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THERMOELECTRIC POWER IN NONSTOICHIOMETRIC $\alpha\text{-Nb}_2\text{O}_5$

by

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Department of Materials Science

The Technological Institute

Northwestern University

Evanston, Illinois



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ABSTRACT

Thermoelectric power measurements have been made on nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ over the temperature range from 300° to 1270°K. The measurements show that, for all compositions in the single-phase, $\alpha\text{-Nb}_2\text{O}_{5-x}$ region ($0.0012 \leq x \leq 0.1545$), the majority charge carriers are electrons. These thermoelectric power data have been interpreted in terms of a simple semiconductor exhibiting conduction in a narrow d-band with the conduction electrons being assigned an effective mass equal to four times that of the rest mass.

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INTRODUCTION

There has been considerable interest shown recently in the electrical properties of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$. The work of Kofstad and Anderson¹ and Kofstad² on the thermogravimetric properties of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ and on the isothermal oxygen partial pressure dependence of the electrical conductivity has been interpreted on the basis of an oxygen-ion defect structure occurring in the nonstoichiometric state. The oxygen ion vacancy is believed to be capable of contributing one or both of its trapped electrons in the conduction process.

Valletta³ has recently reported on the electrical conductivity and thermoelectric power of heavily, tungsten doped Nb_2O_5 . He interpreted his data in terms of mixed-valence semiconduction, ascribing the observed thermoelectric power to an entropy of mixing of electrons on cation sites. However, the experimental values at lower temperatures are much lower than would be predicted by such an entropy of mixing term.

Recently, Janninck and Whitmore⁴ have measured the electrical conductivity of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ in specimens of fixed oxygen concentrations. Their observations may also be rationalized in terms of a nonstoichiometric oxygen-ion defect structure; however, it was found difficult to interpret the negative temperature coefficient of the electrical conductivity at high temperatures in terms of a hopping-type conduction mechanism which has been suggested for this type of material.^{3,5,6} Instead, this phenomenon was interpreted in terms of donor exhaustion at high temperatures with conduction occurring in a narrow d-band.

The purpose of the present investigation was to systematically measure the thermoelectric power of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ in an attempt to gain a better understanding of the mechanism of electrical conduction in this oxide.

EXPERIMENTAL DETAILS

The experimental technique employed in this investigation was very similar to that used in the measurement of the electrical conductivity of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$.⁴ The four electrical probes of the conductivity jig were replaced with two platinum vs platinum - 10% rhodium thermocouples which had been calibrated against each other so that the errors involved in the measurement of small temperature differences would be minimized. The platinum legs of the thermocouples immediately adjacent to the junctions were pressed against the ends of the specimen by means of the quartz jig. Both the temperature at each end of the specimen and the thermoelectric voltage of the specimen between the two platinum probes were measured with the aid of a Leeds and Northrup type K-2 potentiometer. A small auxiliary heater was added at one end of the specimen jig so that a temperature gradient could be established along the oxide specimen.

The specimens employed in this investigation were identical to those used in the electrical conductivity experiments which have been previously reported.⁴ The specimens were prepared from high-purity oxide powder* by pressing in a steel die to a pressure of 20,000 psi and sintering at 1390°C for 3 hours. It has been demonstrated that this treatment produces a very dense $\alpha\text{-Nb}_2\text{O}_5$ specimen.⁷ The thermoelectric power specimens were cut from the sintered bars so as to have an average size of 1.5 cm long by 0.5 cm wide by 0.2 cm thick and a weight of approximately 700 milligrams.

The departures from stoichiometry were produced by means of an isopiestic reduction technique^{4,8} which was followed by an homogenization anneal at 1100°C for several days.

The compositional state or oxygen content of the specimens, prior to and following the thermoelectric power measurements, was determined by means of weight measurements, assuming all of the detectable weight loss was due to a

* High purity Nb_2O_5 powder was kindly supplied by the Fansteel Metallurgical Corp., North Chicago, Illinois, with a total reported impurity content of < 1250 ppm. Identical results were obtained with specimens made from high purity Nb_2O_5 powder obtained from the Johnson-Matthey Co., Ltd., with a reported purity of Ta < 100 ppm, Si 30 ppm, Fe 10 ppm, and Mg < 1 ppm.

loss of oxygen from stoichiometric Nb_2O_5 (the state obtained by firing Nb_2O_5 in air). This assumption was verified by weighing a specimen before reduction, after reduction, and again after reoxidation. The initial and final oxidized weights of the specimen were identical within the precision of weighing ($\pm 20 \mu\text{g}$) for several cycles.

By flowing a highly purified argon gas over the nonstoichiometric specimen, the composition could be held reasonably constant during the course of making the measurements at elevated temperatures. In the case of each thermoelectric power measurement, the temperature of the specimen was allowed to reach a steady value before the temperature gradient and the thermoelectric voltage were measured. The thermoelectric power, Q , is taken as the thermoelectric voltage divided by the temperature difference across the probes. A temperature difference of approximately 10°C was maintained between the probes.

RESULTS AND DISCUSSION

The thermoelectric power of pressed-and-sintered $\alpha\text{-Nb}_2\text{O}_{5-x}$ was measured as a function of the composition ($0.0012 \leq x \leq 0.1545$) and as a function of temperature over the range 300° to 1270°K . This compositional range covers the entire range of stability for the homogeneous phase except for compositions very close to stoichiometry where a fixed oxygen composition could not be maintained in the specimen by means of the present experimental technique. Figures 1 to 3 show the temperature dependence of the thermoelectric power for the various states of nonstoichiometry. The specimen numbers and compositional data are listed in Table I. It is noteworthy that the present data show this oxide to be an n-type semiconductor at all times.

The electrical properties can be accounted for on the basis of a standard semiconductor with a simple band structure. In the light of the earlier electrical conductivity data reported for this oxide,⁴ the compositions and temperatures used here correspond to those of the exhaustion region of the conductivity, except in the case of specimens exhibiting the smallest departures from stoichiometry at the lowest temperatures where complete exhaustion of the donor states may not have occurred.

In such an exhaustion region, the simple band theory for an n-type- extrinsic semiconductor⁹ predicts that the thermoelectric power, Q , will be given by the expression:

$$Q = -\frac{k}{e} \{2 - \ln n_e + \ln n_o\} \quad (1)$$

where n_e is the number of conducting electrons per cm^3 , k is Boltzmann's constant, e is the electronic charge, and n_o is the effective density of electronic states at the conduction band edge. This last quantity is given by the relation:

$$n_o = \frac{2 (2\pi m^* kT)^{3/2}}{h^3} \quad (2)$$

where m^* is the effective mass of the electron, T is the absolute temperature, and h is Planck's constant.

If it is assumed that the nonstoichiometric defect in $\alpha\text{-Nb}_2\text{O}_{5-x}$ is an oxygen-ion vacancy which has contributed both of its trapped electrons to the conduction process, then, in an exhaustion region, $n_e = 2 N_D$ where N_D is the number of oxygen ion vacancies per cm^3 in the nonstoichiometric oxide. Assigning to the effective mass of the conduction electrons a value of $4 m_o$, Eq. (1) becomes

$$Q = -\frac{k}{e} \left\{ 2 - \ln 2 N_D + \ln \left[\frac{2 (8\pi m_o kT)^{3/2}}{h^3} \right] \right\} \quad (3)$$

Since the effective electron mass for nonstoichiometric rutile (TiO_2) has been estimated to be 12 to 32 times that of the rest mass,^{10,11} an effective mass value of $4 m_o$ in the case of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ appears to be reasonable.

Figure 4 is a plot of the isothermal variation at 500° and 1270°K of the thermoelectric power measurements with composition. Also indicated in this figure are the variations in thermoelectric power to be expected at the same two temperatures on the basis of Eq. (3). It is noteworthy that rather good agreement exists between the predictions of Eq. (3) and the empirical results.

If, on the other hand, a polaron conduction mechanism is assumed for this

oxide in spite of the observation of an exhaustion region in the electrical conductivity of this nonstoichiometric oxide, an expression for the thermoelectric power may be obtained in a manner analogous to that given by Aronson et al¹² for nonstoichiometric UO_2 . Accordingly, the thermoelectric power expression for tungsten-doped, $\alpha\text{-Nb}_2\text{O}_5$ has been reported to be:³

$$Q = \frac{\bar{S}_q}{e} + \frac{\bar{S}_{\text{add.}}}{e} + \frac{Q_q^*}{eT} + \left(\frac{kT}{e} \right) \frac{d \ln N_q}{dT} \quad (4)$$

where $\bar{S}_{\text{add}}$ is the entropy change due to factors such as vibrational entropy, Q_q^* is the heat of transport of charge carriers, N_q is the number of charge carriers, and $\bar{S}_q$ is the entropy change due to addition of a charge carrier to the aggregate of cation sites. If only the entropy of mixing term is considered, Eq. (4) reduces to

$$Q = - \frac{k}{e} \ln \left(\frac{1-x}{x} \right) \quad (5)$$

where x is a measure of the departure from stoichiometry as indicated by the formula $\text{Nb}_2\text{O}_{5-x}$ (see Table I for the magnitude of this quantity).

For comparison purposes, a plot of Eq. (5) is also given in Fig. 4 by the dashed line. It should be observed that agreement with the experimental data at 1270°K is not nearly as good in the case of Eq. (5) as that exhibited by Eq. (3). Furthermore, the agreement becomes poorer as the temperature is lowered because the relation given in Eq. (5) shows no temperature dependence. This disparity between the thermoelectric results predicted by Eq. (5) and experiment, as well as the observation of an exhaustion region in the electrical conductivity, tends to indicate that conduction occurs in a narrow d-band.

TABLE I

Table of Specimen Compositions and Defect Concentrations

Specimen Number	Initial Wt.% Loss	Final Wt.% Loss	Average Wt.% Loss	x in $\text{Nb}_2\text{O}_{5-x}$	Oxygen Vacancy Concentration cm^{-3}
59-17	0.00634	0.00817	0.00725	0.0012	1.24×10^{19}
49-23	0.0134	0.00635	0.00987	0.0016	1.69×10^{19}
68-15-JM ^a	---	0.0119	0.0119 ^b	0.0020	2.03×10^{19}
64-19	0.00860	0.0195	0.0141	0.0023	2.41×10^{19}
62-20	0.0300	0.0274	0.0287	0.0048	4.91×10^{19}
45-21	0.0364	0.0382	0.0373	0.0062	6.38×10^{19}
63-16	0.0538	0.0572	0.0555	0.0092	9.49×10^{19}
45-13	0.0760	0.0687	0.0723	0.0120	1.24×10^{20}
60-14	0.0795	0.0801	0.0798	0.0133	1.36×10^{20}
59-28	0.114	0.110	0.112	0.0186	1.91×10^{20}
60-27	0.243	0.230	0.236	0.0392	4.04×10^{20}
68-25-JM ^a	0.250	0.233	0.241	0.0400	4.12×10^{20}
45-2	---	0.458	0.458 ^b	0.0761	7.83×10^{20}
63-26	0.575	0.529	0.552	0.0916	9.44×10^{20}
64-24	0.683	0.654	0.668	0.1110	1.14×10^{21}
49-12	0.958	0.903	0.930	0.1545	1.59×10^{21}

^a Johnson-Matthey material.

^b Final composition only.

FIGURE CAPTIONS

- Fig. 1 - Thermoelectric power of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ as a function of temperature for several different compositions.
- Fig. 2 - Thermoelectric power of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ as a function of temperature for several different compositions.
- Fig. 3 - Thermoelectric power of nonstoichiometric $\alpha\text{-Nb}_2\text{O}_5$ as a function of temperature for several different compositions.
- Fig. 4 - The compositional dependence of the isothermal thermoelectric power of $\text{Nb}_2\text{O}_{5-x}$ at 500° and 1270°K.

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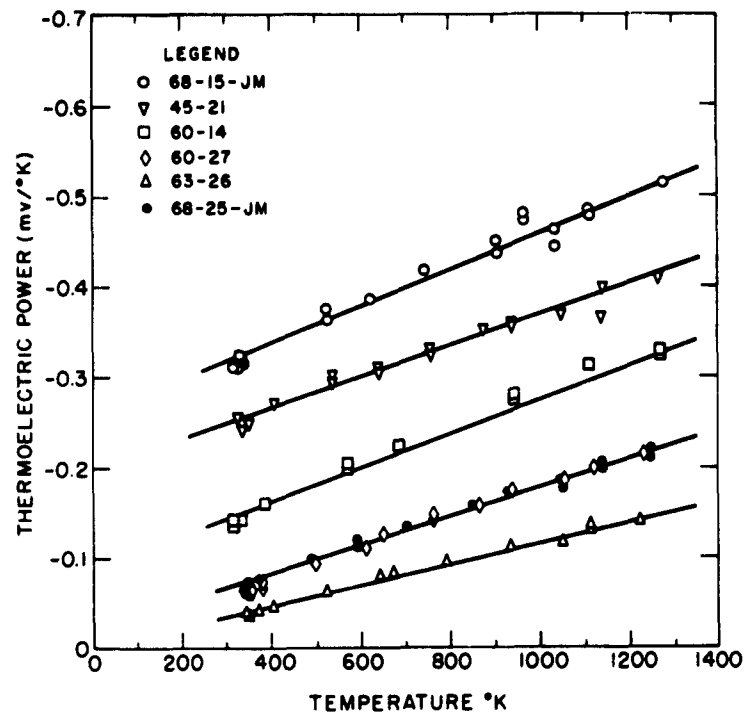


Figure 1

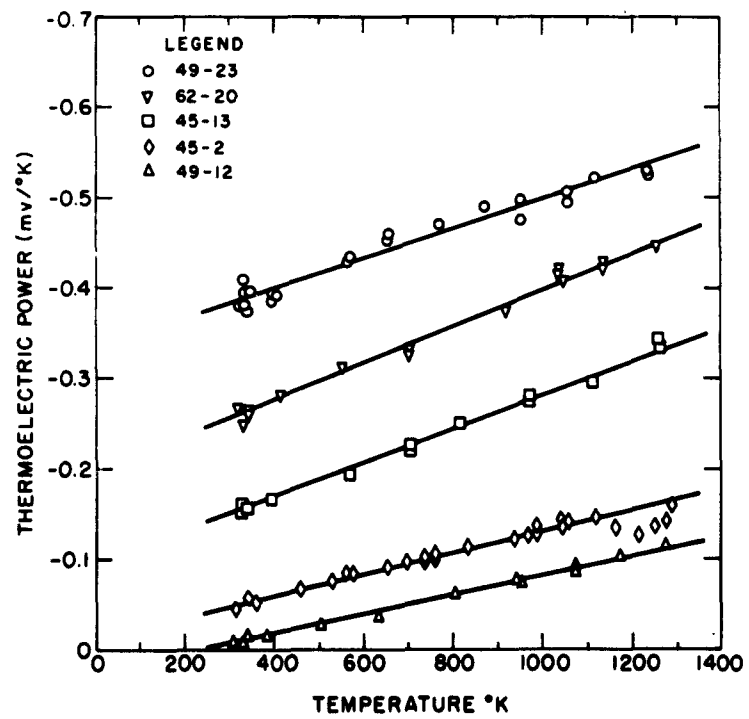


Figure 2

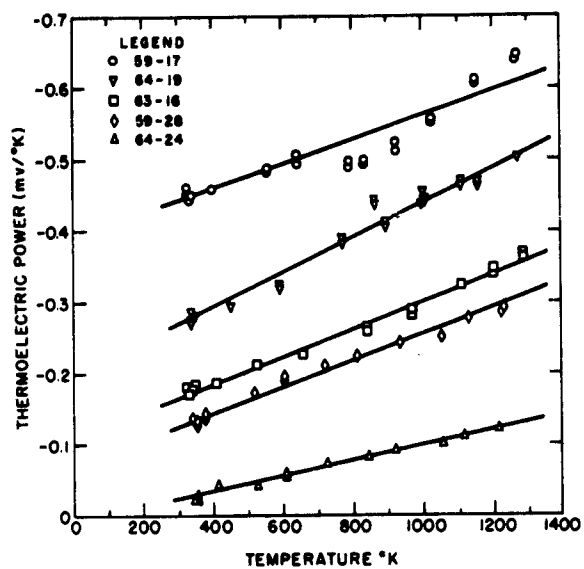


Figure 3

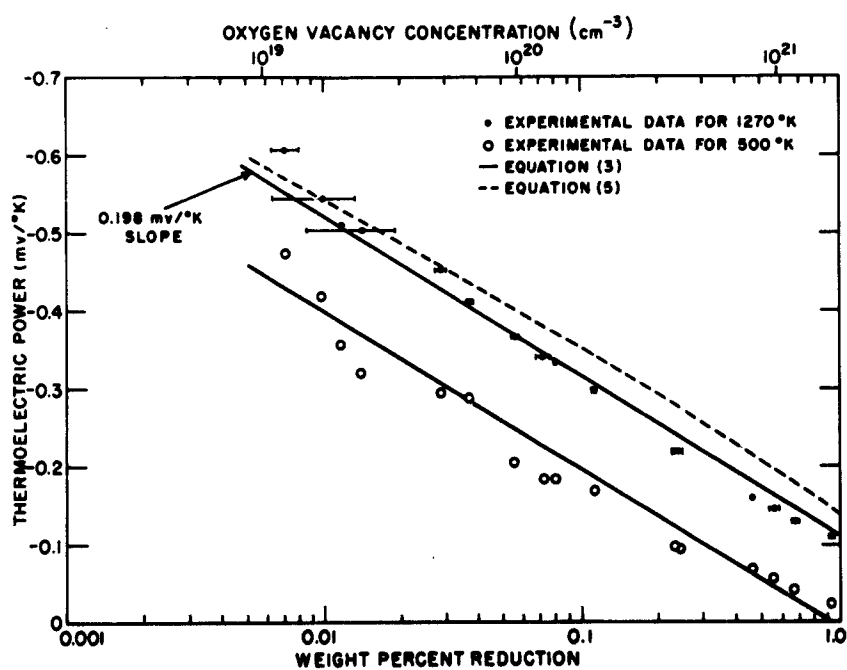


Figure 4

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