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# Non-stoichiometric disorder in $\alpha$ - $Nb_2O_5$ at elevated temperatures

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The electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ was determined for the oxygen partial pressure range of $10^0$ to $10^{-20}$ atm and temperature range 700 to 1150° C. The data were found to be proportional to the $-1/6$th power of the oxygen partial pressure for the oxygen pressure range $10^{-20}$ to $10^{-9}$ atm, and proportional to $P_{O_2}^{-1/4}$ for oxygen pressures greater than $10^{-9}$ atm. The region of linearity where electrical conductivity varies as the $-1/4$th power of $P_{O_2}$ increased as the temperature was decreased. Thermogravimetric measurements were carried out in the temperature range 950 to 1250° C. The deviation from stoichiometry in $\alpha$-$Nb_2O_5$ ($x$ in $Nb_2O_{5-x}$) as a function of partial pressure of oxygen showed two distinct regions, namely a region with an approximately $-1/6$th dependence on $P_{O_2}$ and a region where the deviation was nearly independent of oxygen partial pressure. The electrical conductivity and thermogravimetric data are consistent with the presence of small amounts of acceptor impurities in $\alpha$-$Nb_2O_5$.

## 1. Introduction

The potential use of niobium for high-temperature service has focused attention on its oxides since these make up the barrier layers between the metal and gas phase during oxidation. Unfortunately, little is known about the properties of the oxides formed, resulting in a correspondingly incomplete understanding of the mechanism of oxidation. $Nb_2O_5$ is the main oxide formed during oxidation at temperatures above 500° C [1–3]. It has been shown by many investigators [4–8] that $Nb_2O_5$ crystallizes in five different modifications. The $\alpha$-form of $Nb_2O_5$ is the high-temperature modification. The transformation temperature for the $\alpha$-form from the low-temperature modification has been found to be approximately 830° C [5]. The transformation is irreversible [5] and the temperature of transformation has also been found to be somewhat dependent both on heating rate [6] and the partial pressure of oxygen [3]. The crystal structure of $\alpha$-$Nb_2O_5$ has been found to be monoclinic [5, 9, 10].

$Nb_2O_5$ is non-stoichiometric and the nature of the non-stoichiometry has been a subject of studies by a number of investigators [4, 11–19]. Brauer [4] found that $\alpha$-$Nb_2O_5$ could exist as a single phase with departures from stoichiometry up to $Nb_2O_{4.8}$. Kling [11] measured the electrical conductivity of fused $Nb_2O_5$ as a function of oxygen partial pressure and reported an increase in conductivity with a decrease in partial pressure of oxygen, characteristic of n-type conduction. The deficit in oxygen may arise from either oxygen vacancies or metal interstitials. The electrical conductivity of near-stoichiometric $\alpha$-$Nb_2O_5$ single-crystal and sintered specimens was studied by Greener *et al.* [12]. Under a constant ambient oxygen pressure in the temperature range 300 to 900° C, the conductivity exhibited an exponential temperature dependence with an activation energy of 1.65 eV. The isothermal conductivity in the oxygen pressure range $10^0$ to $10^{-3}$ atm was found to be proportional to $P_{O_2}^{-0.24 \pm 0.01}$. This result was interpreted on the basis of a defect model involving singly ionized oxygen vacancies. Similar results were obtained by Kofstad [14] in the temperature range 750 to 1200° C.

Non-stoichiometry of $\alpha$-$Nb_2O_5$ was studied by Kofstad and Anderson [13], Blumenthal *et al.* [20] and Schafer *et al.* [21] by gravimetric

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measurements. Kofstad and Anderson [13] reported that the relative weight change in $Nb_2O_5$ is proportional to $P_{O_2}^{-1/6}$ at constant temperature over an oxygen pressure range of $10^{-7}$ to $10^{-18}$ atm and a temperature range of 900 to 1400° C. They concluded that the defect structure in this range of oxygen activity involves doubly ionized oxygen vacancies. The electrical conductivity measurements carried out in mixtures of CO and $CO_2$ by Kofstad [14] showed a $-1/6$th dependence for conductivity on $P_{O_2}$ at 750 to 1100° C. The ionic transport number in $\alpha$-$Nb_2O_5$ is found to be less than 0.05 by Elo *et al.* [22]. By combining the available thermogravimetric and electrical conductivity data, Yahia [23] calculated the electronic mobility in $\alpha$-$Nb_2O_5$ at 900° C as $\simeq 7 \times 10^{-2}\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$.

The change in the oxygen pressure dependence of the conductivity from a $-1/6$th to a $-1/4$th power as $P_{O_2}$ is increased has been interpreted in terms of doubly and singly ionized oxygen vacancies [11–19] and acceptor impurities [24]. This report constitutes a further study of the defect structure of $\alpha$-$Nb_2O_5$. The electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ has been determined for the $P_{O_2}$ range of $10^0$ to $10^{-20}$ atm and temperature range 700 to 1150° C. Thermogravimetric measurements are also carried out in the temperature range 950 to 1250° C. The change in the oxygen pressure dependence of the electrical conductivity has been interpreted on the basis of the presence of small amounts of acceptor impurities in the sample.

## 2. Experimental procedure

The specimens used in this investigation were prepared from niobium oxalate solution (Kawecki Berylco Industries, Boyertown, Pennsylvania, USA). Estimates of impurities in the oxalates determined by emission analysis are as follows: Ta, 350 ppm; Fe, 400 ppm; Si, 150 ppm; Ca, 250 ppm; Pb, 25 ppm and Al, Sn, Sb and Mo each less than 15 ppm. The powder samples obtained from the oxalate solution were pressed into thin rectangular slabs (2.1 cm × 0.6 cm × 0.05 cm) under a load of $286\,\mathrm{MN\,m^{-2}}$ and sintered in air at 1350° C for 10 h. The density of the sintered slabs was 96% of the theoretical density. Conductivity specimens were cut from this slab using an S.S. White Industrial Airbrasive Unit, Model F. The specimens were wrapped with four 0.03 cm platinum wires as described in the literature [25, 26]. Small notches were cut in the edges of the sample to help hold the platinum wires in place.

A conventional four-probe direct current technique was employed for all electrical conductivity measurements. The four platinum leads were insulated from one another by recrystallized high-purity alumina insulators. A standard taper Pyrex joint to which capillary tubes had been sealed was mounted on top of the furnace reaction-tube assembly. The platinum wires were led out through the capillary tubes and were glass-sealed vacuum tight into the tubes.

The oxygen partial pressures surrounding the samples were controlled by flowing metered mixtures of gases past the sample. The gases were oxygen, compressed air, argon with known amounts of oxygen and $CO_2/CO$ mixtures. The error in volumetric measurements of the $CO_2/CO$ gas mixtures resulted in an error of about 1% in the $P_{O_2}$ value reported here. The conductivity was measured as a function of $P_{O_2}$ in the temperature range 700 to 1150° C. The conductivity was determined by measuring the voltage across the potential probes using a high-impedance ($> 10^{10}\,\Omega$) digital voltmeter (Keithley 191 digital multimeter). The current was supplied between the two outer leads by a constant-current source (Keithley 225 current source). The voltage was measured with the current in both forward and reverse directions, and the conductivity was calculated from the average values. After each variation of the gas atmosphere surrounding the sample the conductivity was measured as it changed to the new equilibrium value. This process of change was recorded and if the conductivity no longer changed, it was assumed that the state of equilibrium had been attained. This state proved to be attainable reversibly from higher or lower oxygen partial pressures. Current was varied from 10 $\mu$A to 1 mA and no significant change in conductivity was observed. The size and geometry of the samples were altered so that the ratio of surface to bulk was changed with no detected difference in the calculated conductivity; that indicated the measured quantity is the bulk conductivity. The measured conductivity in the forward and reverse directions of the current flow differed by less than 0.1%. The conductivity did not change with time after the current was applied to the sample.

For the thermogravimetric measurements a Cahn RG microbalance enclosed in a glass vacuum-jar was mounted above the furnace. The specimen

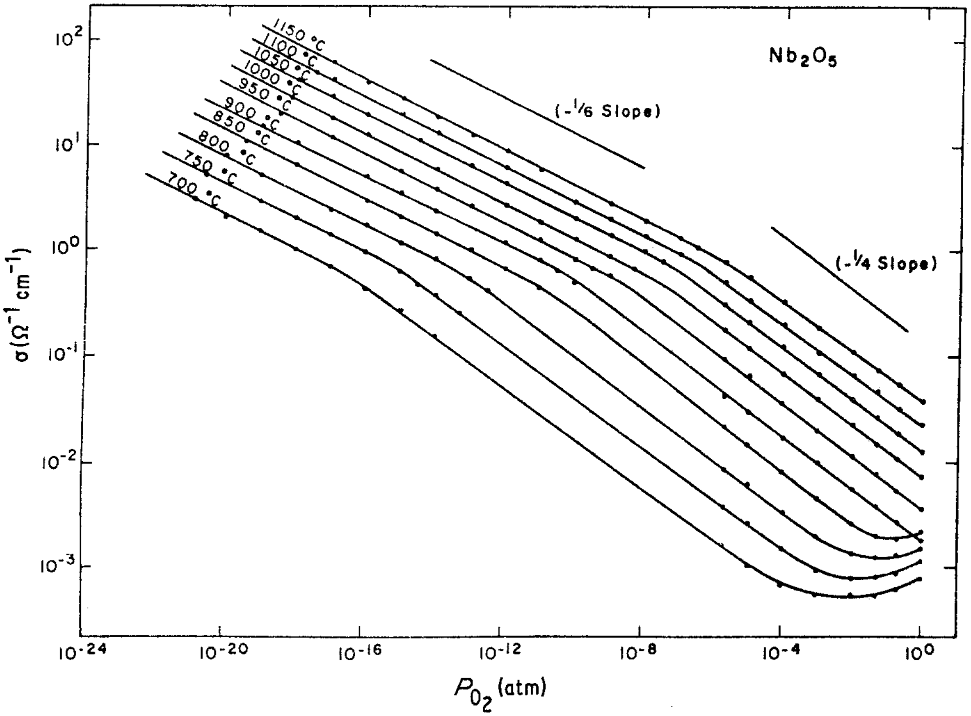

*Figure 1* The electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ as a function of oxygen partial pressure at constant temperature.

(sintered pellet) was suspended in the hot zone of the furnace from the balance with a quartz fibre. The microbalance was calibrated with a sample of recrystallized alumina of similar mass and shape as the $Nb_2O_5$ specimen. The temperature-induced noise was $<2 \times 10^{-5}$ g peak-to-peak so that the weight could be easily estimated to within the selected sensitivity, $4 \times 10^{-6}$ g, of the balance. The calibration of the balance with the "inert" alumina was carried out at each experimental temperature to account for the buoyancy effect. The weight of the $\alpha$-$Nb_2O_5$ specimen was approximately 2 g. Readings were taken at both decreasing and increasing temperature and partial pressures of oxygen. All measurements were carried out at a total gas pressure of 1 atm.

The furnace employed in this investigation consisted of a winding of platinum–40% rhodium alloy around an alumina tube. The temperature was measured with a platinum–platinum–10% rhodium thermocouple. The hot zone of the furnace varied by ±1° C during an on–off cycle of the furnace controller. It was found that the temperature in the centre of the hot zone within the furnace reaction tube was uniform in cross-section and did not change when the gases were flowing. The temperatures reported should, therefore, be accurate to ±1° C.

## 3. Results and discussion

### 3.1. Electrical conductivity measurements

The electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ in the temperature range 700 to 1150° C and in equilibrium with oxygen partial pressures between $10^{-20}$ and $10^0$ atm is shown in Fig. 1. Two distinct regions were found from the $\log \sigma$ against $\log P_{O_2}$ plot (Fig. 1). The slopes of the straight lines drawn through the data points are given in Table IA and B. The results show that the conductivity of $\alpha$-$Nb_2O_5$ is proportional to the $-1/6$th power of oxygen partial pressure at larger deviation from stoichiometry. In the higher oxygen partial pressure regions ($P_{O_2} > 10^{-9}$ atm) the conductivity is found to be proportional to $P_{O_2}^{-1/4}$. The $P_{O_2}$ values where the conductivity changes its dependence on oxygen activity depend on the equilibrium temperature. The present data obtained in the region near atmospheric pressures are in general agreement with the published data [12, 14, 19].

A significant observation of the present work is the p-type behaviour observed at temperatures below approximately 900° C and $P_{O_2}$ values greater

TABLE IA $P_{O_2}$ dependence of electrical conductivity in $Nb_2O_5$ in the region $10^{-20}$ to $10^{-9}$ atm

| $T$ (°C) | $m$ for $\sigma_n \propto P_{O_2}^{-1/m}$ |
|---|---|
| 700 | 6.00 |
| 750 | 6.12 |
| 800 | 6.12 |
| 850 | 6.00 |
| 900 | 6.12 |
| 950 | 6.00 |
| 1000 | 6.00 |
| 1050 | 5.90 |
| 1100 | 6.00 |
| 1150 | 6.00 |

TABLE IB $P_{O_2}$ dependence of electrical conductivity in $Nb_2O_5$ in the region of $P_{O_2}$ greater than $10^{-9}$ atm

| $T$ (°C) | $m$ for $\sigma_n \propto P_{O_2}^{-1/m}$ |
|---|---|
| 700 | 4.18 |
| 750 | 4.18 |
| 800 | 4.09 |
| 850 | 3.96 |
| 900 | 4.18 |
| 950 | 4.00 |
| 1000 | 4.09 |
| 1050 | 4.09 |
| 1100 | 4.19 |
| 1150 | 4.23 |

than $10^{-2}$ atm. The different regions of $P_{O_2}$ dependence for conductivity are discussed separately in Sections 3.1.1. to 3.1.4.

### 3.1.1. Region I ($P_{O_2} = 10^{-20}$ to $10^{-9}$ atm)

The $\log\sigma$ against $\log P_{O_2}$ data (Fig. 1) are linear for as many as nine decades of oxygen partial pressure for a given temperature (above 950°C) and linear for six decades of $P_{O_2}$ for temperatures in the range 900 to 700°C. This extensive region of linearity affords an opportunity to determine the defect model responsible for the n-type electrical conductivity in this region. A slope of approximately $-1/6$ is found for the $\log\sigma$ against $\log P_{O_2}$ data (Table IA). This oxygen partial pressure dependence is in agreement with the thermogravimetric studies reported in Section 3.2 on $\alpha$-$Nb_2O_5$ at corresponding partial pressures of oxygen. The conductivity values are not given by Kofstad [14] (he gives only the resistance measured in ohms) and, hence, the absolute values measured in this work are not compared with any other data available in the literature. The relative, isothermal weight change of $\alpha$-$Nb_2O_5$ equilibrated in mixtures of CO and $CO_2$ has been found to be proportional to $P_{O_2}^{-1/6}$ by Kofstad and Anderson [13], indicating that doubly ionized oxygen vacancies are the predominant defects.

The variation of the electrical conductivity with the oxygen partial pressure is calculated in terms of the oxygen vacancy defect model. The basis for the calculation is the reaction that represents the formation of a doubly ionized oxygen vacancy $[V_o^{\cdot\cdot}]$ and two electrons available for conduction by the removal of an oxygen from a normal lattice site into the gas phase. The reaction is

$$O_o \rightleftharpoons 1/2O_2 + V_o^{\cdot\cdot} + 2e'. \tag{1}$$

The equilibrium constant for Reaction 1 is

$$K_1 \cong [V_o^{\cdot\cdot}]\,[n]^2 P_{O_2}^{1/2} = \exp(-\Delta G_f/RT), \tag{2}$$

where $[n] \equiv e'$. It is assumed that the defects exist in a dilute solution and do not interact. The Gibbs standard free energy change for Reaction 1 is represented by $\Delta G_f$. With two electrons resulting from each oxygen vacancy it follows that

$$[n] \cong 2[V_o^{\cdot\cdot}]. \tag{3}$$

Expressing the free energy change in terms of the enthalpy change, $\Delta H_f$, and entropy change, $\Delta S_f$, and substituting Equation 3 into Equation 2 the result for the electron concentration is

$$[n] = 2^{1/3} P_{O_2}^{-1/6} \exp[\Delta S_f/3R] \exp[-\Delta H_f/3RT]. \tag{4}$$

The electrical conductivity, $\sigma$, for the case where the sole charge carriers are electrons in the conduction band is

$$\sigma = ne\mu, \tag{5}$$

where $e$ is the electronic charge and $\mu$ is the mobility of the conduction electrons. When Equation 4 is substituted into Equation 5, the electrical conductivity becomes

$$\sigma = 2^{1/3} P_{O_2}^{-1/6} e\mu \exp[\Delta S_f/3R] \exp[-\Delta H_f/3RT]. \tag{6}$$

At constant temperature, assuming that mobility is independent of the change in concentration of oxygen vacancies, a plot of the logarithm of the electrical conductivity against the logarithm of $P_{O_2}$ should result in a straight line with a slope of $-1/6$. The data in Fig. 1 and Table IA are in good agreement with the predicted $-1/6$ dependence.

An indication of the magnitude of $\Delta H_f$, the enthalpy of the oxygen extraction reaction, is typically obtained from Arrhenius plots of the

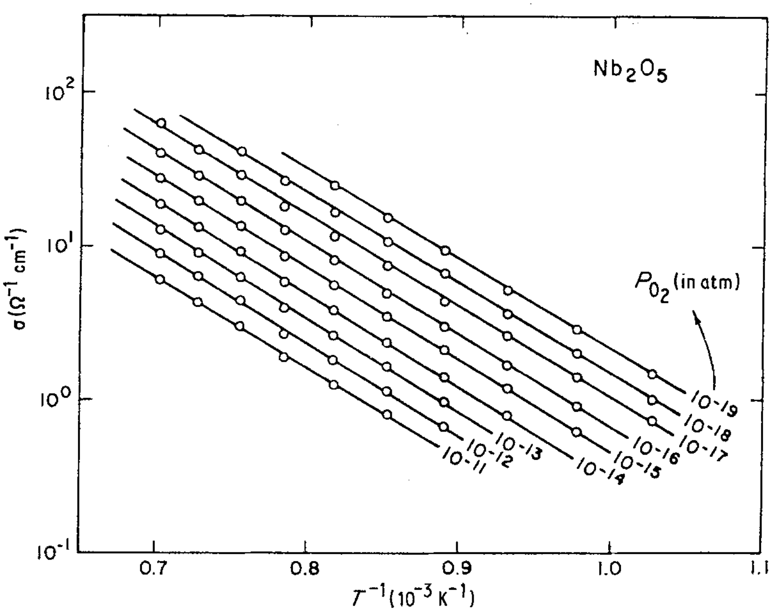

*Figure 2* Temperature dependence of electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ in the region $10^{-19}$ to $10^{-11}$ atm.

conductivity (Fig. 2), as deduced from Equation 6. This procedure neglects contributions from the temperature dependencies of the carrier mobility or density of states. The calculated slope values (in kcal $mol^{-1}$) from the Arrhenius plots are given in Table II. An average value of 1.18 eV (27.20 kcal $mol^{-1}$) is estimated for $(\Delta H_f/3)$. Kofstad [14] obtained a value of 1.19 eV (27.50 kcal $mol^{-1}$). It should be pointed out here that $\Delta H_f$, the enthalpy of oxygen extraction reaction (Equation 1) should be three times the value of the activation energies given in Table II, or 3.54 eV (81.60 kcal $mol^{-1}$).

### 3.1.2. *Region II* ($P_{O_2} > 10^{-9}$ *atm*)

A slope of approximately −1/4 is found for the log $\sigma$ against log $P_{O_2}$ data (see Table IA). A number of conductivity studies at near-atmospheric pressures [14–17, 19] ($1$–$10^{-3}$ atm) all yield an oxygen pressure dependence characterized by values of $n$ ranging from 4 to 4.3 in $\sigma \propto P_{O_2}^{-1/n}$. These relations have often been interpreted to reflect that singly charged oxygen vacancies predominate close to atmospheric pressures. To explain the change in the charge of the oxygen vacancies it has been proposed that the ionization energy of the oxygen vacancies decreases with increasing defect concentration (Meyer–Neldel rule) [14, 17]. However, there appears to be no firm theoretical interpretation for this rule [24].

TABLE II Arrhenius slopes for $Nb_2O_5$ in the region $10^{-20}$ to $10^{-11}$ atm

| $P_{O_2}$ (atm) | Arrhenius slopes (kcal $mol^{-1}$) |
|---|---|
| $10^{-19}$ | 26.64 |
| $10^{-18}$ | 26.52 |
| $10^{-17}$ | 27.65 |
| $10^{-16}$ | 27.44 |
| $10^{-15}$ | 27.44 |
| $10^{-14}$ | 27.44 |
| $10^{-13}$ | 27.44 |
| $10^{-12}$ | 27.40 |
| $10^{-11}$ | 26.75 |

These interpretations presuppose that effects of impurities can be neglected, but this presupposition does not appear probable at near-atmospheric pressures [24]. The low oxygen partial pressure data for non-stoichiometry in $Nb_2O_5$ have been extrapolated [24] to 1 atm oxygen at 900° C. This extrapolation resulted in an estimated native disorder in pure $Nb_2O_{5-x}$, at 1 atm oxygen partial pressure, of $\sim 10^{-6}$ for $x$ (ppm). Lower temperatures would result in even less native disorder. This means that extraordinary purities are required for the electrical properties of $Nb_2O_5$ to be free from impurity effects at high oxygen activities. All reported studies have been made on $Nb_2O_5$ with impurity contents many orders of magnitude larger than this. In the present report, the change in oxygen pressure dependence is discussed in terms of impurity effects.

In discussing the concept of the impurity effect, it is helpful to consider a Kroger–Vink [27] diagram for a binary oxide $M_2O_5$ with an acceptor impurity. We will for the purpose of illustra-

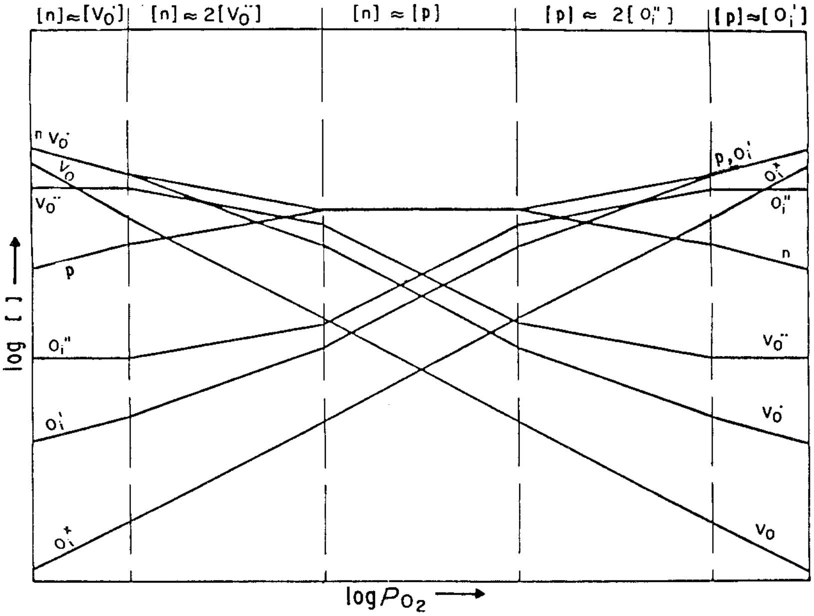

*Figure 3* Concentration of defects as a function of oxygen pressure for the oxide $M_2O_5$ with Frenkel disorder on the anion sublattice.

tion consider Frenkel disorder on the anion sublattice to describe the non-stoichiometry. Fig. 3 illustrates the variation of defect concentrations as a function of oxygen partial pressure for the case of various atomic defects, electrons, [n], and electron holes, [p]. If we consider the left side of Fig. 3 (n-type region) we recognize the familiar [n] $\propto$ $P_{O_2}^{-1/6}$, where [n] $\approx 2[V_O^{••}]$, region of the simplification of the electrical neutrality condition. In Fig. 4 an acceptor impurity, $I_m$, is added (always fully ionized to $I_m'$) to the binary oxide $M_2O_5$ described in Fig. 3. Note that for sufficient

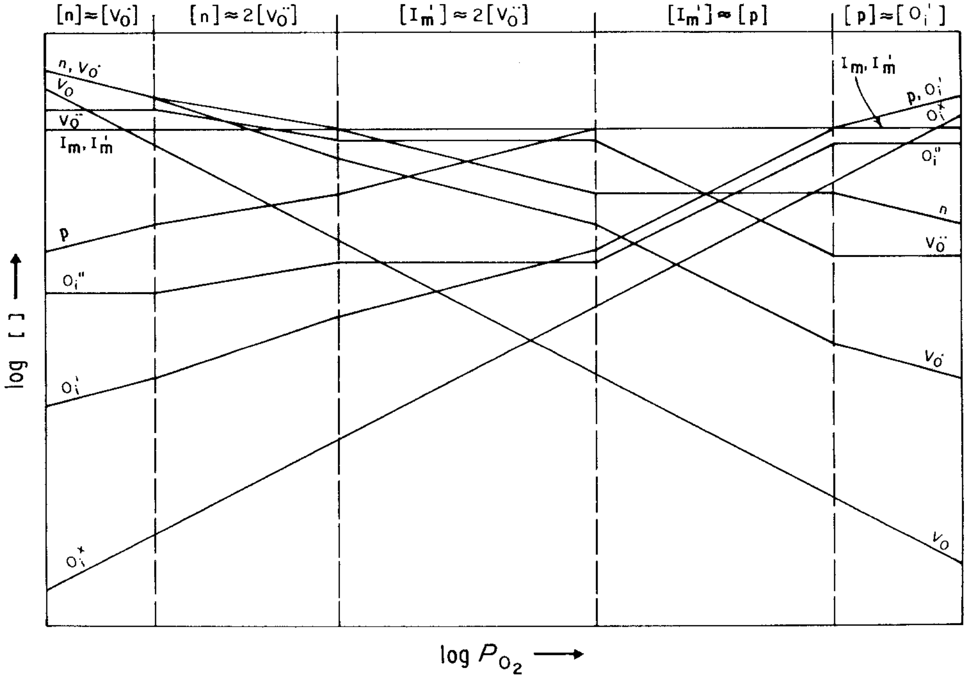

*Figure 4* Concentration of defects as a function of oxygen pressure for the oxide $M_2O_5$ with a fully ionized acceptor impurity, $I_m'$, and Frenkel disorder.

departures from stoichiometry it may be possible for the electrical conductivity to be controlled by $[\mathrm{n}] \approx [\mathrm{V}_\mathrm{o}^{\cdot}]$ and $[\mathrm{n}] \approx 2[\mathrm{V}_\mathrm{o}^{\cdot\cdot}]$ and to thereby mask the effect of the acceptor dopant. The occurrence of an impurity insensitive region within the experimental conditions of temperature and oxygen partial pressure depends on the amount of the acceptor impurity present in the sample.

In Fig. 4, there is a region with an electrical neutrality condition, $[\mathrm{I}'_\mathrm{m}] \approx 2[\mathrm{V}_\mathrm{o}^{\cdot\cdot}]$, in which the electron concentration varies as the $-1/4$th power and the electron hole concentration increases as the $+1/4$th power of oxygen partial pressure. In this region, for certain values of $P_{\mathrm{O}_2}$, the electron concentration is greater than the electron hole concentration and, hence, the conductivity is n-type with a $+1/4$th dependence on $P_{\mathrm{O}_2}$. As the oxygen partial pressure increases, the electron hole concentration becomes greater than the electron concentration after a certain value of $P_{\mathrm{O}_2}$ and the material becomes p-type with a $+1/4$th dependence of the conductivity on $P_{\mathrm{O}_2}$. When the $P_{\mathrm{O}_2}$ value is increased further, the electron hole concentration becomes equal to the acceptor concentration, which is constant, and, hence, the electrical conductivity is independent of $P_{\mathrm{O}_2}$, with the charge neutrality condition, $[\mathrm{I}'_\mathrm{m}] \approx [\mathrm{p}]$, as shown in Fig. 4. The observation of p-type behaviour depends on the concentration of acceptor impurity present, temperature and $P_{\mathrm{O}_2}$.

The observed slope of $-1/4$ in this region of $P_{\mathrm{O}_2}$ is interpreted in terms of the presence of negatively charged impurity, i.e., an acceptor impurity such as Fe, Al or Ca on Nb sites. The $\alpha$-$\mathrm{Nb_2O_5}$ sample used in this investigation as well as those used by earlier workers [11–19] contain Fe as a major impurity (≈400 ppm). Balachandran and Eror [28] were able to observe an extensive range of $P_{\mathrm{O}_2}^{-1/4}$ dependence for conductivity in the oxygen-deficient region below the p–n transition in $\mathrm{SrTiO_3}$ due to the presence of acceptor (Fe, Al) impurities in their samples. The presence of iron in the niobium oxalate solution and iron pick-up, if any, from the hardened steel die used for pressing the sample will lead to the observed slope of $-1/4$ in the $\log \sigma$ against $\log P_{\mathrm{O}_2}$ plots (Fig. 1). Thus, the condition of charge neutrality in this region can be

$$[\mathrm{V}_\mathrm{o}^{\cdot\cdot}] \approx [\mathrm{I}''_\mathrm{m}] = \text{constant}, \tag{7}$$

where $\mathrm{I}''_\mathrm{m}$ is a doubly charged acceptor impurity and in the present case it will represent $\mathrm{Fe}^{3+}$ on $\mathrm{Nb}^{5+}$ site, i.e., $\mathrm{Fe}''_{\mathrm{Nb}}$. This is in agreement with the later interpretation by Kefstad [24].

Two valence states are possible for Nb and Fe, namely $\mathrm{Nb}^{5+}$, $\mathrm{Nb}^{4+}$ and $\mathrm{Fe}^{3+}$, $\mathrm{Fe}^{2+}$. The different valence states will not change the results except for a change in magnitude of the conductivity values.

With the neutrality condition given in Equation 7, Reaction 1 and Equations 2 and 5, the conductivity varies with oxygen partial pressure as:

$$\sigma = [\mathrm{I}''_\mathrm{m}]^{-1/2} P_{\mathrm{O}_2}^{-1/4} e\mu \exp[\Delta S_\mathrm{f}/2R] \exp[-\Delta H_\mathrm{f}/2RT]. \tag{8}$$

The slopes listed in Table IB are in excellent agreement with the value of $-1/4$ predicted by the above impurity model. The values of $(\Delta H_\mathrm{f}/2)$ derived from the Arrhenius slopes (see Fig. 5) are shown in Table III. An average value of 1.68 eV (38.74 kcal mol$^{-1}$) is estimated for $(\Delta H_\mathrm{f}/2)$ in this region. This value is in good agreement with the value of 1.65 eV (38 kcal mol$^{-1}$) reported by Kofstad [14] at 1 atm oxygen. It must be pointed out, however, that in view of the lack of knowledge regarding the temperature dependence of the electron mobility, such an estimation of the value of $\Delta H_\mathrm{f}$ must be taken with caution. In fact, this value of 1.68 eV is considerably larger than the 1.4 eV obtained by Chen and Swalin [19].

If the oxygen vacancy concentrations are determined by the impurity content at higher oxygen partial pressures, and depending on the ratio of oxygen vacancy and electron concentration, one may expect a significant contribution of ionic conductivity. Elo *et al.* [22] measured the potential across sintered $\mathrm{Nb_2O_5}$ specimens when exposing opposite sides to oxygen with partial pressures of 1 atm and $5 \times 10^{-5}$ atm, and could on this basis estimate the ionic transport number to within a factor of two. For undoped $\mathrm{Nb_2O_5}$ (but with unspecified purity) the ionic transport number, $t_\mathrm{i}$, was less than 0.05 between 1000 and 1200 K.

TABLE III Arrhenius slopes for $\mathrm{Nb_2O_5}$ in the $P_{\mathrm{O}_2}$ region greater than $10^{-6}$ atm

| $P_{\mathrm{O}_2}$ (atm) | Arrhenius slopes (kcal mol$^{-1}$) |
|---|---|
| $2.0 \times 10^{-6}$ | 38.16 |
| $10^{-5}$ | 38.30 |
| $10^{-4}$ | 39.21 |
| $10^{-3}$ | 39.44 |
| $10^{-2}$ | 39.10 |
| $5.0 \times 10^{-2}$ | 38.87 |
| $2.1 \times 10^{-1}$ | 38.53 |
| $10^{0}$ | 38.30 |

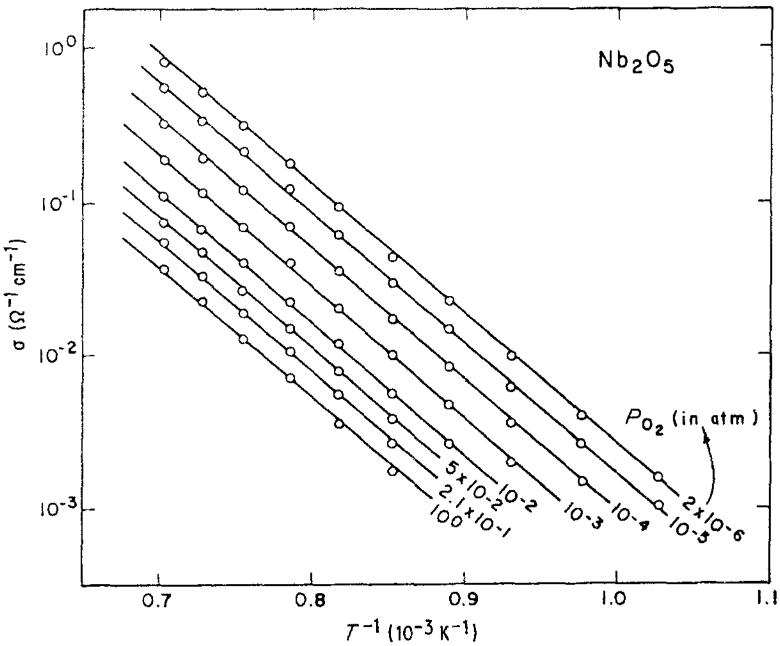

*Figure 5* Temperature dependence of electrical conductivity of polycrystalline $\alpha$-$Nb_2O_5$ in the region $10^0$ to $2 \times 10^{-6}$ atm.

### *3.1.3. p-type region*

The observation of p-type behaviour at oxygen partial pressures greater than $10^{-2}$ atm and temperatures below 900° C can be explained on the basis of the impurity effect. It is seen from Fig. 4 that in the region with the neutrality condition $[I'_m] \approx 2[V_o^{\cdot\cdot}]$, there is a region where $[p] > [n]$. The electronic conductivity would be controlled by the electron holes, where $[p] \propto P_{O_2}^{1/4}$. For the case of $\alpha$-$Nb_2O_5$ the electron hole concentration becomes greater than the electron concentration at temperatures below 900° C and near atmospheric pressures. This results in the p-type behaviour as seen in Fig. 1. It is shown [28] in $SrTiO_3$ and $BaTiO_3$ [29] that the region of linearity in the p-type region (due to the presence of accidental acceptor impurities) increases in width with decreasing temperature as the p–n transition moves to lower $P_{O_2}$. The $P_{O_2}$ value where the p–n transition occurs in the present case also moves to lower $P_{O_2}$ as the temperature is decreased. For temperatures above 900° C, p-type conductivity may be observed at oxygen partial pressures much greater than 1 atm. Under such high $P_{O_2}$ values, the conductivity should vary as the + 1/4 power of oxygen partial pressure as predicted by the Kroger–Vink diagram [27].

The p-type conductivity arises from the incorporation of oxygen into the impurity-related oxygen vacancies where the reaction is,

$$[V_o^{\cdot\cdot}] + 1/2O_2 \rightleftharpoons O_o + 2h^{\cdot} \qquad (9)$$

where $[p] \equiv h^{\cdot}$. The charge neutrality condition in this region would still be as Equation 7. The chemical mass action expression for Equation 9 combined with Equation 7 gives

$$\sigma \propto P_{O_2}^{1/4}, \qquad (10)$$

provided that only a minor fraction of the impurity-related $V_o^{\cdot\cdot}$ is filled.

### *3.1.4. Electrical conductivity at temperatures below 800° C*

One of the critical observations of this investigation is the measurement of the electrical conductivity in $\alpha$-$Nb_2O_5$ at temperatures below 800° C without any hysteresis effect. The $P_{O_2}$ dependence of conductivity at temperatures below 800° C is similar to those measured at higher temperatures except for the p-type behaviour at $P_{O_2} > 10^{-2}$ atm when the measurements are carried out below 800° C. Previous measurements [14, 19] on $\alpha$-$Nb_2O_5$ below approximately 800° C revealed unexpected results with respect to the oxygen pressure dependence of the conductivity. Kofstad [14] reported a sharp decrease in the resistance of the sample at ~750° C and a $P_{O_2}$ value below approximately $10^{-2}$ atm. He also observed hysteresis effects when measuring the electrical resistance at decreasing and increasing oxygen pressures. Chen and Swalin [19] associated their unexpected results below 800° C to the surface-reaction-controlled conduction.

In the present experiments, no hysteresis effect

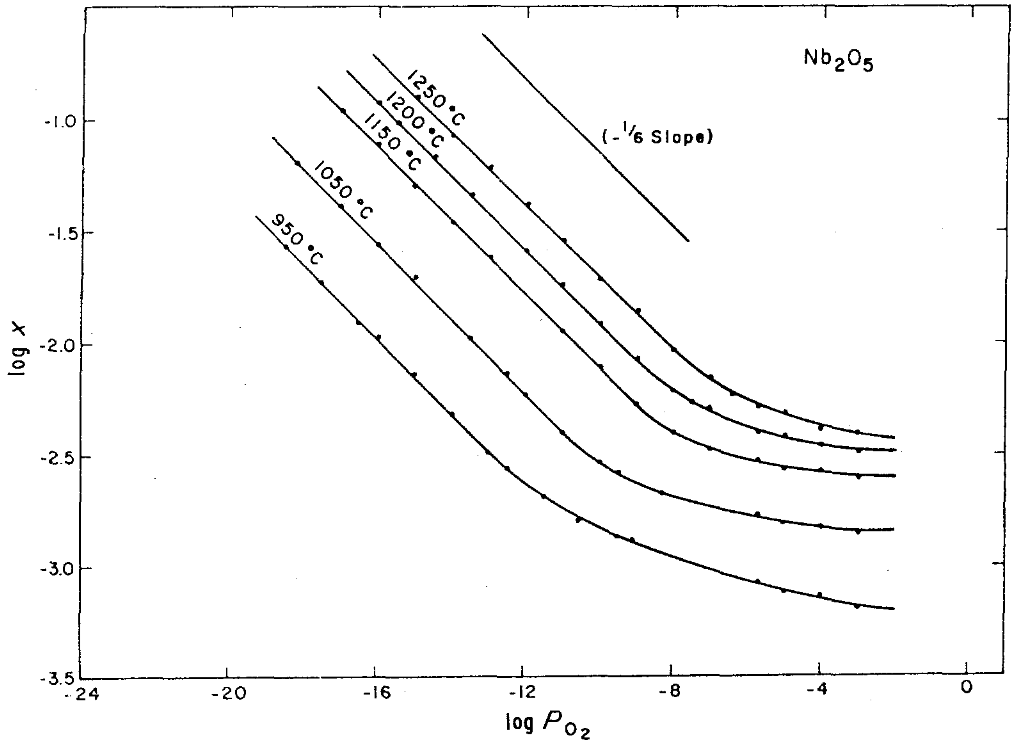

*Figure 6* The logarithm of $x$ (in $Nb_2O_{5-x}$) as a function of the logarithm of oxygen partial pressure in the temperature range 950 to 1250° C.

is observed in the electrical conductivity measurements taken at decreasing and increasing temperature and oxygen partial pressures. The present results are thus in disagreement with the earlier studies [14, 19].

## 3.2. Thermogravimetric measurement

The change in weight of the sample as a function of temperature and oxygen partial pressure gives a measure of the corresponding change in the non-stoichiometry of the oxide. The compositional state or oxygen content of the specimen was determined assuming all of the detectable weight loss observed as the $P_{O_2}$ values were changed was due to a loss of oxygen from stoichiometric $Nb_2O_5$ (the state obtained by firing at infinite oxygen pressure). The weight of the exactly stoichiometric $Nb_2O_5$ sample was obtained by extrapolating the relative weight change of the $\alpha$-$Nb_2O_5$ sample against $P_{O_2}^{-1/6}$ plots (for $P_{O_2} < 10^{-12}$ atm) to infinite oxygen pressure. From the weight changes, values of $x$ in $Nb_2O_{5-x}$ have been evaluated, and in Fig. 6 is shown a plot of $\log x$ as a function of $\log P_{O_2}$. The thermogravimetric isotherms at 950 to 1250° C exhibit a ~ − 1/6th slope in the same $P_{O_2}$ region as those observed in electrical conductivity experiment (conductivity was measured only to 1150° C). For higher $P_{O_2}$ values, the value of $x$ becomes almost independent of $P_{O_2}$.

Earlier studies [13, 20, 21] on the thermogravimetric analysis of $\alpha$-$Nb_2O_5$ were carried out for oxygen partial pressures below $10^{-7}$ atm. The homogeneity range of $Nb_2O_{5-x}$ was proposed to extend to values of $x$ approximately 0.1 at 900° C and 0.155 at 1100° C by Blumenthal *et al.* [20]. The maximum non-stoichiometry obtained in this work corresponds to $x = 0.126$ at 1250° C and $P_{O_2} = 10^{-15}$ atm. This value is in disagreement with the studies of Schäfer *et al.* [21] who estimated that maximum non-stoichiometry at 1300° C corresponded to a value of $x \sim 0.022$. It may be noted that Schäfer *et al.* [21] analysed the oxide compositions after cooling to room temperature, while in the present study the measurements are made thermogravimetrically at elevated temperature [24].

The ~ − 1/6th slope obtained in Fig. 6 indicates that the doubly ionized oxygen vacancies are the predominant defects at concentrations of $x$ larger than approximately $3 \times 10^{-3}$. The defect reaction is

$$O_o \rightleftharpoons 1/2O_2 + V_o^{\cdot\cdot} + 2e', \qquad (11)$$

i.e. identical to Equation 1. Kofstad and Anderson [13] found that $n = 6$ in $x \propto P_{O_2}^{-1/n}$, and this was rationalized assuming that doubly charged oxygen vacancies are the predominant defects. Schäfer *et al.* [21] suggested from their studies that $x \propto P_{O_2}^{-1/4}$, and proposed that the interstitial niobium ions with four effective charges are the predominant defects in $Nb_2O_5$. However, a definite conclusion should not be drawn considering the large scatter in their results [24]. Judging from the present electrical conductivity and thermogravimetric studies, it is more probable that oxygen vacancies are the predominant defects under low oxygen activity regions.

If the interpretation of the results from both electrical conductivity measurements and the thermogravimetric study is correct, there should be a transition of the defect structure from predominantly doubly ionized oxygen vacancy to impurity-controlled defects as the oxygen partial pressure is increased. This is reflected in Fig. 6 where the $\log x$ against $\log P_{O_2}$ curves become almost independent of $P_{O_2}$ in the same oxygen pressure region in which the electrical conductivity was found to be proportional to $P_{O_2}^{-1/4}$ (see Fig. 1). The oxygen vacancy concentrations are determined by the acceptor impurity content in the sample with charge neutrality condition given by Equation 7. The concentration of oxygen vacancies is constant and, therefore, there will be no change in relative weight of the sample as $P_{O_2}$ values are changed in the region where the defect structure is controlled by acceptor impurities. The impurity-controlled region becomes narrow as the temperature is increased. The thermogravimetric measurement (Fig. 6) which gives the oxygen vacancy concentration yields a $-1/6$th dependence on $P_{O_2}$ in the same region where the conductivity was found to be proportional to $P_{O_2}^{-1/6}$ and a region nearly independent of $P_{O_2}$ in which the conductivity was proportional to $P_{O_2}^{-1/4}$.

Thus, the electrical conductivity measurement and the thermogravimetric study on $\alpha$-$Nb_2O_5$ are consistent in explaining the observed behaviour in the entire range of temperature and oxygen partial pressure covered in this work.

## 4. Conclusions

The experimental results on electrical conductivity agree well with the predictions based on a doubly ionized oxygen vacancy defect model in the $P_{O_2}$ range $10^{-20}$ to $10^{-9}$ atm and temperature range 700 to 1150° C. The $P_{O_2}$ region in which the doubly ionized oxygen vacancies are the dominant defects becomes narrow as the temperature is decreased. The logarithm of the electrical conductivity is a linear function of the lograrithm of $P_{O_2}$ at constant temperature. A slope of $-1/6$ is observed in this region of oxygen partial pressure and this agrees with the predicted value.

The defect chemistry of $\alpha$-$Nb_2O_5$ is dominated by accidental acceptor impurities and their related oxygen vacancies, as $P_{O_2}$ is increased, see Equation 7:

$$[I_m''] \approx [V_o^{\cdot\cdot}] = \text{constant}.$$

Because of these acceptor impurities, a region in which there is a $P_{O_2}^{-1/4}$ dependence for conductivity is observed. The p-type conductivity observed in the region $P_{O_2} > 10^{-2}$ atm at temperatures below 900° C results from the incorporation of oxygen into the impurity-related oxygen vacancies, Equation 9.

Measurements on $\alpha$-$Nb_2O_5$ below 800° C revealed no unexpected results with respect to the oxygen pressure dependence of the electrical conductivity. No hysteresis effects were observed when measuring the conductivity at increasing and decreasing oxygen pressures and temperatures.

Thermogravimetric measurements in the temperature range 950 to 1250° C indicated that the deviation from stoichiometry in $\alpha$-$Nb_2O_5$ ($x$ in $Nb_2O_{5-x}$) varies as the $\sim -1/6$th power of $P_{O_2}$ in the same $P_{O_2}$ region in which the conductivity was observed to be proportional to $P_{O_2}^{-1/6}$. A region where $x$ is nearly independent on $P_{O_2}$ is observed at higher $P_{O_2}$ values. The electrical conductivity and thermogravimetric data are consistent with the presence of small amounts of acceptor impurities in the $\alpha$-$Nb_2O_5$.

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