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Electronic Conduction in Oxides at Elevated Temperatures*†

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A brief discussion of the defect models and experimental techniques used to characterize the electrical conductivity of insulating and semiconducting oxides are presented. Emphasis is on the electronic conduction at elevated temperatures, where the oxide may be equilibrated with the ambient atmosphere.

Where appropriate, typical examples of oxides are selected to emphasize (1) how information about defect structures and transport properties of the defects in oxides may be obtained from a combined analysis of different types of experimental data, and (2) some of the experimental and theoretical problems which are limiting our understanding of the electronic conductivity of insulating and semiconducting oxides and their application to technology.

Introduction

The electrical conductivity of metal oxides encompasses a wide range of values which characterize insulators, semiconductors, and metallic conductors. The electrical behavior is usually strongly dependent upon temperature and composition. For example, a small change in the composition may transform an insulating ceramic into a semiconductor. When the resistivity is high, conduction may occur by both electronic and ionic processes. The electrical conductivity of a homogeneous single-phase material is generally described by the following expression

$$\sigma = \sum_i n_i q_i \mu_i, \qquad (1)$$

where n_i is the concentration of charge carriers with charge q_i and mobility μ_i. A complete characterization of the electrical conductivity requires that the charge, concentration and mobility of each charge carrier be determined as a function of the appropriate parameters (e.g., temperature, composition, atmosphere).

Discussion of electrical conductivity in this paper will be restricted to those oxides which exhibit insulating or semiconducting behavior. For these type of oxides the charge carriers in Eq. (1) are referred to as defects. These defects can be produced by thermal disorder, deviation from stoichiometry and the incorporation of foreign atoms into the lattice.

If an oxide is heated in an atmosphere such that the stoichiometric ratio of M/O is maintained, defects will be produced by thermal disorder. Several types of disorder may occur (*1*, *2*), for example, Schottky disorder in a binary oxide MO corresponds to the creation of equal concentrations of anion and cation vacancies,[1] i.e.,

$$[V_{\mathrm{M}}^{x}] = [V_{\mathrm{O}}^{x}]. \qquad (2)$$

If the concentration of defects is small defect interaction can be ignored and the mass action law may be employed to obtain the expression

$$[V_{\mathrm{M}}^{x}]\,[V_{\mathrm{O}}^{x}] = K_s \qquad (3)$$

relating the concentration of cation and anion vacancies to the temperature dependent Schottky disorder constant K_s.

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† Invited paper.

[1] The notation used in this paper is the same as used by Kröger (*2*).

The lattice defects may also ionize, for example

$$V_O^x = V_O^{\cdot} + e' \tag{4}$$

where

$$K_5 = ([V_O^{\cdot}][e'])/[V_O^x]. \tag{5}$$

Kröger and Vink (*1*) and Kröger (*2*) have presented a comprehensive treatment of this subject matter.

Based on thermodynamic considerations all oxides exhibit deviations from stoichiometry. According to the phase rule the number of degrees of freedom is two for a binary oxide system. Thus, for example if a sample of TiO_{2-x} is equilibrated at a given temperature with a fixed oxygen pressure the deviation from stoichiometry is uniquely determined, i.e., $x = f(T, P_{O_2})$. For a ternary system such as $BaTiO_{3-x}$ one additional degree of freedom must be controlled. If the cation ratio, Ba/Ti, is fixed than $x = f(T, P_{O_2})_{Ba/Ti}$.

When a binary oxide is equilibrated with a gaseous phase containing oxygen or the metal component, M, an excess or deficit of one of the components is accommodated in the lattice. If limiting cases are considered for an oxide of the type $MO_{2\pm x}$ the excess oxygen may be incorporated by the following defect reactions

$$V_i^x + \tfrac{1}{2}O_2(g) \rightarrow O_i^x \tag{6}$$

or

$$\tfrac{1}{2}O_2(g) \rightarrow O_O^x + \tfrac{1}{2}V_M^x \tag{7}$$

Applying the law of mass action to Eqs. (6) and (7), we obtain the following expressions

$$K_8 = [O_i^x]/P_{O_2}^{1/2} \tag{8}$$

and

$$K_9 = ([V_M^x]^{1/2})/(P)_{O_2}^{1/2} \tag{9}$$

If the oxide is oxygen deficit

$$O_O^x \rightarrow \tfrac{1}{2}O_2(g) + V_O^x \tag{10}$$

or

$$V_i^x + M_M^x + 2O_O^x \rightarrow M_i + O_2(g). \tag{11}$$

The mass action constants for Eqs. (10) and (11), respectively, are

$$K_{12} = [V_O^x]P_{O_2}^{1/2} \tag{12}$$

and

$$K_{13} = [M_i]P_{O_2} \tag{13}$$

In addition each of the above types of defects may ionize and the resulting equations may be expressed with equilibrium constants.

The problem in characterizing the defect behavior of a metal oxide is to determine which of the above defect reactions predominate. Usually, the magnitude of the enthalpies associated with defect reaction are quite different so that only a few of the reactions have to be considered.

As an example, consider an oxygen deficit oxide, MO_{2-x}, where the predominant nonstoichiometric defects are oxygen vacancies. Then by combining Eqs. (5) and (12) we obtain

$$K_{14} = K_5 K_{12} = [V_O^{\cdot}][e']P_{O_2}^{1/2}. \tag{14}$$

If the oxide is an electronic conductor and we employ the simplified electroneutrality equation

$$[V_O^{\cdot}] = [e'], \tag{15}$$

then since

$$\sigma = [e']q\mu_e \tag{16}$$

$$\sigma\alpha[e'] = (K_5 K_{12})^{1/2} P_{O_2}^{-1/4} \tag{17}$$

if the electron mobility μ_e is a function of temperature only.

For this simplified case we are ignoring the thermally created defects and are assuming that the nonstoichiometric defects are controlling the physical properties of the oxide.

In addition to the formation of defects by thermal disorder and nonstoichiometry, defects may also be incorporated into the crystal by addition of foreign atoms. These atoms may be incorporated in either substitutional or interstitial positions or both. To maintain electroneutrality in the doped crystal additional lattice point defects or electronic defects may be formed. For a detailed discussion of the incorporation of foreign atoms in oxides the reader is referred to the comprehensive discussion by Kröger (*2*).

In the aforementioned discussion of defect models the law of mass action has been used to obtain expressions relating the concentration of defects to the external variables temperature, partial pressure of the components, and concentration of foreign impurities. The law of mass action treatment is limited to the case of dilute defect concentration where (1) the interaction of defects is negligible (i.e., the partial molal enthalpies $\bar{H}_i$ of the defect is independent of defect concentration) and (2) the defects may be considered to be randomly distributed (i.e., the partial molal entropy, $\bar{S}_i$, may be divided into vibrational, S_i^v, and configurational, S_i^c, terms where S_i^v is independent of defect concentration and $S_i^c = -R \ln x_i$; and (3) Boltzmann statistics may be used instead of Fermi–Dirac statistics.

As the concentration of defects increase the mass action treatment may be invalidated because of defect interaction. If the defects interact over a short range and the force is attractive, the closely interacting defects may be treated as a new species (i.e., an associated or complex type defect). This type of defect may then be used in the mass action equations (*2*, *3*). On the other hand, if the short range forces between the defects are repulsive it may be possible to treat the case using a "blocking" method (*3–5*) (e.g., a defect located within the crystal may prevent the neighboring sites from being occupied).

When the forces between defects are long range coulombic interaction it may be possible to make corrections to the mass action expression by employing the Debye–Hückel theory. This approach has been discussed by Lidiard (*6*).

At large deviations from stoichiometry the nonstoichiometric behavior may be controlled by the formation of microdomains or shear structures. For a discussion of extended defects see for example *Problems of Nonstoichiometry* (*7*) and *The Chemistry of Extended Defects in Non-Metallic Solids* (*8*).

The electronic mobility, μ, in oxides at elevated temperatures is generally determined to a large extent by the interaction of the electrons with the polar modes of the crystal. The theories describing the temperature dependence of the electron mobility are usually based on the large polaron case or small polaron case. A comprehensive review of the subject is given by Appel (*9*). Large polarons correspond to band type conduction. The lower limit for μ is approximately 0.5–1 cm^2/V sec and μ decreases with temperature. The small polaron mobility is a hopping type process. For this case the upper limit for μ is approximately 0.1 cm^2/V sec and $\mu \propto T^{-n} e^{-Q/kT}$. Thus, an accurate determination of the magnitude or the temperature dependence of the mobility will allow one to distinguish band type conduction from hopping type conduction.

As discussed previously a complete characterization of the electrical conductivity requires that the charge, concentration and mobility of each charge carrier be determined as a function of the pertinent parameters (e.g., temperature, composition, atmosphere). In general these quantities cannot be determined directly by experiment. Usually the results from several different experimental measurements must be used in combination with the theoretical interpretation in order to provide this information. These experimental methods usually include one or more of the following types of measurements: thermodynamic, electrical conductivity, transference number, thermoelectric, and mobility. An extensive discussion of the experimental details involved in these experimental techniques is presented in a recent text on *Electrical Conductivity In Ceramics and Glass* (*10*).

The selection of an oxide for a particular application is usually dependent on the magnitude of its electrical conductivity. Thus, it is convenient to describe the electrical behavior of oxides in terms of three conductivity regions, insulating, semiconducting, and metallic. Since metallic conducting oxides will be described in other papers in the Symposium, we will restrict our discussion to those oxides which exhibit insulating or semiconducting behavior. Where appropriate typical examples of oxides will be selected to emphasize (1) how information about defect structure and transport properties of the defects in oxides may be obtained from a combined analysis of different type experimental data, and (2) some of the experimental and theoretical problems which are limiting our understanding of the electronic conductivity of insulating and semiconducting oxides and their application to technology.

Metal Oxide Insulators

Oxide insulators (e.g., Al_2O_3, MgO, BeO, CaO, SrO) are what Kröger (*2*) has referred to as normal ionic compounds in which the cations and anions have a rare-gas configuration. The low concentration of defects is a result of the large band-gap energies and small deviations from stoichiometry. Thermal disorder defects (e.g., Frenkel or Schottky disorder) may be important in these oxides at very high temperatures. Thus, one of the problems with oxides of this type is that the electrical conductivity tends to be extrinsically controlled unless the measurements are made on very high purity specimens at high temperatures. Even if high purity specimens can be prepared the problem of preventing contamination with impurities *in situ* at high temperatures remains.

Because of the large band-gap energies the electronic mobilities of these type of oxides are usually quite low. According to Steele (*11*), at present it appears that 10^{-3} cm^2/V sec probably represents an operational lower limit for electron and hole mobilities in ionic type solids. In contrast, the higher reported ionic mobility (in β-Al_2O_3) is approximately 10^{-3} cm^2/V sec and values of the ionic mobility are usually much lower for other oxide systems. Because of the low concentration of electronic defects and their low mobilities insulating type oxides may exhibit an appreciable ionic conductivity.

To illustrate some of the experimental problems encountered with the electrical conductivity measurements and interpretation of the defect structure and transport

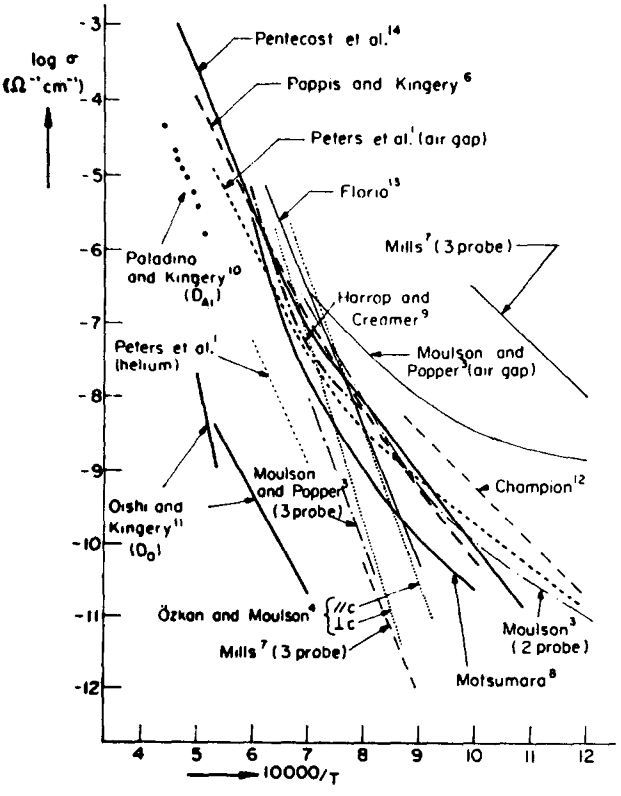

FIG. 1. Comparison of the specific conductivity of Al_2O_3 reported in the literature with the corresponding air gap conductivity and conductivity calculated from self-diffusion of O and Al after Brook et al. (*12*).

properties of insulating oxides at elevated temperatures consider the results of some recent studies on Al_2O_3.

The electrical conductivity of Al_2O_3 has been investigated many times and several different explanations have been used to explain the observed behavior. Figure 1 was used by Brook et al. (*12*) to illustrate the wide variation of reported results on the conductivity of Al_2O_3. Many of the earlier studies have been shown to be in error because external leakage paths were not eliminated in the experimental measurements. When the electrical behavior of materials with high resistance are investigated care must be exercised to avoid leakage paths arising from either surface or gas-phase conduction. A number of investigators (*12*, *13–16*) have shown that for high resistance materials the conductivity of the gas phase around the sample can be comparable to or greater than that of the sample. The gas-phase conduction involves thermionic emission from the sample, the leads, or the supporting structure and is probably dependent on the design of the experimental system. The effects of gas-phase and surface conduction may be either eliminated or minimized using a guarded circuit and isolating the gas phase at the electrodes. As an example, a schematic diagram of the guarded system used by Brook et al. (*12*) to measure the electrical conductivity and transference number of Al_2O_3 is shown in Fig. 2. The platinum shielding which acted as the guard was maintained at the same potential as the Pt-wire contact by adjusting the potential of the guard until no current flowed. The results of their measurements on the ionic transference number on a cell of the type

$$\mathrm{Pt, O_2|Al_2O_3|air, Pt}$$

is shown in Fig. 3. They observed that with the guarded circuit the measured emf between 1000 and 1400°C agreed with the theoretical values within experimental error indicating that $t_i \simeq 1$ and that the ionic species have conventional charges. Without the guard t_i appeared to decrease with increasing temperature. This reduction in the apparent value of t_i was attributed to an increase in the conduction of the gas phase.

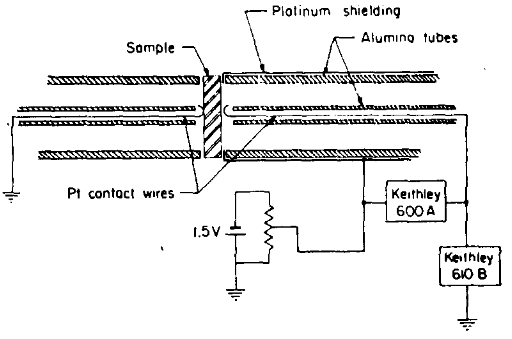

FIG. 2. Arrangement for measuring bulk conductivity or emf using a cylindrical volume guard. The guard and the electrode boosted to the same potential should be under identical P_{O_2} and temperature after Brook et al. (*12*).

Electrical conductivity measurements in air between 1000 and 1600°C were obtained by Brook et al. (*12*) using the three terminal dc techniques shown in Fig. 2. They interpret the conduction in Al_2O_3 as substantially ionic with aluminum interstitial ions as charge carriers at high oxygen activity.

Using a similar measuring system Yee and Kröger (*17*) extended the transference measurements on Al_2O_3 to higher temperatures, 1650°C. Single crystals of Al_2O_3 were shown to have an ionic transference number, t_i, of $\simeq 1$ with a possible small decrease as a result of electronic (hole) conduction at $T > 1450°C$. Polycrystalline

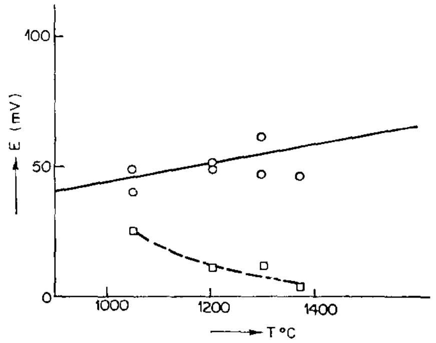

FIG. 3. Measurements on a cell Pt, $O_2|Al_2O_3|Pt$, air with and without volume guard after Brook et al. (*12*). □ Unguarded; ○ with volume guard —— theoretical value assuming conventional charges.

samples exhibit t_i values of <1, with $t_{el} = (1 - t_i)$ increasing with decreasing temperature and increasing O_2 pressure. The electronic conduction was attributed to the movement of holes along grain boundaries.

In a recent study Kitazawa and Coble (*18*) measured the electrical conductivity and transference number in Al_2O_3 as a function of P_{O_2} and temperature. They employed a sample configuration where the sample wall extends through a temperature gradient, so that both surface and gas-phase conduction was negligible in the low temperature part of the sample. Unguarded four-electrode measurements were also made to permit assessment of surface and gas-phase contributions in previous results. With decreasing partial pressures of oxygen over single-crystal Al_2O_3 at 1000 to 1650°C, the conductivities decreased, then remained constant, and finally increased when strong reducing atmospheres were attained, The intermediate flat region became dominant at the lower temperature. The emf measurements showed predominantly ionic conduction in the flat region; the electronic conduction is exhibited in the branches of both ends. These results are shown in Fig. 4 as a diagram of the conduction mechanisms in single-crystal Al_2O_3. In pure O_2 (1 atm) the conductivity above 1400°C was $\sigma \simeq 3 \times 10^3 \exp(-80\ \text{kcal}/RT)\Omega^{-1}\ \text{cm}^{-1}$ which corresponds to electronic conductivity. Below 1400°C, the activation energy was <57 kcal, corresponding to an extrinsic ionic conduction. Polycrystalline samples showed significantly higher conductivity because of additional electronic conduction in the grain boundaries.

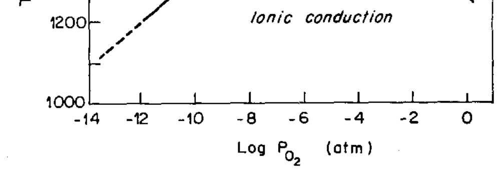

FIG. 4. Diagram of conduction mechanism in single-crystal Al_2O_3 after Kitazawa and Coble (*18*).

In a recent study the electrical conductivity of polycrystalline and single crystal Al_2O_3 was measured between 1000 and 1650°C (*19*). A novel sample geometry (i.e., a thin walled hollow tube), similar to that employed by Kitazawa and Coble (*18*), was used to eliminate the effects of gas or surface conduction. According to Frederiske and Hosler (*19*), "An interesting aspect of electrical conduction in Al_2O_3 is the fact that the magnitude of its conductivity at 1500°C and above is relatively large and very similar to that observed in a 'no-sample' measurement where the charge transport takes place through the vacuum or through the gas between the electrodes." Based on a review of the possible conduction mechanisms in Al_2O_3 (i.e., gas, surface, thermionic emission from an electrode into the insulator, an electronic and ionic transport) they conclude that none of these processes fully account for the magnitude of the observed conductivity. However, they feel that the migration of Al^{3+} ions (or Al^{+3} vacancies) yield the largest value and offers at present the best explanation for electrical conduction in Al_2O_3.

In summary it appears that there is general agreement that below 1400°C extrinsically controlled ionic conductivity predominates which may be attributed to the migration of Al ions. However, for $T >$ 1400°C the relative amount of ionic and electronic conductivity present appears to be in question. For example in contrast to the results of Kitazawa and Coble (*18*), Frederiske and Hosler (*19*) do not observe much variation of the conductivity with oxygen pressure. The question of purity and lack of other types of reliable experimental measurements (e.g., the need for more Al and O tracer experiments on very pure Al_2O_3 single crystals over a wide range of oxygen pressure and temperature) also complicates the defect analysis of the data.

Semiconducting Oxides

As discussed above, the electrical properties of semiinsulating oxides are very dependent on the presence of impurities because of the limited range of nonstoichiometry. "Pure" semiconducting oxides, however, are usually very dependent on the nonstoichiometric behavior, in this discussion we will refer to nonstoichiometric oxides as those oxides which have a measurable range of nonstoichiometry. One characteristic of nonstoichiometric oxides is that the cations usually exhibit more than one state of ionization. This is a result of incomplete inner shells (e.g., transition metals).

We will limit our discussion of the electrical conductivity of semiconducting oxides to the temperature region where the oxide may be readily equilibrated with its environment. We will attempt to emphasize (1) some of the experimental and theoretical problems limiting our understanding of these oxides and (2) how a combined analysis of different types of experimental data can be used to obtain information about the defect structure and mobility of defects by discussing some simple oxide systems that exhibit (a) small deviations from stoichiometry and (b) large deviations from stoichiometry.

A. Oxides Exhibiting Small Deviations from Stoichiometry

Although there are many oxides which fall in this classification (e.g., TiO_{2-x}, $BaTiO_{3-x}$, NiO, etc.), we will arbitrarily select only a few of these to emphasize some of the problem areas.

In the temperature and composition region where the nonstoichiometric defects predominate in a single state of ionization a conductivity expression of the type

$$\sigma \propto P_{O_2}^{\pm 1/n} \qquad (18)$$

can be derived using the law of mass action where the sign and the value of n is related to a nonstoichiometric defect reaction (*1*, *2*). If the simple defect model is valid then from a plot of $\log \sigma$ vs $\log P_{O_2}$ the defect reaction may be inferred from the experimentally determined value of n. One of the problems with this simple approach is that it is frequently observed that the value of n is a noninteger value which changes with both P_{O_2} and temperature.

As an example of this consider the results of an electrical conductivity study on TiO_{2-x} shown in Fig. 5 (*20*, *21*). The conductivity data shown in this figure were obtained on single crystals of rutile using a four-probe dc technique. Because of the higher conductivity no difficulties were experienced with leakage current as were observed for the semi-insulating oxides. However, two important considerations should be observed regarding the measurement of σ as a function of T and P_{O_2}:

1. The stability limits (i.e., T and P_{O_2} region where the oxide is thermodynamically stable) should be ascertained before making property measurements.
2. As shown in Fig. 5, there is a "triangular P_{O_2} region" where data cannot be readily obtained.

Point 1 is important for example because much of the early low-temperature conductivity and Hall mobility data obtained on reduced specimens of TiO_{2-x} were made on samples that were exposed to H_2 at elevated temperatures. According to the phase diagram these reduced specimens would be in a region where Magnéli phases are present, and thus would not be representative of reduced TiO_{2-x}.

Point 2 is important because of the experimental difficulties encountered in controlling the P_{O_2} in this region. Problems associated with "buffering," impurities in the gas phase,

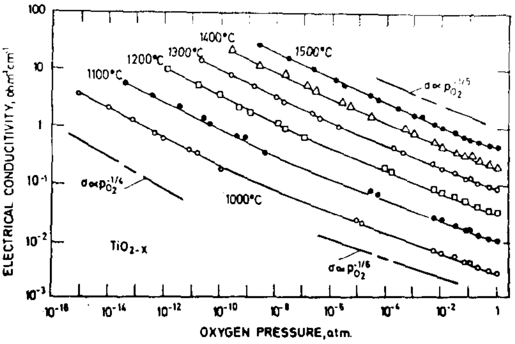

FIG. 5. The electrical conductivity in the *c* direction of rutile single crystals as a function of the partial pressure of oxygen in the temperature range 1000–1500°C. Results of Blumenthal et al. (*20*, *21*).

and thermal diffusion are discussed elsewhere for example see Ref. (*10*).

As shown in Fig. 5 the value of n in Eq. (4) varies both with temperature and P_{O_2}. At lower P_{O_2} the values of n varies between 4 and 5 and decreases with decreasing P_{O_2}. This behavior was interpreted in terms of a defect model involving the nonstoichiometric defect (titanium interstitials) in multiple states of ionization (i.e., $Ti_i^{\cdot\cdot\cdot}$ and $Ti_i^{\cdot\cdot\cdot\cdot}$) and quasifree electrons (*20*, *21*). At higher P_{O_2} and lower temperature the value of n was larger than 5. This region which corresponds to the near stoichiometric condition was assumed to be influenced by a contribution to the electrical conductivity due to either impurity or intrinsic type conduction. The defect model of TiO_{2-x} was inferred by comparing the theoretical relation

$$\sigma^5 = (A\sigma + B)P_{O_2}^{-1} + l'\sigma^3 \tag{19}$$

based on the law of mass action with the electrical conductivity data shown in Fig. 5 (*21*).

One of the problems of analysis of this type is that the defect model is inferred on the basis of comparison with only one type of experimental data (i.e., $\sigma = \sigma(T, P_{O_2})$). For example, Kofstad (*22*) interprets the same conductivity data on the basis of a defect model involving

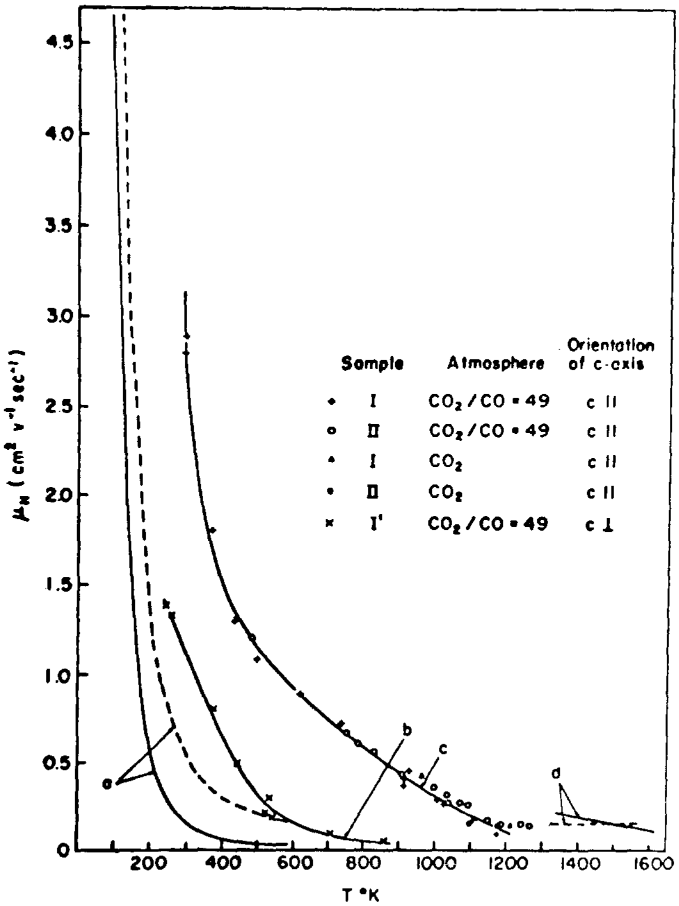

FIG. 6. a. Hall mobility of rutile measured by Bogomolov and Zhuze: — samples with $c_\perp$, --- samples with $c_\parallel$. Hall mobility measurements, Bransky and Tannhauser: (*24*). b. Samples with $c_\perp$. c. Samples with $c_\parallel$. d. Drift mobility of single crystal of rutile with $c_\parallel$, calculated by Blumenthal et al. (*23*) from combined electrical conductivity and thermogravimetric measurements after Bransky and Tannhauser (*24*).

oxygen vacancies and interstitial titanium ions with three and four effective charges.

Experimental data on the dependence of $x = x(T, P_{O_2})$ for TiO_{2-x} would be useful for testing the above defect model. Unfortunately the existing thermodynamic data exhibits too much scatter to reliably test the difference between these two defect models.

Although the $x = x(T, P_{O_2})$ data could not be used to test the above defect model, it was used to obtain an estimate of the electronic carrier concentration which was then combined with the conductivity data to obtain an estimate of the drift mobility of electrons (i.e., $\mu_D \simeq 10^{-1}$ cm^2/V sec) in rutile at temperatures in excess of 1300°K (*23*).

Hall mobility measurements are difficult to make at elevated temperatures because of thermal noise problems (*10*). To minimize these problems, Bransky and Tannhauser (*24*) employed a double ac technique to measure the Hall mobility, μ_H, of electrons in reduced rutile from 300 to 1250°K. As shown in Fig. 6, μ_H is independent of the CO/CO_2 ratio employed and decreases with increasing temperature. The agreement between the magnitude of μ_H and μ_D and the fact that μ_H decreases rapidly with temperature are not consistent with a small-polaron model. It appears that the mobility data can be better interpreted by a phonon scattering law of the type $\mu \sim T^{-n}$ (*24*).

Information on the temperature dependence of the mobility can also be obtained by combining conductivity and thermoelectric power data (*25*). Such an analysis was used to demonstrate the absence of an activated hole mobility in Li-doped NiO (*26*) and CoO (*27*) and nonstoichiometric CoO (*28*) and NiO (*29*). Unfortunately, this type of analysis requires (1) a very accurate determination of the temperature dependence of the conductivity and thermoelectric power and (2) a knowledge of certain parameters (e.g., effective density of states and a transport energy term).

Because of experimental problems attempts to measure the temperature dependence of the mobility using the above combined property measurements has resulted in somewhat confusing results (*25*). To circumvent some of these problems improved experimental techniques for measuring the thermoelectric power, deviations from stoichiometry and Hall mobility are required.

B. Oxides Exhibiting Large Deviations from Stoichiometry

There are several oxides which exhibit a large deviation from stoichiometry (e.g., $Mn_{1-x}O$, $Fe_{1-x}O$, UO_{2+x}, CeO_{2-x}, etc.).

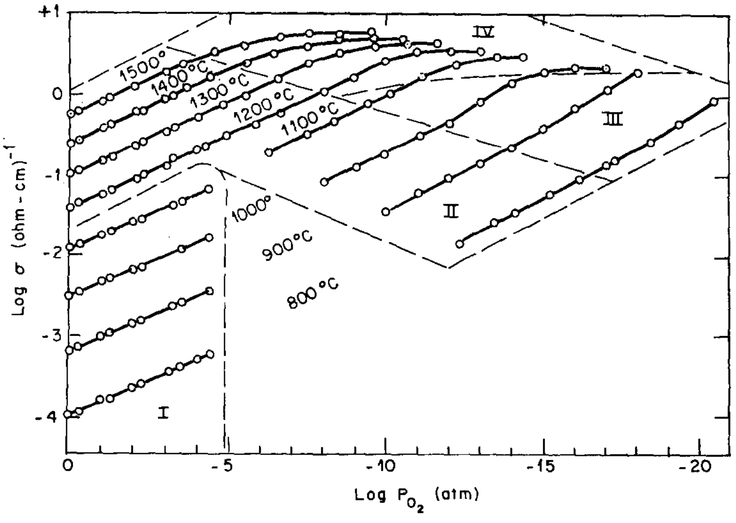

FIG. 7. Isothermal relation between the electrical conductivity of sintered and oxygen partial pressure (*34*).

However, for purposes of illustrating some of the problems associated with the characterization of the defect structure and transport properties of defects in an oxide exhibiting large deviations from stoichiometry, we will limit our discussion to the CeO_{2-x} system.

The electrical conductivity of CeO_{2-x} has been measured by several investigators *(30–34)* On the basis of the P_{O_2} dependence of the conductivity the results of these studies have been rationalized in terms of defect models involving oxygen vacancies or cerium interstitials or a combination of both types of defects. The isothermal relation between the electrical conductivity of CeO_{2-x} and the oxygen partial pressure is shown in Fig. 7. Some of the problems associated with a defect structure analysis of this data are:

1. The oxygen partial pressure dependence (n in $\sigma \alpha P_{O_2}^{-1/n}$) is a function of both temperature and partial pressure of oxygen.
2. At low oxygen pressures the deviation from stoichiometry is large (i.e., $x > 0.1$) and it would be expected that some type defect interaction would occur which would invalidate the mass action approach.
3. The electronic mobility may exhibit both temperature and compositional dependence particularly at larger deviations from stoichiometry.

A recent study *(35)* of the dependence of $x = x(T,P_{O_2})$ for CeO_{2-x} was undertaken to check the previously obtained results *(36)* at larger deviations from stoichiometry and to obtain additional data for $x < 10^{-2}$ in order to test the assumptions used in the law of mass action and to help clarify the interpretation of the defect structure.

The results of the recent thermogravimetric study *(35)* are shown in Fig. 8 where isotherms of $\log x$ in CeO_{2-x} are plotted vs $\log P_{O_2}$ from 750 to 1500°C and from 10^{-2} to 10^{-26} atm of oxygen. The thermodynamic quantities $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ were calculated in the region $0.001 \leqslant x \leqslant 0.3$ from the data in Fig. 8 and found to be independent of temperature. In the composition region $0.001 < x < 0.01$, the variation of $\Delta\bar{S}_{O_2}$ with x is consistent with the defect reaction

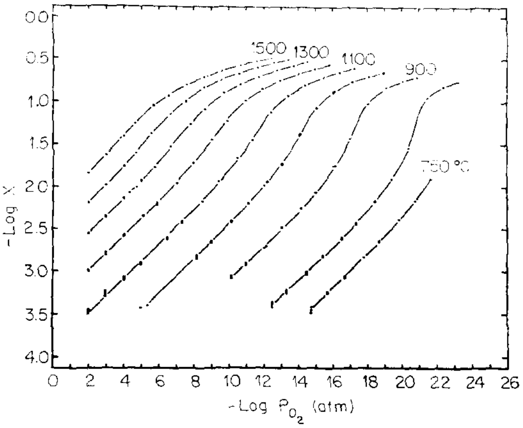

FIG. 8. Isothermal relation between $\log x$ and $\log P_{O_2}$ for nonstoichiometric CeO_{2-x} from 750 to 1500°C *(35)*.

$$2Ce_{Ce}^{x} + O_O^{x} = \tfrac{1}{2}O_2(g) + V_O^{\cdot\cdot} + 2Ce'_{Ce} \qquad (20)$$

involving randomly distributed doubly ionized oxygen vacancies. The experimental $P_{O_2}^{-1/5}$ dependence of x and σ was rationalized on the basis of the above defect model and the observation that $\Delta\bar{H}_{O_2}$ (≈ 10 eV) exhibits a slight dependence on x. Thus, the application of the law of mass action is invalid in this composition range because $\Delta\bar{H}_{O_2}$ is a function of x. At large deviations from stoichiometry $\Delta\bar{H}_{O_2}$ changes rapidly with x as shown in Fig. 9. The nonstoichiometric behavior in this region appears to be more strongly dependent on defect interaction.

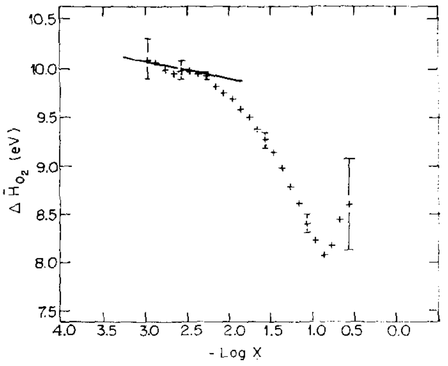

FIG. 9. $\Delta\bar{H}_{O_2}$ vs x in CeO_{2-x} *(35)*.

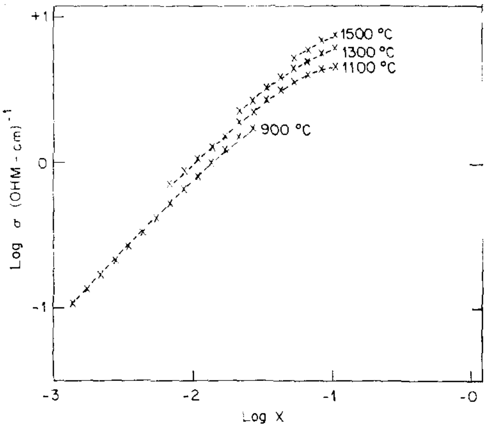

FIG. 10. Isothermal plot of logσ vs log$x$ at 800, 1000, 1200, and 1400°C (*39*). × experimental data; ---- plot of Eq. 21.

Two recent studies have provided convincing evidence that the predominant nonstoichiometric defects in CeO_{2-x} are oxygen vacancies; Steele and Floyd (*37*) by measurements of oxygen self diffusion from 850 to 1150°C and Faber (*38*) by X-ray and neutron diffraction measurements from 800 to 1000°C.

In a recent study (*39*) the isothermal compositional dependence of the electrical conductivity of CeO_{2-x} was determined by combining thermogravimetric data, $x = x(P_{O_2}, T)$, with the appropriate conductivity data, $\sigma = \sigma(P_{O_2}, T)$. These results are shown in Figs. 10 and 11 as isothermal plots of logσ vs log$x$. As shown by the dashed lines, the compositional and temperature dependence of the electrical conductivity may be represented by the expression

$$\sigma = 410\,[x]\,e^{-(0.158+x)/kT}\,(\text{ohm cm})^{-1} \qquad (21)$$

over the temperature range 750–1500°C and from $x = 0.001$ to $x = 0.1$.

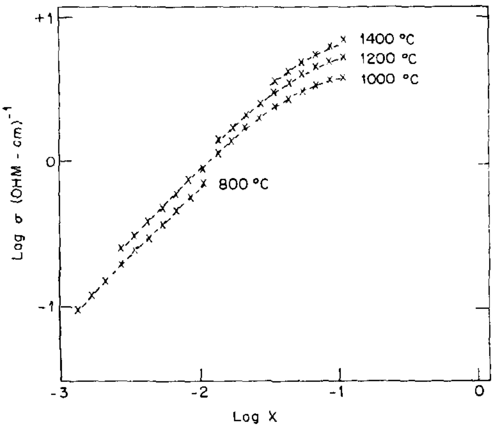

FIG. 11. Isothermal plot of logσ vs log$x$ at 900, 1100, 1300, and 1500°C (39). × experimental data; ---- plot of Eq. 21.

This expression was rationalized in terms of the following simple relations for (a) the electron carrier concentration

$$^{n}\mathrm{Ce}'_{\mathrm{Ce}} = 8x/(a_0^{\,3}) \qquad (22)$$

where $^{n}\mathrm{Ce}'_{\mathrm{Ce}}$ is the number of $\mathrm{Ce}'_{\mathrm{Ce}}$ per cm^3 and a_0 is the lattice parameter and (b) the electron mobility

$$\mu = 5.2 \times 10^{-2}\,e^{-(0.158+x)/kT}\,(\text{cm}^2/\text{V sec}) \qquad (23)$$

It is interesting to note that the activation energy for the hopping type process increases linearly with x. Since the lattice parameter a_0 has been shown to vary linearly with x for $x < 0.1$, it appears that the activation energy is associated with the dilatation of the lattice. It would be very helpful if Hall mobility measurements could be made on reduced specimens at elevated temperatures to determine the validity of the compositional dependence of the mobility.

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