ELECTRICAL CONDUCTIVITY OF UO_2 :
PART II. FINAL REPORT

J. LAMBERT BATES

NOVEMBER, 1967

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PART II. FINAL REPORT

By

J. Lambert Bates

Materials Research Section
Materials Department

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ELECTRICAL CONDUCTIVITY OF UO_2 : PART II. FINAL REPORT

INTRODUCTION

The electrical conductivity of single-crystal UO_2 has previously been determined by direct current (dc) measurements from 298 to 3000 °K.⁽¹⁾ The purpose of this study was to determine the electrical conductivity of single-crystal UO_2 by alternating current (ac) measurements as a function of frequency; and to determine the ac and dc conductivities of polycrystalline, sintered UO_2 . A statistical analysis of the intrinsic conduction above 1400 °K was made using a least squares, polynomial-fitting, computer program.

Reported effects of grain size and porosity on the extrinsic electrical conductivity of UO_2 have been largely incomplete. Wolfe⁽²⁾ observed a significant difference in extrinsic conductivity as a function of grain size, the larger grain oxide having the higher conductivity. Iida⁽³⁾ reported that sintered, hypostoichiometric UO_{2-x} exhibited a much higher conductivity than the single crystal UO_{2-x} .

Above temperatures of 1100 to 1300 °K, intrinsic conduction is reported.^(2,4,5) In this temperature range (1100 to 1400 °K) the conduction in nearly stoichiometric UO_2 changes from p-type to n-type which is typical of intrinsic semiconductors. The reported activation energies vary from 1.5 to 0.95 eV.^(2,4) However, the high-temperature intrinsic data were deter-

mined over a relatively small temperature range.

It was thus evident from the available data that electrical conductivity in UO_2 at high temperatures was not understood and that there was an important need to determine the electrical conductivity of UO_2 by both ac and dc measurements and to compare the conductivity of single crystal and polycrystalline UO_2 over the entire temperature range to 3000 °K.

SUMMARY

The electrical conductivity of nearly stoichiometric single crystal and polycrystalline UO_2 was measured from room temperature to 3000 °K. The electrical conductivity values of polycrystalline UO_2 were the same as the values for single crystal UO_2 . The results show no significant difference between the ac (5 to 5000 Hz) and dc conductivity values at all temperatures. The electrical conductivity is intrinsic above 1400 °K. The best linear fit of the $\ln \sigma$ versus T^{-1} curve above 1400 °K showed

$$\sigma = 3.57 \times 10^3 e^{-1.15 \text{ eV}/kT}$$

The best fit of the data above 1900 °K is obtained with the equation

$$\sigma = 2.104 \times 10^{-2} T^{1.40} e^{-0.916 \text{ eV}/kT}$$

EXPERIMENTAL DETAILSURANIUM DIOXIDE SAMPLES

Electrical conductivity measurements were determined for three single crystal and two polycrystalline specimens. The UO_2 single crystal specimens were machined from large crystal boules grown from an arc-fused melt. Crystals were heated for 12 hr in commercial grade hydrogen at 1700 °C prior to machining. The specimens were of undetermined crystallographic orientation.

The polycrystalline UO_2 specimen was machined from a large UO_2 cylinder which had been cold pressed and sintered in commercial grade hydrogen at 1700 °C for 12 hr.

Each specimen was heat-treated in the electrical-conductivity apparatus for 8 to 12 hr at 1125 °K in purified 8% hydrogen-argon prior to conductivity measurements.⁽¹⁾ The O:U ratio of the crystals after this heat treatment deviated only slightly from stoichiometric UO_2 (O:U < 2.001). The O:U ratio, density, and impurity level of each specimen is given in Table I.

TABLE I. Description of Uranium Dioxide Specimens

	Specimen Designation	O:U ^(a) Ratio	Density, ^(b) g/cm ³	Impurity Content, ^(c) ppm
A. <u>Single Crystal UO_2</u>				
	MR-5	2.001	10.97	Al 2 Cr <5 Si 35 As <2 Fe 41 Zn <50 Ca 2 Mg 1 Co <10 Na <2 All others total <1.
	B-40-A	2.001	10.97	Al 5 Mg 1 V <50 Ca 1 Ni <5 Zn <50 Cr <5 Pb 3 Fe 10 Si 21 All others total <1.
B. <u>Polycrystalline UO_2</u>				
	EC-P-3A	2.001	10.39	Al 500 Mn 5 Te <10 Cr <5 Ni <5 V <50 Cu 20 P 50 Zn <50 Mg 10 Pb 5 All others total <1.
	B-38-C	2.001	10.19	Al 1000 Fe 66 Ni 5 Ca 2 Mg 10 Si 27 Cr 5 Mo 5 Sn <50 Cu 5 Na <2
	EC-P-1A	2.001	10.29	Al 1000 Cu 0.5 Mo <5 Bi 1 Fe 43 Na <2 Ca 5 Ge <0.5 Ni 5 Cr <5 Mg 5 Si 27 Sn <5 V <50 All others <1.

(a) O:U were determined by coulometry after electrical conductivity measurements.

(b) Determined by mercury displacement.

(c) Determined by emission spectroscopy.

ELECTRICAL-CONDUCTIVITY APPARATUS

Electrical conductivity was measured using a four-contact method (Figure 1). A tungsten mesh element with a hot zone, 3.5 cm diam and 9 cm long, was heated by direct current from motor-driven generators. The oxide specimens (0.63 cm diam and 1.9 cm long) were held in the furnace between two tungsten holders. These holders were also used as current leads during conductivity measurements. Two sharp-pointed, tungsten rods were set into very shallow holes 0.63 cm apart on the specimen surface to measure the voltage drop across the specimen. Good contacts were main-

tained by applying a small pressure to these probes. Since no current was permitted to flow through these probes, relatively high contact resistances could be tolerated.

The electrical measurement consisted of passing a constant alternating or direct current through the specimen and measuring the resulting potential difference between the two probes, (Figure 2). Direct current was provided from a solid-state power supply. The direction of the current was reversed as rapidly as possible and the current-voltage relationship was measured with current flow in both directions. An average of the two values was used to calculate the resistance. The alternating current was provided from a wide-range oscillator (5 Hz to 600 kHz). Most measurements were made

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FIGURE 1. Schematic Representation of Four Probe, Electric Conductivity Apparatus

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FIGURE 2. Schematic Representation of the Electrical Circuit for the Four Probe, Electrical Conductivity Apparatus

at frequencies less than 5000 Hz since measurements were complicated by a frequency dependence of the measuring circuit not associated with the oxide specimens. No frequency dependence of the conductivity was observed between 5 to 5000 Hz. Voltages were measured with a high resistance voltmeter. The current through the specimen was determined by measuring the voltage difference across a standard resistor in series with the specimen. The size of the resistor varied from 2.5 to 1000 ohms to provide the best current-voltage combination.

The measuring potential was varied between 0.01 and 10 V with most measurements between 0.01 to 1.0 V. The current through the specimen varied between 1 and 100 mA.

A switching device was used to conveniently change from the ac to dc measuring circuit. Approximately 10 to 30 sec were required for both ac and dc measurements at any one temperature.

ATMOSPHERE

Measurements were made in purified 8% hydrogen-92% argon at atmospheric pressure. The oxygen and water content of the gas introduced into the furnace was <1 ppm and <5 ppm, respectively. The partial pressure of oxygen during measurements at high temperatures was calculated using thermodynamic data for the decomposition of water in hydrogen. The calculated partial pressures of oxygen at 1125, 2025, and 2675 °K were 2.5×10^{-26} , 6.3×10^{-14} , and 8×10^{-13} atmospheres, respectively.

Measurements were initially made in purified dry argon and 8% hydrogen-argon with a relatively high water content. However, the measurements in the low-temperature range in these atmospheres were not reproducible during thermal cycles, apparently because of O:U changes in the relatively non-reducing atmosphere.

TEMPERATURE MEASUREMENTS

Temperatures were measured from 298 to 1850 °K using a Pt-Pt 13% Rh thermocouple positioned adjacent to the sample. At the higher temperatures the thermocouples were removed and temperatures were measured above 1050 °K with an optical brightness pyrometer. The system was calibrated using a UO_2 sample with a 0.040 cm diam, 0.32 cm deep hole drilled into the center of the rod. Corrections were made for the absorption of the pyrex window. Both thermocouple and pyrometer temperatures agreed to within ± 5 °K in the temperature range from 1100 to 1850 °K where both measurements could be made simultaneously. No temperature gradient across the sample was observed.

Measurements were made during both increases and decreases in temperature during a thermal cycle. The rate of temperature change (stepwise) was varied from approximately 2 °K/min to approximately 25 °K/min.

RESULTS AND DISCUSSION

The electrical conductivity below 1250 °K was not reproducible during

the initial measurements of a nonheat-treated specimen or when measurements were conducted in purified argon (1ppm O_2 and <10 ppm H_2O) or in 8% hydrogen-argon with a relatively high water content (approximately 100 ppm).⁽¹⁾ A hysteresis in the electrical conductivity occurred below 1250 °K during thermal cycling. The conductivity was higher on heating than during cooling. Above approximately 1250 °K, the conductivity values were the same in all atmospheres.

To eliminate the effects of the residual oxygen, measurements were made in a reducing atmosphere of 8% hydrogen-92% argon. Data which are reported represent reproducible conductivity values from as many as five thermal cycles from room temperature to 3000 °K.

Similar changes in UO_2 electrical conductivity in this temperature range (300 to 1150 °K) have been observed by other investigators.^(2,6-13) This nonreproducibility has been attributed to stoichiometric changes during heating resulting from the high oxygen content of the inert gases. Wolfe⁽²⁾ suggested that the variations were probably due to the oxidation of the specimen surface and not a homogeneous change in specimen stoichiometry.

Initial ac measurements indicated that the electrical conductivity of both polycrystalline and single crystal UO_2 increased with increasing frequency above 5 kHz at low temperatures and decreased with increasing frequency above 5 kHz at temperatures above 1250 °K (See Appendix A). Because of the unusual nature of these results,

further ac measurements were performed using other materials (such as graphite) to determine if these results were characteristic of the UO_2 or of the measuring system. The results indicated that high-frequency resistance effects in the measuring system could have caused these changes in conductivity. For this reason, all ac conductivity data above 5 kHz are questionable. Further tests will be required to determine if a frequency dependence of conductivity exists for UO_2 . The low-frequency data (<5 kHz) where conductivity is independent of frequency are accurate and are reported in this study.

The ac (<5 kHz) electrical conductivity of UO_2 is identical within experimental error to the dc electrical conductivity at all temperatures (Figure 3).^{*} No time dependence of the conductivity was observed between 1 and 60 sec. The similarity of the ac and dc conductivity suggests that the conduction in nearly stoichiometric UO_2 is primarily electronic.

The electrical conductivity values for polycrystalline UO_2 were the same at all temperatures as the conductivity values for single crystal UO_2 (Figure 4). It can be concluded that for nearly stoichiometric UO_2 , there is no significant attenuation of the electronic carriers due to grain boundaries or pores. In light of these results, it is difficult to understand the data reported by Wolfe⁽²⁾ which showed an increase in conductivity with grain

* The electrical conductivity data for all UO_2 specimens are given in Appendix B.

size for nearly stoichiometric UO_2 , and the very large increase in conductivity of polycrystalline, hypostoichiometric UO_2 observed by Iida over single crystal UO_2 of the same stoichiometry.

The electrical conductivity of polycrystalline UO_2 for both ac and dc measurements shows the same variations

in $\log \sigma$ versus T^{-1} curve below 1250 °K that was observed for single crystal UO_2 .^{(1)*} At approximately 1250 °K there is a sharp break in the $\log \sigma$ versus T^{-1} curve where the conduction

* The electrical conductivity data for all UO_2 specimens are given in Appendix B.

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FIGURE 3. The Electrical Conductivity of Polycrystalline UO_2 (B-38-C) Comparing the ac and dc Electrical Conductivity Data

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FIGURE 4. The Electrical Conductivity of Polycrystalline and Single Crystal Uranium Dioxide Including Both ac and dc Measurements

is intrinsic n-type with an activation energy above 1.0 eV.

Below 575 °K the $\log \sigma$ versus T^{-1} curve for all the specimens appears to be linear with an activation energy of approximately 0.17 eV (Figure 4). The conductivity values at any single temperature varies between samples; however, the slope is approximately the same.

Above 575 °K, however, an effect occurs that causes a change in slope. Single crystal B-40-A exhibits an "S" shape between 575 and 1250 °K. The curves for single crystal MR-5 and polycrystalline B-38-C appear as humps. However, the change in slope for B-38-C occurs at a higher temperature, approximately 675 °K. These changes are reproducible and occur both on heating and cooling.

Such differences between specimens can result from differences in impurity content or in stoichiometry. However, the differences in conductivity are small compared to the differences in impurity content between samples (See Table I). The stoichiometry of the samples is the same to within the accuracy of the analytical measurements.

Similar changes in slope of the $\log \sigma$ versus T^{-1} curve have been observed by other investigators. Wolfe⁽²⁾ observed a break in the curve at 675 °K for polycrystalline UO_2 similar to that observed in polycrystalline sample B-38-C. He reported on activation energy of 0.13 eV between 675 and 1250 °K. The slope for B-38-A is approximately the same. However, the activation energy for data of Wolfe below 675 °K was 0.20 eV, slightly higher than the 0.17 eV observed in

these data. Wolfe⁽²⁾ suggests that above 675 °K, the activation energy (0.13 eV) represents that of the transfer of a positive hole from U^{5+} cation to an adjacent U^{4+} cation. The activation energy (0.20 eV) below 675 °K, in addition to the energy of the jump process, includes the energy for freeing holes that are bound to defect centers.

Amelinckx, et al.⁽¹¹⁾ observed a similar change in slope at approximately 475 °K; this change was most pronounced in specimens that had been quenched. He attributed this change to the phase transition in the specimen from UO_{2+x} to UO_2 plus U_4O_9 .

Iida⁽³⁾ detected a rapid change in conductivity near 175 °K which he attributed to a high impurity concentration.

Other possible causes could involve changes in the thermally activated process (e.g., in addition to the mobility, the carrier density might also be changing). The effect would also be even more complex, if the difference in charge between the polarized ion and lattice ion was greater than unity. Further measurements to lower temperatures and measurements as a function of oxygen pressure may be required to clarify the exact cause of this change.

The electrical-conductivity data has been plotted in the form $\log \sigma$ versus T^{-1} and the activation energy reported here is obtained from the relation

$$\sigma = \sigma_0 e^{-E/kT} \quad (1)$$

Although the correct temperature relationship for the hopping mechanism has not been clearly determined, other

investigators have used a plot of $\log \sigma T$ versus T^{-1} , calculating their activation energy from the expression

$$\sigma = \sigma_0 \frac{1}{T} e^{-E/kT} \quad (2)$$

The activation energy using the latter method is approximately 20% higher than the value obtained from a $\log \sigma$ versus T^{-1} curve. The $\log \sigma T$ versus T^{-1} curve did not improve the linearity of the data in this temperature range.

Above 1250 °K, there is a sharp rise in the electrical conductivity. The data for all of the specimens show a similar reciprocal temperature relationship indicating intrinsic conduction. This large change in activation energy at 1250 °K corresponds to the p-to-n transition observed in thermoelectric property measurement.⁽⁹⁾ Evidence for the existence of intrinsic conduction has also been reported by Willardson, et al.⁽⁶⁾ and by Wolfe.⁽²⁾

The intrinsic electrical conductivity of solids can be given by

$$\sigma = n e \mu \quad (1)$$

where n is the intrinsic carrier concentration, e is the electronic charge, and μ is the carrier mobility. The electronic charge is constant. The mobility of an electron or hole does not change significantly above the characteristic temperature. (For UO_2 the characteristic temperature is <300 °K).⁽⁵⁾ The carrier concentration based upon the quantum mechanical treatment of free electron carriers in a nondegenerate state can be expressed as

$$n = \frac{2(2\pi m^* kT)^{3/2}}{h^3} e^{-E_g/2 kT} \quad (2)$$

where m^* is the effective mass and E_g is the energy difference between the valence and conduction bands. This equation also assumes that $m^* = m_+^* = m_-^*$ and $n = (n_- n_+)^{1/2}$, i.e., the Fermi level lies exactly between the valence and conduction bands. Thus, the equation for conductivity is given as

$$\sigma = e \mu \frac{2(2\pi m^* kT)^{3/2}}{h^3} e^{-E_g/2 kT} \quad (3)$$

For temperatures where $2 kT \ll E_g$, the exponential term is very much more important than $T^{3/2}$. The equation is then approximated to the familiar form

$$\sigma = \sigma_0 e^{-E_g/2 kT} \quad (4)$$

where σ_0 is a constant and E_g is twice the activation energy, E . By plotting $\log \sigma$ as a function of T^{-1} , the activation energy may be obtained from the slope of the straight line.

The least square curve of $\log \sigma$ versus T^{-1} above 1400 °K was determined for each specimen and for the combined data from the three specimens (Table II). The results show no significant differences in the conductivities of single crystal and polycrystalline UO_2 , nor between the ac and dc data. A reasonable linear fit of the data is obtained with the activation energies varying from 1.14 to 1.21 eV. For all data, the electrical conductivity above 1400 °K can be expressed as

$$\sigma = 3.569 \times 10^3 e^{-1.15/kT} \quad (5)$$

TABLE II. Linear Fit of Electrical Conductivity
of UO_2 Above 1400 °K $\sigma = \sigma_0 e^{-E/kT}$

Specimen	Data Points	σ_0 , mho/cm	Activation Energy, eV	Standard ^(a) Deviation
MR-5	24	5.240×10^3	1.212	0.0068
B-40-A	36	4.141×10^3	1.168	0.0015
B-38-C	133	3.370×10^3	1.144	0.00098
ECP3A	21	3.255×10^3	1.058	0.0113
All Data	193	3.569×10^3	1.151	0.00056

(a) 95% Confidence Level

Although a reasonable fit of the data is obtained from a linear equation, a better fit of the data is obtained statistically with a third order polynomial. For all data

$$\ln \sigma = 9.646 - 2.087 \times 10^4 T^{-1} + 1.231 \times 10^7 T^{-2} - 6.484 \times 10^9 T^{-3} \quad (6)$$

These results show that the slope of the $\ln \sigma$ versus T^{-1} curve above 1900 °K increases slightly with increasing temperature. A plot of $\frac{\Delta(\ln \sigma)}{\Delta(T^{-1})}$ versus

temperature is shown in Figure 5. Above 1900 °K, the incrementally determined slope varies linearly with temperature as

$$\frac{\Delta(\ln \sigma)}{\Delta(T^{-1})} = -10.627 \times 10^3 - 1.4013 T \quad (7)$$

Between 1400 and 1900 °K, $\frac{\Delta(\ln \sigma)}{\Delta(T^{-1})}$ varies only slightly with temperature. From Equation 3, the temperature dependence of σ above 1900 °K can be expressed as

$$\sigma = \sigma_0^1 T^{3/2} e^{-E'/2kT} \quad (8)$$

or

$$\ln \sigma = \ln \sigma_0^1 + 3/2 \ln T - \frac{E'}{2kT} \quad (9)$$

It can be easily shown by differentiation that

$$\frac{\Delta(\ln \sigma)}{\Delta(T^{-1})} = -\frac{E'}{2k} - \frac{3}{2} T \quad (10)$$

This is the same form as Equation (7) obtained from a plot of the data above 1900 °K (Equation 7) where

$$\sigma = 2.104 \times 10^{-2} T^{1.401} e^{\frac{-0.9157 \text{ eV}}{kT}} \quad (11)$$

This would suggest that above 1900 °K, the $T^{3/2}$ cannot be neglected. At 2000 °K, $2kT$ is approximately 0.1 the activation energy and $2kT$ is not $\ll E_g$. It is interesting to note that the power of T from the data (1.401) is close to the theoretical value of 1.5.

The exact meaning of the 0.916 eV for E' is somewhat obscure since it applies only to the data above 1900 °K.

It need not agree with the activation energy obtained from the linear curve (1.15 eV) since the activation energy could be a function of temperature without altering the slope of the $\ln \sigma$ versus T^{-1} curve, ($E_g = E_0 + \alpha T$). It can be shown that the α/k term would become a part of the σ_0 term during differentiation.

Although there is a significant statistical difference between the first and third order relationships for the conductivity, the linear equation is representative of the data within experimental error. It can be concluded that until more data are available for many UO_2 specimens, the best expression of conductivity above 1400 °K is linear Equation (5).

A significant difference exists between the energy gap derived from con-

ductivity data (2.3 eV) and that derived from optical absorption data.⁽⁵⁾ Of the reported values for the optical energy gap (2.0 to 5.25 eV), the highest is probably the most valid. The lower energy values were determined by using thin sections where absorption densities are very large and a measurement of the absorption edge is very difficult.⁽¹²⁾ In addition, in very thin sections, single crystals appear yellow in transmitted light,⁽⁵⁾ suggesting an optical energy gap greater than 2.0 eV.

As suggested by Wolfe,⁽²⁾ the absorption spectrum for UO_2 between 2000 and 7000 Å probably consists of a strong absorption edge at 2400 Å (5.25 eV), two intense bands between 2500 Å (5.0 eV) and 5000 Å (2.5 eV) with an absorption edge near 6600 Å (2.00 eV).

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FIGURE 5. The Temperature Dependence of $\frac{\Delta(\ln \sigma)}{\Delta(T^{-1})}$ for the Intrinsic Electrical Conductivity of UO_2 Above 1400 °C

A direct numerical agreement between the thermal energy gap and the optical energy gap should not be expected in polar solids.⁽¹²⁻¹⁵⁾ The optical energy transition occurs without relaxation obeying selection rules which require no change of momentum. The thermal energy transition occurs with an energy change in equilibrium configuration. The selection rules may be relaxed, if the electron (or hole) interacts with the lattice and the transition is accompanied by the emission or absorption of a phonon. This latter energy is measured from electrical conductivity data. Thus, the optical energy gap should always be larger than the thermal energy gap, making it difficult to compare directly the absorption energy spectra and electrical conductivity data.

An additional distinction exists between the thermal and optical energy gap in polar crystals. The redistribution of ionic charge can change the relative configuration of the bands. This change is a relatively slow, thermally-activated process. During the faster, optical excitation process, this charge redistribution does not occur. The differences in the thermal and optical excitation processes can be

described in terms of the low frequency (ϵ_s) and high frequency (ϵ_o) dielectric constants. This difference is proportional to $(\epsilon_s - \epsilon_o)/\epsilon_s \epsilon_o$.⁽¹⁴⁾

If ϵ_s is larger than ϵ_o as is probable in ionic crystals, the optical energy gap would be larger than the thermal energy gap.

The ratio of the optical to thermal energy transitions is approximately equal to ϵ_s/ϵ_o .⁽⁵⁾ This value for UO_2 has been reported as 24/5.8.⁽⁵⁾ Assuming the optical energy gap is 5.25 eV, the corresponding thermal energy gap would be 1.27 eV, substantially less than half the measured value.

However, a simple band model is assumed in this analysis, and it has been pointed out previously that simple band theory may not be valid for UO_2 . Thus, a correlation of electrical and optical properties is complicated and does not appear feasible using present theory.

The difference between the optical and thermal energy gaps could also indicate the presence of an intense extrinsic band in UO_2 near 2.3 eV. This band would be independent of O:U ratio of the UO_2 and the conductivity associated with this band would mask the true intrinsic conductivity representative of the higher (~ 5.0 eV) energy gap.

REFERENCES

1. J. L. Bates, C. A. Hinman and T. Kawada. Electrical Conductivity of UO_2 : Part I, Single Crystals, BNWL-296 PT 1, Pacific Northwest Laboratory, Richland, Washington, August, 1966.
2. R. A. Wolfe. The Electrical Conductivity and Thermoelectric Power of Uranium Dioxide, WAPD-270, Westinghouse Atomic Power Department, Pittsburgh, Pennsylvania, 1963.
3. Shoji Iida. "Electrical Properties of Nonstoichiometric Uranium Dioxide," Jap. J. Appl. Phys., vol. 4, no. 11, pp. 833-838. 1965.
4. R. K. Willardson and J. M. Moody. "Electrical, Magnetic, and Optical Properties," Uranium Dioxide: Properties and Nuclear Applications, J. Belle, edited by U. S. Government Printing Office, Washington, D. C., pp. 211-219. 1961.
5. Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases, Technical Report Series No. 39, International Atomic Energy Agency, Vienna, Austria, pp. 60-72. 1965.
6. R. K. Willardson, J. W. Moody and H. L. Goering. "The Electrical Properties of Uranium Dioxide," J. Inorg. Nucl. Chem. vol. 6, pp. 19-33. 1958.
7. P. Chiotti. "II. Crucibles of Mixtures of Tuballoy Dioxide with Other Materials," in Technological Research--Metallurgy for Period October 10 to November 10, 1944, pp. 7-8. 1945.
8. S. Aronson, J. E. Rulli and Be. E. Schaner. "Electrical Properties of Nonstoichiometric Uranium Dioxide," J. Chem. Phys., vol. 35, pp. 1382-1388. 1961.
9. J. L. Bates. "Ionic Diffusion in High Temperature Uranium Dioxide," Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids, paper no. Sm-66/67, IAEA Vienna, Austria, July 22-27.
10. R. J. Ackerman, R. J. Thorn and G. H. Winslow. "Visible and Ultraviolet Absorption Properties of Uranium Dioxide Films," J. Opt. Soc. Am., vol. 49, no. 11, pp. 1107-1112. 1959.
11. S. Amelinckx. Physical Properties of UO_2 Single Crystals, EUR 1414.e, Centre d'Etude de l'Energie Nucleaire, MOL, Belgium. 1965.
12. J. L. Bates. "Visible and Infra-red Absorption Spectra of Uranium Dioxide," Nucl. Sci. and Eng., vol. 21, pp. 26-29. 1965.
13. N. F. Mott and R. W. Gurnery. Electronic Processes in Ionic Crystals. Oxford University Press, London, 1953. 2nd ed., pp. 160-162.
14. W. W. Scanlon. "Polar Semiconductors," Solid State Physics, Academic Press, New York, 1959, vol. 9, pp. 109-118.
15. E. J. W. Verwey. "Oxidic Semiconductors," Semi-Conducting Materials, edited by R. W. Ditchburn and N. F. Mott. Butterworths Scientific Publication, Ltd., London, 1951. p.151-161.

APPENDIX A

FREQUENCY DEPENDENCE OF ELECTRICAL
CONDUCTIVITY OF UO_2

Initial measurements of the ac electrical conductivity of both polycrystalline and single crystal UO_2 exhibited unusual frequency dependence above 50 kHz. However, further measurements above 50 kHz were performed on other materials (such as graphite). The results suggested that the high frequency changes in conductivity were

probably due to resistance effects in the measuring system. For this reason all ac data above 10 kHz can be questioned. Further study and refinement of the equipment will be required to determine if a frequency dependence of conductivity exists for UO_2 . Two examples of the frequency dependence are illustrated in Figures A-1 through A-3.

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FIGURE A-1. Electrical Conductivity of Single Crystal UO_2 Temperature and Frequency Dependence (Specimen EC-S2A)

The polycrystalline UO_2 appeared to exhibit more pronounced changes than the single crystal oxide. In addition, the values of the conductivity were different during increasing or decreasing temperature changes during a thermal cycle.

The exact cause of these variations is not known. It has been suggested that the frequency variations are due to the resistance of the voltage probes or current leads, or to surface conduction effects which are strongly frequency dependent.

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FIGURE A-2. Electrical Conductivity of Polycrystalline UO_2 Temperature and Frequency Dependence (Specimen EC-P1A)

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FIGURE A-3. Electrical Conductivity of Polycrystalline UO_2 Temperature and Frequency Dependence (Specimen EC-P3A)

APPENDIX B

ELECTRICAL CONDUCTIVITY OF UO_2
ac AND dc DATA

SPECIMEN B-40-A (Alternating Current)

Run Number 3		Run Number 4	
Temperature, °K	Conductivity ohm-1-cm-1	Temperature, °K	Conductivity ohm-1-cm-1
1293	0.19	1066	0.14
1423	0.32	1221	0.17
1543	0.60	1438	0.35
1656	1.10	1631	0.96
1757	1.80	1753	1.70
1833	2.40	1871	2.60
1673	1.30	2118	6.00
1474	0.44	2348	12.0
1273	0.20	2543	21.0
1073	0.14	2648	25.0
878	0.090	2483	18.0
776	0.068	2033	5.8
478	0.013	1473	0.42
		1198	0.15

SPECIMEN B-40-A (Direct Current)

Run Number 1	
Temperature, °K	Conductivity, ohm-1-cm-1
654	0.0401
658	0.0374
788	0.0710
825	0.0811
852	0.0887
878	0.0903
883	0.0942
989	0.125
1011	0.129
1031	0.131
1031	0.136
1121	0.158
1128	0.159
1111	0.154
1112	0.154
1130	0.158
1127	0.159
1126	0.158
1137	0.162
1138	0.162
1128	0.160
1144	0.163

Run Number 2	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1114	0.154
1120	0.147
1116	0.156
1114	0.155
1114	0.153
1068	0.142
1068	0.143
1002	0.132
1000	0.133
972	0.120
960	0.122
897	0.0985
885	0.0966
771	0.0643
778	0.0657
702	0.0477
688	0.0436
613	0.0339
570	0.0300
538	0.0226
523	0.0210
453	0.0127
444	0.0113
410	0.0080
399	0.0070
363	0.0042
358	0.0037
342	0.0027
332	0.0024
318	0.0017
312	0.0016

Run Number 3	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1143	0.1464
1136	0.1450
1130	0.1461
1273	0.1871
1268	0.1880
1273	0.1876
1480	0.4477
1473	0.4249
1473	0.4267
1673	1.223
1673	1.201
1673	1.223
1873	3.114
1880	3.095
1876	3.095
1923	3.756
1923	3.721
1929	3.721
1773	1.866
1773	1.832
1773	1.823
1573	0.721
1573	0.721
1575	0.719
1373	0.274
1373	0.276
1373	0.279
1173	0.165
1173	0.163
1173	0.164
1173	0.168
973	0.120
973	0.117
973	0.119
773	0.6686
777	0.0683
773	0.0674

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FIGURE B-1. Electrical Conductivity of Single Crystal UO_2 (B-40-A) Comparing ac and dc Data

SPECIMEN EC-P1A (Direct Current)

Run Number 1		Run Number 2	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹	Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1048	0.209	293	0.00147
1073	0.201	333	0.00243
1120	0.218	388	0.00574
1173	0.275	418	0.00850
1205	0.298	443	0.0109
1267	0.328	468	0.0147
1314	0.362	498	0.0209
1363	0.429	573	0.0345
1433	0.452	628	0.0467
1494	0.627	653	0.0568
1573	0.809	688	0.0722
1673	1.15	733	0.0924
1857	2.23	788	0.120
2013	3.65	913	0.181
2158	7.04	988	0.265
2276	8.73	1210	0.567
2394	12.4	1263	0.709
2483	18.2	1221	0.709
2477	14.9	1123	0.397
2441	16.2	1023	0.378
2317	9.38	813	0.107
2152	5.75	728	0.0795
1845	2.47	638	0.0497
1633	1.30	538	0.0209
		473	0.0181
		373	0.00722
		303	0.00208

SPECIMEN EC-P1A (Alternating Current)

Run Number 3		Run Number 4	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹	Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
293	0.0016	1118	0.50
483	0.024	1181	0.58
778	0.16	1445	0.91
1058	0.44	1648	1.70
1138	0.60	1928	4.40
1273	0.67	2133	8.00
1178	0.50	2488	13.0
943	0.16		
768	0.023		
298	0.0025

Neg 0671421-2

FIGURE B-2. Electrical Conductivity
of Polycrystalline UO_2 (EC-P1A)
Comparing ac and dc Data

SPECIMEN EC-P3A (Direct Current)

Run Number 1	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1268	0.177
1278	0.182
1283	0.183
1273	0.174
1273	0.179
1273	0.199
1273	0.185
1273	0.199
1273	0.107
1273	0.187
1223	0.173
1113	0.151
1843	0.0904
803	0.0839
693	0.0530
628	0.0426
563	0.0275
518	0.0186
423	0.00902

SPECIMEN EC-P3A (Alternating Current)

Run Number 2	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1163	0.158
1333	0.214
1623	0.903
1793	1.47
2053	3.66
2313	17.36
2581	14.37
2901	21.31
3178	30.11
2793	23.00

SPECIMEN B-38-C (Direct Current)

Run Number 1	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
293	0.00136
303	0.00183
305	0.00211
335	0.00564
335	0.00612
520	0.0240
520	0.0241
598	0.0408
598	0.0445
603	0.0444
696	0.0625
783	0.0839

Run Number 2	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
796	0.0790
880	0.0926
937	0.101
953	0.107
1139	0.185
1208	0.159
1323	0.239
1466	0.494
1523	0.849
1674	1.38
1748	1.97
1817	2.61
1817	2.67
1822	2.79

Neg 0671421-1

FIGURE B-3. Electrical Conductivity
of Polycrystalline UO_2 (EC-P3A)
Comparing ac and dc Data

Run Number 3	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1549	0.593
1623	0.817
	0.839
1708	1.31
1782	1.86
1877	2.73
1965	3.63
2076	5.42
2256	7.77
2851	3.42
2134	6.17
2213	8.19
2434	11.8
2434	14.3
2434	16.9
2555	22.8
2673	27.2
2075	5.70
2075	5.35

Run Number 4	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1519	0.486
1519	0.506
1672	1.20
1669	1.13
1885	2.51
2145	7.24
2332	9.74
2296	0.8
2127	6.37
1971	3.50
1733	1.53

Run Number 5	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1873	2.77
2093	5.65
2148	6.51
2213	8.36
2368	13.4
2373	13.6
2569	18.2
2713	27.5
2713	32.1
2011	5.81

SPECIMEN B-38-C (Alternating Current)

Run Number 1	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
293	0.00096
293	0.00100
293	0.00102
303	0.00143
305	0.00154
329	0.0309
468	0.0128
520	0.0228
520	
598	0.0416
598	
603	0.0431
696	0.0627
783	0.0746

Run Number 2	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
796	0.0771
880	0.0920
923	0.0983
937	0.100
953	0.102
1139	0.131
1208	0.155
1323	0.240
1453	0.476
1523	0.815
1674	1.319
1748	1.823
1793	1.892
1817	2.388
1825	2.79

Run Number 3	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1479	0.577
1549	0.567
1623	0.815
1623	0.819
1688	1.20
1708	1.25
1782	1.76
1788	1.81
1869	2.52
1877	2.60
1877	2.67
1965	3.49
1965	3.04
2071	4.56
2074	4.78
2190	6.89
1851	3.38
2134	6.21
2213	8.02
2434	11.51
2434	15.2
2434	17.3
	15.9
2555	20.1
2809	36.5
2075	5.73
2075	5.33
1910	5.23
1868	2.82
1841	2.55
1735	1.70
1701	1.40
1674	1.29
1628	1.03
1588	0.836
1558	0.701
1521	0.535
1483	0.436
1431	0.369
1423	0.313
1388	0.271
1318	0.222
1273	0.1985

Run Number 4	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1519	0.486
1591	0.490
1672	1.12
1669	1.10
1858	2.11
1858	2.40
2145	6.33
2274	8.53
2332	9.24
2332	11.3
2296	10.2
2321	3.4
2321	15.7
2603	19.86
2244	9.67
2127	6.04
1971	3.37
1733	1.47
1626	0.918

Run Number 5	
Temperature, °K	Conductivity, ohm ⁻¹ -cm ⁻¹
1873	2.80
2093	5.41
2148	6.56
2213	8.12
2368	12.3
2368	12.7
2373	12.7
2569	18.6
2569	23.7
2686	22.9
2555	19.6
2320	12.8
2236	9.12
2011	5.76
2823	29.4
2838	31.7
2838	32.5
2908	41.5
2973	41.6
2105	6.10
2073	5.75

B-4 Neg 0671421-3

FIGURE B-4. Electrical Conductivity of Polycrystalline UO_2 (B-38-C) Comparing ac and dc Data

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