

will depend upon ionic mass. Since ions of differing isotopic mass will have unequal amplitudes of oscillation, they will consequently sample the crystalline electric fields in different manners.¹⁵ Such oscillations would have to occur in nonsymmetric modes since small changes of oscillation amplitude in symmetric modes would cause no changes in the sampling of the electric field. A complete description of the dependence of the shift of the crystalline field parameters of the spin Hamiltonian on isotope mass differences would require

¹⁵ A. L. Schawlow, *J. Appl. Phys.* **33**, 395 (1962).

detailed information on the relevant vibrational energy levels. The lack of any temperature dependence of the observed shift over the range 4.2–112°K suggests, however, that only the zero-point vibrational states of the ground electronic level need be considered.

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Oxygen Vacancies and Electrical Conduction in Metal Oxides*

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Oxygen vacancies and their effects on electrical conduction in some metal oxides were considered through an exact solution of the equilibrium relations between oxygen partial pressure in the ambient gas and concentrations of oxygen vacancies and conduction electrons in the oxide. The mass-action law was assumed but no state of ionization of oxygen vacancies was neglected. Concentrations of electrons in conduction states and total oxygen vacancies were considered. The results, which possess considerable complexity not contained in the usual limiting-case solutions, were compared with pertinent experiments.

I. INTRODUCTION

ELECTRICAL conductivity σ and concentrations of oxygen vacancies, $[V_A]_{\text{tot}}$, in some solid metal oxides such as TiO₂, Nb₂O₅, and CeO₂ show a dependence on oxygen partial pressure P at constant temperature T according to the laws

$$\sigma = C_1(T)P^{-1/n}, \quad (1)$$

and

$$[V_A]_{\text{tot}} = C_2(T)P^{-1/m}, \quad (2)$$

where $C_1(T)$ and $C_2(T)$ are functions of temperature and n and m are constants. It has been reported that n has values $n=5$ for CeO₂,¹ $n=4$ for Nb₂O₅,² $n=5$ or $n=6$ for TiO₂,³ and that n can take on various nonintegral values.⁴ It has also been reported that m has values $m=6$ or $m=2$ for TiO₂,^{5,6} and $m=6$ for Nb₂O₅.⁷

It has generally been concluded that Eq. (1) with $n=5$ is not compatible with a defect model wherein oxygen vacancies are the sole source of conduction electrons. This conclusion has been reached on the basis that the oxygen-vacancy model leads to Eq. (1) with $n=4$ if all oxygen vacancies are singly ionized, and to Eq. (1) with $n=6$ if all oxygen vacancies are doubly ionized.^{2,3,5,7,8} Because of this, interstitial cations,^{1,3,8} or associated vacancies⁹ have been postulated as conduction electron sources in order to explain experimental results which appear to follow the law of Eq. (1) with $n=5$.

The purpose here is to treat the oxygen-vacancy model exactly, not making any assumption about the states of ionization of oxygen vacancies. Because both electrical-conductivity measurements and gravimetric determination of oxygen-vacancy concentration are used to determine the defect structure, concentrations of both conduction electrons and oxygen vacancies are considered. The case discussed is that of pure oxide with oxygen vacancies being the only source of conduction electrons. Thus, impurity atoms and all other sources of carriers including intrinsic formation of electron-hole pairs are not considered here. It is assumed that there is only one type of conduction state for the electrons and that electrons are the only carriers. After the characteristics of the oxygen-vacancy defect model

* This work was supported by the U. S. Air Force Office of Scientific Research.

¹ E. H. Greener, J. M. Wimmer and W. M. Hirthe, presented at the Third Rare-Earth Conference, Clearwater, Florida, April 1963 (unpublished).

² E. H. Greener, D. H. Whitmore, and M. E. Fine, *J. Chem. Phys.* **34**, 1017 (1961).

³ J. Yahia, *Phys. Rev.* **130**, 1711 (1963).

⁴ J. Rudolph, *Z. Naturforsch.* **14a**, 727 (1959).

⁵ P. Kofstad, *Phys. Chem. Solids* **23**, 1579 (1962).

⁶ W. R. Buessem and S. R. Butler, in *Kinetics of High Temperature Processes*, edited by E. Kingery (John Wiley & Sons, Inc., New York, 1958).

⁷ P. Kofstad and B. Anderson, *Phys. Chem. Solids* **21**, 280 (1962).

⁸ T. Hurlen, *Acta Chem. Scand.* **13**, 365 (1959).

⁹ D. J. M. Bevan and B. Hyde (private communication).

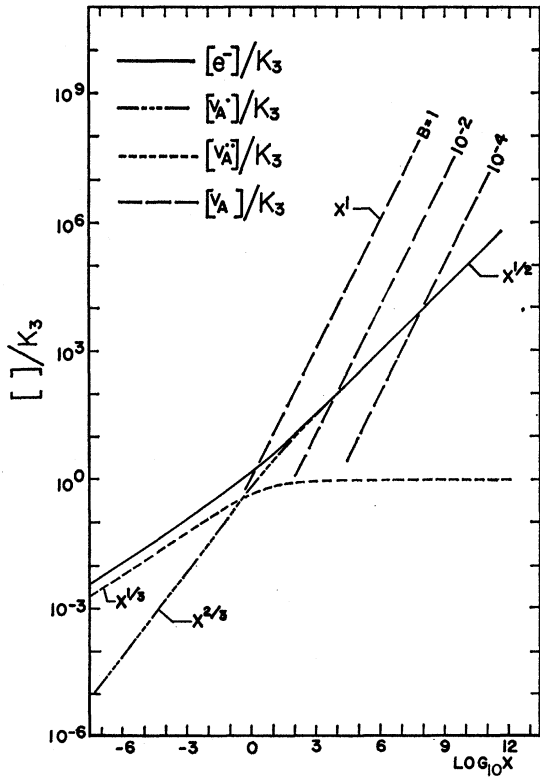
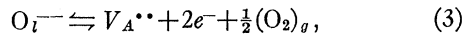


FIG. 1. Conduction-electron and oxygen-vacancy concentrations. The quantities $[e^-]/K_3$, $[V_A^*]/K_3$, $[V_A^{**}]/K_3$, and $[V_A]/K_3$ are plotted as functions of $X = (K_2/K_3)P^{-1/2}$. The quantity relating to the concentration of un-ionized vacancies, $[V_A]/K_3$, is plotted for several values of the parameter $B = K_3/K_4$, upon which it also depends.

are obtained and discussed, they are compared with the results of several experiments.

II. THE OXYGEN-VACANCY MODEL

The oxygen-vacancy model discussed here falls within the general framework of the defects treated by Kröger and Vink.¹⁰ The reactions between the oxygen vacancies, the ambient oxygen gas, and the conduction electrons are:



where e^- , V_A^{**} , V_A^* , V_A , $\frac{1}{2}(O_2)_g$, and O_i^{--} represent, respectively, a conduction electron, a doubly ionized oxygen vacancy, a singly ionized oxygen vacancy, an un-ionized oxygen vacancy, an atom of oxygen in the ambient gas, and an oxygen ion at an anion lattice position.

Assuming the law of mass action,¹¹ leads to relations

¹⁰ F. A. Kröger and H. J. Vink, in *Solid State Physics, Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. III.

¹¹ R. F. Brebeck, *Phys. Chem. Solids* 4, 190 (1958).

involving concentrations of the quantities appearing in Eqs. (3), (4), and (5) and equilibrium constants. They are

$$[e^-]^2[V_A^{**}]P^{1/2} = K_2(T), \quad (6)$$

$$[e^-][V_A^{**}] = K_3(T)[V_A^*], \quad (7)$$

and

$$[e^-][V_A^*] = K_4(T)[V_A], \quad (8)$$

where the square bracket terms indicate the concentrations in numbers per cm^3 of the quantity in the bracket and P is the oxygen partial pressure in atmospheres. For TiO_2 , for instance, $[e^-]$ is identical with the number of Ti^{3+} ions³ per cm^3 .

The equilibrium constants K_3 and K_4 are given by¹²

$$K_3(T) = (2\pi m^* kT/h^2)^{3/2} \exp[-eV_2/kT], \quad (9)$$

and

$$K_4(T) = (2\pi m^* kT/h^2)^{3/2} \exp[-eV_1/kT], \quad (10)$$

where m^* , k , h , e , T , V_1 , and V_2 are, respectively, the electron effective mass, Boltzmann's constant, Planck's constant, electronic charge, absolute temperature, first ionization potential, and second ionization potential.¹³

Equations (6), (7), and (8), along with the equation for electrical neutrality,

$$[e^-] = [V_A^*] + 2[V_A^{**}], \quad (11)$$

lead to the expressions for $[e^-]$, $[V_A^*]$, $[V_A^{**}]$, and $[V_A]$:

$$[e^-]^3 - (K_2/K_3)P^{-1/2}[e^-] - 2K_2P^{-1/2} = 0, \quad (12)$$

$$[V_A^*] = (K_2/K_3)P^{-1/2}[e^-]^{-1}, \quad (13)$$

$$[V_A^{**}] = K_2P^{-1/2}[e^-]^{-2}, \quad (14)$$

and

$$[V_A] = (K_2/K_3K_4)P^{-1/2}. \quad (15)$$

The solution of these as well as the general clarification of the entire problem is facilitated by introducing the following quantities:

$$A(T) = K_2/K_3^3, \quad (16)$$

$$B(T) = K_3/K_4, \quad (17)$$

$$X(T, P) = A(T)P^{-1/2}, \quad (18)$$

$$R = [e^-]/K_3, \quad (19)$$

$$S = [V_A^*]/K_3, \quad (20)$$

$$T^2 = [V_A^{**}]/K_3, \quad (21)$$

and

$$U = [V_A]/K_3. \quad (22)$$

With the introduction of these quantities, Eqs. (12),

¹² F. A. Grant, *Rev. Mod. Phys.* 31, 646 (1959).

¹³ The ionization potentials for a vacancy could be assigned values corresponding to a helium atom embedded in a dielectric [cf. D. C. Cronemeyer and M. A. Gillette, *Phys. Rev.* 82, 975 (1951)]. There is a question about the validity of such a procedure because of the relative size of a vacancy and the extent of the charge distribution about the vacancy.

(13), (14), and (15) become

$$R^3 - XR - 2X = 0, \quad (23)$$

$$S = X/R, \quad (24)$$

$$T^2 = X/R^2, \quad (25)$$

and

$$U = BX. \quad (26)$$

The appropriate solution of the cubic equation is easily obtained by ordinary means¹⁴ and is given by

$$R = X^{1/3} \{ [1 + (1 - X/27)^{1/2}]^{1/3} + [1 - (1 - X/27)^{1/2}]^{1/3} \} \quad (X \leq 27), \quad (27)$$

$$R = (2/\sqrt{3})X^{1/2} \cos\{\frac{1}{3} \tan^{-1}[(X/27) - 1]^{1/2}\} \quad (X \geq 27).$$

Figure 1 shows the quantities $[e^-]/K_3$, $[V_A^*]/K_3$, $[V_A^{**}]/K_3$, and $[V_A]/K_3$ as functions of X , as obtained from the solutions of these equations. The quantity U is not completely determined by X but depends also on the parameter B . In Fig. 1, $[V_A]/K_3$ is shown as a function of X for several values of the parameter B .

The general nature of the exact solution shown in Fig. 1 is in complete agreement with the limiting cases discussed earlier.^{2,3,5,7,8} At small X , the oxygen vacancies tend to be doubly ionized and both conductivity- and the gravimetric-vacancy concentration should vary as $X^{1/3}$, and therefore as $P^{-1/6}$. At large X , lower states of vacancy ionization are favored¹⁵ and conductivity would vary as $X^{1/2}$ or $P^{-1/4}$. The gravimetric-vacancy concentration in the region of large X could vary as $X^{1/2}$ or $P^{-1/4}$ for small values of B or it could vary as X^1 or $P^{-1/2}$ for larger values of B .

There are also intermediate regions where more than one ionization state must be considered. The first is associated with the change from predominantly double ionization to predominantly single ionization of vacancies and it affects both electrical and gravimetric experiments. The second is associated with the change from predominantly singly ionized to predominantly un-ionized vacancies and will affect only the vacancy concentration and not the conduction-electron concentration.

The results to be expected from a given isothermal experiment will be determined by values of X over which the experiment runs in addition to the value of B for that experiment. Varying the oxygen partial pressure varies X , but rather slowly since X varies as $P^{-1/2}$. The general location of the experimental range for an isotherm measurement is also determined by the temperature according to Eqs. (18) and (16). If one assumes

¹⁴ N. B. Conkwright, *Introduction to the Theory of Equations* (Ginn and Company, New York, 1941).

¹⁵ This is a direct consequence of the fact that $[e^-]$ increases with X . Inspection of Eqs. (7) and (8) shows that increasing the electron concentration at constant temperature causes lower ionization states to be favored. It should be noted, however, that all concentrations increase with increasing X .

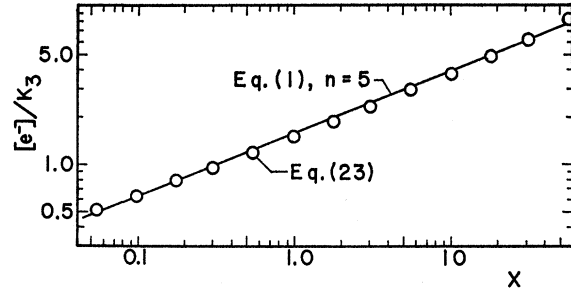


FIG. 2. Conduction-electron concentration in the first intermediate region. The quantity $[e^-]/K_3$ is plotted as a function of X . The circles represent the exact solution of the problem while the straight line is a least-squares fit of Eq. (1) to the calculated points.

that K_3 and K_4 are given by Eqs. (9) and (10) and that K_2 is given by $K_2 = K_{20} \exp[-eV_{fi}/kT]$, where eV_{fi} is the energy to form a doubly-ionized oxygen vacancy, then Eqs. (16) and (18) lead to the equations for X and B :

$$X(T, P) = K_{20} P^{-1/2} (2\pi m^* k/h^2)^{-3/2} T^{-9/2} \times \exp[(-e/kT)(V_{fi} - 3V_2)], \quad (28)$$

and

$$B(T) = \exp[(-e/kT)(V_2 - V_1)]. \quad (29)$$

From Eq. (29) it appears probable that $B(T)$ always increases with increasing temperature. It is also probable that X increases with temperature although the term $3V_2$ in Eq. (28) may make the rate of increase relatively small. The temperature dependences of X and B as given in Eqs. (28) and (29) lead to a characteristic appearance of gravimetric isotherms at large X which will be discussed below.

The most important factor which determines the X position of an experimental range is the value of the parameter $A(T)$. The things which determine the value of A are the energy of formation of an un-ionized vacancy, and the first and second ionization potentials. These latter are determined mainly by the effective dielectric constant and by the effective mass of an electron bound to a vacancy.¹⁸ None of these are directly susceptible to experimental manipulation so that it may not be possible to investigate every interesting range of X .

Following these general remarks about the exact solution of the oxygen-vacancy case, the conduction-electron concentration and the oxygen-vacancy concentration will be discussed separately.

III. CONDUCTION-ELECTRON CONCENTRATION

If the mobility of conduction electrons is independent of their concentration, the electrical conductivity will be proportional to the concentration of conduction electrons, $[e^-]$. The curve labeled $[e^-]/K_3$ in Fig. 1 then gives the consequences of the oxygen-vacancy defect model for electrical conduction. The pressure dependences for large X and for small X are $P^{-1/4}$ and $P^{-1/6}$,

respectively. As mentioned above, the $[e^-]/K_3$ curve shows the intermediate region extending from about $X=3\times 10^{-4}$ to $X=3\times 10^{+3}$. In this intermediate region, neither singly ionized nor doubly ionized vacancies may be neglected and the result is that Eq. (1) with $n=4$ or $n=6$ will not be satisfied. Instead, a conductivity isotherm will show a curvature upward and will only approximate Eq. (1) with $n=5$ over a limited range of X .

The approximation to Eq. (1) with $n=5$ can be rather good over a range of X of three orders of magnitude. This range corresponds to six orders of magnitude of oxygen partial pressure, which is a typical experimental range. The exact solutions of Eq. (23) for thirteen values of X between $X=5.4\times 10^{-2}$ and $X=5.4\times 10^1$ are shown in Fig. 2 as the circles. The straight line represents a least-squares fit to these points of a law corresponding to Eq. (1). The least-squares value of n is $n=5.0002$. The exact values of R in this range depart from the least-squares line by a maximum of 5.5% and the rms value of the departure is about 3%. This suggests that unless the conductivity isotherms are taken over a sufficiently large range of X or unless the measurements are sufficiently precise, it may not be possible to distinguish between the law of Eq. (1) with $n=5$ and the exact behavior in the intermediate region for oxygen-vacancy defects.

If the same range of X were moved to larger X , the approximation to the law of Eq. (1) would become better and n would decrease from $n=5$ toward $n=4$ as a limiting value. Moving the same range of X to smaller X also would lead to a better approximation to Eq. (1) and to a larger value of n , approaching $n=6$ as a limit.

IV. OXYGEN-VACANCY CONCENTRATION

The solutions S , T , and U of Eqs. (23), (24), (25), and (26) can be used to obtain an expression for the total oxygen-vacancy concentration:

$$[V_A]_{\text{tot}} = [V_A^{\bullet\bullet}] + [V_A^\bullet] + [V_A]. \quad (30)$$

This expression includes all vacancies in all states of ionization and corresponds to the result of a gravimetric determination of oxygen-vacancy concentration. Figure 1 shows that for $X < 10^{-5}$ and $B < 1$, the vacancies are essentially all doubly ionized and the total vacancy concentration follows Eq. (2) with $m=6$. For $10^4 < X < 10^8$ and $B < 10^{-4}$, the vacancies are essentially all singly ionized and Eq. (2) with $m=4$ would apply. For larger X and/or larger B , the vacancies would be predominately un-ionized and the total vacancy concentration would follow Eq. (2) with $m=2$.

For the total oxygen-vacancy concentration there are two intermediate regions. As X increases, the first corresponds to the transition from double to single ionization and the second to the transition from single ionization to no ionization. For large enough B , the two intermediate regions could merge into a single one in the vicinity of $X=1$. Formally, if $B > 1$, the second inter-

mediate region would move past the first to smaller X and there would be only one observable intermediate region corresponding to the direct transition from double ionization to no ionization. It should be noted, however, that for equal electron effective masses, Eqs. (9), (10), and (17) show that the largest possible value of B is unity for $V_2 > V_1$. Thus, one would not expect the second intermediate region to pass completely through the first.

The parameter B is potentially of considerable importance for gravimetric experiments although it probably has little to do with electrical-conductivity experiments.

V. COMPARISON WITH EXPERIMENT

A. TiO_2

Because of the large extent of the intermediate region for electrical conductivity, it would seem possible that part of some experiment actually would lie in it. The experiment of Yahia³ on TiO_2 may be just such a case. Using Yahia's values of K_2 and K_3 at 1170°K, the value of A from Eq. (16) is about 1.6×10^{-3} .

From his range of oxygen partial pressures, Eq. (18) shows that the range of X for his experiment at that temperature would be from $X=1.6\times 10^{-3}$ to about $X=1.6$. Reference to Fig. 1 shows that the low-pressure end at that temperature would extend well into the intermediate region while the high-pressure end would be at a place where Eq. (1) with $n=6$ is closely approximated. Because the experiments were actually carried out at a higher temperature, the range for the actual experiments would be expected to be shifted further into the intermediate region.

Yahia did not neglect any states of ionization but also solved exactly for the carrier concentration. His calculated results at 1170°K were fairly close to Eq. (1) with $n=6$. Therefore, he invoked the cation-interstitial model at low-oxygen partial pressure to explain the approximation to Eq. (1) with $n=5$ in that pressure range.³ It is suggested here that the experimental results of Yahia are just the type to be expected from oxygen vacancies alone when the low-pressure measurements extend about halfway into the first intermediate region. By way of further illustration, a value of 1.35×10^{-2} for A (which is close to, but slightly larger than that obtained from Yahia's values of K_2 and K_3 at 1170°K) and a range of oxygen partial pressure from 1.0 to 1.0×10^{-6} atm gives a range of X from 1.35×10^{-2} to 1.35×10^1 . Reference to Figs. (1) and (2) shows that the high-pressure end of this range should give an isotherm closely approximating Eq. (1) with $n=6$, while the low-pressure end should give an isotherm closely approximating Eq. (1) with $n=5$. This is just the behavior found for TiO_2 by Yahia.³

There are two gravimetric experiments which relate to the present discussion. The experiments of Buessem and Butler⁶ were carried out between 860 and 1050°C and between 1.0 and 2×10^{-2} atm of oxygen partial

pressure. Using their values of K_2 and the helium-atom vacancy model¹³ it is possible to find the range of X for their experiment. Use of Eqs. (9), (16), and (18) gives $4.35 \times 10^{-4} \leq X \leq 9.90 \times 10^{-2}$ for the case $m^* = 30m_0$. From this result and Figs. 1 and 2 it is seen that the gravimetric experiment of Buessem and Butler also extends part way into the first intermediate region. Because of this, it would appear questionable to interpret the results in terms of the limiting case that all vacancies are doubly ionized. Instead, it would appear that K_2 should be evaluated from the exact solution in the intermediate region.

Another gravimetric experiment at lower oxygen partial pressures also showed a $P^{-1/6}$ dependence and was interpreted on the basis of doubly ionized vacancies.⁵ It does not seem possible to reconcile all of these interpretations with noninteracting oxygen vacancies acting as electron donors.

B. Nb_2O_5

A gravimetric determination of oxygen-vacancy concentration in $\alpha\text{-Nb}_2\text{O}_5$ showed a $P^{-1/6}$ dependence on oxygen partial pressure⁷ and was interpreted in terms of doubly ionized oxygen vacancies. The range of that experiment was between 927 and 1410°C and between 10^{-18} and 10^{-7} atm of oxygen partial pressure. Taking the values of K_2 from the gravimetric experiment, using Eq. (9) with $m^* = 30m_0$, and taking the dielectric constant to be 280,¹⁶ the range of X for the gravimetric experiment is from $X = 4.6 \times 10^{-18}$ to $X = 2.5 \times 10^{-5}$. This is below the first intermediate region and entirely consistent with the $P^{-1/6}$ dependence and supports the evaluation of K_2 in terms of doubly-ionized vacancies.

On the other hand, two conductivity experiments in approximately the same temperature range as the gravimetric experiment show a $P^{-1/4}$ dependence near one atmosphere of oxygen partial pressure.^{2,17} At low pressure, the conductivity shows a change to a $P^{-1/6}$ dependence.¹⁷ Kofstad interprets the change to the $P^{-1/6}$ dependence in terms of interaction between vacancies¹⁷ and attributes the $P^{-1/4}$ dependence at higher pressures to singly ionized vacancies. The treatment presented here would appear to indicate that something other than noninteracting oxygen-vacancy donors is required to explain those experimental results.

C. CeO_2

Conductivity experiments have been reported to show a $P^{-1/5}$ dependence for CeO_2 between 1100 and 1400°C and between 1.0 and 0.006 atm of oxygen partial pressure. Because of the $P^{-1/5}$ dependence, the results were interpreted on the basis of cation interstitial defects with all interstitials being quadruply ionized.¹ Gravimetric experiments on CeO_2 have been conducted by

Bevan and Kordis¹⁸ in the range between 777 and 1080°C and between 10^{-10} and 10^{-22} atm of oxygen. The results appear to show a $P^{-1/4}$ dependence changing to a $P^{-1/2}$ dependence at lower oxygen pressures although there is considerable scatter in the data at higher pressures due to the small departure from stoichiometry. The composition range for the gravimetric experiment was $1.900 \leq x \leq 1.999$ in CeO_x .

While it is possible that the range of the gravimetric experiments is such that ideal-solution theory might not apply throughout, a reasonable choice of effective mass, dielectric constant, and K_2 may be able to account in a general way, at least, for the results of both experiments in terms of oxygen vacancies alone. By choosing $m^* = 30m_0$ for both bound electrons, $V_2 = 0.795$ V, $V_1 = 0.36$ V and $K_2 = (4.29 \times 10^{78}) \exp[(-6.11e)/kT]$, Eqs. (9), (10), (16), and (17) give the following relations:

$$K_3 = (3.88 \times 10^{17}) T^{3/2} \exp[(-0.795e)/kT], \quad (31)$$

$$B = \exp[(-0.435e)/kT], \quad (32)$$

and

$$A(T) = (7.33 \times 10^{25}) T^{-9/2} \exp[(-3.72e)/kT]. \quad (33)$$

At a temperature in the range of the conductivity experiments, Eq. (33) gives $A(1500^\circ\text{K}) = 9.23 \times 10^{-2}$. For this case, the conductivity experiments, which were carried out near 1.0 atm oxygen partial pressure, would fall in the first intermediate region. This is approximate, but it might be possible to account for the $P^{-1/5}$ dependence found in the conductivity. On the other hand, Eq. (33) gives $A(777^\circ\text{C}) = 6.60 \times 10^{-7}$ and Eq. (32) gives $B(777^\circ\text{C}) = 6.97 \times 10^{-3}$. Figure 1 shows that this value of B should place the second intermediate region in the vicinity of $X = 10^4$ and this together with the value of A should correspond to $P = 10^{-21}$ atm of oxygen partial pressure. This is approximately where the gravimetric data showed a transition from $P^{-1/4}$ to a $P^{-1/2}$ dependence at 777°C.¹⁸

Equations (31), (32), and (33) can be used to construct a family of oxygen-vacancy concentration isotherms in the vicinity of the second intermediate region. Figure 1 shows that the concentration of doubly ionized vacancies is negligible in the vicinity of $X = 10^4$. From the exact solutions given in Eqs. (23), (24), and (26), we may use the following forms for $[V_A^*]$ and $[V_A]$ at large X :

$$[V_A^*] = K_3 X^{1/2} = K_3 A^{1/2} P^{-1/4} \quad (34)$$

and

$$[V_A] = K_3 B X = K_3 B A P^{-1/2}. \quad (35)$$

Figure 3 shows a family of oxygen-vacancy concentration isotherms calculated from Eqs. (31), (32), (33), (34), and (35). The general appearance of this family of isotherms is characteristic of the exact treatment of the

¹⁶ E. Wainer and C. Wentworth, J. Am. Ceram. Soc. **35**, 207 (1952).

¹⁷ P. Kofstad, Phys. Chem. Solids **23**, 1571 (1962).

¹⁸ D. J. M. Bevan and J. Kordis (private communication and to be published).

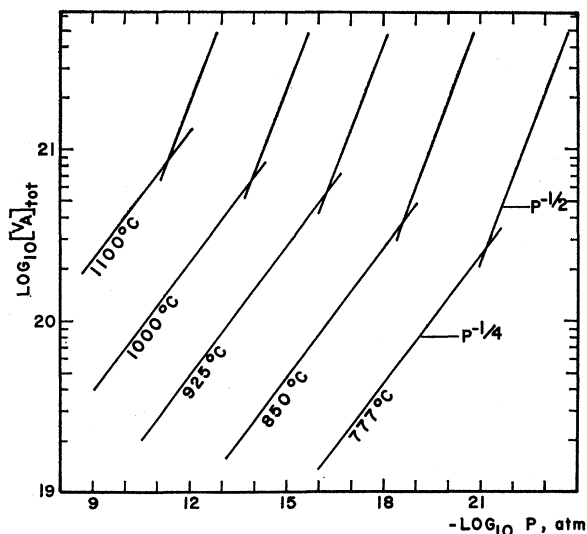


FIG. 3. Family of isotherms of oxygen-vacancy concentration calculated from the limiting forms of the solutions of Eqs. (25) and (26) at large X .

oxygen-vacancy defect model in this region and is very similar to that reported by Bevan and Kordis¹⁸ for CeO_2 . From this it appears to be possible to account for both the conductivity and gravimetric results for CeO_2 on the basis of an oxygen-vacancy model alone without

making unreasonable assumptions regarding effective mass, dielectric constant, vacancy model, or vacancy-formation energies.

VI. DISCUSSION

The exact treatment of oxygen-vacancy defects in metal oxides may account, in some cases, at least, for the departure from a $P^{-1/4}$ or a $P^{-1/6}$ dependence without the necessity of introducing other defects such as cation interstitials. There are some experimental observations which would be in clear contradiction with the oxygen-vacancy model and a search for such contradictions may be the best way to proceed. For instance, a $P^{-1/5}$ dependence of conductivity over approximately ten orders of magnitude of oxygen partial pressure should rule out oxygen vacancies. The experiments on^{2,7,17} Nb_2O_5 also seem to be clearly in contradiction with simple oxygen-vacancy defects. On the other hand, in the two cases where a $P^{-1/5}$ dependence of conductivity is observed,^{1,3} there seem to be indications that the experiments could be located in the first intermediate region for oxygen vacancies. Also, if the gravimetric experiments on¹⁸ CeO_2 do not involve serious departure from ideality, the transition from a $P^{-1/4}$ to a $P^{-1/2}$ dependence on oxygen partial pressure should represent a confirmation of the vacancy model. The cation interstitial defect should give a transition from $P^{-1/4}$ to $P^{-1/3}$.

Electronic Structure of the M Center in LiCl and LiF *

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Experimental work of the past few years has fairly conclusively established that the M center in alkali halides consists of two F centers bound together at neighboring halide sites. Using this model, the wave functions and energy levels of the M center in LiCl and LiF are calculated in the Heitler-London approximation. The F -electron wave functions used in the calculations are of the vacancy-centered type. The finite extension of the neighboring alkali ions is treated but all other ions are considered to be point charges. The results of the calculations show that there is a transition energy which corresponds closely to the observed M_1 band. In addition, there are numerous possibilities for other transitions, all giving energies which cluster in the vicinity of the main F -band energy. The results for the M_1 band follow the empirical Ivey relationship quite well.

I. INTRODUCTION

OF the various models for the M center, the one proposed by van Doorn and Haven¹ has been the most successful in explaining the experimental data.

* A preliminary report on this work was given in the Bull. Am. Phys. Soc. 8, 352 (1963).

† Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

¹ C. Z. van Doorn and Y. Haven, Philips Res. Rept. 11, 479 (1956).

According to this model, the M center consists of two F centers bound together at nearest-neighbor halide sites. Thus, the M center, in a sense, can be considered a lattice analog of the hydrogen molecule in free space. We shall sometimes refer to it as the F_2 molecule and speak of the F_2 model of the M center.

Very few theoretical calculations have been carried out on the M center, and, as far as we know, there have been no published results of detailed calculations based