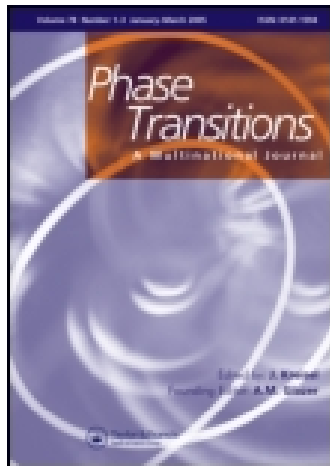


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Defect chemistry in metal oxides

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DEFECT CHEMISTRY IN METAL OXIDES

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The presentation gives a brief overview and description of point defects and extended defects that may be considered to arise from clustering or ordering of point defects. Defect chemistry and the relations between defect concentrations and transport properties are exemplified and illustrated by a review of nonstoichiometry, electrical conductivity, diffusion of cobalt and oxygen tracers, chemical diffusion, and high temperature creep of $\text{Co}_{1-\beta}\text{O}$.

Crystals are like people,
it is the defects that make them interesting

F.C. Frank

1 INTRODUCTION

What is a defect in a crystal? To answer this it is interesting to take a brief look at the history of classical chemistry and crystallography. During the 19th century crystallographers concluded that the atoms or structural units in crystals were arranged in ideal structures where all the structural sites were occupied. Chemists, on their side, generally believed that inorganic compounds had an exact stoichiometric composition. There were considerable discussions regarding these concepts, and it was not until the beginning of 20th century that it became clearly established that intermetallics and inorganic compounds can have variable compositions. The question was theoretically resolved at about 1930 when Wagner and Schottky (1931) through statistical thermodynamic treatments of mixed phases showed that crystal structures of solids are not ideal. Some lattice sites will be empty (vacant) and extra atoms may occupy the interstitial space between the atoms on the lattice sites. The empty lattice sites are termed vacancies

and the extra atoms interstitial atoms. Following Wagner and Schottky all crystalline solids will at any temperature contain vacancies and extra atoms and will as such exhibit deviations from the ideal structure. Furthermore, all inorganic compounds may in principle have variable composition and thus exhibit nonstoichiometry, and the very exact stoichiometric composition is an exception rather than the rule and can under equilibrium conditions only be achieved at definite sets of temperature and activities of the components in a crystal. These aspects have been discussed in a number of books, e.g. by Kröger (1974) and Kofstad (1971).

Even though these structural imperfections and deviations from the ideal structures are present at any temperature and occur naturally in all crystalline compounds, they are called defects. The reason for this is that the ideal structure is by convention used as the reference state, and any deviation from this ideal state is termed a defect.

Crystalline solids contain different types of structural defects. When a defect is limited to a lattice site and its immediate vicinity, the defect is called a point defect. Vacancies and interstitial atoms are point defects. An impurity atom that occupy a normal lattice site or an interstitial site is also termed a point defect. But the structural defects also comprise line and plane defects. The line defects are dislocations which are characterized by displacements in the structure in certain directions. The plane defects comprise stacking faults, grain boundaries, internal and external surfaces. This presentation will be limited to point defects and more extended defects that may be considered to arise from clustering or ordering of point defects.

1.1 Nonstoichiometry and Point Defects

The deviation from the exact stoichiometric composition, i.e. nonstoichiometry, is directly related to the presence of point defects and their aggregates. Nonstoichiometric metal oxides may — depending on the oxide, temperature and activities of the components — have an excess or deficit of metal or oxygen. In view of this, nonstoichiometric oxides may be divided in four limiting groups:

- metal deficient oxides, e.g. $M_{1-\beta}O$ such as $Ni_{1-\beta}O$, $Co_{1-\beta}O$ a.o. in which metal vacancies are the majority point defects,
- metal excess oxides, e.g. $M_{1+\beta}O$ such as $Cd_{1+\beta}O$ with metal interstitials as the prevalent defects,

oxygen deficient oxides, e.g. $\text{MO}_{2-\delta}$ exemplified by, for instance, $\text{CeO}_{2-\delta}$ and other oxides with fluorite structure and where oxygen vacancies prevail,
oxygen excess oxides, e.g. $\text{MO}_{2+\delta}$ such as, for instance, $\text{UO}_{2+\delta}$, where oxygen interstitial defects predominate.

Although a particular type of defect predominates in an oxide and as such constitutes the majority defect in the crystal, it is important to emphasize that the crystal will also contain all other defects in varying concentrations in the form of minority defects. Furthermore, the majority defect in the crystal may also change with temperature or activity of the components in the crystal (e.g. metal and oxygen). By way of example, in an oxide MO_2 the predominant defects may in principle change from oxygen vacancies to interstitial metal ions on changing the oxygen activity, and under these conditions the nonstoichiometry may be written $\text{M}_{1+\delta}\text{O}_{2-\delta}$. In addition to these defects that are native to the oxide, other defects comprise impurity or dopant atoms. In ambient hydrogen-containing atmospheres hydrogen may dissolve in oxides in the form of protonic defects.

1.2 Electronic Defects

In addition to these structural defects, inorganic compounds are also considered to contain electronic defects. These constitute electrons and electron holes which are relatively free to move in the crystal. If the electrons or holes are located at the regular ions in the structure of inorganic compounds, the electronic defects are termed polarons or — from a chemical point of view — a valence defect. Electrons or holes may also be trapped at defects and as a result otherwise transparent materials may become coloured. Composite defects involving defects and trapped electronic defects are termed colour centers.

1.3 Defect Structure

An overall description of the point and electronic defects is often termed the defect structure of the compound. Defect chemistry describes how the concentrations of point and electronic defects and their aggregates vary with composition, temperature and activities of the components of the inorganic compounds and will be further exemplified below.

1.4 Defect-dependent Properties

The defects determine or affect a number of physical and chemical properties. For instance, diffusion takes place because of the presence of defects. Thus point defects are responsible for lattice diffusion. Dislocations and grain boundaries greatly influence the mechanical properties of solids and at the same time play an important part in diffusional transport and solid state reactions. Electronic defects determine properties such as electronic conductivity, thermoelectric power, etc. Heterogeneous catalysis involving metal oxides is also closely related to their defect chemistry.

The perovskite-like compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ provides an illustration where change in nonstoichiometry produces a dramatic change in properties. The value of δ can vary from 0 to 1 and the changes in nonstoichiometry results in gradual structural changes and in the properties. As discussed by Cava, Hewat, Batlogg, Mareziosa, Rabe, Krajewski, Peck and Rupp (1990) the compound is a superconductor for values of δ smaller than 0.65 and a semiconductor at higher values of δ . At $\delta = 0$ the value of T_c is 93 K and at $d \sim 0.5 T_c$ is close to 60 K.

2 EXAMPLES OF DEFECT STRUCTURES

2.1 Stoichiometric Oxides

Although inorganic compounds under equilibrium conditions have in principle an exact stoichiometric composition only at definite sets of temperature and activities of the components, a number of compounds exhibit so small nonstoichiometry that they can be considered to be essentially stoichiometric. Such crystalline compounds may have two main types of defect disorder, and these are termed Schottky and Frenkel disorder, respectively. Schottky disorder means that the stoichiometric compound contains equivalent concentrations of cation and anion vacancies while for Frenkel-type disorder the crystal contains the same concentration of vacancies and interstitial ions for the same component (metal or oxygen).

2.2 Nonstoichiometric Oxides

As mentioned above, the nonstoichiometry may involve excess or deficit of metal or oxygen. Thus in an oxygen-deficient oxide, e.g. $\text{MO}_{2-\delta}$, the

predominant defects constitute oxygen vacancies. The point defects in a crystal may be charged or uncharged. Fully charged oxygen vacancies have two positive effective charges, and in order to conserve the electroneutrality of the crystal, complementary electronic charges in the form of electrons are formed. Similarly, an oxide with metal deficit has a defect structure where metal vacancies are the predominating point defects. When these are charged, complementary electronic defects in the form of electron holes are formed. When the nonstoichiometry involves excess metal ions, the complementary electronic defects are electrons, and when the oxide has excess oxygen in the form of oxygen ions, the complementary defects are electron holes. Nonstoichiometric oxides with electronic defects in the form of electrons and electron holes are *n*- and *p*-conductors, respectively.

In these examples it is assumed that the defects are dissolved and randomly distributed in the oxides. In other oxides the defects may be constrained to certain sites in the structure. By way of example, β -alumina, a sodium aluminium oxide with composition $\text{Na}_{2+x}\text{Al}_{21-x/3}\text{O}_{34}$, may be considered to consist of blocks consisting of four layers with oxygen in a cubic close-packed arrangement as in a spinel and between these spinel blocks are more open layers containing the sodium ions.

3 ASSOCIATIONS OF POINT DEFECTS, POINT DEFECT CLUSTERS

Point defects are often assumed to be unassociated and randomly distributed in the structure. However, this is in principle only applicable for small defect concentrations, i.e. for $\delta < 0.001$ – 0.01 . For larger defect concentrations one expects that defects begin to interact to form associations or clusters of defects.

A simple example is the association of a defect and an impurity or dopant ion with opposite effective charges. Examples of larger point defect clusters are, for instance, found for oxides with metal deficit and with excess oxygen or oxygen deficit.

3.1 Defect Clusters in a Metal-deficient Oxide: $\text{Fe}_{1-\delta}\text{O}$

A well known and extensively studied oxide where the point defects form clusters is wustite, $\text{Fe}_{1-\delta}\text{O}$. Under normal equilibrium conditions this oxide is never stoichiometric. The value of δ has values that range from 0.05

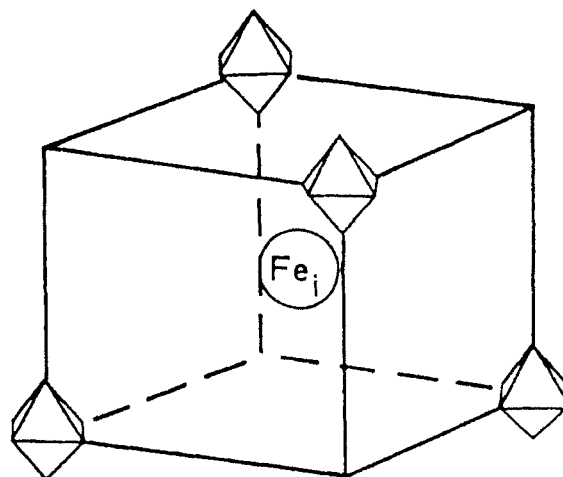


FIGURE 1 The basic unit cell for clusters in $\text{Fe}_{1-\beta}\text{O}$ and other metal deficient oxides with rock salt structure. The unit cell consists of four metal vacancies and one interstitial metal ion.

to 0.15 depending upon the temperature and oxygen activity. The composition of the oxide suggests that the predominant defects are iron ion vacancies. However, extensive structural investigations by X-ray, electron and neutron diffraction have shown that the defects not only comprise Fe-vacancies, but also Fe-interstitials with ratios of vacancies to interstitials ranging from 3 to 4 and that the vacancies and interstitials form defect clusters. As discussed by Catlow (1981) the basic unit of such clusters consists of four vacancies and one interstitial ion (a 4:1 cluster) and is illustrated in Figure 1. Such units may further combine to form more complex clusters through side-, edge- and corner-sharing and for these the ratio of vacancies to interstitials are close to 3:1. It is interesting to note that larger corner-sharing clusters have the same local atomic arrangement as magnetite, Fe_3O_4 , to which $\text{Fe}_{1-\beta}\text{O}$ transforms when the defect concentrations exceed the critical values on increasing the oxygen activity.

3.2 Defect Clusters in an Oxide with Excess Oxygen, $\text{UO}_{2+\delta}$

Uranium dioxide may depending on the temperature and oxygen activity either have a deficit or an excess of oxygen. Under conditions when it has

excess oxygen the composition of the oxide may be written $\text{UO}_{2+\delta}$. The maximum value that δ may have is about 0.25. This hyperstoichiometric composition may suggest that the predominant defects are oxygen interstitials. However, as shown by Willis (1964) through neutron diffraction studies the defects are not single, unassociated interstitials, but comprise clusters of oxygen interstitials and vacancies. The real composition of the clusters is still a matter of discussion, but the formation of the clusters may be qualitatively visualized as follows: when an oxygen atom on a normal site is dissolved interstitially an oxygen atom on a normal neighbouring site is simultaneously displaced to a neighbouring interstitial site leaving behind an unoccupied normal oxygen site. This model would suggest that the cluster consists of two oxygen interstitials and an oxygen vacancy. Other compositions with more complex geometries of the clusters have also been proposed.

4 EXTENDED DEFECTS, SHEAR STRUCTURES

Extended defects are planar defects and these may be considered to be formed by ordering and elimination of point defects, e.g. of oxygen vacancies, along specific crystallographic planes. Eyring (1981) has given an overview of these aspects. Such crystallographic planes are called shear planes, and these produce layers of lower oxides which are termed crystallographic shear phases. Crystallographic shear occurs in the transition metal oxides WO_3 , Nb_2O_5 , the rutile form of TiO_2 , a.o. The formation of shear phases gives rise to the homologous series of oxide structures, e.g. $\text{W}_n\text{O}_{3n-1}$ and $\text{Ti}_n\text{O}_{2n-1}$. In this way the crystals may be able to have variable composition and may as such be termed nonstoichiometric.

5 MODULATED STRUCTURES/INFINITELY ADAPTIVE STRUCTURES

As discussed by Anderson (1977) some oxide systems may accommodate nonstoichiometry by continuous adjustment of a parent structure without forming point defects. Such structures are now called modulated nonstoichiometric compounds, but these have also in the literature been termed vernier structures or infinitely adaptive structures. An example of an oxide with so-called infinitely adaptive structure is the low temperature modification

of Ta_2O_5 , L- Ta_2O_5 . The oxide becomes oxygen-deficient on reducing the ambient oxygen activity, but the monophasic structure is maintained through the creation or elimination of oxygen sites in the oxygen sublattice while the number of tantalum sites remain unchanged. The structure of L- Ta_2O_5 have been described by Roth (1980) and the electrical conductivity of the oxide with different dopants have been reported by Bredesen and Kofstad (1988).

6 DEFECT CHEMISTRY

As mentioned above defects determine or affect a number of physical and chemical properties of metal oxides and other crystalline solids. By way of example, the electronic conductivity is proportional to the concentrations of electronic defects and their mobility and lattice diffusion is proportional to the concentrations of point defects and their mobilities. Diffusion, in turn, determines solid state reactions, protective oxidation behaviour, sintering, creep, a.o. In order to predict how these properties vary with temperature and with oxygen and/or metal activities, it is essential then to be able to express the concentrations of point and electronic defects as a function of the same parameters.

This is achieved through defect chemistry. This in turn, requires that one has a notational system to describe the various defects, to write equations for their formation and interactions and to treat these in terms of thermodynamics.

6.1 Notational System and Rules for Writing Defect Reactions

The most widely used notational system for defects is that of Kröger and Vink (1956). In this system the defects are indicated by the major symbol and the site it occupies by a subscript. A vacancy is written as V and oxygen and metal vacancies are then written as V_{O} and V_{M} , respectively. An interstitial site is indicated by a subscript i and an oxygen interstitial is then written O_i . A metal atom and an oxygen atom on a normal lattice sites in the oxide MO are written M_{M} and O_{O} , respectively.

The defects may be charged and such charges are in defect chemistry usually expressed in terms of effective charges rather than in real charges. The effective charge is the charge relative to that in an ideal crystal. Special

symbols are used to describe the effective charges, thus a positive effective charge is indicated by a superior dot and a negative effective charge by a superior prime. An oxygen vacancy with two (positive) effective charges is thus written $V_{\text{O}}^{2\cdot}$ and a metal vacancy with two effective (negative) charges as $V_{\text{M}}^{2\prime}$. If it is desirable to indicate that a defect or an atom have zero effective charge, then this is indicated by a superior "x". An oxygen vacancy with zero effective charge is thus written V_{O}^x .

The writing of defect equations involve the same principles and procedure as for ordinary chemical reactions in that it is necessary to take into account mass balance and electroneutrality. But in addition, the ratio of regular metal and oxygen sites must remain constant. Thus if an oxygen site is created in an oxide MO by reaction with the ambient oxygen, a metal site is also created in order that the ratio of the two sites remains 1:1.

Numerous defect reactions may be written involving various oxides, defects and defect structures, dopant additions, etc. In order to illustrate the principles involved, the treatment and discussion will focus on various aspects of the defect structure of $\text{Co}_{1-\delta}\text{O}$. It is one of the most extensively studied oxides with regards to defects and defect-dependent properties and provides illustrative examples of the relations between defect chemistry and properties.

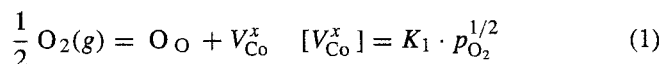
7 DEFECTS AND DEFECT DEPENDENT PROPERTIES OF $\text{Co}_{1-\delta}\text{O}$

Following the thermodynamic data evaluated and reported by Kubachewski, Evans and Alcock (1967) the standard Gibbs free energy of formation of CoO ($\text{Co} + \frac{1}{2}\text{O}_2$) is given by $\Delta G^\circ = -223.9 + 0.707 \cdot T$ kJ/mole. By way of example, this means that CoO decomposes to cobalt metal and oxygen at $1 \cdot 10^{-11}$ atm O_2 at 1000°C and $3.2 \cdot 10^{-9}$ atm O_2 at 1200°C. At sufficiently high oxygen pressures the oxide is oxidized to Co_3O_4 and by way of example this takes place at 970°C in 1 atm O_2 .

CoO is assumed to be essentially stoichiometric at the decomposition pressures and to be metal deficient at higher oxygen activities. In all practical cases CoO becomes nonstoichiometric by exchanging oxygen with the ambient atmosphere. On increasing the ambient oxygen pressure oxygen reacts with CoO and as such the nonstoichiometry of this oxide may be written $\text{CoO}_{1+\delta}$. However, the oxygen atoms form new normal oxygen sites

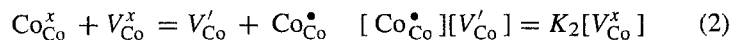
and to conserve the 1:1 ratio between regular cobalt and oxygen sites, an equivalent number of cobalt vacancies are formed, i.e. the oxide is metal deficient and the composition is more correctly written $\text{Co}_{1-\beta}\text{O}$.

Thus when CoO reacts with oxygen gas, the formation of cobalt vacancies and the corresponding defect equilibrium using the law of mass action may be written

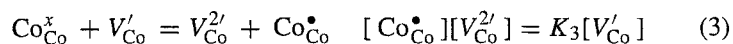


where V_{Co}^x represents a cobalt vacancy with zero effective charge and K_1 the equilibrium constant. If one can assume that the electronic defects in CoO are small polarons and (thus that the electronic charges are located at the cobalt ions on regular lattice sites), a neutral vacancy may be considered to constitute a vacant cobalt site (with two negative effective charges) associated with two neighbouring cobalt ions each with a positive effective charge (Co^{3+} -ions).

One may further envisage that the positive effective charges may be excited away from the vacancy. When one of the charges is excited, the defect reaction and equilibrium may be written



where $\text{Co}_{\text{Co}}^\bullet$ represents a cobalt ion with one effective positive charge located away from the vacancy region, V_{Co}' a cobalt vacancy with one negative effective charge (i.e. a vacant cobalt site with two negative effective charges associated with one neighbouring cobalt ion with a positive effective charge) and K_2 the corresponding equilibrium constant. This vacancy may be further ionized to yield a cobalt vacancy with two negative effective charges and a new cobalt ion with one positive effective charge:



where K_3 is the equilibrium constant.

In this description of the cobalt vacancies the charge or charges associated with the metal vacancies should not be considered to be fixed at one of the neighbouring cobalt ions, but rather that they move around at different Co sites. The number of associated positive charges should as such be viewed as the average number of positive charges located at one of the nearest-neighbour Co-sites. In these terms the average number of associated positive charges

may vary from zero to two and the negative effective charge on the defects correspondingly varies from 2 to zero.

When the cobalt vacancies are the prevalent point defects, the concentration of the point defects and the electronic defects (electron holes/ $\text{Co}_{\text{Co}}^{\bullet}$) may be expressed by combining the expressions for the defect equilibria with the electroneutrality condition involving the point and electronic defects:

$$[\text{Co}_{\text{Co}}^{\bullet}] = [V'_{\text{Co}}] + 2[V^{2'}_{\text{Co}}] \quad (4)$$

7.1 Nonstoichiometry

If the defects comprise single vacancies only, the deviation from stoichiometry is given by the sum of the neutral, singly, and doubly charged cobalt vacancies. The above relations show that the deviation from stoichiometry δ is proportional to $p_{\text{O}_2}^{1/2}$ if the neutral vacancies predominate, to $p_{\text{O}_2}^{1/4}$ if singly charged vacancies prevail, and to $p_{\text{O}_2}^{1/6}$ if doubly charged vacancies predominate. The expression for the concentration of vacancies when the singly charged vacancies predominate is, for instance, approximated by

$$[V'_{\text{Co}}] = (K_1 K_2)^{1/2} p_{\text{O}_2}^{1/4} \quad (5)$$

The equilibrium constant may be expressed in terms of the enthalpies of the different defect reactions, i.e.

$$K_n = K_o \exp\left(-\frac{\Delta H_n}{RT}\right) \quad (6)$$

where n has values of 0, 1, and 2 corresponding to the effective charge on the defect. By way of example the expression for the concentration of singly charged cobalt vacancies is given by

$$[V'_{\text{Co}}] = (K_{o1} K_{o2})^{1/2} \exp\left(-\frac{\Delta H_1 + \Delta H_2}{2RT}\right) p_{\text{O}_2}^{1/4} \quad (7)$$

where ΔH_1 is the enthalpy of formation of neutral cobalt vacancies and ΔH_2 for the excitation of the neutral to singly charged cobalt vacancies. The sum of ΔH_1 and ΔH_2 , $\Delta H_{12} = \Delta H_1 + \Delta H_2$, represents the enthalpy of formation of the singly charged cobalt vacancies.

The deviation from stoichiometry has been directly measured by means of thermogravimetry in several investigations by Fisher and Tannhauser (1964, 1966), Sockel and Schmalzried (1968), Bransky and Wimmer (1972), Sykora (1988), and Persels, Mason and Routbort (1991). By this method the most accurate values are obtained at near-atmospheric oxygen pressures. As a measure of the nonstoichiometry the value of δ is 0.01 at 1150°C at 1 atm O₂.

The results at 1200°C show that the δ has an oxygen pressure dependence that gradually changes from $p_{\text{O}_2}^{1/6}$ at reduced oxygen pressures ($< 10^{-5}$ atm O₂) to $p_{\text{O}_2}^{1/2}$ (and even a somewhat higher value) at oxygen pressures larger than about 1 atm. On the basis of these results alone it would not be unreasonable to interpret the defect structure in terms of the ideal model involving cobalt vacancies as described above with effective charges gradually changing from 2' at reduced oxygen activities and correspondingly low defect concentrations to 0 at oxygen pressures larger than 1.

7.2 Electrical Conductivity (14,17–20)

The electrical conductivity has also been studied by a number of investigators, e.g. by Fisher and Tannhauser (1964, 1966), Sykora (1988), Persels *et al.* (1991), Eror and Wagner (1969) and Gvishi and Tannhauser (1972) and it exhibits essentially the same oxygen pressure dependence as that for δ at 1200°C varies from about $p_{\text{O}_2}^{1/6}$ at reduced oxygen pressures to $p_{\text{O}_2}^{1/2}$ and even somewhat higher values at oxygen pressures higher than 1. Petot-Érvas, Ochin and Mason (1985) and Chen, Gartstein and Mason (1982) have shown through studies of the thermoelectric power that the charge carriers are positive and thus that the oxide is an electronic *p*-conductor.

When one only considers the transport of electron holes, the electrical conductivity is given by

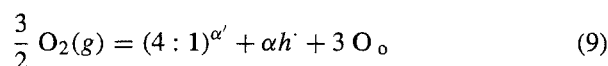
$$\sigma = z_h e \mu_h p \quad (8)$$

where z_h is the charge number of the electron holes ($z_h = 1$), e the electronic charge, μ_h the mobility and p the concentration of electron holes. Chen *et al.* (1982) measured the temperature dependence of the mobility by measuring the conductivity at constant thermoelectric power, i.e. at constant concentration of electron holes. They found that the mobility could be expressed as a thermally activated process with an activation energy of

0.37 eV. This result clearly suggest that the electron holes can be considered to be small polarons as is assumed above.

The ideal defect model involving single cobalt vacancies with different effective charges predicts that the oxygen pressure dependence of the electrical conductivity should be no higher than $p_{O_2}^{1/4}$ as no mobile electronic charges are available when neutral cobalt vacancies are the prevailing point defects. As the conductivity has a higher oxygen pressure dependence at high oxygen pressures, this means that the ideal defect model involving single cobalt vacancies has to be modified at the larger defect concentrations.

In view of the defect cluster formation that has been both experimentally observed and theoretically modelled for $Fe_{1-\delta}O$, several authors, Gesmundo, Viani, Petot-Ervas, Petot and Buscaglia (1987), Tomlinson, Calow and Harding (1985), and Anderson, Grimes and Heuer (1985), have proposed that similar clusters may be formed in $Co_{1-\delta}O$. By way of example, a 4:1 cluster composed of 4 cobalt vacancies and 1 cobalt interstitial ion may be written



where α' is the negative effective charge of the defect cluster. If this type of cluster prevales at high oxygen pressures, the oxygen pressure dependence of both the nonstoichiometry and the electrical conductivity will be dependent on the charge of the cluster. Thus if the effective charge on the cluster is $\alpha = 1$, the oxygen pressure dependence of the hole concentration (conductivity) will be $p_{O_2}^{3/4}$ and for $\alpha = 2$ an oxygen pressure dependence of $p_{O_2}^{1/2}$. This is in the range of experimentally observed values.

7.3 Cobalt Tracer Self-diffusion

Cobalt self-diffusion has also been studied by several investigators and the results are in good agreement. Some of the results reported by Carter and Richardson (1954, 1955), Dieckmann (1977), and Rahman and Berard (1977) are given in Figure 2. As shown from these results the oxygen pressure dependence in the oxygen pressure range 10^{-4} –1 atm range from $p_{O_2}^{1/4}$ to $p_{O_2}^{1/3}$ depending on the temperature and oxygen pressure. This is what is expected in view of the oxygen pressure dependences observed for the nonstoichiometry in the same oxygen pressure and temperature range.

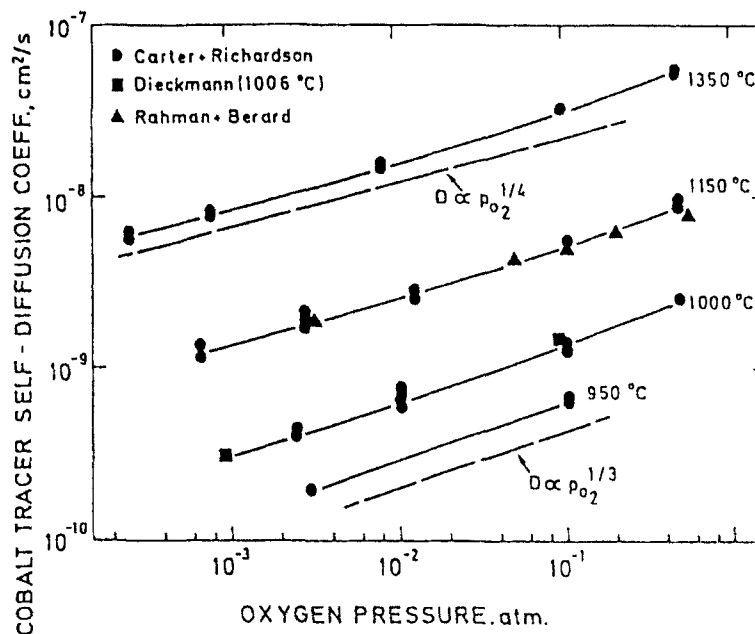


FIGURE 2 Literature values of the cobalt tracer self-diffusion coefficient in $\text{Co}_{1-\delta}\text{O}$ as a function of the partial pressure of oxygen at temperatures from 950 to 1350°C. Results of Carter and Richardson (1954, 1955), Dieckmann (1977), and Rahman and Berard (1977).

Results reported by Aggarwal and Dieckmann (1991) suggest that the values of ∂ exhibits a somewhat larger oxygen pressure dependence than that of the cobalt tracer diffusion coefficient in the oxygen pressure. If cobalt diffuses by the vacancy diffusion mechanism, the cobalt tracer diffusion coefficient is related to ∂ through the relation

$$D_{\text{Co}}^{\text{tr}} = f D_{\text{Co}} = f \partial D_{V_{\text{Co}}} \quad (10)$$

where f is correlation coefficient ($f = 0.78$ for diffusion of cobalt in CoO by the vacancy mechanism) and $D_{V_{\text{Co}}}$ is the vacancy diffusion coefficient. The difference in oxygen pressure dependence between ∂ and $D_{\text{Co}}^{\text{tr}}$ may suggest that the vacancy diffusion coefficient changes with the oxygen pressure or that the type of diffusing defect gradually changes with the oxygen pressure.

7.4 Chemical Diffusion Coefficient

A large number of studies of the chemical diffusion coefficient has been reported in the literature using either thermogravimetric or electrical conductivity measurements and results of these studies have been summarized by Nowotny and Sadowski (1985). In these type of studies a specimen is equilibrated at a definite oxygen pressure, the oxygen pressure is then suddenly changed and the weight change or electrical conductivity is measured as the specimen equilibrates with the new ambient oxygen pressure. Thermogravimetric measurements is the more direct method for measuring the chemical diffusion. The reported results show considerable discrepancies both with regards to the absolute values and the activation energies. The results also clearly suggest that the chemical diffusion coefficient increases with increasing oxygen pressure.

Under ideal conditions and when cobalt diffuses by the vacancy mechanism, the chemical diffusion coefficient for $\text{Co}_{1-\delta}\text{O}$ is related to the cobalt vacancy diffusion coefficient by

$$D_{\text{CoO}}^{\text{chem}} = (1 + \alpha)D_{V_{\text{Co}}} \quad (11)$$

where α is the charge on the cobalt vacancy. If the cobalt vacancy diffusion coefficient is independent of the deviation from stoichiometry, one would then expect that the chemical diffusion coefficient decreases with increasing oxygen pressure as the value of α decreases with increasing oxygen pressure. The opposite behaviour is observed, and this may suggest that the cobalt vacancy diffusion varies with δ or that the type of mobile defect gradually changes with oxygen pressure.

7.5 Interference Between Ionic and Electronic Flows in $\text{Co}_{1-\delta}\text{O}$

In considerations of simultaneous transport of electrons and ions in oxides with prevalent electronic conduction it is generally assumed that the ions and electrons move independently of each other, i.e. that there is no interference between the ionic and electronic flows. However, Lee and Yoo (1994) and Yoo, Lee, Martin and Scmalzried (1994) have through several studies on $\text{Co}_{1-\delta}\text{O}$ in recent years shown that this is not necessarily the case.

This interference may be described in terms of the linear transport theory and for a metal deficient oxide like $\text{Co}_{1-\beta}\text{O}$ the flux of cobalt ions, J_1 , and of electrons, J_2 , in a gradient of the electrochemical potential of the cobalt ions, $\nabla\eta_1$, and in a gradient of the electronic electrochemical potential, $\nabla\eta_2$. The flux of cobalt ions and of electrons are given by

$$J_1 = -L_{11}\nabla\eta_1 - L_{12}\nabla\eta_2 \quad (12a)$$

$$J_2 = -L_{21}\nabla\eta_1 - L_{22}\nabla\eta_2 \quad (12b)$$

where L_{11} , L_{22} , L_{12} , and L_{21} represent the transport coefficients. Following Onsager and irreversible thermodynamics $L_{12} = L_{21}$.

It is common practice to neglect the coefficients L_{12} and L_{21} and assume that these are zero. Transport-related quantities such as the Nernst-Einstein relation, the open cell voltage a.o. are normally based on this assumption. However, recent studies by Lee and Yoo (1994) and Yoo *et al.* (1994) have shown that the cross coefficient is not negligible.

One way of expressing this is to define the so-called charge of transport of the cations, a_1^* . If there is no electronic electrochemical potential gradient ($\Delta\eta_2 = 0$) present in the oxide and one takes Co^{2+} and electrons as the mobile units in $\text{Co}_{1-\beta}\text{O}$, a_1^* given by

$$a_1^* = \frac{J_2}{J_1} = \frac{L_{12}}{L_{11}} \quad (13)$$

On the basis of this model the charge of transport of the cation is defined as the number of electrons dragged along by a moving cation when $\nabla\eta_2 = 0$.

Values of a_1^* has in recent years been measured by various techniques including electrotransport and electrochemical techniques. The values of a_1^* have been found to decrease from about 1.5 at 950°C to about 0.5 at 1100°C for measurements carried out in air (0.21 atm O_2). Other studies show that a_1^* increases with increasing oxygen pressure at constant temperature. As discussed by Yoo *et al.* (1994) these results have important consequences for the expressions for the Nernst-Einstein relation, the open cell voltage for a cell involving a mixed conductor a.o.

As the cobalt ions diffuse by the vacancy mechanism, the cationic charge of transport can alternatively be viewed in terms of the cobalt vacancy diffusion. Consider, for instance, the diffusion of a cobalt vacancy with an effective charge α' . When this diffuses and exchanges sites with a Co^{2+} -ion, it means that α' associated positive charges moves along with the vacancy. Thus as a Co^{2+} -ion moves in the lattice, α' positive charges moves in the opposite direction. Thus the net charge that is moved when Co^{2+} -ions move in the lattice is equal to $2 - \alpha'$. In these terms $2 - \alpha'$ can be considered to be equal to α_1^* . Generally interference between ionic and electronic flows in $\text{A}_{1-\beta}\text{O}$ oxides are expected when the defects (vacancies) have an effective charge that differs from the formal charge of the cations.

7.6 Oxygen Defects in $\text{Co}_{1-\beta}\text{O}$

Oxygen defects are minority defects in $\text{Co}_{1-\beta}\text{O}$ and studies of nonstoichiometry, electrical conductivity and cobalt tracer diffusion provide no information regarding the type of oxygen point defects that are present and their concentrations. The most direct way of obtaining such information is through measurements of oxygen diffusion in monocrystalline $\text{Co}_{1-\beta}\text{O}$. Studies of high temperature creep, which is controlled by the slower moving (oxygen) defects, may also provide relevant information.

Tarento and Monty (1988) have studied oxygen self diffusion in $\text{Co}_{1-\beta}\text{O}$ between 10^{-8} and 0.21 atm O_2 at 1150, 1200, 1300, and 1400°C. The studies involved diffusion of ^{18}O into monocrystalline species and subsequent analysis of ^{18}O concentration/penetration curves by SIMS. The oxygen tracer diffusion coefficient decreases with decreasing oxygen pressure in the pressure range 0.21– 10^{-4} atm O_2 and then goes through a minimum and increases with further decrease of the oxygen pressure. The authors conclude that the predominating oxygen defects are doubly charged oxygen vacancies at the low oxygen pressures and singly charged oxygen interstitials at high oxygen pressures.

Studies of stationary creep in $\text{Co}_{1-\beta}\text{O}$ at 1100–1400°C has been reported by Dominguez-Rodriguez, Sanchez, Marquez, Castaing and Monty (1981), Dominguez-Rodriguez, Sanchez, Marquez, Castaing, Monty and Philibert (1982), and Clauss, Tarento, Monty, Dominguez-Rodriguez, Castaing and Philibert (1985). The stationary creep exhibits a similar oxygen

pressure dependence as for oxygen diffusion and the creep rates goes through a minimum at about 10^{-4} atm O₂. This is also the behaviour predicted by the creep models based on the results of oxygen diffusion in Co_{1- δ} O.

All in all, nonstoichiometry and transport properties of Co_{1- δ} O have been extensively studied. The main features of the defect structure is understood, but there are still various aspects with regards to the nature of the defects and their diffusional properties that are in need of improved understanding.

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