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"The Defect Structure of Nonstoichiometric CeO_{2-x} " *

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The electrical conductivity of pressed and sintered specimens of CeO_{2-x} was measured over the temperature range $800^\circ - 1500^\circ\text{C}$ and from 1 to 10^{-17} atm of oxygen. Based on the excellent fit observed between the theoretically derived relation

$$\sigma^3 = (A\sigma + B)P_{\text{O}_2}^{-1/2}$$

and the experimental conductivity data from 1000° to 1500°C , in the "high" and "intermediate" oxygen pressure region, the nonstoichiometric defect structure of CeO_{2-x} was interpreted in terms of a defect model involving quasi-free electrons and both singly and doubly ionized oxygen vacancies.

The standard enthalpy of formation for the following defect reactions in CeO_{2-x} :

were determined from the temperature dependence of A and B obtained from the above relation.

At the lowest oxygen pressures in the range 1200° to 1500°C the electrical conductivity of CeO_{2-x} appears to be relatively insensitive to oxygen pressure. In this region CeO_{2-x} exhibits a large departure from stoichiometry and thus may behave as a degenerate semiconductor.

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1. INTRODUCTION

Nonstoichiometric cerium dioxide (CeO_{2-x}) has been the subject of several x-ray,^{1,2,3} thermodynamic,^{4,5,6} and electrical conductivity investigations.^{7,8,9,10} Based upon these experimental observations, CeO_{2-x} may be classified as a metal-excess, n-type semiconductor. Such a metal excess may arise from the presence of a defect structure involving anion vacancies or cation interstitials in the crystal. However, in spite of all this scientific interest in CeO_{2-x} , there has been no conclusive experimental evidence to indicate which of the above defect models predominates.

Brauer and Gingerich^{3,4} studied the influence of temperature on the cerium oxide system by measuring the oxygen dissociation pressure in the region $\text{CeO}_{2.0} - \text{CeO}_{1.5}$, from 600 to 1000°C, and by high-temperature x-ray powder-diffraction analysis in the region $\text{CeO}_{2.0} - \text{CeO}_{1.8}$ over the temperature range 20 - 1050°C. From the results of their investigation, it can be concluded that above 800°C, a continuous homogeneous series of the cubic solid solution extends from CeO_2 to about $\text{CeO}_{1.67}$ and in the region $\text{CeO}_{1.67} - \text{CeO}_{1.50}$ there exists a two phase region.

Kuznetsov et al⁵ utilized both a galvanic cell technique and a gas equilibrium method to obtain the thermodynamic properties of cerium oxide over the composition range $\text{CeO}_{1.581}$ to $\text{CeO}_{1.960}$. The results of their investigation indicate the existence of a single phase region between $\text{CeO}_{1.66}$ and $\text{CeO}_{1.96}$ above 700°C. More recently Bevan and Kordis⁶ measured the oxygen dissociation pressure of CeO_{2-x} and found that a single phase region exists between $\text{CeO}_{2.00}$ and $\text{CeO}_{1.72}$ at all temperatures above 685°C. Thus the phase field limits of CeO_{2-x} determined by high temperature x-ray and thermodynamic measurements appear to be in good agreement.

Although CeO_{2-x} is thermodynamically stable^{4,5,6} over a wide range of P_{O_2} and temperature (e.g. CeO_{2-x} is thermodynamically stable to values of P_{O_2} as low as 10^{-20} atm at 1023°C) the electrical conductivity^{7,8,9,10} of CeO_{2-x} has been measured only between approximately 1 and 10^{-4} atm of oxygen.

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Rudolph⁷ measured the electrical conductivity of CeO_{2-x} as a function of P_{O_2} at only one temperature, 987°C , and found

$$\sigma \propto P_{\text{O}_2}^{-1/5.7}$$

Greener et al⁸ using a two probe method measured the electrical conductivity of CeO_{2-x} in the temperature range 650° to 1400°C and from 0.006 to 1 atm of oxygen. They found that their experimental data could be represented by the following relation:

$$\sigma_T = \sigma_0 \exp \frac{(-2.2)}{kT} P_{\text{O}_2}^{-1/5} + \sigma_{\text{O}_i} \exp \frac{(-1.45)}{kT}$$

They interpreted their results in terms of a defect structure involving either quadruply ionized cerium interstitials or completely ionized oxygen vacancy pairs.

Kevane⁹ analyzed the conductivity data of Greener et al⁸ and the gravimetric data of Bevan and Kordis⁶ and concludes that it is possible to interpret these results for CeO_{2-x} on the basis of an oxygen vacancy model.

The results of these conductivity measurements over a very limited range of P_{O_2} have not provided an unambiguous determination of the defect structure in CeO_{2-x} . Thus, in order to help elucidate the defect structure in CeO_{2-x} , work was initiated in this investigation on the electrical conductivity of CeO_{2-x} as a function of temperature and oxygen partial pressure from 800° to 1500°C and from 10^{-17} to 1 atm of oxygen.

II. EXPERIMENTAL

A. Specimen Preparation

Both Fisher certified CeO_2 powder (99.5% minimum with respect to CeO_2) and American Potash and Chemical Company high purity CeO_2 powder (99.9% minimum with respect to CeO_2 and 99.999% minimum with respect to rare earth impurities only) were used for the electrical conductivity studies.

The conductivity specimens were prepared by cold pressing the CeO_2 powder without a binder at 15,000 to 20,000 psi. into a bar $3/16$ in. x $3/16$ in. x 1 in. A surface layer was removed from the specimens to avoid contamination from the die walls. The specimens were then placed in an alumina boat lined with a layer of CeO_2 powder and sintered at 1550°C for at least two hours in argon. The color of the specimens prepared from the

Fisher certified CeO_2 powder appeared to be light pink whereas specimens prepared from the high purity CeO_2 powder were white. Conductivity specimens were cut with a diamond saw from the pressed and sintered bars. The final specimen dimensions were 0.2 cm x 0.2 cm x 2 cm long. The current probes were made by wrapping 0.018" diameter platinum wire tightly around the specimen at both ends. The ends of the sample were coated with platinum paste (Engelhard No. 6926) to reduce the contact resistance. The potential probes were made by wrapping two 0.010" diameter platinum wires around the sample with a spacing of 1 cm.

B. Experimental Procedure

The electrical conductivity measurements of CeO_{2-x} as a function of P_{O_2} in the temperature range 700 to 1500°C were made in a molybdenum wound resistance furnace. A standard four probe D.C. technique was employed for the electrical conductivity measurements. The experimental apparatus employed was essentially the same as that described in an earlier publication.^{11,12}

Oxygen partial pressures were achieved by means of two methods. For pressures from 1 to 10^{-3} atm an appropriate mixture of purified oxygen and argon was obtained by use of calibrated flowmeters.^{11,12} In addition, premixed and analyzed O_2 -Ar mixtures with P_{O_2} values of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} atm were used in the study. Controlled oxygen partial pressures in the low pressure region were obtained by introducing known mixtures of CO and CO_2 . The well known free energy values for the CO- CO_2 reaction were then used to calculate the oxygen partial pressure. A linear flow rate of 0.9 cm/sec was maintained for all gas mixtures used in this investigation to avoid errors arising from thermal diffusion.¹³ Isothermal electrical conductivity measurements at 100° intervals between 800° and 1500°C were made for both increasing and decreasing partial pressures of oxygen. Since the composition of CeO_{2-x} has a unique equilibrium value for each oxygen partial pressure and temperature, the above procedure insures the measurement of equilibrium values of the conductivity, because the equilibrium state was approached from both higher and lower compositions of oxygen.

III. RESULTS AND DISCUSSION

A specimen prepared from Fisher certified CeO_2 was used in the preliminary study¹¹ of the electrical conductivity of CeO_{2-x} as a function of temperature and oxygen partial pressure. Based on the preliminary study, a plot of the logarithm of the electrical conductivity of CeO_{2-x} versus $1/T$ in 1 atm of oxygen exhibited a two slope behavior similar to that reported by Greener et al.⁸ The conduction mechanism for the lower temperature slope was attributed to either impurity or intrinsic type conduction.¹¹ To check the effect of impurities, the electrical conductivity data obtained in 1 atm oxygen on high purity specimens used in this study was plotted as shown in Fig. 1 with the results from the previous study. The plot of the logarithm of the conductivity versus $1/T$ for the high purity specimen is characterized by a one slope behavior. It is interesting to note that the value of the experimental activation energy (2.1 eV) calculated for the high purity specimen has the same value as that calculated from the high temperature slope in the previous study. Thus, it appears that the electrical conduction from $700^\circ - 1050^\circ\text{C}$ reported in the previous study and by Greener et al.⁸ was controlled by impurities.

The metal excess nature of nonstoichiometric CeO_{2-x} may arise from the presence of a defect structure involving either anion vacancies or cation interstitials. Using the law of mass action in combination with appropriate simplified electroneutrality equations, the concentration of conduction electrons can be obtained as a function of the partial pressure of oxygen. The electrical conductivity is, however, directly proportional to the concentration of conduction electrons. Consequently, if the assumptions made in deriving these equations are valid and the mobility is assumed to be a function of temperature only, theoretical equations for the pressure dependence of the electrical conductivity can be derived. For the defect reaction

and the simplified electroneutrality equation

$$2[\text{O}_v^{++}] = n \quad (2)$$

the expression for the conductivity is

$$\sigma = 2(K_1 K_2 K_3)^{1/3} q \mu P_{O_2}^{-1/6} \quad (3)$$

or simply the pressure dependence is

$$\sigma P_{O_2}^{-1/6} \sim P_{O_2}^{-1/x} \quad (4)$$

where $x = 6$; K_1 , the equilibrium constant for the formation of oxygen vacancies; K_2 , the equilibrium constant for the ionization of the first electron; K_3 , the equilibrium constant for the ionization of the second electron; $[O_v^+]$ is the concentration of singly ionized oxygen vacancies; $[O_v^{++}]$ is the concentration of doubly ionized oxygen vacancies; n , is the concentration of electrons; q , is the charge on an electron and μ , is the electron mobility.

Similarly for the defect reaction

and the simplified electroneutrality equation

$$[O_v^+] = n \quad (6)$$

the expression for the conductivity is

$$\sigma = (K_1 K_2)^{1/2} q \mu P_{O_2}^{-1/4} \quad (7)$$

or simply the pressure dependence is

$$\sigma P_{O_2}^{-1/4} \sim P_{O_2}^{-1/x} \quad (8)$$

where $x = 4$.

For the cerium interstitial defect model, $x = 2, 3, 4$ or 5 respectively, for the case where the cerium interstitial is singly, doubly, triply or quadruply ionized. Thus, if the assumptions made in deriving the above equations are valid, the defect structure in CeO_{2-x} can be determined from a plot of the logarithm of σ versus the logarithm of P_{O_2} .

The electrical conductivity of high purity CeO_2 specimens was measured as a function of the partial pressure of oxygen at $100^\circ C$ intervals between 800° and $1500^\circ C$. The results of the conductivity measurements on samples 7 and 8 are shown in Fig. 2 as isothermal plots, at $100^\circ C$ intervals between 800° and $1500^\circ C$, of $\log \sigma$ versus $\log P_{O_2}$. The results shown in Fig. 2 were

for two different ceramic samples, sample 7 from 1000° to 1500°C and sample 8 at 800° and 900°C. The question arises as to the reproducibility of the results obtained using different ceramic specimens in the same temperature and oxygen pressure region. To check this effect the electrical conductivity of samples 6 and 7 was measured over approximately the same oxygen pressure region at 1000° and 1100°C. As shown in Fig. 3, the values of x in the intermediate and high oxygen pressure region is approximately the same for both specimens. The ratio of the absolute values of the conductivity of sample 7 to sample 6 was 1.3 ± 0.1 , this ratio does not appear to vary with either temperature or oxygen pressure. The ratio can not be simply accounted for since the ratio of densities of specimen 7 to specimen 6 was only 1.1.

As shown in Fig. 2, the data below 1200°C can be represented by two straight lines, with two different slopes for each isotherm. The values of x calculated from these slopes are shown in Fig. 2. Since the value of x is not an integer and it appears to vary both with temperature and partial pressure of oxygen, the nonstoichiometric defect structure cannot be accounted for in terms of a point defect in a single predominant state of ionization.¹²

For the purpose of convenience, the conductivity data shown in Fig. 2 can be described in terms of three oxygen pressure regions, high, intermediate and low. A qualitative explanation of the observed electrical conductivity data is described as follows:

1. The value of x in the intermediate and high oxygen pressure region increases with increasing temperature. This can be interpreted as the result of increased ionization of the nonstoichiometric point defect as the temperature is increased.

2. The values of x in the intermediate and high oxygen pressure region vary between the integers 4 and 6. Thus, it would appear that the defect structure of CeO_{2-x} could best be interpreted on the basis of an oxygen vacancy model involving singly and doubly ionized oxygen vacancies.

3. The low oxygen pressure region is characterized by a range of oxygen pressures where the electrical conductivity does not appear to be very dependent on the oxygen pressure. One possible explanation for this observation is that in this region the CeO_{2-x} specimen is heavily reduced

and may behave as a degenerate semiconductor because the concentration of electrons in the conduction band is large.

Therefore, in order to obtain a quantitative relation between σ and P_{O_2} the following electroneutrality expression should be utilized:

$$n = [O_v^{+}] + 2 [O_v^{++}] \quad (9)$$

(in the intermediate and high oxygen pressure region) for a defect structure involving both singly and doubly ionized oxygen vacancies.

From the equations for defect equilibria and the law of mass action, an expression is obtained which relates the concentration of singly ionized oxygen vacancies to the concentration of conduction electrons and the partial pressure of oxygen; that is,

$$[O_v^{+}] = K_1 K_2 P_{O_2}^{-1/2} n^{-1} \quad (10)$$

The concentration of doubly ionized oxygen vacancies is,

$$[O_v^{++}] = K_1 K_2 K_3 P_{O_2}^{-1/2} n^{-2} \quad (11)$$

Substitution of Eqs. 10 and 11 into Eq. 9 yields the expression

$$n = (K_1 K_2 n^{-1} + 2 K_1 K_2 K_3 n^{-2}) P_{O_2}^{-1/2} \quad (12)$$

which relates the concentration of conduction electron to the partial pressure of oxygen.

For extrinsic electronic conduction

$$\sigma = nq\mu \quad (13)$$

and

$$n = \frac{\sigma}{c} \quad (14)$$

where $c = \mu q$, and μ is assumed to be a function of temperature only.

By combining equations (12) and (14) and rearranging terms the following expression was obtained which relates the electrical conductivity to the partial pressure of oxygen:

$$\sigma^3 = (A\sigma + B)P_{O_2}^{-1/2} \quad (15)$$

where

$$A = K_1 K_2 c^2 \quad (16)$$

$$B = 2K_1 K_2 K_3 c^3 \quad (17)$$

Similarly, for a defect structure involving both triply and quadruply ionized cerium interstitials the electroneutrality equation is

$$n = 3[\text{Ce}_i^{+3}] + 4[\text{Ce}_i^{+4}] \quad (18)$$

Accordingly,

$$\sigma^5 = (D\sigma + E)P_{\text{O}_2}^{-1} \quad (19)$$

where

$$D = 3K_4K_5K_6K_7C^4 \quad (20)$$

$$E = 4K_4K_5K_6K_7K_8C^5 \quad (21)$$

K_4 is the equilibrium constant for the formation of the cerium interstitial; K_5 , the equilibrium constant for the ionization of the first electron; and K_6 , K_7 and K_8 , the equilibrium constants for subsequent ionization reactions.

A computer program was written for equations (15) and (19) and the values of σ and P_{O_2} in the "high" and "intermediate" oxygen pressure region shown in Fig. 2 were used to calculate the values of the parameters in these equations at 100° intervals between 1000° and 1500°C for specimen 7 only.

The values of these parameters were used to calculate the solid and dashed lines representing Eqs. 15 and 19 respectively and shown in Fig. 4. It is readily apparent from Fig. 4 that Eq. 15 represents an acceptable fit of the experimental data, whereas Eq. 19 is not an acceptable representation of the data.

Thus, the excellent agreement between the expression

$$\sigma^3 = (A\sigma + B)P_{\text{O}_2}^{-1/2} \quad (15)$$

and the experimental data of the electrical conductivity as a function of the partial pressure of oxygen and temperature provides a quantitative confirmation of the qualitative interpretation of the data in the "high" and "intermediate" oxygen pressure region (which was interpreted in terms of a defect structure involving both singly and doubly ionized oxygen vacancies).

The standard enthalpy of formation for the nonstoichiometric defect reaction

is related to the product of the thermodynamic equilibrium constants, K_1 and K_2 , by the well-known expression

$$K_1 K_2 \propto \exp(\Delta S_a^0/k) \exp(-\Delta H_a^0/kT) \quad (22)$$

Since,

$$A = K_1 K_2 C^2 \quad (16)$$

and if μ is much less temperature dependent than $\exp(-\Delta H_a^0/kT)$ then the slope of the line obtained from a plot of $\log A$ vs. $1/T$ would be equal to the expression

$$\frac{d(\log A)}{d(1/T)} \approx \frac{-\Delta H_a^0}{2 \cdot 303k} \quad (23)$$

The result, $\Delta H_a^0 = 4.5(\text{eV})$ was obtained by equating the right hand side of equation (23) with the slope of the line shown in Fig. 5, where $\log A$ is plotted as a function of $1/T$.

In a similar manner, the standard enthalpy of formation for the non-stoichiometric defect reaction

was found to be equal to $5.3(\text{eV})$. This result was obtained by equating the relation

$$\frac{d(\log B)}{d(1/T)} = \frac{-\Delta H_b^0}{2 \cdot 303k} \quad (24)$$

with the slope of the line shown in Fig. 6, where the $\log B$ is plotted as a function of $1/T$.

The standard enthalpy of formation for the ionization reaction

was calculated from the relation

$$\Delta H_c^0 = \Delta H_b^0 - \Delta H_a^0 \quad (26)$$

IV. CONCLUSIONS

The nonstoichiometric defect structure of CeO_{2-x} in the "high" and "intermediate" oxygen pressure region was assumed to be a defect model involving quasi-free electrons and both singly and doubly ionized oxygen vacancies.

An experimental confirmation of this defect model was obtained from the excellent fit observed between the theoretical relation

$$\sigma^3 = (A\sigma + B)P_{\text{O}_2}^{-1/2}$$

based on the above defect model, and the electrical conductivity data measured in the temperature range $1000^\circ - 1500^\circ\text{C}$ and over the range of oxygen partial pressure from 10^{-12} to 1 atm.

The standard enthalpy of formation for the following defect reactions in CeO_{2-x} :

were determined from the temperature dependence of A and B obtained from the aforementioned relation and the assumption that the electron mobility is much less temperature dependent than the equilibrium constants for the above defect reactions.

At the lowest oxygen pressures in the range 1200° to 1500°C the electrical conductivity of CeO_{2-x} appears to be relatively insensitive to oxygen pressure. In this region CeO_{2-x} exhibits a large departure from stoichiometry and thus may behave a degenerate semiconductor.

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REFERENCES

1. G. Brauer and H. Gradinger, *Z. Anorg. Allg. Chem.*, 277, 89 (1954).
2. D. J. M. Bevan, *J. Inorg. Nucl. Chem.*, 1, 49 (1955).
3. G. Brauer, K. A. Gingerich and U. Holtzschmidt, *J. Inorg. Nucl. Chem.*, 16, 77 (1960).
4. G. Brauer and K. A. Gingerich, *J. Inorg. Nucl. Chem.*, 16, 87 (1960).
5. F. A. Kuznetsov, V. I. Beliy, T. N. Rezhukhina, *Doklady An SSR, Fiz-Khim.* 139, No. 6, 1405 (1961).
6. D. J. M. Bevan and J. Kordis, *J. Inorg. Nucl. Chem.*, 26, 1509 (1964).
7. J. Rudolph, *Z. Naturforsch.*, 14a, 727 (1959).
8. E. H. Greener, J. M. Wimmer and W. M. Hirthe, in *Rare Earth Research II*, edited by Karl S. Vorres (Gordon and Breach, New York, 1964).
9. C. J. Kevane, *Phys. Rev.*, 133, A1431 (1964).
10. C. J. Kevane, E. L. Holverson and James B. Armstrong, presented at the Fifth Rare Earth Research Conference, Ames, Iowa, August 1965.
11. R. N. Blumenthal, Atomic Energy Commission, Technical Progress Report, COO-1441-1.
12. R. N. Blumenthal, J. Coburn, J. Baukus and W. M. Hirthe, *J. Phys. Chem. Solids*, 27, 643 (1966).
13. L. S. Darken and R. W. Gurry, *J. Am. Chem. Soc.*, 67, 1398 (1945).

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