BNWL-927

UC-25, Metals, Ceramics
and Materials

THE EFFECT OF OXYGEN STOICHIOMETRY
ON THE THERMAL DIFFUSIVITY AND CONDUCTIVITY
OF $U_{0.75}Pu_{0.25}O_{2-x}$

By

R. L. Gibby

Ceramics Department
Chemistry and Metallurgy Division

FIRST UNRESTRICTED
DISTRIBUTION MADE

JAN 31 '69

January 1969

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

leg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THE EFFECT OF OXYGEN STOICHIOMETRY
ON THE THERMAL DIFFUSIVITY AND CONDUCTIVITY
OF $U_{0.75}Pu_{0.25}O_{2-x}$

R. L. Gibby

ABSTRACT

The effect of oxygen content on the thermal diffusivity (α) of $U_{0.75}Pu_{0.25}O_{2-x}$ was measured for values of x from 0.00 to 0.07 at temperatures from 100 to 1200 °C. Corresponding values of thermal conductivity (λ) were calculated from the thermal diffusivity data using estimated values for the heat capacity of the mixed oxide. Thermal diffusivity and conductivity were observed to decrease with decreasing oxygen content and increasing temperature, obeying the empirical relationships:

$$1/\alpha = 0.110T + 1.08 \times 10^3 x + 4 \text{ (sec/cm}^2\text{)}$$

$$1/\lambda = 0.0312T + 3.55 \times 10^2 x + 1.5 \text{ (cm-}^\circ\text{K/W)}$$

with T expressed in °C and x representing the amount of missing oxygen. The dependence of thermal conductivity on oxygen content was shown to be associated with oxygen ion vacancies and Pu^{+3} ions which form as oxygen is removed from the lattice. The calculated thermal resistances are in reasonable quantitative agreement with values estimated using the Klemens-Callaway model for phonon scattering by point defects.

CONTENTS

LIST OF FIGURES	v
INTRODUCTION	1
SUMMARY	2
EXPERIMENTAL PROCEDURE.	4
Materials	4
Method	7
THEORY.	9
RESULTS AND DISCUSSION.	15
Thermal Diffusivity	15
Thermal Conductivity.	19
Temperature Coefficient (B)	21
Defect Thermal Resistance (A)	23
ACKNOWLEDGMENTS	31
REFERENCES.	31
APPENDIX	35

FIGURES

1	Photomicrographs of Sintered $U_{0.75}Pu_{0.25}O_{2.00}$	6
2	Lattice Parameter (a_o) of $U_{0.75}Pu_{0.25}O_{2-x}$ as a Function of Missing Oxygen, x	8
3	Reciprocal Thermal Diffusivity as a Function of Absolute Temperatures and Oxygen Stoichiometry	16
4	Thermal Diffusivity of $U_{0.75}Pu_{0.25}O_{2-x}$ According to Equation (17)	18
5	Calculated Thermal Resistance as a Function of Absolute Temperature and Oxygen Stoichiometry	20
6	Thermal Conductivity of $U_{0.7}Pu_{0.25}O_{2-x}$ According to Equation (19).	22
7	Defect Thermal Resistance (A) as a Function of Oxygen Stoichiometry	24

THE EFFECT OF OXYGEN STOICHIOMETRY
ON THE THERMAL DIFFUSIVITY AND CONDUCTIVITY
OF $U_{0.75}Pu_{0.25}O_{2-x}$

R. L. Gibby

INTRODUCTION

Uranium-plutonium solid solutions containing 20 to 30 wt% PuO_2 are candidates for fast-reactor fuels. To predict their thermal behavior during irradiation, their thermal and physical properties (of which thermal diffusivity and thermal conductivity are especially important) must be known. Experimental measurements from this⁽¹⁾ and other laboratories^(2,3) have already shown solid solutions containing up to 20 wt% PuO_2 possess out-of-reactor thermal conductivities very similar to that of pure UO_2 at temperatures as high as 1600 °C. Schmidt and Richter,⁽³⁾ and more recently Van Craeynest and Weilbacher,⁽⁴⁾ have also shown the thermal conductivity of the mixed oxide decreases similarly to UO_{2+x} , when the oxygen stoichiometry deviates from stoichiometric composition ($O/M = 2.000$). However, unlike UO_2 , the oxygen stoichiometry of UO_2 - PuO_2 solid solutions may be varied to either slightly hyper- or hypostoichiometric compositions without precipitation of additional phases. In both cases, the thermal conductivity decreases. Consequently, for nonstoichiometric compositions, oxygen-associated defects are present in the fluorite lattice and, moreover, these defects are responsible for the decrease in thermal conductivity.

Klemens⁽⁵⁾ and Callaway⁽⁶⁾ have developed simple phenomenological models to calculate from first principles the thermal resistance contributions from lattice defects. Their relationships and those developed by others using their model have been shown to be in reasonable quantitative agreement with experimental results.

The purpose of this study was to determine the thermal diffusivity and conductivity of a uranium-plutonium solid solution containing 25 wt% PuO_2 as a function of temperature and oxygen stoichiometry for hypostoichiometric compositions. This study also proposed to show these results in quantitative agreement with the theoretical relationships for point defect resistance at high temperatures developed by Ambegaokar⁽⁷⁾ and Abeles⁽⁸⁾ using the Klemens-Callaway theory.

SUMMARY

The thermal diffusivity of sintered $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2-x}$ was measured with a laser heat-pulse apparatus from 100 to 1200 °C for oxygen stoichiometries in which x varied from 0.00 (stoichiometric) to 0.07 (oxygen-to-metal ratio = 1.93). Thermal conductivity was calculated from the measured thermal diffusivity data and estimated heat capacity data.

The thermal diffusivity and conductivity data determined for each oxygen stoichiometry obeyed the relationships

$$1/\alpha = A' + B'T$$

$$1/\lambda = A + BT$$

where α and λ are the thermal diffusivity and thermal conductivity, respectively. The temperature coefficients B' and B were independent of oxygen content, while the terms A' and A increased linearly with x . The general expression for thermal diffusivity and conductivity in terms of the absolute temperature T and the number of moles of missing oxygen atoms, x , are

$$1/\alpha = 0.110T + 1.08 \times 10^3 x + 4 \text{ (sec/cm}^2\text{)}$$

$$1/\lambda = 0.0312T + 3.55 \times 10^2 x + 1.5 \text{ (cm-}^\circ\text{K/W)}$$

The values for thermal conductivity determined in this study are in reasonable agreement with the data reported for mixed oxides containing 20 wt% PuO_2 , and also with data reported for UO_2 , even though the higher temperature data of this study are slightly lower in all cases than that reported by others for the mixed oxide. Since the other data for mixed oxides are in good agreement with the UO_2 data at all temperatures, the high temperature results of this study are not understood at this time.

The temperature coefficient (B) was found, by means of the Leibfreid-Schlömann relationship, to correspond to a Debye temperature (θ) of 190 °K. This value is in very good agreement with the values reported from X-ray diffraction for UO_2 .

The value of the defect resistance (A) was calculated in terms of the oxygen-associated defect concentrations from the theoretical relationship of Ambegaokar, derived on the basis of Klemen's theory of phonon scattering by point imperfections. The value of A calculated from the basic properties of the mixed oxide, assuming a defect structure model for oxygen removal, agreed to within a factor of 1.3 with the experimental value. In view of this excellent agreement, the assumed defect model was concluded to be essentially correct and Pu^{+3} ions and oxygen ion vacancies to be the principal phonon scattering centers in the hypostoichiometric mixed oxide. Moreover, these defects were concluded to scatter phonons because of their size difference in relationship to the host lattice site which they occupied. The size difference, also responsible for a lattice expansion when oxygen is removed from the structure, results in localized strains around the defects which scatter the phonons. Calculations indicated phonon scattering due to the mass difference of vacant oxygen sites to be negligible.

EXPERIMENTAL PROCEDURE

MATERIALS

Dense specimens of a UO_2 -25 wt% PuO_2 solid solution were made by sintering dry pressed pellets prepared from physically blended powder. The combined powder, consisting of ceramic grade UO_2 and high purity PuO_2 prepared by low temperature oxidation of plutonium metal, was dry blended for 72 hr in a rubber-lined ball mill using high density alumina balls. A 2 to 3 wt% solution of carbowax was added for pelletizing and the pellets were sintered at 1650 °C for 12 hr. A cover gas of argon-8% hydrogen was used to prevent oxidation during sintering.

The properties of the sintered material are summarized in Table 1. The impurities nickel, iron, aluminum, and zinc were present in the starting powders, while most of the carbon came from the carbowax binder. No additional impurities were introduced during the milling process.

The X-ray diffraction pattern showed only a single fluorite phase with a lattice parameter corresponding to that expected from a Vegard's law relationship for an ideal UO_2 -25 wt% PuO_2 solid solution. In addition, the high angle diffraction peaks were also well resolved, a further indication of complete solid solution formation. The microstructure shown in Figure 1, on the other hand, was not uniform but showed small regions with the appearance of incomplete chemical reaction. These regions represent only a small percentage of the total sample volume, however, and therefore would not be detectable by X-ray diffraction analysis. Consequently, the X-ray and microscopic data are not inconsistent.

As seen in Figure 1, the porosity consists of numerous large as well as fine pores. Many of the pores were lamellar in shape. In spite of the apparently high porosity, the measured density was determined to be 95.5% of theoretical density (TD).

TABLE 1. *Properties of Physically-Blended
Sintered $U_{0.75}Pu_{0.25}O_{2-x}$*

Lattice Parameter, O/M = 2.00	5.4515 $\pm$ 0.0003 Å
Weight Percent Plutonium (Isotopic Dilution)	21.6 wt%
Density (from weight and size measurements)	10.59 g/cm ³
Percent of Theoretical Density (11.08 g/cm ³)	95.5%
Average Grain Size	17 x 10 ⁻⁴ cm
Chemical Impurities	

<u>Element</u>	<u>ppm</u>	<u>Element</u>	<u>ppm</u>
Ag	<0.1	Mg	2
Al	50	Mn	2
B	<0.1	Mo	<5
C	280	Na	2
Ca	<1	Ni	50
Cl	29	P	<50
Cr	<5	Pb	2
Cu	20	Si	12
F	7	Sn	5
Fe	120	V	<20
K	20	Zn	50

The oxygen-to-metal ratio (O/M) of approximately 1.98 for the sintered compacts was adjusted to the desired value by subsequent heat treatments in controlled oxidizing or reducing atmospheres. For hypostoichiometric (O/M < 2.00) compositions, the samples were heated in a static high purity hydrogen atmosphere. In order to obtain the desired oxygen composition, the reduction temperature was varied while the reduction time was fixed at 1 hr. Reduction at 1150 °C resulted in an O/M of approximately 1.99 while, at 1750 °C, the O/M was about 1.93.

Neg 47269G

250X

a.

Neg 48208D

250X

b.

FIGURE 1. Photomicrographs of Sintered $U_{0.75}Pu_{0.25}O_{2.00}$
(a) Polished Section - Normal to Pellet Axis
(b) Polished Section - Parallel to Pellet Axis

The O/M of the test specimen was determined primarily by thermogravimetric analysis. However, the lattice parameter was also measured as an additional check. Samples were heated at 800 °C in a flowing atmosphere of argon-8% hydrogen passed through 0 °C water. After approximately 6 hr in this environment, the samples were stoichiometric and the original O/M was determined from the weight gain associated with the oxidation process. The test specimens could obviously not be used in this process since their stoichiometry would be changed. Therefore, additional samples were reduced with the test specimen to be used for O/M analysis. Generally, the O/M was determined for three different samples from each run. The O/M's varied by as much as ± 0.02 , an excessive amount when considering the maximum total variation in oxygen content obtainable for single-phase hypostoichiometric compositions to be about 0.10 mole/mole of mixed oxide. The lattice parameter, much more sensitive to oxygen content, was therefore measured as a function of stoichiometry and the results, shown in Figure 2, were used in conjunction with TGA data to better define the oxygen composition.

METHOD

The laser heat-pulse apparatus used in this study has been described in a previous report.⁽¹⁾ A ruby laser was used to transiently heat one surface of a small wafer specimen, while the subsequent thermal response on the opposite surface was monitored with an indium antimonide infrared detector. The ambient sample temperature was controlled with a molybdenum-rhenium wire-wound tube furnace.

The two test specimens used in this study were 0.625 cm in diameter, with thicknesses of 0.0762 and 0.0798 cm, respectively. The thickness was measured with a dial gage with an accuracy of ± 0.00025 cm.

Neg 0681780

FIGURE 2. Lattice Parameter (a_0) of $U_{0.75}Pu_{0.25}O_{2-x}$ as a Function of Missing Oxygen, x . (Numbers designate the experimental run.)

The samples were protected from oxidation during a run with a flowing atmosphere of argon-8% hydrogen. When the O/M was less than 2.00, the cover gas was dried using a molecular sieve and heated zirconium chips. For stoichiometric compositions, the gas was passed through an ice-water mixture to maintain stoichiometry to measurement temperatures up to approximately 1400 °C.

The ambient temperature of the sample was measured with a Pt-Pt10% rhodium thermocouple located immediately adjacent to the sample. Thermal diffusivity measurements were made at ~50 °C intervals on heating, and at ~100 °C intervals on cooling. The samples tended to oxidize at the higher temperatures when the oxygen content was less than about 1.97. Consequently, data were not obtained on cooling for these compositions. For the same reason, data were not obtained above 1200 °C for any hypostoichiometric compositions.

THEORY

Heat in most metal oxides is transported almost entirely by phonons, and thermal resistance arises from the interaction of the phonons with one another or with crystalline defects. The phonon-phonon interactions consist of three phonon processes which conserve crystalline momentum, called N-processes, and those in which momentum is not conserved, called U-processes. While U-processes account for most of the thermal resistance at high temperatures, Abeles⁽⁸⁾ has shown that N-processes may account for a sizeable amount of high temperature thermal resistance when the point defects are stronger scatterers of phonons than the intrinsic processes.

Crystalline defects which scatter phonons include internal and external crystalline boundaries, dislocations, colloidal precipitates, and point imperfections. Within a given

temperature interval, only one or two of these imperfection types may be important contributors to thermal resistance. For instance, point defects may contribute strongly to thermal resistance at either low or high temperatures, while internal and external crystalline boundaries, dislocations, and colloidal precipitates generally are important only at temperatures below the Debye temperature. Generally, therefore, the only important sources of thermal resistance at high temperatures are point defects and the intrinsic phonon interactions.

The thermal diffusivity, α , and thermal conductivity, λ , can be expressed in terms of an average phonon relaxation time, τ_i , by the kinetics formulas:

$$\alpha = \frac{1}{3} v^2 \tau_i \quad (1)$$

$$\lambda = \frac{1}{3} C_v v^2 \tau_i \quad (2)$$

where v is the average phonon velocity and C_v is the heat content per unit volume.

The total average phonon relaxation time, τ_T , in terms of the relaxation times associated with the intrinsic processes and the point defect processes, can be written as

$$\frac{1}{\tau_T} = \frac{1}{\tau_U} + \sum_i \frac{1}{\tau_i} \quad (3)$$

where τ_U is the relaxation time for U-processes and τ_i is the time for the i th type point defect. N-processes are not included in this summation since the reciprocal relaxation time is not directly additive but must receive special considerations.⁽⁶⁾ Callaway⁽⁶⁾ has included N-processes in a phenomenological model for lattice conduction at low temperatures, and Abeles⁽⁸⁾ has extended Callaway's formalism to high

temperatures. According to Klemens,⁽⁵⁾ however, if the relaxation time for defect scattering is less than that for U-processes, the effect of N-processes on thermal resistance will be small. This condition appeared to apply for (U,Pu)O₂. Therefore, the effect of N-processes was not included in Equation (3).

By combining Equation (3) with Equations (1) and (2), the thermal diffusivity and thermal conductivity are expressed as a summation of the thermal resistance of the intrinsic processes and the point defect processes. Thus,

$$R' = \frac{1}{\alpha} = R_I' + R_U' \quad (4)$$

$$R = \frac{1}{\lambda} = R_I + R_U \quad (5)$$

where R_I and R_U are the thermal resistance due to the point defects and U-processes, respectively, and R_I' and R_U' are equivalent expressions for reciprocal thermal diffusivity.

The intrinsic thermal resistance, R_U , can be estimated from basic material properties with the Leibfreid-Schlömann relationship⁽⁹⁾

$$R_U = \frac{\gamma^2 T}{\left(\frac{24}{10}\right)(4)^{1/3} \left(\frac{k}{h}\right)^3 M \theta^3 \delta} = BT \quad (6)$$

where

- γ = Gruneisen constant
- T = absolute temperature
- k = Boltzmann's constant
- h = Plank's constant
- M = mass per atom
- δ^3 = volume per atom
- θ = Debye temperature

Although this equation is based on an idealized model, the dependence of R_U on T , as well as θ , δ , and M is essentially correct.

Klemens⁽⁵⁾ has shown that point defects scatter phonons because of (1) a difference in mass compared with the host atom, (2) a difference in bonding strength, and/or (3) a difference in size compared to the normal lattice site. The phonon relaxation time $\tau(w)$ in the Debye approximation, according to Klemens' model, is

$$\tau_i(w) = \frac{4\pi v^3}{V_o \Gamma_i w^4} \quad (7)$$

where Γ_i characterizes the scattering cross section of the i th point defect (vacancy, interstitial, substitutional impurity, isotopic impurity, etc.) and is given by

$$\Gamma_i = \frac{V_o \epsilon_i}{12} \left\{ \left(\frac{\Delta M_i}{M} \right)^2 + 2 \left[\left(\frac{\Delta G_i}{G} \right) - 6.4 \gamma \left(\frac{\Delta R_i}{R} \right)^2 \right] \right\} \quad (8)$$

In Equation (7)

v = the average phonon velocity
 V_o = the atomic volume
 w = the phonon frequency

and in Equation (8)

ϵ_i = the defect concentration per unit volume
 M_i = mass of the i th defect
 R_i = radius of the i th defect
 G_i = An average stiffness constant of the nearest neighbor bonds of defect atoms to the host lattice atoms.

$$\left. \begin{aligned} \Delta G_i &= G_i - G \\ \Delta R_i &= R_i - R \\ \Delta M_i &= M_i - M \end{aligned} \right\} \begin{array}{l} \text{where } G, R, \text{ and } M \text{ are the average stiff-} \\ \text{ness constant, average interatomic} \\ \text{distance, and average mass per atoms,} \\ \text{respectively, in the host lattice} \end{array}$$

$\gamma = \text{Gruneisen constant.}$

Assuming the elastic constants, C_{ik} , to be only a function of the atomic volume, according to the relationship

$$C_{ik} R^4 \approx \text{constant} \quad (9)$$

where R is the interatomic spacing, Abeles⁽⁸⁾ derived a simple equation expressing $\Delta G_i/G$ in terms of $\Delta R_i/R$ and, consequently, reduced Klemen's expression for Γ_i to

$$\Gamma_i = \frac{V_o \epsilon_i}{12} \left[\left(\frac{\Delta M_i}{M} \right)^2 + \eta \left(\frac{\Delta R_i}{R} \right)^2 \right] \quad (10)$$

where

$$\eta = 32 (1 + 1.6 \gamma)^2$$

Because of the many simplifying assumptions required in the overall derivation of the above expression for Γ_i , Abeles suggests that, in general, η should be regarded as a phenomenological, adjustable parameter.

Using Klemens expression [Equation (7)] for the relaxation time for point-defect scattering, Ambegaokar⁽⁷⁾ derived the following expression for the impurity resistance, R_I , at high temperatures:

$$R_I = \frac{4\pi^2 V_o^2 \Gamma_o}{v^2 h} \quad (11)$$

$$\Gamma = \sum_i \Gamma_i$$

This relationship should apply in the limit of weak point-defect scattering and, accordingly, R_I would be essentially independent of temperature.

Klemens⁽¹⁰⁾ has shown that for strong point-defect scattering in the absence of N-processes

$$R_I \propto T^{1/2} \epsilon^{1/2} \quad (12)$$

Abeles⁽⁸⁾ arrived at a similar expression when N-processes were included in the analysis. However, the quantitative agreement between theory and experiment was improved.

If the expressions for R_U and R_I given in Equations (6) and (11), respectively, are substituted into Equation (5), the total thermal resistance, in the case of weak defect scattering, can be expressed in terms of absolute temperature by a relationship of the form

$$R = A + BT \quad (13)$$

where $A = R_I$ and the temperature coefficient, B , is given in the Liebfreid-Schlömann relationship [Equation (6)]. In the case of strong defect scattering, since $R_I \propto T^{1/2}$, then

$$R = DT^{1/2} + BT \quad (14)$$

Variation in the concentration of one defect will, according to Equation (11), permit the thermal resistance for small defect concentrations to be expressed by relationships of the form

$$R = A_1 \epsilon + A_2 + BT \quad (15)$$

$$R = D_1 \epsilon^{1/2} T^{1/2} + D_2 T^{1/2} + BT \quad (16)$$

for the cases of weak and strong point-defect scattering, respectively. The quantities A_2 and $D_2 T^{1/2}$, in these expressions, are the thermal resistance contributions from all point defects whose concentrations are fixed, and ϵ is the variable defect concentration per unit volume.

Since C_v is essentially constant at high temperatures, reciprocal thermal diffusivity may also be expressed by relationships similar to those of Equations (13) through (16), differing only by C_v .

RESULTS AND DISCUSSION

THERMAL DIFFUSIVITY

The thermal diffusivity data for sintered $U_{0.75}Pu_{0.25}O_{2-x}$ samples prepared from mechanically mixed powder are tabulated in the Appendix, and the reciprocal thermal diffusivities are plotted against absolute temperature for each oxygen stoichiometry in Figure 3. The results for successive measurements on a stoichiometric sample to 1600 °C agreed to better than $\pm 5\%$, the calculated precision of the apparatus. The original plan of this study was to use the same sample in each run and, by varying only stoichiometry, to eliminate the normal variation in density and impurity content from sample to sample which could mask the effects of oxygen content. However, after approximately six runs at different stoichiometries, the thermal diffusivity of the sample measured again at stoichiometric composition was observed to be slightly lower than originally determined. This difference, previously unobserved, was attributed to damage of the microstructure from the volume changes associated with successive adjustments of stoichiometry. For this reason, a second sample from the same pellet was used in the investigation for a measurement at

an O/M = 1.97. The thermal diffusivity of this sample at stoichiometric composition was in excellent agreement with the original results for the first sample.

In most cases, the thermal diffusivity data for hypostoichiometric compositions were not reproducible because (1) a given stoichiometry was difficult to reproduce by the reduction process, (2) the actual stoichiometry attained in the process could not be determined accurately, and (3) the hypostoichiometric samples oxidized slightly during the measurements at the higher measurement temperatures because of oxygen contamination in the protective atmosphere, thus eliminating the possibility of successive measurements on the sample at the same stoichiometry. The data obtained, however, for the several different oxygen stoichiometries studied were self consistent.

Neg 0683641-4

FIGURE 3. Reciprocal Thermal Diffusivity as a Function of Absolute Temperature and Oxygen Stoichiometry (Dashed line indicates extrapolation for A' .)

As can be seen in Figure 3, the reciprocal thermal diffusivity varied linearly with absolute temperature as predicted by Equation (13). Deviation from linearity at the higher measurement temperatures is attributed to changes in stoichiometry from sample oxidation.

The intercepts (A') of the curves in Figure 3 varied linearly with the amount of missing oxygen, x , as predicted by Equation (15), while the slopes (B') were independent of oxygen concentration. The general equation for the thermal diffusivity of $U_{0.75}Pu_{0.25}O_{2-x}$ in terms of temperature and oxygen content which best fit the experimental data was

$$1/\alpha = 0.110T + 1.08 \times 10^3 x + 4 \text{ (sec/cm}^2\text{)} \quad (17)$$

The results of this study as given by the preceding relationship are compared in Figure 4 with the results reported previously⁽¹⁾ for $U_{0.80}Pu_{0.20}O_{2.00}$ samples prepared from coprecipitated powder and the results of Van Craeynest and Weilbacher⁽⁴⁾ for a $U_{0.80}Pu_{0.20}O_{2-x}$ material prepared from physically blended powder. The present data for stoichiometric mixed oxide are approximately 16% lower than the data obtained previously for $U_{0.80}Pu_{0.20}O_{2.00}$, and are up to 20% lower than Van Craeynest and Weilbacher's data for stoichiometric mixed oxide. The differences between the results of this study and those reported previously are attributed to differences in homogeneity and porosity rather than to the 5% difference in PuO_2 content. The microstructure of the coprecipitated material showed no evidence of additional phases. However, the microstructure of the present material, prepared from physically blended powder, does indicate regions of incomplete solid solution formation. In addition, although the measured densities of the two materials are

Neg 0683641-3

FIGURE 4. Thermal Diffusivity of $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2-x}$ According to Equation (17) (Other data are shown for comparison.)

supposed to be the same, the microstructure of the present material shows a larger amount of porosity as well as some lamellar-shaped pores oriented with their large surfaces normal to the direction of heat flow. The orientation of these pores also may account for the lower thermal diffusivity.

For hypostoichiometric mixed oxides, Van Craeynest and Weilbacher's data appear to show a much stronger dependence of thermal diffusivity on oxygen concentration than do the results of this study, at least for a small deviation from stoichiometric composition. However, in view of the general difficulty in accurately determining the oxygen content of the hypostoichiometric mixed oxides, the data are in reasonable agreement.

THERMAL CONDUCTIVITY

Thermal conductivity λ was calculated using the expression

$$\lambda = 4.185 \alpha \rho C_p, \text{ W/cm-}^\circ\text{K} \quad (18)$$

where α is the measured thermal diffusivity (cm^2/sec), ρ is the measured density (g/cm^3) and C_p is the heat capacity at constant pressure ($\text{cal/g-}^\circ\text{K}$).

The variation of density with O/M was calculated from lattice parameters measured as a function of O/M. The theoretical densities were converted to actual densities by assuming no change in porosity during the high-temperature reduction treatments. The variation of density with temperature was calculated from thermal expansion data.⁽¹¹⁾ The effect of oxygen content on the thermal expansion coefficient has not been reported. However, this effect was not expected to greatly alter the calculated high-temperature densities.

The heat capacity of UO_2 -20 wt% PuO_2 from 1100 to 2400 $^\circ\text{K}$ has been reported by Ogard and Leary⁽¹²⁾ for O/M ratios of 2.00 and 1.98. According to their results, the heat capacity of the mixed oxides above 1400 $^\circ\text{K}$ is higher than the heat capacity of UO_2 as reported by Conway and Hein,⁽¹³⁾ and the stoichiometric mixed oxide is slightly higher than the hypostoichiometric composition. Below 1400 $^\circ\text{K}$, their heat capacity data are lower than the UO_2 data of Moore and Kelley.⁽¹⁴⁾ Since data are not available for $\text{U}_{0.75}\text{Pu}_{0.25}\text{O}_{2-x}$, the heat capacities used in this study were calculated by combining the heat capacities for UO_2 ⁽¹⁵⁾ and PuO_2 ⁽¹⁶⁾ in proportion to their respective mole fractions (Kopp's law) in the solid solution. Since the heat capacity of PuO_2 is

higher than UO_2 at lower temperatures, the calculated heat capacity of the mixed oxide is also slightly higher and in qualitative agreement with the results of Ogard and Leary. Observations by Ogard and Leary of a slight heat capacity decrease with oxygen content were neglected in these calculations inasmuch as the magnitude of this effect does not appear to be great.

The calculated thermal conductivities for each oxygen composition are tabulated in the Appendix, and reciprocal thermal conductivity (thermal resistance) is plotted against absolute temperature in Figure 5.

Neg 0683641-2

FIGURE 5. Calculated Thermal Resistance as a Function of Absolute Temperature and Oxygen Stoichiometry (Dashed line indicates extrapolations for A.)

The thermal resistance, like reciprocal thermal diffusivity, obeyed a linear temperature relationship for all oxygen compositions. The slopes (B) of the curves were essentially the same for all oxygen compositions, while the intercepts (A) increased linearly with a decrease in oxygen content. The general equation for the thermal resistance best fit by the data of this study is

$$W = 1/\lambda = 0.0312T + 3.55 \times 10^2 x + 1.5 \text{ (cm-}^\circ\text{K/W)} . \text{ (19)}$$

This expression is plotted in Figure 6 as a function of x and T . The steady-state data of Schmidt and Richter⁽³⁾ for $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{2-x}$ compositions and of Godfrey et al.⁽¹⁷⁾ for UO_2 are shown for comparison. Our results, considering the use in this study of estimated heat capacities for calculating thermal conductivity, are in reasonable agreement with those for the mixed oxides.

Temperature Coefficient (B)

The thermal conductivity determined in this study shows a much stronger temperature dependence than Schmidt and Richter's data. Moreover, this difference cannot be completely attributed to the possible use of incorrect heat capacities in the calculations. A comparison of temperature coefficients (B) in Table 2 shows the coefficient reported by Schmidt and Richter for $\text{U}_{0.80}\text{Pu}_{0.20}\text{O}_{2-x}$ to be in excellent agreement with the values of Godfrey et al. for UO_2 as expected in accordance with the Leibfreid-Schlömann relationship of Equation (6), since the similarity in properties affecting the intrinsic thermal conduction for UO_2 and PuO_2 would be expected to extend to their solid solutions as well. Since results of this study show a stronger temperature dependence than Schmidt and Richter's data (Figure 6), the temperature coefficient is

Neg 0683641-1

FIGURE 6. Thermal Conductivity of $U_{0.75}Pu_{0.25}O_{2-x}$ According to Equation (19) (Other data shown for Comparison.)

also obviously higher. The temperature coefficient reported by Van Craeynest and Weilbacher for $U_{0.80}Pu_{0.20}O_{2-x}$ is also higher than the Schmidt and Richter value, although less than our value. Because the Van Craeynest and Weilbacher data were calculated from transient measurements, the value of their temperature coefficient may also be related to the use of incorrect heat capacities. However, heat transport differences arising, for instance, from measurement techniques, i.e., transient versus steady state, are also possible and should not be dismissed. The temperature coefficient determined in this study, although apparently too high, is not an unreasonable value since, from the Leibfreid-Schlömann relationship it corresponds to a Debye temperature of 190 °K. This value is in excellent agreement with the Debye temperature of 188 °K determined for UO_2 ⁽¹⁸⁾ by X-ray diffraction studies.

TABLE 2. *Values of the Temperature Coefficient (B) [Equation (13)] for (U,Pu)O₂ Compositions and UO₂*

<u>Material</u>	<u>B (cm-°K/W)</u>	<u>Source</u>
UO ₂	0.0223	Godfrey et al. ⁽¹⁷⁾
U _{0.80} Pu _{0.20} O _{2-x}	0.0213	Schmidt and Richter ⁽¹³⁾
U _{0.80} Pu _{0.20} O _{2-x}	0.0269*	Van Craeynest and Weilbacher ⁽⁴⁾
U _{0.75} Pu _{0.25} O _{2-x}	0.0312*	This study

* Determined from calculated thermal conductivities.

Defect Thermal Resistance (A)

The thermal resistance due to lattice defects (A) is shown as a function of the amount of missing oxygen, x, in Figure 7. The data of Schmidt and Richter, and of Van Craeynest and Weilbacher, are also shown for comparison. The results of this study are in excellent agreement with the Schmidt and Richter data and, although Van Craeynest and Weilbacher's data are somewhat higher, the close similarity of their curve slope shows a similar dependence on x.

A linear increase in A as oxygen is removed from the lattice is consistent with the assumption of Equation (15) that the defect resistance (A) is much less than the intrinsic resistance (BT). A comparison of the respective values of A and BT shows this assumption to be valid for U_{0.75}Pu_{0.25}O_{2-x}.

The experimental data in Figure (7) obeys the linear relationship

$$A = 355x + 1.5 \quad (20)$$

The first term on the right-hand-side (R.H.S.) of the expression corresponds to the defect resistance arising from oxygen removal, while the second term is the thermal resistance

Neg 0683413

FIGURE 7. Defect Thermal Resistance (A) as a Function of Oxygen Stoichiometry (Dashed line indicates theoretical relationship expected according to phenomenological model of Klemen's.)

associated with all other point defects. Therefore, in comparing this relationship with that expected from theoretical consideration, only the first term on the R.H.S. of this equation need be considered.

Calculation of the defect thermal resistance, according to Equation (11), requires information concerning the defects such as types of defects, mass differences, size differences, etc. As oxygen is removed from $U_{0.75}Pu_{0.25}O_{2-x}$, the lattice expands and, simultaneously, the density decreases. The charge imbalance created by removal of an oxygen ion is compensated by reduction of two Pu^{+4} ions to a valence of +3. The size of the +3 ion (1.07 Å compared to 0.93 Å for the +4)⁽¹⁹⁾ accounts for some of the observed expansion. However, as will be shown later, oxygen vacancies also account for some expansion. This expansion is reasonable since the removal of an oxygen ion leaves four cations as nearest neighbors to the vacant site. Mutual interaction of their coulombic repulsive forces in the absence of the attractive force of the oxygen ion will therefore result in an effective expansion of the vacant site. Klemens⁽⁵⁾ has estimated that, in KCl doped with Ca^{+2} ions, the K^{+} vacancies are approximately 10% larger than the replaced K^{+} ion.

According to Equation (10), the thermal resistance from defect-phonon interactions can result from both mass and size difference. These effects are now considered separately in order to assess the individual contribution to thermal resistance. The effect of the mass difference due to the missing oxygen ion will be considered first, followed by the effect of the size difference for both the Pu^{+3} ion and the oxygen ion vacancy.

In the case of compounds, the value of Γ resulting from mass fluctuations cannot be calculated directly from Equation (10). However, Slack⁽²⁰⁾ gives relationships applicable to this calculation as follows:

$$\begin{aligned} \Gamma(A_x B_y C_z) = & \frac{x}{x+y+z} \left(\frac{M_A}{\bar{M}} \right)^2 \Gamma(A) + \frac{y}{x+y+z} \left(\frac{M_B}{\bar{M}} \right)^2 \Gamma(B) \\ & + \frac{z}{x+y+z} \left(\frac{M_C}{\bar{M}} \right)^2 \Gamma(C) \end{aligned} \quad (21)$$

where

$$\bar{M} = \frac{xM_A + yM_B + zM_C}{x + y + z}$$

and

$$\Gamma(A) = \frac{1}{12} \sum_j f_j \left(\frac{M_j - M_A}{M_A} \right)^2 = \frac{1}{12} \sum_j f_j \left(\frac{\Delta M_A}{M_A} \right)^2$$

$$M_A = \sum_j f_j M_j$$

and $\Gamma(B)$ and $\Gamma(C)$ are also given by similar expressions. The fractional concentration, f_j , is for the j th isotope of mass M_j . In using these relationships, the compound is treated as a monatomic solid with an average mass per atom of $\bar{M}$ and an average volume per atom of V_0 .

For an oxygen ion vacancy, $\frac{\Delta M}{\bar{M}} = -1$, and Γ value for the oxygen is

$$\Gamma(O) = \frac{1}{12} f_v \quad (22)$$

where $f_v = \frac{x}{2}$ is the fraction of vacant oxygen sites according to the formula MO_{2-x} . The Γ values for the isotopes of uranium and plutonium, as well as those for chemical impurities, are not included in this calculation since the thermal resistances resulting from these sources are not a function of

oxygen content and, consequently, are included in the second term on the R.H.S. of Equation (20). The Γ value for the compound MO_{2-x} is, therefore,

$$\Gamma = \frac{2-x}{3-x} \times \left(\frac{16}{90.3}\right)^2 \times \frac{1}{12} \times \frac{x}{2}$$

which, for $x \ll 1$, reduces to

$$\Gamma = 8.72 \times 10^{-4} x \quad (23)$$

Inserting this relationship in Equation (11), and assuming

$$\theta = 190^\circ \text{K},$$

$$V = 3.7 \times 10^5 \text{ cm/sec, and}$$

$$V_o = 13.56 \times 10^{-24} \text{ cm}^3$$

then the thermal resistance resulting from oxygen vacancies is

$$R_I = 0.93x \quad (24)$$

This expression gives a much smaller increase in thermal resistance with vacancy concentration (x) than the experimental results of Equation (20). Although estimated values of θ and V were used in evaluation of Equation (11), reasonable variation of these quantities does not result in significantly better agreement with experimental results. Since these calculations should agree to within at least an order of magnitude with the experimental results, mass fluctuations due to the oxygen vacancies are not concluded to be the important source of the defect resistance. Damon⁽²¹⁾ has observed in tin-telluride that the defect resistance due to tin vacancies

is also not completely accounted for by mass fluctuations. Like $(U,Pu)O_{2-x}$, tin shows appreciable lattice dilatation as vacancies are formed. Damon showed that the defect resistance in SnTe could be correlated with a localized strain model in which strains occurred around the tin vacancies which were smaller in size than the occupied tin sites.

The contribution to point defect thermal resistance from bonding and size differences can be calculated using Equation (11), and using Equation (10) for r . The term involving mass fluctuations in the latter relationship has already been considered and, hence, is ignored in this calculation. Since there are size differences associated with both the Pu^{+3} ion and the oxygen ion vacancy, the total r value is the sum of the r determined for each defect.

The value of $\Delta r/r$ for each defect type was determined from the total increase in volume of the unit cell upon removal of a known amount of oxygen. Because this volume is a sum of the volume increase associated with both defects, individual assessments of $\Delta r/r$ from just the total volume change alone were not possible. To evaluate $\Delta r/r$ for each defect, therefore, the value for the Pu^{+3} ion was estimated using the following relationship:⁽²²⁾

$$\frac{\Delta r}{r} = \frac{r_i - r}{r} = \frac{\mu}{1 + \mu} \frac{r'_i - r}{r} \quad (25)$$

where

$$\mu = \frac{(1 + \nu) G_i}{2G (1 - 2\nu)}$$

and G and ν are the bulk modulus and Poisson's ratio of the matrix, respectively, and G_i is the bulk modulus of the impurity atom. The radius of the impurity atom in its own lattice is r'_i , while r_i is its radius in the host lattice.

Taking $r'_i = 1.07 \text{ \AA}$, $r_i = 0.93$, $G_i/G \approx 1$, and $\nu \approx 0.3$, then $\Delta r_i/r$ for the Pu^{+3} ion was determined as 0.09. Using this quantity, a volume change was calculated and the difference between this volume and measured volume change was attributed to oxygen ion vacancies. Thus, $\Delta r_i/r$ for oxygen ion vacancies, estimated to be 0.15, is in reasonable agreement with Klemens' suggested value of 0.10 for vacancies in an ionic solid.

Using these values of $\Delta r_i/r$ for Pu^{+3} ions and oxygen vacancies, the value of Γ as a function of the respective defect concentrations per unit volume, $\epsilon_{\text{Pu}^{+3}}$ and ϵ_v , was

$$\Gamma = \frac{V_o}{12} \left[9.1 \epsilon_v + 3.4 \epsilon_{\text{Pu}^{+3}} \right] \quad (26)$$

where the Gruneisen constant (Γ) was taken as 1.6. Since

$$\epsilon_v = \frac{4x}{a_o^3} \quad (27)$$

where a_o is the lattice parameter, and since $\epsilon_{\text{Pu}^{+3}} = 2\epsilon_v$, then Equation (26) reduces to

$$\Gamma = 0.454x \quad (28)$$

which, substituted into Equation (11), yields the following expression for the defect thermal resistance:

$$R_I = 475x \quad (29)$$

This expression is shown in Figure 7 with the experimental results. The total defect resistance for all other point defects has been added to the immediately preceding expression for the comparison. The theoretical expression overestimates the experimental values of thermal resistance by a

factor of 1.3. The agreement of this factor is considered excellent, especially in view of the necessarily simple model employed in deriving the theoretical relationship.

The number of associated defect complexes at any temperature is an important though unconsidered variable in this discussion. Although the degree of defect association is not known in the hypostoichiometric mixed oxide, these defect complexes could result in a reduced defect thermal resistance contribution which, if taken into account, could result in even better agreement with the experimental value.

Schmidt and Richter⁽³⁾ found that, for $U_{0.80}Pu_{0.20}O_{2-x}$ compositions, the defect thermal resistance (A) was the same for an O/M = 1.95 and an O/M = 1.88. According to Equation (29), (A) should continue to increase linearly as oxygen is removed from the lattice. However, in the uranium-plutonium oxide system when the PuO_2 content is less than 40 wt%, the amount of oxygen which can be removed is limited by the number of Pu^{+4} ions available to be reduced to the +3 valence state.⁽²³⁾ In other words, for a composition containing 20 wt% PuO_2 , the minimum possible O/M ratio is 1.90 ($x = 0.10$), and for 25 wt% PuO_2 , 1.88 ($x = 0.12$). Under strongly reducing conditions at sufficiently high temperatures, lower oxygen contents may be obtained, but the final product is no longer single phase. When a second phase is precipitated, therefore, the concentration of oxygen associated defects remains constant and, consequently, (A) should also remain constant. For small amounts of second-phase precipitate, the thermal resistance should not be affected unless the particle size of the precipitate is equal to, or less than, the wavelength of the vibration modes primarily responsible for heat transfer. Schmidt and Richter indicate that (A) is constant below an O/M = 1.95 which, for 20 wt% PuO_2 , is somewhat higher than the expected value of 1.90. In spite of this difference

in O/M, however, their results appear to exhibit the expected behavior of (A) when additional oxygen removal does not further increase the number of oxygen associated defects.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. R. J. Shogren for preparing the sintered mixed oxide pellets used in this study, Mr. R. V. Olson for his assistance with metallography, and Mr. T. C. Berry and Mr. H. C. Buchanan for preparing the test samples and making the experimental measurements.

REFERENCES

1. R. L. Gibby. The Thermal Diffusivity and Thermal Conductivity of Stoichiometric $(U_{0.8}Pu_{0.2})O_2$, BNWL-704. Pacific Northwest Laboratory, Richland, Washington, May 1968.
2. F. J. Hetzler, T. E. Lannin, K. J. Perry, and E. L. Zebroski. "Thermal Conductivity of 20:80 (Pu:U)O₂," Trans. Am. Nucl. Soc., vol. 8, no. 1. June 1965.
3. H. E. Schmidt and J. Richter. "The Influence of Stoichiometry on the Thermal Conductivity of $(U_{0.8}Pu_{0.2})O_{2+x}$," presented at Oxide Fuel Thermal Conductivity Symposium, Stockholm, Sweden, June 1, 1967.
4. J. C. Van Craeynest and J. C. Weilbacher. "Etude de la Conductibilite Thermique des Oxydes Mixtes D'Uranium et de Plutonium," J. Nucl. Mater., vol. 26, no. 1, pp. 132-136. 1968.
5. P. G. Klemens. "The Scattering of Low-Frequency Lattice Waves by Static Imperfections," Proc. Phys. Soc. (London), A-68, p. 1113. 1955.
6. Joseph Callaway. "Model for Lattice Thermal Conductivity at Low Temperatures," Phys. Rev., vol. 113, no. 4, pp. 1046-1051. 1959.
7. V. Ambegaokar. "Thermal Resistance Due to Isotope at High Temperatures," Phys. Rev., vol. 114, no. 2, pp. 488-489. 1959.

8. B. Abeles. "Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures," Phys. Rev., vol. 131, no. 5, pp. 1906-1911. 1963.
9. G. Leibfreid and E. Schlömann. "Heat Conduction in Electrically Insulating Crystals," Nachr. Akad. Wiss. Gottingen, Math-Physik. Kl., II-a, p. 71. 1954.
10. P. G. Klemens. "Thermal Resistance Due to Point Defects at High Temperatures," Phys. Rev., vol. 119, no. 2, pp. 507-509. 1960.
11. G. Berggren and R. S. Forsyth. "Some Studies of the High Temperature Behavior of PuO_2 and $\text{PuO}_2\text{-UO}_2$ Mixtures," Plutonium 1965, edited by A. E. Kay and M. B. Waldron. Chapman and Hall Ltd., London, 1967.
12. A. E. Ogard and J. A. Leary. "High Temperature Heat Content and Heat Capacity of Uranium Dioxide and Uranium Dioxide - Plutonium Dioxide Solid Solutions," presented at IAEA Symposium on Thermodynamics of Nuclear Materials, Conf. 6.70915-5, Vienna, September 4-8, 1967.
13. J. B. Conway and R. A. Hein. "Enthalpy of Uranium Dioxide to 2350 °C," J. Nucl. Mater., vol. 15, no. 1, pp. 149-150. 1965.
14. G. E. Moore and K. K. Kelley. "High Temperature Heat Contents of Uranium, Uranium-Dioxide, and Uranium Trioxide," J. Am. Chem. Soc., vol. 69, no. 9, pp. 2105-2107. 1947.
15. T. G. Godfrey, J. A. Wooley, and J. M. Leitnaker. Thermodynamic Functions of Nuclear Materials: UC, UC_2 , UO_2 , ThO_2 , and UN, ORNL-TM-1596, Oak Ridge National Laboratory, December 1966.
16. T. K. Engle. "Heat Capacity of Plutonium Dioxide from 300 to 1100 °K," presented at Pacific Coast Regional Meeting, Am. Cer. Soc., San Francisco, Cal., November 1-3, 1967.
17. T. G. Godfrey, W. Fulkerson, T. G. Kollie, J. P. Moore, and D. L. McElroy. "Thermal Conductivity of Uranium Dioxide from -57 °C to 1100 °C by a Radial Heat Flow Technique," J. Am. Cer. Soc., vol. 48, no. 6, pp. 297-305. 1965.

18. C. J. Sparks and B. S. Borie. "Advances in X-Ray Analysis," Proceedings of the Eleventh Annual Conference on Applications of X-Ray Analysis, August 1962, Denver, edited by W. M. Mueller and Marie Fay. Plenum Press, New York, 1963. vol. 6, pp. 177-184.
19. Linus Pauling. The Nature of the Chemical Bond. Cornell University Press, Ithica, New York, 1960. Third Edition, p. 518.
20. G. A. Slack. "Thermal Conductivity of MgO , Al_2O_3 , $MgAl_2O_4$, and Fe_2O_4 Crystals from 3 to 300 °K," Phys. Rev., vol. 126, no. 2, pp. 427-441. 1962.
21. D. H. Damon. "Thermal Conductivity of SnTe Between 100 °K and 500 °K," J. Appl. Phys., vol. 37, no. 8, pp. 3181-3190. 1960.
22. J. D. Eshelby. "The Continuum Theory of Lattice Defects," Solid State Physics, edited by F. Seitz and D. Turnbull, Academic Press Inc., New York, 1956. vol. 3, p. 107.
23. T. L. Markin and R. S. Street. "The Uranium-Plutonium-Oxygen Ternary Phase Diagram," J. Inorg. Nucl. Chem., vol. 29, pp. 2265-2280. 1967.

APPENDIX

THERMAL DIFFUSIVITY AND CONDUCTIVITYOF $U_{0.75}Pu_{0.25}O_{2-x}$

SAMPLE NO. 032768

 $\chi = 0.007 - 0.015$ $a_o = 5.4561 \text{ \AA}$

$T, \text{ } ^\circ\text{C}$	$\alpha, \text{ cm}^2/\text{sec}$	$C_p, \text{ cal/g-}^\circ\text{K}$	$\rho, \text{ g/cm}^3$	$\lambda, \text{ W/cm-}^\circ\text{K}$
133	0.0147	0.0689	10.51	0.0446
156	0.0154	0.0701	10.50	0.0475
203	0.0141	0.0724	10.48	0.0448
251	0.0127	0.0744	10.46	0.0414
300	0.0121	0.0759	10.45	0.0402
350	0.0115	0.0773	10.43	0.0388
403	0.0107	0.0783	10.42	0.0365
452	0.0101	0.0791	10.40	0.0347
501	0.00940	0.0796	10.38	0.0325
576	0.00862	0.0800	10.36	0.0300
602	0.00858	0.0802	10.35	0.0299
650	0.00837	0.0803	10.33	0.0291
701	0.00803	0.0804	10.31	0.0279
751	0.00776	0.0804	10.29	0.0269
807	0.00714	0.0803	10.28	0.0247
850	0.00704	0.0802	10.26	0.0243
901	0.00690	0.0801	10.24	0.0237
975	0.00694	0.0801	10.22	0.0238
1002	0.00655	0.0801	10.21	0.0225
1054	0.00635	0.0802	10.19	0.0217
1103	0.00624	0.0803	10.17	0.0213
1152	0.00611	0.0805	10.15	0.0209
1207	0.00590	0.0808	10.13	0.0202

SAMPLE NO. 122768

$$\chi = 0.000$$

$$a_0 = 5.4515 \text{ \AA}$$

$T, \text{ } ^\circ\text{C}$	$\alpha, \text{ cm}^2/\text{sec}$	$C_p, \text{ cal/g-}^\circ\text{K}$	$\rho, \text{ g/cm}^3$	$\lambda, \text{ W/cm-}^\circ\text{K}$
174	0.0199	0.0710	10.54	0.0623
200	0.0203	0.0723	10.53	0.0647
251	0.0179	0.0744	10.51	0.0586
300	0.0166	0.0759	10.50	0.0554
350	0.0148	0.0773	10.48	0.0502
402	0.0131	0.0783	10.47	0.0450
452	0.0124	0.0791	10.45	0.0429
500	0.0115	0.0795	10.43	0.0399
552	0.0112	0.0799	10.41	0.0390
603	0.00994	0.0802	10.40	0.0347
650	0.00949	0.0803	10.38	0.0331
700	0.00873	0.0804	10.36	0.0304
752	0.00814	0.0804	10.34	0.0283
800	0.00793	0.0803	10.33	0.0275
850	0.00756	0.0802	10.31	0.0262
901	0.00739	0.0801	10.29	0.0255
954	0.00696	0.0801	10.27	0.0240
1001	0.00678	0.0801	10.26	0.0233
1050	0.00671	0.0801	10.24	0.0230
1104	0.00657	0.0803	10.22	0.0226
1151	0.00639	0.0805	10.20	0.0220
1200	0.00620	0.0808	10.18	0.0213
1095	0.00654	0.0803	10.23	0.0225
999	0.00705	0.0801	10.26	0.0243
901	0.00754	0.0801	10.29	0.0260

SAMPLE NO. 122768 (contd)

<u>T,</u> <u>°C</u>	<u>α,</u> <u>cm²/sec</u>	<u>C_p,</u> <u>cal/g-°K</u>	<u>ρ,</u> <u>g/cm³</u>	<u>λ,</u> <u>W/cm-°K</u>
795	0.00797	0.0803	10.33	0.0277
666	0.00920	0.0803	10.38	0.0321
594	0.0102	0.0801	10.40	0.0356
493	0.0117	0.0795	10.44	0.0406
408	0.0135	0.0784	10.47	0.0464
287	0.0157	0.0755	10.50	0.0521
198	0.0192	0.0722	10.53	0.0611
153	0.0204	0.0699	10.55	0.0630

SAMPLE NO. 122167

$$\chi = 0.000$$

$$a_o = 5.4515 \text{ \AA}$$

$T, ^\circ\text{C}$	$\alpha, \text{cm}^2/\text{sec}$	$C_p, \text{cal/g-}^\circ\text{K}$	$\rho, \text{g/cm}^3$	$\lambda, \text{W/cm-}^\circ\text{K}$
143	0.0157	0.0694	10.55	0.0481
143	0.0165	0.0694	10.55	0.0506
143	0.0173	0.0694	10.55	0.0530
169	0.0148	0.0707	10.54	0.0462
210	0.0145	0.0728	10.53	0.0465
257	0.0140	0.0746	10.51	0.0459
300	0.0131	0.0759	10.50	0.0437
357	0.0126	0.0774	10.48	0.0428
400	0.0119	0.0783	10.47	0.0408
460	0.0112	0.0791	10.45	0.0388
500	0.0110	0.0795	10.43	0.0382
554	0.0104	0.0799	10.41	0.0362
600	0.00975	0.0802	10.40	0.0340
652	0.00946	0.0803	10.38	0.0330
703	0.00863	0.0803	10.36	0.0301
754	0.00846	0.0804	10.34	0.0294
819	0.00783	0.0803	10.32	0.0272
858	0.00761	0.0802	10.31	0.0263
940	0.00736	0.0801	10.28	0.0254
988	0.00674	0.0801	10.26	0.0232
1050	0.00673	0.0802	10.24	0.0231
1103	0.00668	0.0803	10.22	0.0229
1154	0.00622	0.0805	10.20	0.0214
1201	0.00606	0.0808	10.18	0.0209
1254	0.00612	0.0813	10.16	0.0212
1303	0.00571	0.0817	10.14	0.0198
1350	0.00561	0.0824	10.12	0.0196

SAMPLE NO. 122167 (contd)

<u>T,</u> <u>°C</u>	<u>α,</u> <u>cm²/sec</u>	<u>C_p,</u> <u>cal/g-°K</u>	<u>ρ,</u> <u>g/cm³</u>	<u>λ,</u> <u>W/cm-°K</u>
1409	0.00571	0.0832	10.10	0.0201
1447	0.00532	0.0840	10.08	0.0189
1500	0.00529	0.0853	10.06	0.0190
1549	0.00532	0.0863	10.04	0.0193
1600	0.00506	0.0877	10.03	0.0186
1553	0.00544	0.0863	10.04	0.0197
1486	0.00581	0.0847	10.07	0.0207
1479	0.00491	0.0847	10.07	0.0175
1375	0.00550	0.0828	10.11	0.0193
1263	0.00615	0.0813	10.16	0.0213
1150	0.00661	0.0805	10.20	0.0227
1039	0.00674	0.0801	10.24	0.0231
949	0.00728	0.0801	10.27	0.0251
838	0.00762	0.0803	10.32	0.0264
735	0.00816	0.0804	10.35	0.0284
616	0.0110	0.0802	10.39	0.0384
361	0.0138	0.0774	10.48	0.0469
350	0.0137	0.0772	10.48	0.0464
285	0.0166	0.0752	10.50	0.0549
252	0.0174	0.0744	10.51	0.0570
191	0.0194	0.0716	10.54	0.0613
150	0.0207	0.0676	10.55	0.0617

SAMPLE NO. 010968

$$\chi = 0.067 - 0.068$$

$$a_o = 5.4715 \text{ \AA}$$

$T, \text{ } ^\circ\text{C}$	$\alpha, \text{ cm}^2/\text{sec}$	$C_p, \text{ cal/g-}^\circ\text{K}$	$\rho, \text{ g/cm}^3$	$\lambda, \text{ W/cm-}^\circ\text{K}$
184	0.00829	0.0715	10.37	0.0258
202	0.00794	0.0724	10.36	0.0249
274	0.00716	0.0752	10.34	0.0233
311	0.00725	0.0763	10.33	0.0239
319	0.00684	0.0765	10.32	0.0226
352	0.00674	0.0773	10.31	0.0225
423	0.00649	0.0788	10.29	0.0220
425	0.00637	0.0788	10.29	0.0216
458	0.00618	0.0791	10.28	0.0211
500	0.00609	0.0796	10.26	0.0209
614	0.00564	0.0802	10.22	0.0194
650	0.00543	0.0803	10.21	0.0186
706	0.00538	0.0804	10.19	0.0185
751	0.00514	0.0803	10.17	0.0176
800	0.00511	0.0802	10.16	0.0174
854	0.00487	0.0802	10.14	0.0166
909	0.00476	0.0801	10.12	0.0161
950	0.00465	0.0801	10.10	0.0157
1005	0.00452	0.0801	10.09	0.0152
1060	0.00444	0.0802	10.07	0.0150
1102	0.00448	0.0803	10.05	0.0152
1150	0.00437	0.0805	10.03	0.0148

SAMPLE NO. 012368

 $\chi = 0.031 - 0.042$ $a_0 = 5.4607 \text{ \AA}$

$T,$ $^{\circ}\text{C}$	$\alpha,$ cm^2/sec	$C_p,$ $\text{cal/g} - ^{\circ}\text{K}$	$\rho,$ g/cm^3	$\lambda,$ $\text{W/cm} - ^{\circ}\text{K}$
105	0.0120	0.0668	10.47	0.0352
168	0.0113	0.0707	10.44	0.0349
202	0.0106	0.0724	10.43	0.0335
263	0.00980	0.0748	10.41	0.0320
300	0.00893	0.0759	10.40	0.0295
364	0.00843	0.0775	10.38	0.0284
400	0.00801	0.0783	10.37	0.0272
460	0.00772	0.0791	10.35	0.0264
517	0.00741	0.0797	10.32	0.0256
554	0.00717	0.0799	10.31	0.0248
603	0.00693	0.0802	10.30	0.0240
648	0.00643	0.0803	10.28	0.0222
703	0.00638	0.0803	10.26	0.0220
752	0.00608	0.0803	10.24	0.0209
800	0.00607	0.0803	10.23	0.0209
851	0.00568	0.0802	10.21	0.0195
908	0.00567	0.0802	10.19	0.0194
952	0.00551	0.0801	10.17	0.0188
1003	0.00529	0.0801	10.16	0.0180
1052	0.00506	0.0802	10.14	0.0172
1117	0.00476	0.0804	10.11	0.0162
1162	0.00508	0.0806	10.10	0.0173
1200	0.00491	0.0808	10.08	0.0167

SAMPLE NO. 011668

 $\chi = 0.045 - 0.046$ $a_o = 5.4650 \text{ \AA}$

<u>T,</u> <u>°C</u>	<u>α,</u> <u>cm²/sec</u>	<u>Cp,</u> <u>cal/g-°K</u>	<u>ρ,</u> <u>g/cm³</u>	<u>λ,</u> <u>W/cm-°K</u>
156	0.0118	0.0701	10.45	0.0362
204	0.00994	0.0725	10.43	0.0315
263	0.00935	0.0748	10.41	0.0305
318	0.00883	0.0765	10.39	0.0294
352	0.00833	0.0773	10.38	0.0279
399	0.00746	0.0782	10.37	0.0254
464	0.00781	0.0791	10.35	0.0267
506	0.00708	0.0796	10.33	0.0244
550	0.00713	0.0799	10.31	0.0246
604	0.00671	0.0802	10.30	0.0232
651	0.00660	0.0803	10.27	0.0228
712	0.00615	0.0804	10.26	0.0212
751	0.00597	0.0803	10.24	0.0205
811	0.00584	0.0803	10.23	0.0201
855	0.00566	0.0802	10.21	0.0194
899	0.00566	0.0802	10.19	0.0194
951	0.00540	0.0801	10.17	0.0184
1004	0.00523	0.0801	10.16	0.0178
1047	0.00529	0.0802	10.14	0.0180
1110	0.00497	0.0803	10.12	0.0169
1159	0.00509	0.0805	10.10	0.0173
1200	0.00476	0.0808	10.08	0.0162

SAMPLE NO. 021968

 $\chi = 0.027 - 0.028$ $a_0 = 5.4600 \text{ \AA}$

$T,$ $^{\circ}\text{C}$	$\alpha,$ cm^2/sec	$C_p,$ $\text{cal/g-}^{\circ}\text{K}$	$\rho,$ g/cm^3	$\lambda,$ $\text{W/cm-}^{\circ}\text{K}$
124	0.0123	0.0684	10.48	0.0369
167	0.0121	0.0756	10.46	0.0401
212	0.0110	0.0729	10.45	0.0350
289	0.00984	0.0756	10.42	0.0325
309	0.00974	0.0762	10.42	0.0324
350	0.00931	0.0773	10.40	0.0314
401	0.00887	0.0782	10.39	0.0302
452	0.00829	0.0791	10.37	0.0285
500	0.00825	0.0796	10.35	0.0285
550	0.00759	0.0799	10.33	0.0262
589	0.00733	0.0801	10.32	0.0254
651	0.00691	0.0803	10.30	0.0239
701	0.00652	0.0804	10.28	0.0225
766	0.00642	0.0804	10.26	0.0221
805	0.00613	0.0803	10.25	0.0211
850	0.00597	0.0803	10.23	0.0205
910	0.00567	0.0802	10.21	0.0195
960	0.00562	0.0801	10.19	0.0193
1002	0.00563	0.0801	10.18	0.0193
1051	0.00549	0.0802	10.16	0.0188
1106	0.00531	0.0803	10.14	0.0181
1152	0.00517	0.0805	10.12	0.0177
1200	0.00533	0.0808	10.08	0.0182

DISTRIBUTION

No. of
Copies

OFFSITE

1	<u>AEC Chicago Patent Group</u> G. H. Lee
260	<u>AEC Division of Technical Information Extension</u>

ONSITE-HANFORD

1	<u>AEC Chicago Patent Group</u> R. K. Sharp (Richland)
2	<u>AEC RDT Site Representative</u> P. G. Holsted
1	<u>AEC Richland Operations Office</u> C. L. Robinson
3	<u>Battelle Memorial Institute</u>
71	<u>Battelle-Northwest</u> E. A. Astley W. J. Bailey D. E. Baker R. J. Baker J. L. Bates R. E. Bardsley J. A. Basmajian T. C. Berry D. W. Brite H. C. Buchanan C. A. Burgess T. B. Burley M. P. Burns D. C. Carlson T. D. Chikalla J. A. Christensen P. D. Cohn R. G. Curran G. M. Dalen J. L. Daniel D. R. de Halas D. Doran

Battelle Northwest (contd)

K. Drumheller
E. A. Evans
P. L. Farnsworth (2)
G. L. Fox
M. D. Freshley
R. L. Gibby (10)
W. J. Gray
W. J. Gruber
W. L. Hampson
J. E. Hanson
P. E. Hart
B. R. Hayward
R. J. Hennig
G. R. Horn
R. J. Lobsinger
S. J. Mayhan
C. E. McNeilly
M. K. Millhollen
R. P. Nelson
R. E. Nightingale
L. A. Pember
A. L. Pitner
W. E. Roake
R. K. Robinson
O. D. Slagle
F. M. Smith
H. A. Taylor
R. Teats
G. L. Tingey
E. T. Weber
H. H. Yoshikawa
F. R. Zaloudek
Technical Information Files (5)
Technical Publications (2)