PARTIAL PRESSURES OF δ IN $\text{LaMO}_{3-\delta}$ ($M = \text{Mn, Co}$) BY KAMATA *et al.* (22) (Mn) AND SEPPÄNEN *et al.* (5) (Co), ACCORDING TO THE CLUSTER MODEL AND THE RANDOM MODEL

δ	$\log p_{\text{O}_2}$ (obs)	$\log p_{\text{O}_2}$ (calc)	
		Cluster	Random
LaMnO _{3-δ} , Kamata <i>et al.</i> (22), 1473 K			
0.006	-9.55	-9.54	-6.94
0.019	-10.60	-10.59	-9.99
0.033	-11.13	-11.12	-11.49
0.040	-11.31	-11.32	-12.02
0.046	-11.46	-11.46	-12.41
0.053	-11.60	-11.62	-12.80
LaCoO _{3-δ} , Seppänen <i>et al.</i> (5), 1236 K			
0.0006	-1.18	-1.15	0.48
0.0007	-1.35	-1.32	-0.03
0.0009	-1.54	-1.53	-0.65
0.0010	-1.70	-1.70	-1.15
0.0016	-2.04	-2.05	-2.22
0.0019	-2.22	-2.23	-2.74
0.0024	-2.42	-2.44	-3.38
0.0029	-2.58	-2.60	-3.85
0.0033	-2.71	-2.72	-4.22

model is also valid for $\text{LaFeO}_{3-\delta}$. It can thus be concluded that the cluster model describes the defects in $\text{LaMO}_{3-\delta}$ ($M = \text{Mn, Co, Fe, . . .}$) properly.

5. Other Systems in Which the Cluster Model is Valid

As was discussed in Section 3, the cluster model is probably also valid in a number of other perovskite-type oxides over a very wide composition range. Due to the different valencies of the ions there might be other, similar extended defects in these systems. An example of such defect formation is proposed for $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$.

In LaCrO_3 the introduction of Mg^{2+} on Cr^{3+} sites brings about the formation of Cr^{4+} in equal amounts. If the compound becomes

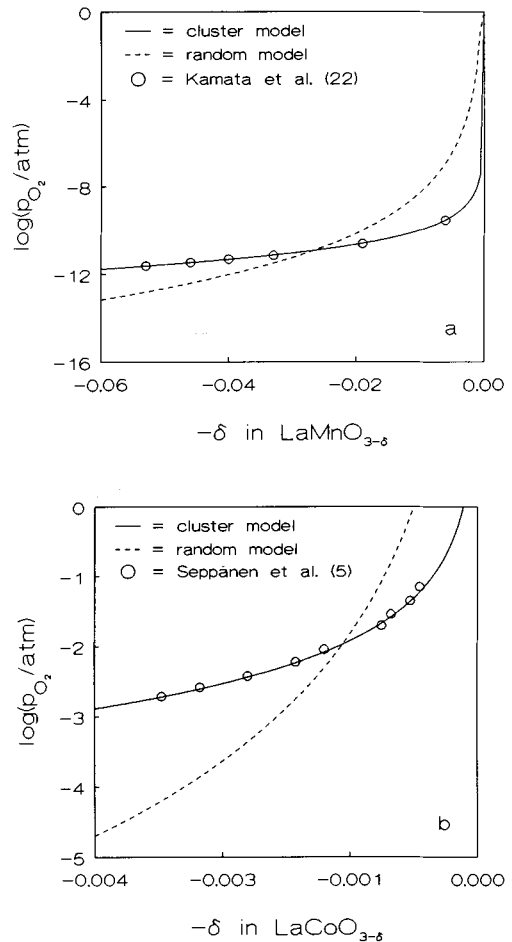


FIG. 2. Phase diagrams of defect concentration versus oxygen partial pressure. Lines are calculated according to the $M^{2+}-V_O-M^{2+}$ cluster model and the random model. (a) δ in $\text{LaMnO}_{3-\delta}$ at 1473 K by Kamata *et al.* (22). (b) δ in $\text{LaCoO}_{3-\delta}$ at 1236 K by Seppänen *et al.* (5) (from the graph).

nonstoichiometric, Cr^{4+} is reduced to Cr^{3+} . Instead of $M^{2+}-V_O-M^{2+}$ clusters $\text{Cr}^{3+}-V_O-\text{Cr}^{3+}$ clusters can be formed. The equilibrium reaction for the cluster model becomes

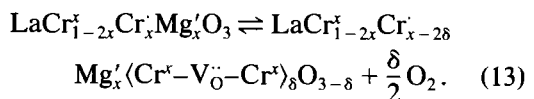


TABLE II

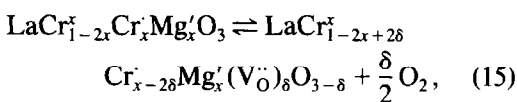
EXPERIMENTAL AND CALCULATED OXYGEN PARTIAL PRESSURES OF δ IN $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ AT 1577 K BY ANDERSON *et al.* (7), ACCORDING TO THE $\text{Cr}^{3+}-\text{V}_O-\text{Cr}^{3+}$ CLUSTER MODEL, THE RANDOM MODEL, AND THE $\text{Mg}^{2+}-\text{V}_O-\text{Mg}^{2+}$ CLUSTER MODEL

δ	$\log p_{\text{O}_2}$ (obs)	$\log p_{\text{O}_2}$ (calc)		
		Cr^{3+} cluster	Random	Mg^{2+} cluster
0.0016	3.19	1.73	1.87	2.75
0.0039	2.38	0.89	1.04	1.88
0.0114	0.60	-0.19	-0.07	0.62
0.0177	0.00	-0.70	-0.62	-0.05
0.0256	-0.95	-1.19	-1.16	-0.77
0.0351	-1.97	-1.71	-1.73	-1.57
0.0452	-3.06	-2.23	-2.29	-2.43
0.0681	-4.74	-3.53	-3.71	-4.78
0.0845	-7.35	-4.98	-5.23	-7.56

This results in an equilibrium constant (similar to Eqs (3)–(6)):

$$K_{\text{III}} = \frac{\delta \cdot p_{\text{O}_2}^{1/2}}{(x - 2\delta)^2 \cdot (3 - \delta)}. \quad (14)$$

Data of Anderson *et al.* (7) (from the graph) on $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ at 1577 K were used to check whether the cluster model is valid in this system (Table II, Fig. 3). This seems not to be the case. The random model does not apply also; the equilibrium reaction would become

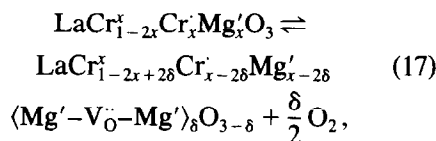


resulting in the equilibrium constant

$$K_{\text{IV}} = \frac{(1 - 2x + 2\delta)^2 \cdot p_{\text{O}_2}^{1/2}}{(x - 2\delta)^2 \cdot (3 - \delta)}. \quad (16)$$

It is probably energetically more favorable to form $\text{Mg}^{2+}-\text{V}_O-\text{Mg}^{2+}$ clusters, since the charge distribution will be similar to the formation of $\text{M}^{2+}-\text{V}_O-\text{M}^{2+}$ clusters in $\text{LaMO}_{3-\delta}$. The equilibrium reaction for the

formation of $\text{Mg}^{2+}-\text{V}_O-\text{Mg}^{2+}$ clusters becomes



resulting in the equilibrium constant

$$K_{\text{V}} = \frac{(1 - 2x + 2\delta)^2 \cdot p_{\text{O}_2}^{1/2}}{(x - 2\delta)^4 \cdot (3 - \delta)}. \quad (18)$$

Although the absolute values of the calculated oxygen partial pressures are in less agreement with the experimental data (Table II) than for the cluster model in $\text{LaMO}_{3-\delta}$ (Table I), from Fig. 3 it can be seen that this cluster formation does describe the data. The appearance of Mg^{2+} in a 5-coordinated site seems a little surprising, since Mg^{2+} usually occupies octahedral sites. It is also surprising that Mg^{2+} would not be randomly distributed in oxygen-deficient $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$. According to the defect model it

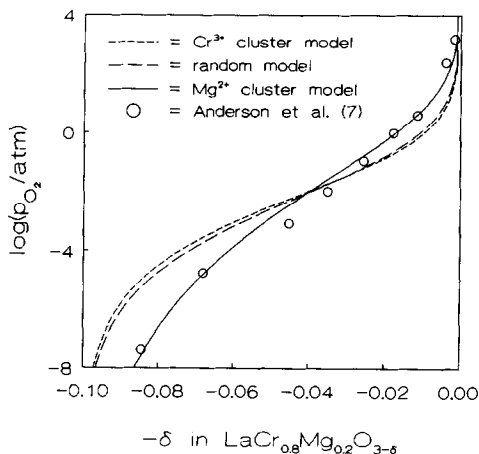


FIG. 3. Phase diagram of defect concentration versus oxygen partial pressure for δ in $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ at 1577 K by Anderson *et al.* (7) (from the graph). Lines are calculated according to the $\text{Cr}^{3+}-\text{V}_O-\text{Cr}^{3+}$ cluster model, the random model, and the $\text{Mg}^{2+}-\text{V}_O-\text{Mg}^{2+}$ cluster model.

nevertheless seems to be the case. In similar systems $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ ($M = \text{Mn, Co, Cr, Fe}$) (3, 4, 6, 8) the behavior is much more complicated and can not be described by the simple defect model. Nevertheless, it seems logical that in these systems similar clusters will be the main (extended) defects.

6. Conclusions

It can be concluded that in perovskite-type oxides the oxygen deficiency can be described by extended defects rather than by point defects. The simple cluster model does describe the phase diagrams of defect concentration versus oxygen partial pressure in $\text{LaMO}_{3-\delta}$ ($M = \text{Mn, Co, Fe}$) perovskite-type oxides. The defect chemistry of a number of other perovskite-type oxides can probably be described by similar, more complicated clusters.

The clusters should be regarded as building blocks for a number of highly defective phases that are formed at high defect concentrations (depending on the temperature). The model can be of great help to further investigate the physical properties, such as the electrical conductivity, of the perovskite-type oxides.

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