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THE ELECTRICAL PROPERTIES OF URANIUM OXIDES

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THE ELECTRICAL PROPERTIES OF URANIUM OXIDES

Robert K. Willardson, Jerry W. Moody,
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The electrical conductivity and thermoelectric power of uranium oxides in the UO_2 - U_3O_7 range have been studied at temperatures between 27 and 400 C after annealing at 200, 400, 600, 800, and 1000 C. The following compounds were identified: UO_{2+x} , as a metal-deficit semiconductor; U_4O_9-y , as a metal-excess semiconductor; and U_3O_7-z , as a metal-excess semiconductor. The presence of all major phases was confirmed by X-ray powder techniques. The basic crystal lattice is the same for the three compounds. However, oxygen in excess of an oxygen/uranium ratio of 2.00 goes into interstitial positions and uniformly contracts the lattice of UO_2 with increasing interstitial oxygen, contracts the lattice a fixed amount for U_4O_9 , or contracts the lattice preferentially to give the slightly tetragonal U_3O_7 structure. An energy of about 0.4 ev is required to free a positive carrier from the interstitial oxygen in UO_{2+x} . In U_4O_9 or U_3O_7 , the energy required to free an electron from the hexavalent uranium varied from 0.4 ev at high carrier concentrations to 0.9 ev at the lower concentrations.

A correlation between the p-type electrical conductivity, and the reduction in volume of pressed UO_2 at elevated temperatures was observed. The percentage shrinkage of p-type uranium dioxide is a linear function of conductivity (and oxygen content) when sintering is done under conditions which minimize loss of oxygen.

The electrical conductivity of sintered UO_2 which did not sinter to high densities exhibited an anomalous decrease as a function of increasing temperature at about 400 C. This decrease was not observed in the active oxides, which sintered to high densities.

INTRODUCTION

The work described here was part of an integrated investigation of the fundamental properties of uranium oxides done for the Mallinckrodt Chemical Works. Electrical measurements were employed to characterize the oxides produced by various processes from different starting materials. The basic objective of the program was to determine those factors which affect the sintering characteristics of uranium dioxide.

The electrical conductivity of the oxides of uranium has been studied by many investigators⁽¹⁻¹¹⁾ and the results of their work have been summarized

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by Meyer⁽¹²⁾ and by Katz and Rabinowitch⁽¹³⁾. The oxides UO_3 and U_3O_8 are reported to be metal-excess semiconductors, while UO_2 is said to be an amphoteric semiconductor. The conductivity of UO_3 at room temperature is very low - the reported values range from 10^{-7} to less than 10^{-8} (ohm-cm)⁻¹. Part of the conductivity of U_3O_8 is ionic in nature. The reported values, which include both the ionic and electronic contributions to the conductivity, vary from 2×10^{-4} to 1×10^{-7} (ohm-cm)⁻¹. In UO_2 , conductivities ranging from 3×10^{-1} to 4×10^{-8} (ohm-cm)⁻¹ have been measured at 27 C. The ranges of conductivities are, of course, caused by variations in the composition, purity, apparent density, and crystalline perfection of the specimens studied.

The studies of Meyer and co-workers⁽¹⁻³⁾, of Chiotti⁽⁴⁾, and of Hartmann⁽⁵⁾ on UO_2 are probably the most significant. Meyer studied the electrical conductivity of UO_2 as a function of temperature to determine "activation energies" for free carriers in samples of widely different conductivities, and obtained values ranging from 0.3 to 0.9 ev. Chiotti also studied the conductivity of UO_2 as a function of temperature, but extended the measurements to higher temperatures where intrinsic conductivity became predominant. A summary of some of this early work is shown in Figure 1.

Hartmann pointed out that the increase of electrical conductivity with the addition of oxygen makes UO_2 a metal-deficit semiconductor in which the current carriers are positive holes. He confirmed this hypothesis by Hall-coefficient measurements. His specimen had a conductivity of 0.013 (ohm-cm)⁻¹ and a Hall coefficient of 770 cm³ per coulomb. These data can be interpreted to give a free-carrier concentration of 1×10^{16} positive holes per cm³ and a mobility of 10 cm² per v-sec.

In most of these investigations only one or two specimens were studied. The purity and excess oxygen content were not known. The type of conductivity (electron or positive hole) was not determined nor was the possibility of the existence of several phases considered. It, therefore, seemed of interest to the authors to extend the work on UO_2 and carefully consider more of the factors involved in producing different conductivities and activation energies in UO_2 and to use the electrical properties to obtain a better understanding of the sintering processes.

EXPERIMENTAL WORK

During the course of this investigation, it was found necessary to study the electrical properties of UO_2 produced by several different processes. Both sintered and nonsintered specimens were studied. Since

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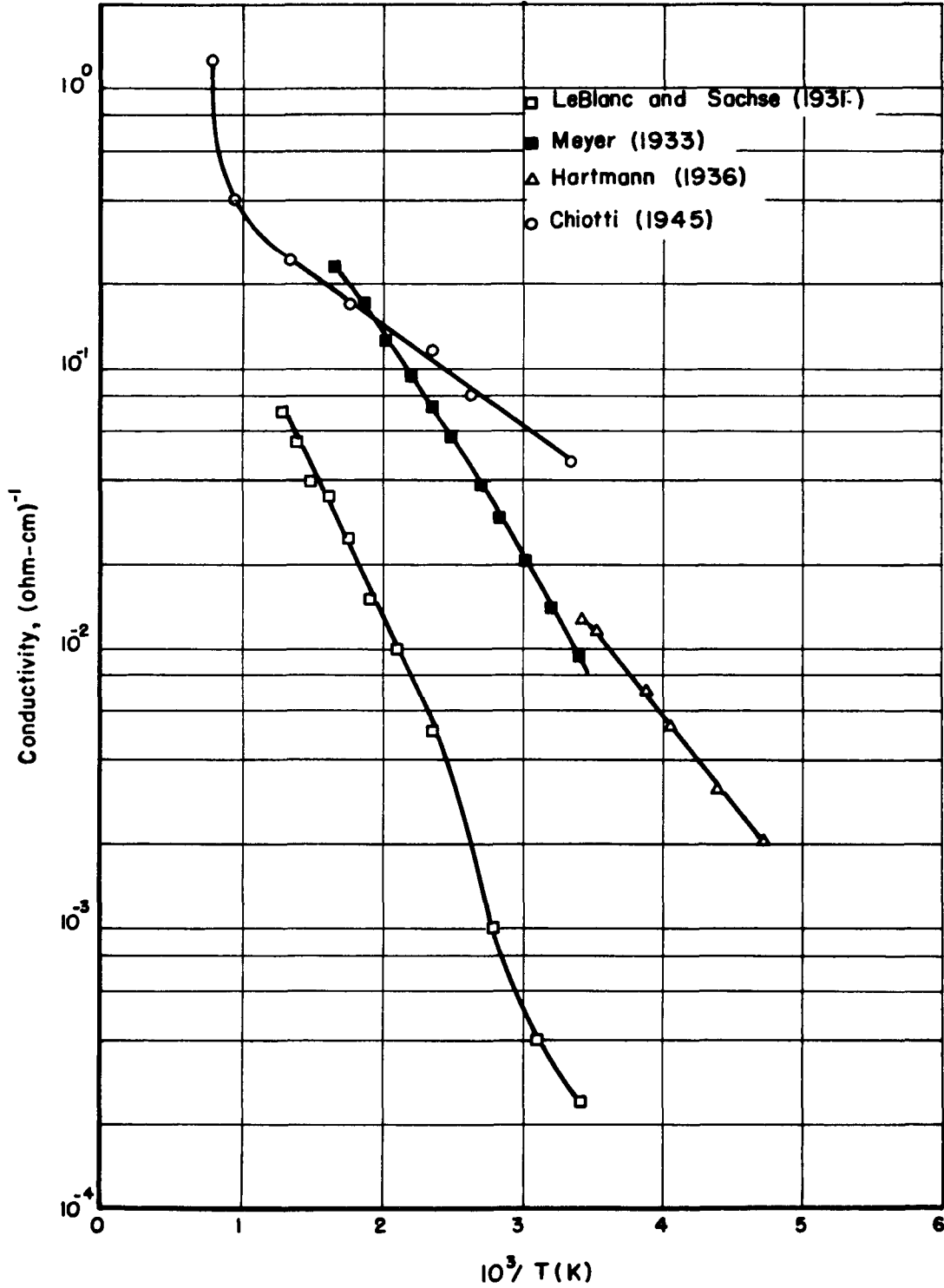
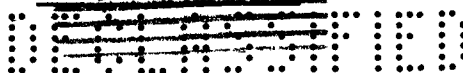


FIGURE 1. LITERATURE DATA ON THE ELECTRICAL CONDUCTIVITY OF URANIUM DIOXIDE AS A FUNCTION OF RECIPROCAL TEMPERATURE



the electrical properties of UO_2 were found so dependent upon its past history, a detailed description of the preparation of samples will be deferred until the electrical properties of a particular sample are discussed. However, all specimens studied were prepared from UO_2 powder and were hydrostatically pressed at 100,000 psi (without a binder) into cylindrical rods about 1/4 by 4 in. These rods were sintered in a hydrogen atmosphere at 1650 or 2050 C for 1 hr. Specimens for electrical measurements were cut from the rods either before or after sintering.

Spectrographic analysis of these materials indicated the metallic impurity content to be very low - a few parts per million at most. Because of the rather high excess-oxygen content of the samples, it was assumed that the effect of the metallic impurities was negligible. Oxygen/uranium ratios were calculated from the weight gain on ignition of the UO_2 powder to U_3O_8 .

After the electrical measurements were completed on a particular sample, the phases present were determined by X-ray techniques, in most cases.

The specimens for electrical measurements were lapped to 1/8 by 1/4 by 1/2 in. on silicon carbide paper. They were mounted in a Lavite holder so constructed that electrical contact could be made on the ends and one face of the sample. The end contacts were Chromel plates to which were welded Chromel-Alumel thermocouples. The thermocouple wires were also used as current leads and thermoelectric power probes. The contacts on the face of the sample were platinum beads and served as conductivity probes. All contacts were spring loaded.

During the measurements as a function of temperature, the holder was enclosed in a Vycor tube and connected to a vacuum system with a pressure of about 10^{-3} mm of mercury. Room-temperature measurements were made in air at atmospheric pressure.

The arrangement used for the measurement of conductivity is shown in Figure 2. The potential drop (V_1) between the two probes is compared with the potential drop across a standard resistor (R_s). The measured conductivity is obtained by using the expression:

$$\sigma_m = \frac{V_2}{V_1} \frac{l}{R_s b d} \quad (1)$$

where

b is the width of the specimen

d is the thickness of the specimen

λ is the distance between the conductivity probes.

Conductivity was converted to "corrected" conductivity by the expression⁽¹⁴⁾:

$$\sigma_c = \left(1 + \frac{P}{1-P^2/3} \right) \sigma_m , \quad (2)$$

where P represents the volume pore fraction of the specimen. The conductivities were referred to the theoretical density of UO₂ because the excess oxygen was determined on a weight per cent basis, whereas the conductivity depends on the number of carriers per unit volume. This correction made it possible to compare the conductivity of specimens of different densities. However, caution must be exercised in any quantitative interpretation of the data because of the effects of grain boundaries.

The voltages were measured with a Leeds and Northrup K-2 potentiometer. The use of potential probes insured against contact-resistance errors. The accuracy of the measurement was limited by the effect of grain boundaries and by the degree of homogeneity of the sample.

The basic circuit for the measurement of thermoelectric power is shown in Figure 3. The thermoelectric power, Q, was determined by establishing a thermal gradient along the specimen and measuring the thermal emf (V_{th}) generated. The thermal gradient is produced by contacting one end of the specimen with a heat source (electric heater) and the other end with a heat sink. The thermoelectric power is obtained from the expression:

$$Q_{(T_{avg})} = \frac{V_{th}}{\Delta T} \quad (3)$$

for small temperature gradients.

The thermal emf (V_{th}) was measured with a Leeds and Northrup K-2 potentiometer, as was the emf of the thermocouples. The thermoelectric power was measured with respect to the Chromel wire in contact with the ends of the specimen. To obtain the absolute thermoelectric power, the value for Chromel was added for p-type materials (and subtracted for n-type materials) to those calculated by Equation (3).

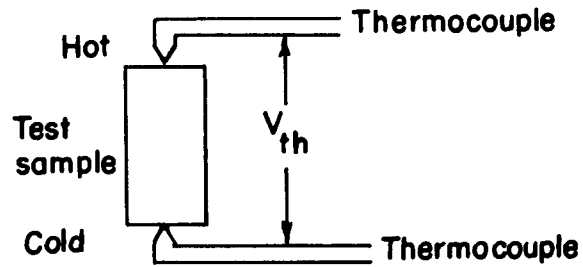


FIGURE 2. BASIC CIRCUIT FOR CONDUCTIVITY MEASUREMENT

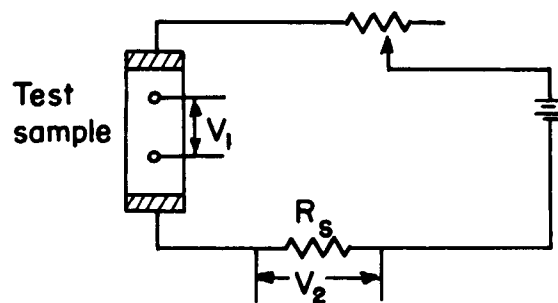


FIGURE 3. BASIC CIRCUIT FOR THERMOELECTRIC-POWER MEASUREMENT

The accuracy of the value obtained for the thermoelectric power is limited by the precision with which the differences in the temperatures at the ends of the specimen was determined (a relatively large gradient, 15-20 C, was employed) and by the homogeneity of the sample.

Characteristics of Sintered Specimens

Initial experiments on the variation of the electrical conductivity of uranium dioxide with oxygen/uranium ratio indicated that the conductivity (by positive carriers) increased linearly with oxygen content, at least up to ratios of about 2.10. However, extended measurements on one specimen revealed that heat treatment could change not only the magnitude of the conductivity but also the sign of the majority carriers. This result is represented by the curves in Figures 4 and 5. These curves were obtained on specimens cut from a rod of MCW UO_2 sintered for 1 hr at 2050 C in a hydrogen atmosphere. After sintering, the oxygen/uranium ratio by ignition analysis was 2.011 and the density of the rod was 86.3 per cent of theoretical density.

The initial data were obtained using the whole length of the rod (about 3 in.) as the specimen and are represented in Figure 4 by the open triangles on Curve A. These measurements were made under about 10^{-5} mm of mercury pressure. Although *n*-type conductivity is assigned to this curve, the thermoelectric power (and sign of the carriers) was not measured during the initial runs. Actually, in view of subsequent measurements, it appears that the rod was nonhomogeneous. Of particular interest is the anomaly occurring between 200 and 350 C (represented by the broken portion of the curve). The general shape of this curve could be duplicated, but the magnitude of the conductivity changed slightly during the temperature cycles.

The other curves of Figure 4 and those of Figure 5 were obtained on specimens 1/8 by 1/4 by 1/2 in. cut from the original rod. These measurements were made under a pressure of about 10^{-3} mm of mercury. The measurements on the *n*-type specimens, represented by the open circles and squares on Curves B and C were completely reproducible and several cycles were made between 20 and 200 C. When these samples were heated above 200 C, the conductivity decreased in the same anomalous manner as the conductivity of the rod, Curve A, and the thermoelectric power became *p*-type. As the temperature was increased to 400 C, where the intrinsic conductivity became apparent, the thermoelectric power again became *n*-type. However, now when the temperature was reduced the extrinsic conductivity was *p*-type, and additional measurements of conductivity as a function of temperature resulted in the data shown by Curve D in Figures 4 and 5.

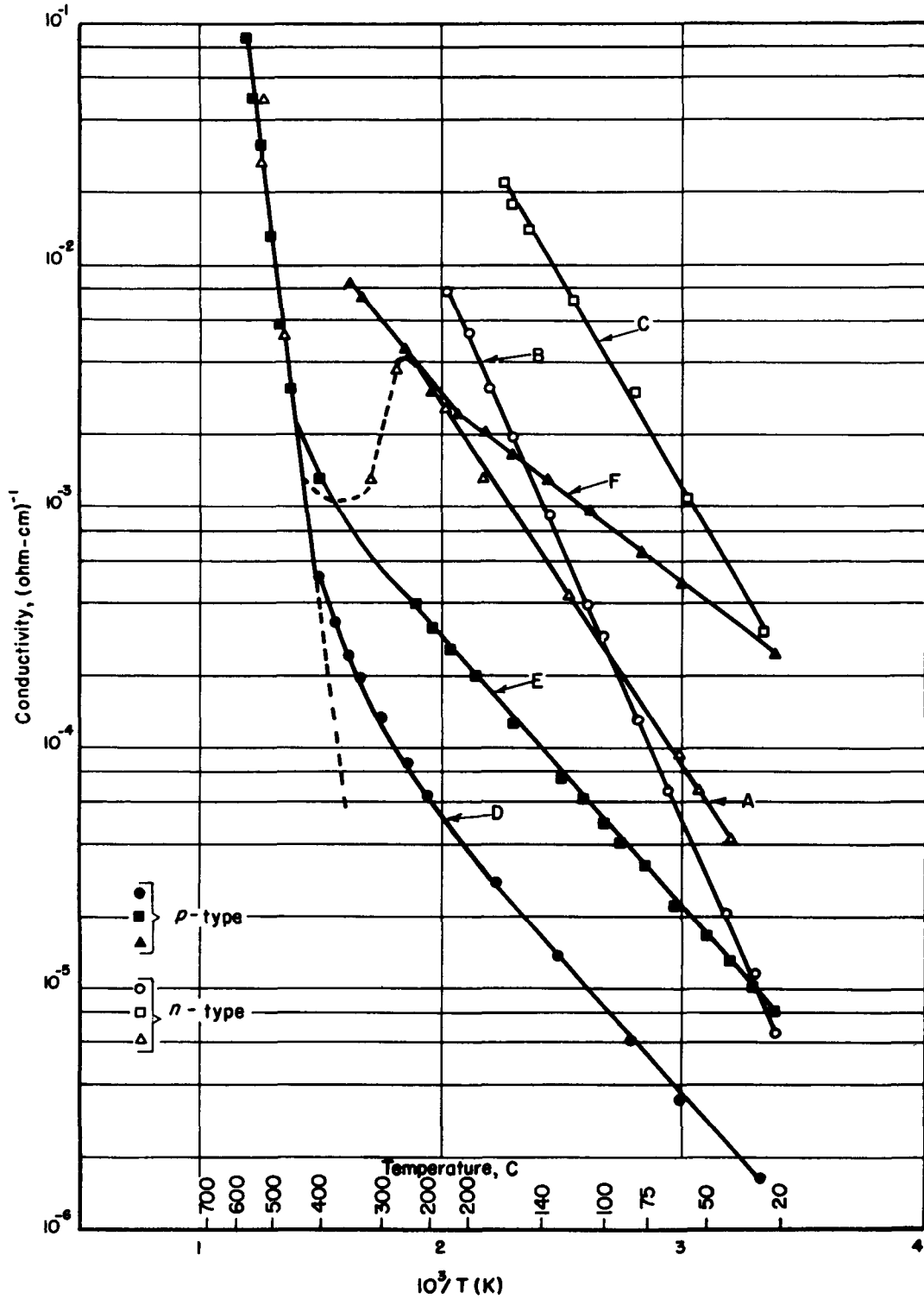


FIGURE 4. CONDUCTIVITY OF SINTERED SPECIMENS OF n - AND p-TYPE UO_2



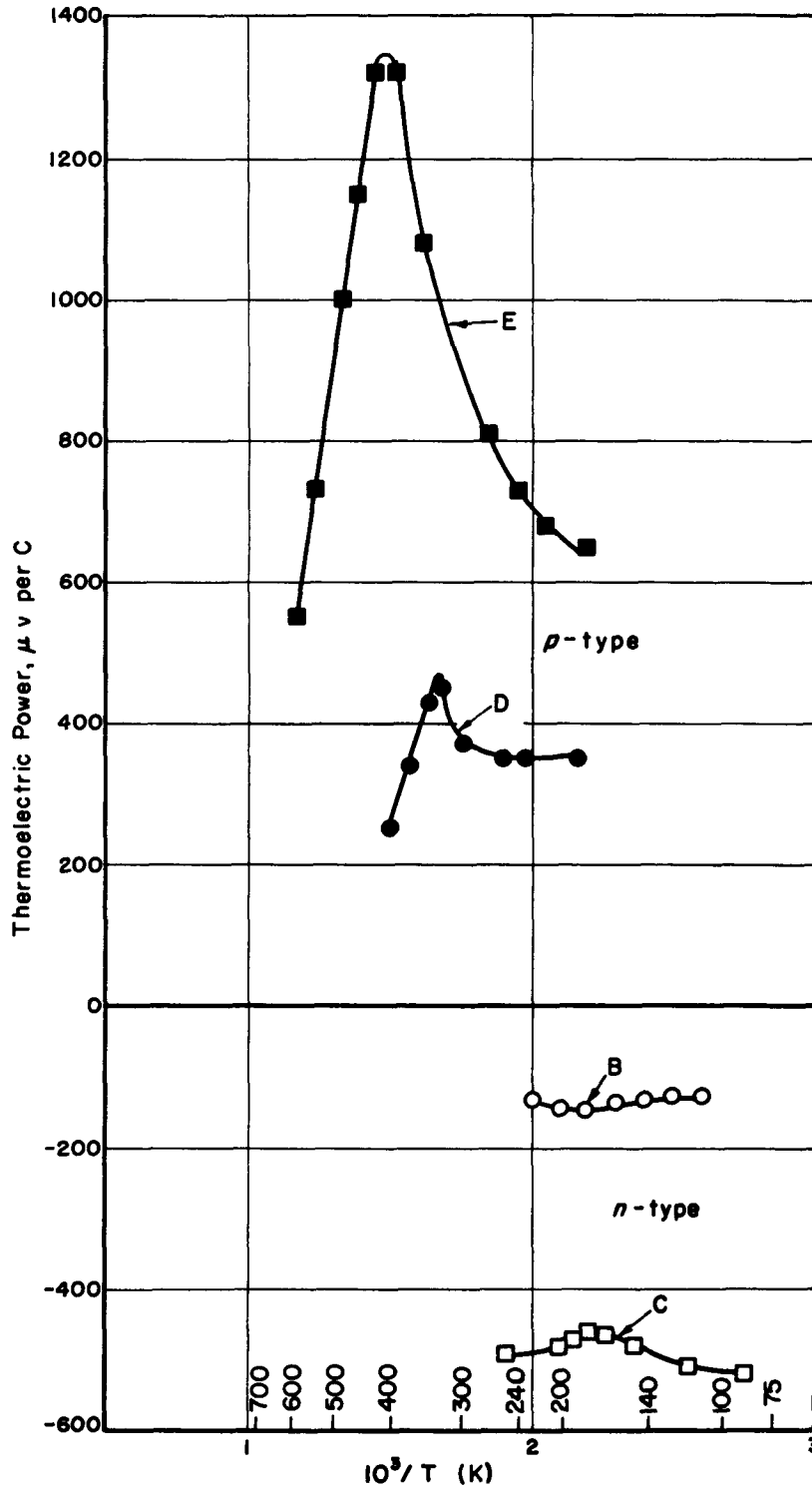


FIGURE 5. THERMOELECTRIC POWER OF SINTERED SPECIMENS OF *n*- AND *p*-TYPE URANIUM DIOXIDE

Additional temperature cycling for several days increased the extrinsic p -type conductivity and resulted in the data shown by the Curves E and F of Figures 4 and 5. Evidently a small amount of oxygen was absorbed above 200 C, even though the measurements were carried out in a vacuum of about 10^{-3} mm of mercury. When the vacuum of 10^{-5} mm of mercury was used, it appears that a negligible amount of oxygen was absorbed. Thus, the anomaly seems to be caused by a reversible phase change in which the conductivity changes from n -type to p -type. Also, the anomaly can be eliminated by the addition of a very small amount of oxygen into the lattice, which makes the material p -type throughout the extrinsic region.

The appearance of n -type conductivity was rather surprising, since the oxygen/uranium ratio of 2.011 ± 0.005 indicated about 3×10^{20} excess oxygen atoms per cm^3 and interstitial oxygen atoms in UO_2 are associated with positive conduction. If the oxygen content had been below the stoichiometric ratio 2.00, then the negative carriers could be supplied by the excess uranium atoms. Also, in view of the anomalous decrease in conductivity with increasing temperature above 200 C, the n -type conductivity seems to be explained only by assuming the presence of excess uranium in a phase other than UO_2 .

It is readily apparent from Figure 4 that the curves of log conductivity as a function of reciprocal temperature, in general, consist of two straight lines and that the conductivity of each portion can be fitted to an expression of the type

$$\sigma = Ae^{-\Delta E/2kT}, \quad (4)$$

where

A is a constant

k is Boltzman's constant

ΔE is the energy necessary to free a charge carrier.

The application of this equation to the conductivity at high temperatures is of particular significance. It is noticed that this portion of the curves appeared to be reproducible, regardless of the behavior of the conductivity at low temperatures. Therefore, it is reasonable to suppose that the high-temperature portions of the curves of Figure 4 represent the intrinsic conductivity of UO_2 . From the slope of the curve and Equation (4), a value of 3.0 ev was calculated for the energy-band separation in uranium dioxide.

However, this value of the energy gap must be taken with caution, since by using the measured value of the conductivity and reasonable values

for the mobility and effective mass of the carriers one would predict a value between 1 and 2 ev. An explanation may be found in the ratio of the electron-to-hole mobility. In the intrinsic range, the conductivity of these specimens was invariably *n*-type, indicating an electron-to-hole mobility ratio greater than one. When such is the case, for a given carrier concentration, extrinsic *p*-type specimens will have a lower conductivity than *n*-type specimens. Also, the approach to the intrinsic conductivity will be different. It can be shown that when the above condition prevails the initial intrinsic slope of *p*-type specimens will be greater than the slope corresponding to the band separation of the material. The reverse is true for *n*-type specimens; that is, the "near-intrinsic" slope of the conductivity curve will be less than the slope corresponding to the band separation. The amount of "overshoot" or "undershoot" is dependent upon the density of acceptor or donor levels as well as the electron-to-hole mobility ratio. At sufficiently high temperatures, when intrinsic conductivity predominates, the slopes of *p*- and *n*-type material are equal and correspond to the band separation. Except for the fact that electrons have a greater mobility than holes, little else is known of the magnitude of the mobilities of charge carriers in uranium dioxide. Therefore, the value of 3.0 ev for the band separation in uranium dioxide, based on a calculation in the near-intrinsic range, should be regarded as the maximum value possible, with the actual value being perhaps as low as half of this value.

The low-temperature portions of the curves of Figure 4 also reveal some interesting characteristics. A rather large difference in the slopes of the *n*- and *p*-type curves is obvious. Applying Equation (4) to the extrinsic portions of Figure 4, activation energies of about 0.9 ev are obtained for *n*-type carriers and about 0.4 ev for positive carriers. It is also interesting to note that the extrinsic slope of Curve A (open triangles) lies between these values.

The thermoelectric power of this specimen (Curve E, Figure 5) poses a difficult problem. Simple theory predicts a thermoelectric power which decreases with increasing temperature for a temperature-dependent population of current carriers. This is obviously not the case for the *p*-type curves where an initial sharp rise in thermoelectric power (although the conductivity increases) is noted. Even the *n*-type curves are relatively flat and do not decrease as would be expected.

Some further measurements on the electrical properties of sintered specimens of uranium dioxide are shown in Figures 6 and 7. These measurements were made on:

- (1) A specimen (Curve G, open circles) cut from a rod of regular MCW minus 325-mesh UO₂, sintered in hydrogen for 1 hr at 1600 C to 79 per cent of theoretical density

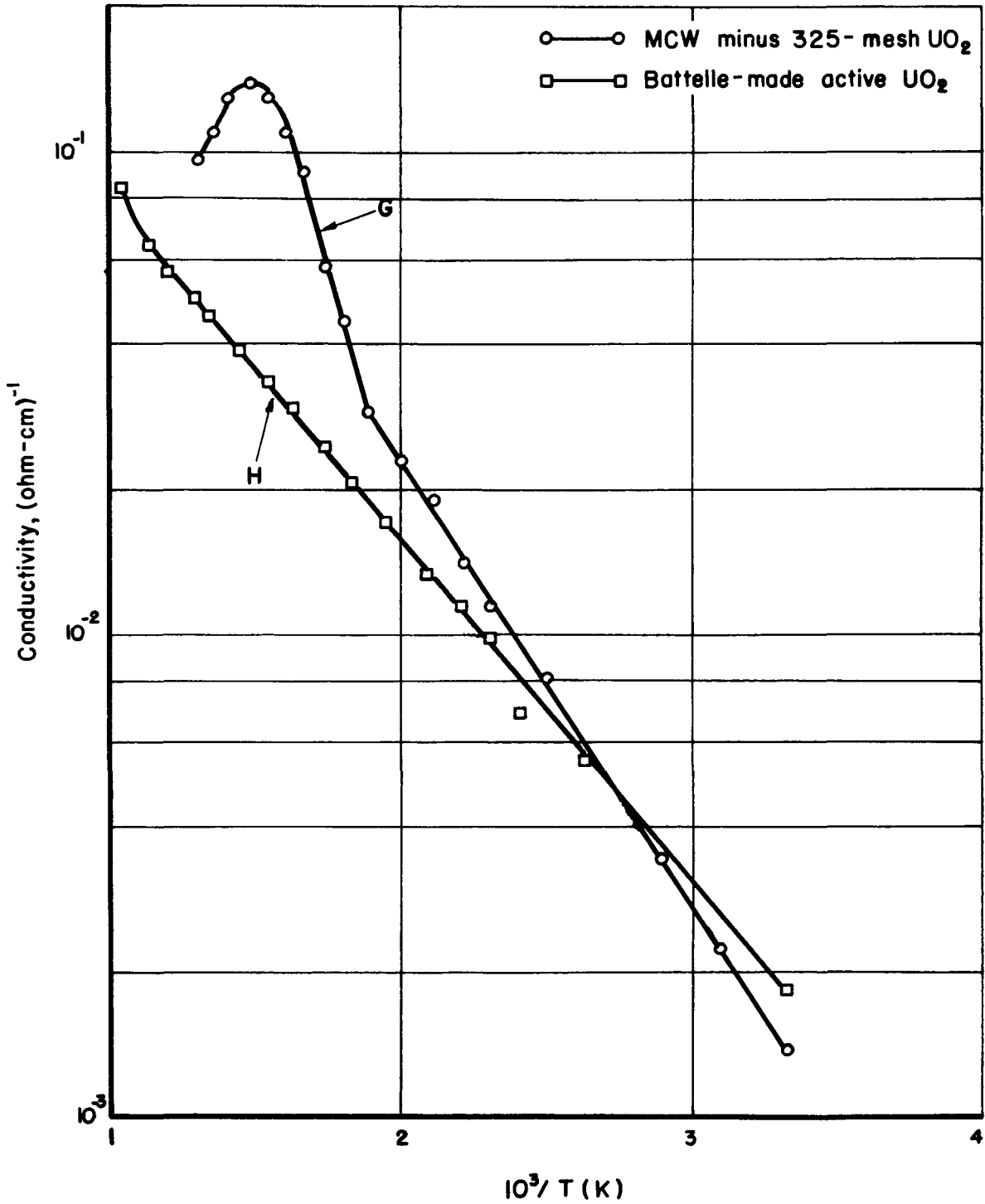


FIGURE 6. CONDUCTIVITY OF SINTERED SPECIMENS OF URANIUM DIOXIDE OF VARIOUS HISTORIES

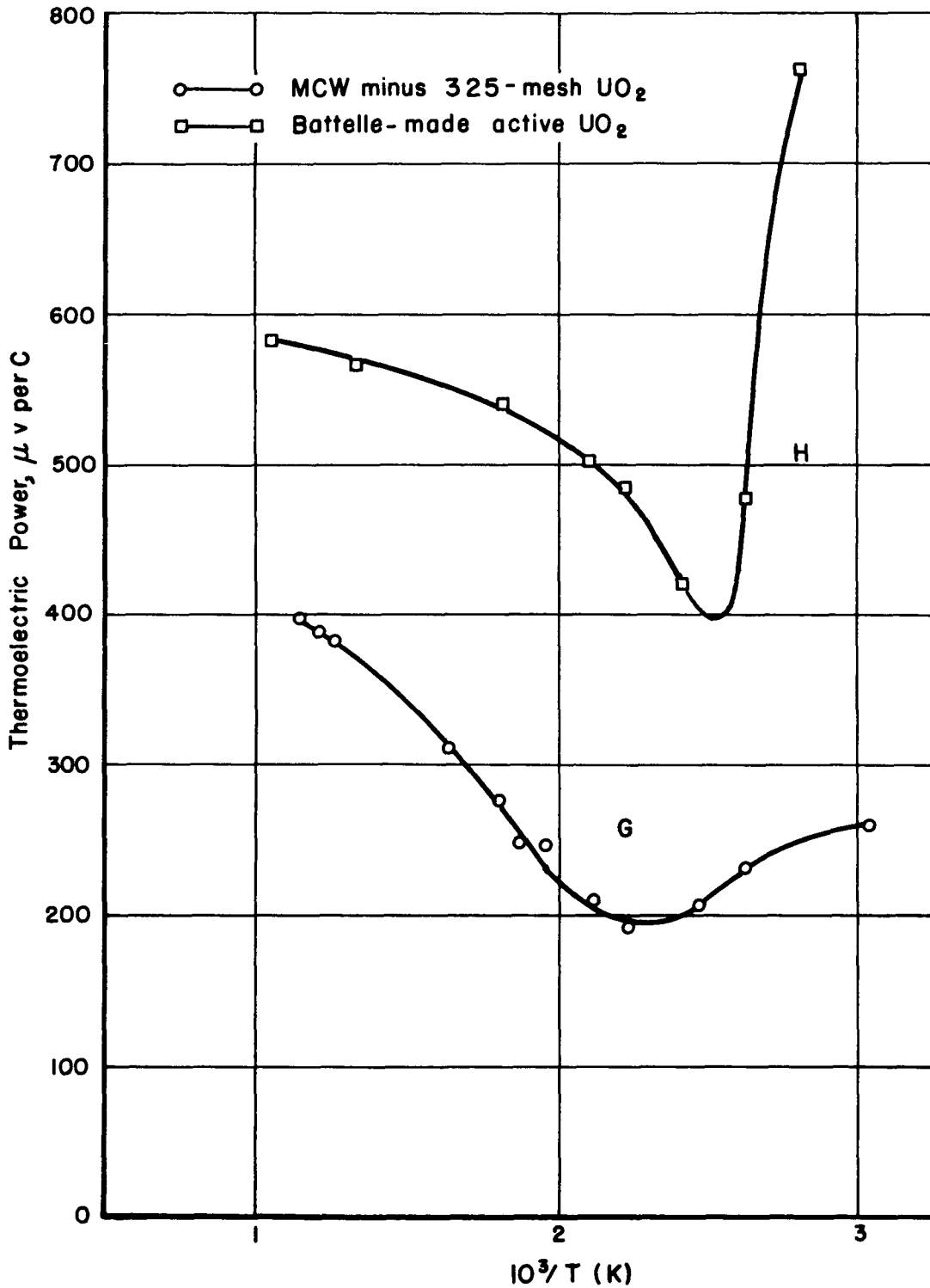


FIGURE 7. THERMOELECTRIC POWER OF SINTERED SPECIMENS OF URANIUM DIOXIDE OF VARIOUS HISTORIES

- (2) A specimen (Curve H, open rectangles) cut from a rod of Battelle-made "active" UO_2 , sintered in hydrogen for 1 hr at 1600 C to 95 per cent of theoretical density.

The measurements were made under a pressure of about 10^{-3} mm of mercury.

Figures 6 and 7 are of particular interest since they compare the electrical properties of a specimen of UO_2 which sintered to high density with those of a specimen which sintered to the usual density (about 80 per cent of theoretical). The conductivity curves display a remarkable difference at the higher temperatures. The anomaly in the electrical conductivity as the temperature is increased noted for the previous sample is obvious on the conductivity curve of the normal UO_2 (Curve G), but does not appear on the curve of the active material (Curve H). Even the slopes of the two curves of conductivity versus temperature are significantly different, that of the normal MCW specimen being 0.36 ev at the lower temperatures and changing to 0.84 ev above 200 C, while that of the active specimen was 0.28 ev.

An examination of the thermoelectric-power curves (Figure 7) also reveals some interesting differences. Although the curves are somewhat similar in general shape, there is a large difference in the magnitude of the thermoelectric powers, even though the conductivities are nearly identical. Again the increase of thermoelectric power with increasing carrier concentration is to be noted. The shape of these curves was reproducible but the magnitudes changed on further temperature cycling.

An explanation of the differences in Figures 6 and 7 is rather difficult to advance. If it is assumed that the anomaly in the conductivity curve of the normal specimen was due to a phase change, the transition is clearly lacking in the active specimen. The question is then why does not the active material change phases at higher temperatures. A possible answer to this question would be the presence of an impurity. The starting material of both normal and active UO_2 is uranyl nitrate, which is decomposed to UO_3 and finally reduced by hydrogen to UO_2 . The difference in the materials is that in the case of the active material the UO_3 is ball milled, thoroughly washed, and then reduced to produce the active UO_2 . If any nitrates had persisted through the decomposition, they probably are removed by the washing. Thus it is possible that the normal UO_2 may contain nitrogen impurities absent in the active material. But even if nitrogen is present in the normal material, it is not understood how it could cause UO_2 to undergo a phase change at elevated temperatures.

Anneal and Quench Experiments

The questions raised in the preceding sections concerning the phase relationships in the $\text{UO}_2\text{-U}_3\text{O}_8$ system made it imperative to investigate the electrical properties of nonsintered specimens with larger oxygen/uranium ratios. It was obvious that no correlation between electrical properties and sintering characteristics would be possible until the dependence of electrical properties on structure was explored. Accordingly, an extended series of anneal-quench experiments was undertaken on pressed specimens of UO_2 containing various amounts of excess oxygen. During these experiments it was found necessary to verify the phase relationships by X-ray analysis.

Regular MCW minus 325-mesh UO_2 powder (Lot No. 77016, oxygen/uranium ratio = 2.032) was exposed to dry oxygen for various lengths of time at 180 C. Care was taken to exclude nitrogen from the system. After the exposure, an oxygen assay was made on the material by ignition analysis. The powder was then hydrostatically pressed, without a binder, under 100,000 psi into cylindrical rods. Since the method of sintering removes most of the excess oxygen, specimens for these anneal-quench experiments and electrical measurements were cut from the pressed rods.

Room-temperature measurements on the as-prepared specimens revealed that all the specimens were p-type and that the conductivity rose slightly in a linear fashion with increasing oxygen content (see Figure 10).

The specimens were then sealed in small Vycor capsules under a partial pressure of argon. The capsules were mounted in a furnace and the specimens annealed at 200 C for an extended period of time. Periodically the specimens were quenched by dropping into an oil bath, removed from the capsules and the magnitude and type of conductivity at room temperature determined. In Figure 8 are plotted the room-temperature conductivities as a function of anneal time at 200 C.

At first glance the curves of Figure 8 might be taken as representing a process of homogenization. It is conceivable that the as-prepared specimens were nonhomogeneous, that oxygen had been absorbed on the surface of the UO_2 granules and was not distributed throughout the crystal lattice. Indeed, this is indicated to some extent by the as-prepared curve of Figure 10. This curve does not rise as sharply as would be expected if the conductivity of UO_2 increased in a one-to-one correspondence with the concentration of excess oxygen atoms. Therefore, part of the changes in conductivity represented in Figure 8 might be considered due to a simple process of homogenization. Yet such a process would not account for all the features of Figure 8. The appearance of n-type conductivity after the first 16-hr anneal, the annealing of regular MCW UO_2 (oxygen/uranium =

Fig. 8

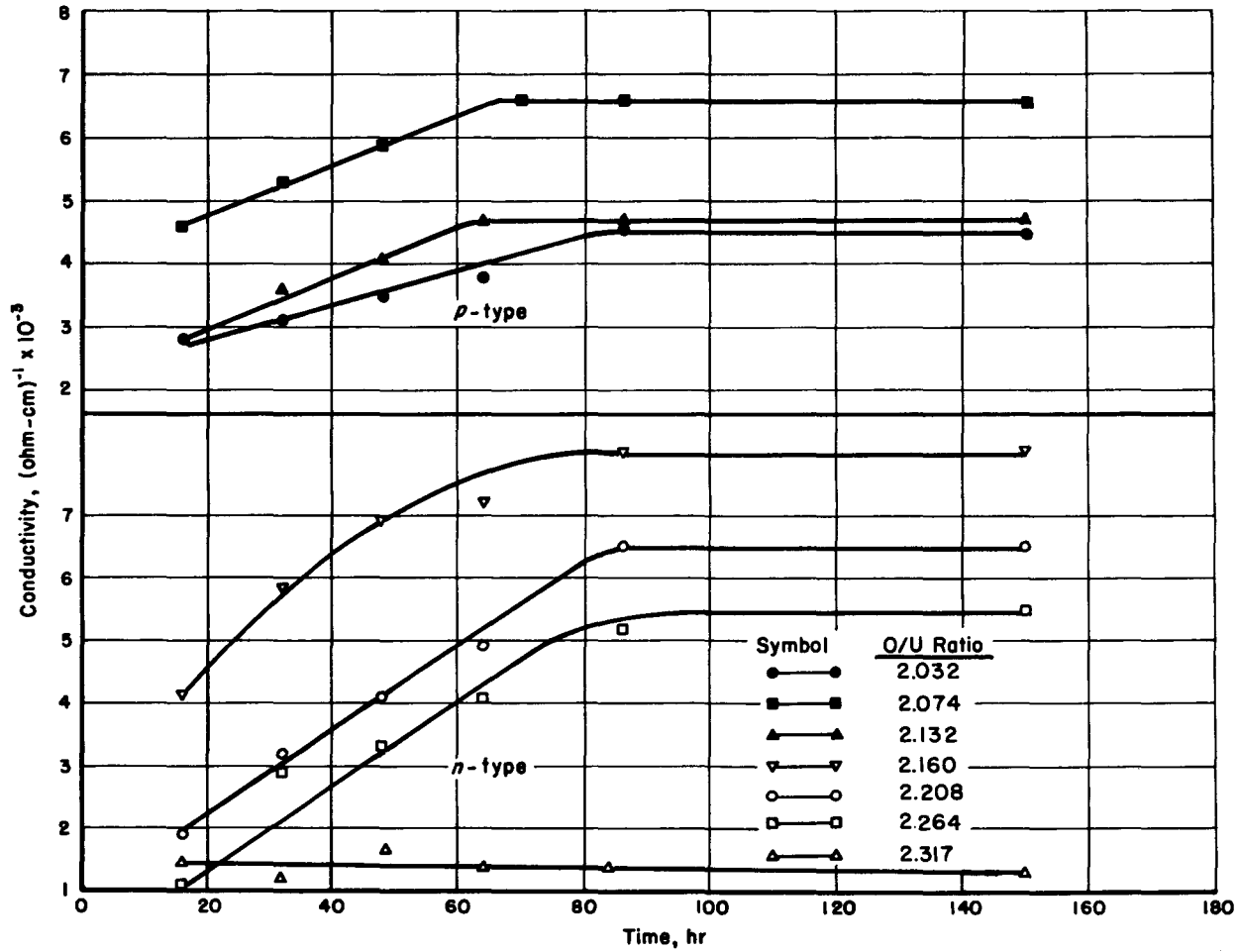


FIGURE 8. CHANGE OF CONDUCTIVITY WITH ANNEAL TIME AT 200 C FOR PRESSED SPECIMENS OF URANIUM DIOXIDE OF VARIOUS OXYGEN/URANIUM RATIOS

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2.032) and the behavior of the specimen of oxygen/uranium ratio of 2.317 strongly suggest an ordering of the excess oxygen atoms at the anneal temperature. Thus, along with the simple process of diffusion and homogenization, there must be postulated an ordering process in which the bonding orbitals in the lattice of UO_2 are affected (increase in conductivity) and in which a new phase or phases appear (appearance of n -type conductivity).

After about 60 hr annealing, the conductivity of the p -type specimens reached a constant value. A somewhat longer time, about 80 hr, was required for the n -type specimens to come to equilibrium. It is interesting to note the differences in which the various specimens approached the steady-state value. The slopes of the annealing curves of p -type material of relatively high oxygen content (oxygen/uranium ratio = 2.074 and 2.132) are nearly parallel and are greater than the slope for the regular MCW material. Even greater parallel slopes are obtained for the n -type specimens, with the exception of the one with an oxygen/uranium ratio of 2.317. This specimen showed a slight decrease in conductivity when annealed at 200 C.

In Figure 9 are plotted the results obtained on the same specimens during an anneal at 400 C. Here it can be seen that the steady state was reached in a much shorter time (about 30-40 hr for both p - and n -type specimens). It will also be noted that the specimen of oxygen to uranium ratio of 2.160 is now p -type. Attention is again called to the manner in which the various specimens approach the steady-state value. As at 200 C, nearly parallel slopes are obtained for both n - and p -type material, with the n -type slopes being somewhat greater. Once again the specimens of lowest and highest oxygen content were different from the other specimens.

If the steady-state values of Figures 8 and 9 are plotted as a function of oxygen/uranium ratio, the curves of Figure 10 are obtained. The significance of Curve A in Figure 10 has been discussed previously. Considering Curve B, the steady-state values of conductivity after annealing at 200 C and quenching to room temperature, it can be seen that as oxygen is added up to an oxygen/uranium ratio of about 2.06, the p -type conductivity of UO_2 increases. Beyond this point the conductivity begins to decrease with increasing oxygen content. Finally, between the oxygen/uranium ratios of 2.13 to 2.16, the conductivity becomes n -type. Between the p - and n -type branches of Curve B there appears to be a discontinuity. Further increasing oxygen content results in decreasing n -type conductivity. The steady-state values of conductivity after annealing at 400 C are shown by Curve C, which is similar in shape to Curve B, but displaced to much higher values of conductivity. Attention is called to the specimen of oxygen/uranium ratio of 2.160. After annealing at 400 C, the conductivity of the specimen fits on neither branch of Curve C.

The anneal-quench experiments were also performed at temperatures of 600, 800, and 1000 C. At these temperatures a steady state was obtained

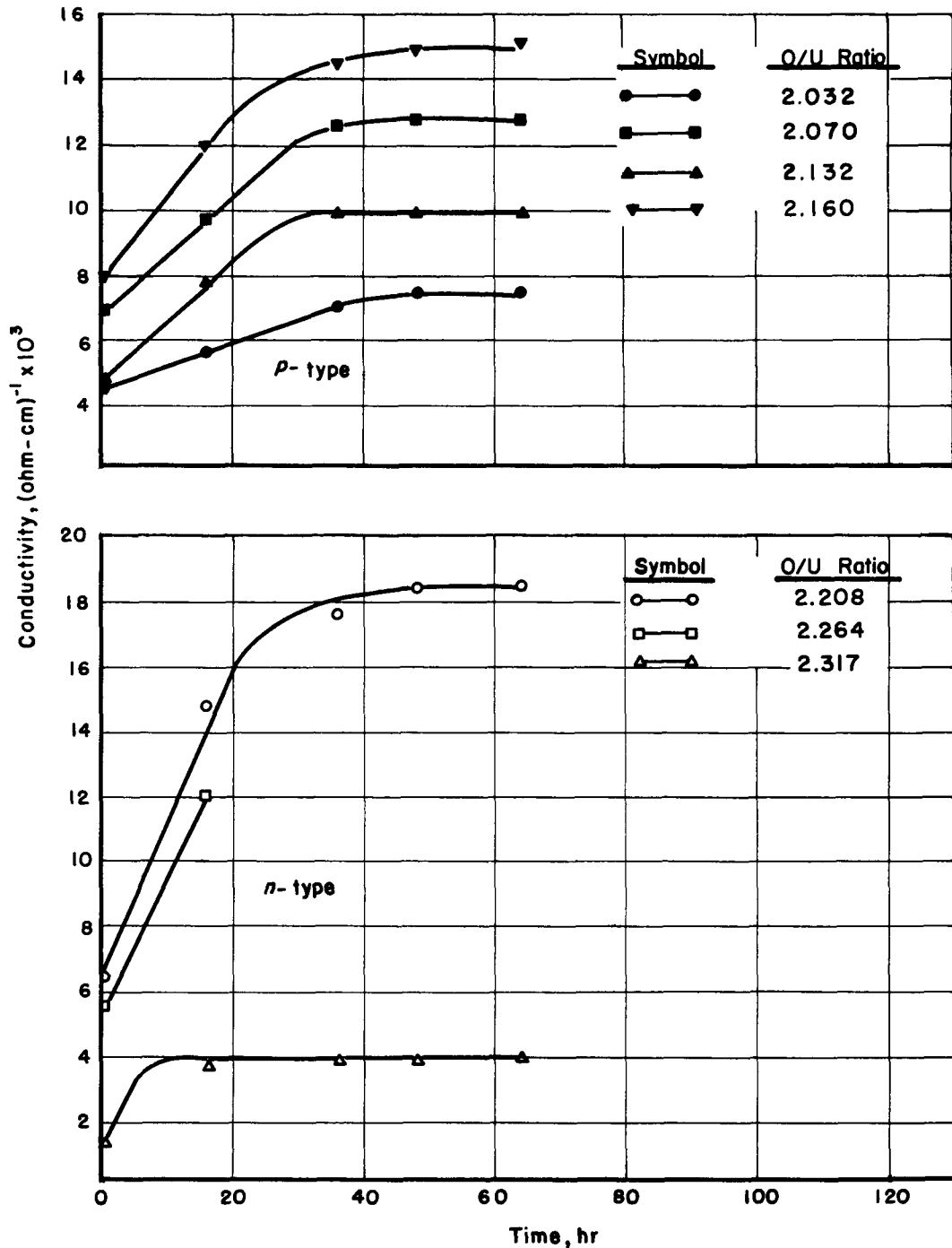


FIGURE 9. CHANGE OF CONDUCTIVITY WITH ANNEAL TIME AT 400 C FOR PRESSED SPECIMENS OF UO_2 OF VARIOUS OXYGEN/URANIUM RATIOS

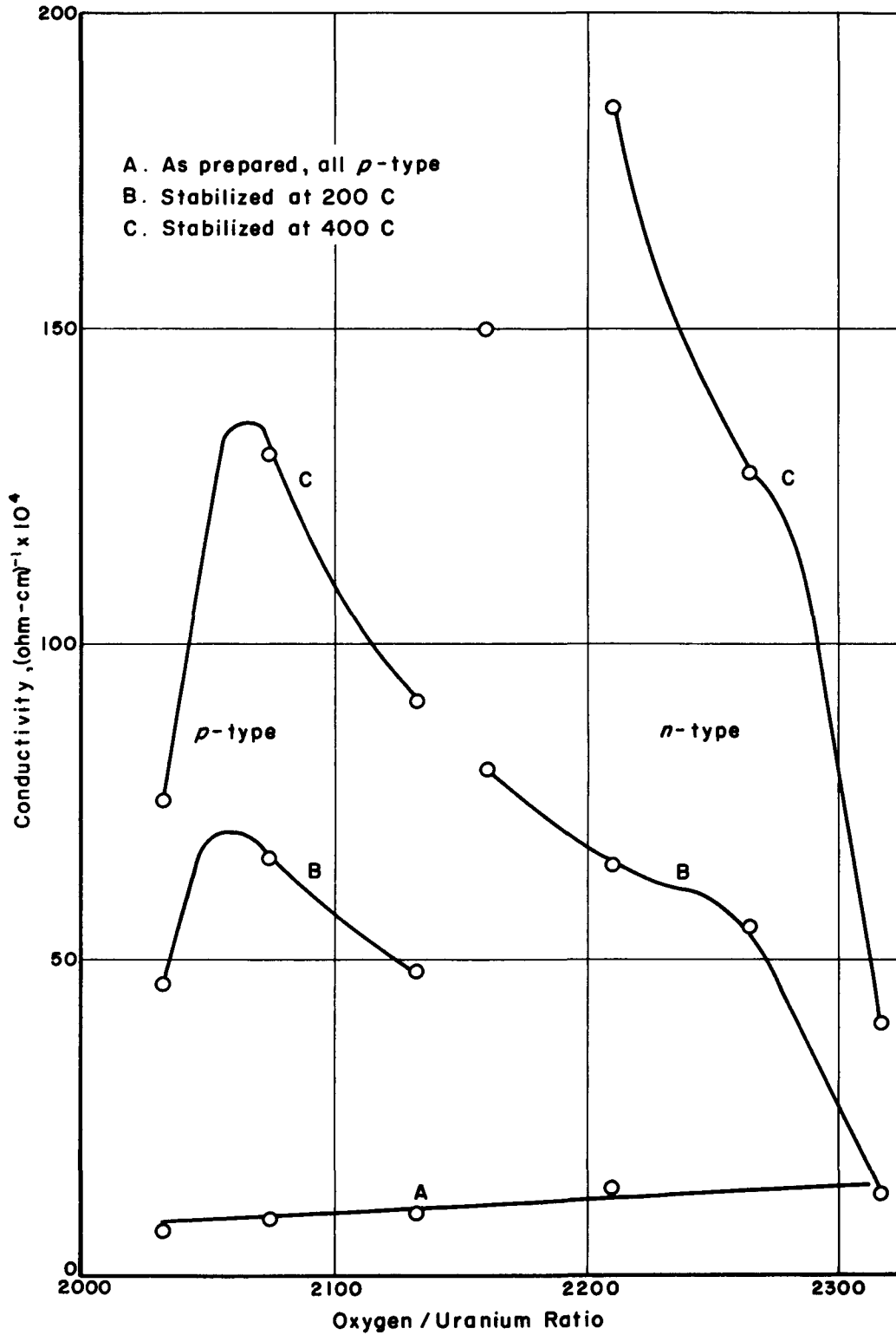
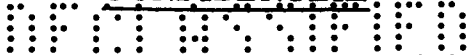


FIGURE 10. ROOM-TEMPERATURE CONDUCTIVITY AS A FUNCTION OF OXYGEN/URANIUM RATIO OF PRESSED SPECIMENS OF URANIUM DIOXIDE



in a few hours. But at these higher temperatures considerable oxygen was lost from the specimens so that a quantitative description of the behavior of the specimens was not possible. However, indications were that annealing up to 800 C resulted in still further increases of conductivity and that curves similar to Curves B and C of Figure 10 could be plotted. No further changes of type of conductivity were noted for these specimens. The *n*-type specimens remained *n*-type, even after annealing at 1000 C. Annealing above 800 C seemed to have little effect on the magnitude of the conductivity after quenching of the specimens. However, the loss of oxygen above 800 C could mask the effects of annealing.

The curves of Figure 10 assume a vital significance when interpreted in the light of the X-ray data obtained on the specimens. If the end points of the branches of the curves of Figure 10 are extrapolated to zero conductivity, they are found to intersect this axis close to oxygen/uranium ratios corresponding to the formulas UO_2 and U_3O_7 . The X-ray analysis of the specimens of high oxygen/uranium ratios (2.264 and, especially 2.317) revealed that the specimens consisted of a tetragonal phase whose pattern corresponds to that reported for U_3O_7 . The UO_2 phase was, of course, verified at the lower oxygen contents. Furthermore, the behavior of the conductivity of the specimens of intermediate oxygen/uranium ratio strongly indicates the presence of an additional phase. X-ray analysis of these specimens revealed that they consisted of UO_2 or U_3O_7 and considerable amounts of a cubic structure corresponding to a formula of U_4O_9 .

Thus, the anneal-quench experiments clarify the dependence of the electrical properties of UO_2 on the phase relationships in the UO_2 - U_3O_8 system. They confirm the existence of phases other than UO_2 as was so strongly indicated by the measurements on the sintered specimens presented in the preceding section. Because of their electrical behavior the phases should be identified as

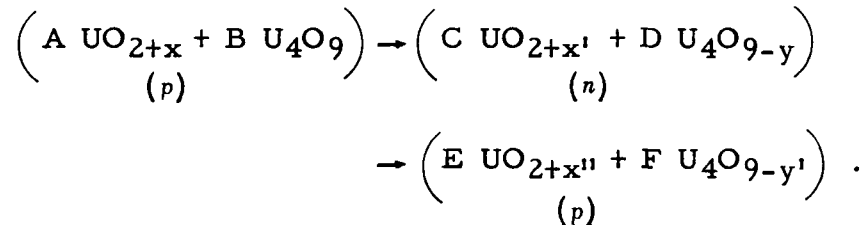
- (1) UO_{2+x} , a metal-deficit semiconductor
- (2) U_4O_{9-y} , a metal-excess semiconductor
- (3) U_3O_{7-z} , a metal-excess semiconductor.

The presence of metal-deficit phases of U_4O_9 and U_3O_7 was not revealed by these experiments, yet their existence should not be excluded. Electrical measurements on specimens with oxygen/uranium ratios slightly above 2.250 and 2.333 would perhaps confirm their existence. One specimen with an oxygen/uranium ratio above U_3O_7 was investigated. It had an oxygen/uranium ratio of 2.353 and after annealing at 400 C was *n*-type. Since a phase corresponding to U_3O_{7+x} would be *p*-type, this specimen was clearly a metal-excess phase of some higher oxide of uranium. From X-ray analysis the new phase was determined to be U_3O_8 .

New specimens were cut from the original rods and their electrical properties were determined as a function of temperature after annealing at 400 C for 100 hr. The electrical measurements were not extended to above 400 C in order to minimize the chance of loss or gain of oxygen in the measuring apparatus.

In Figures 11 and 12 is plotted the behavior of the conductivity of the *p*- and *n*-type specimens, respectively, as functions of reciprocal temperature. These curves represent the extrinsic behavior of typical pressed specimens in the $\text{UO}_2\text{-U}_3\text{O}_7$ system and are to be compared with the extrinsic portion of the curves of Figures 4 and 6. In general, corresponding to their higher oxygen content, the pressed specimens have somewhat higher conductivities than the sintered specimen. The slopes of the pressed *p*-type specimens are comparable to those of the *p*-type sintered specimens, but there is considerable difference between the *n*-type slopes of Figure 4 and those of Figure 12.

The thermoelectric power of the pressed specimens (Figure 13) can be compared with the data shown in Figures 5 and 7. The decrease in thermoelectric power with increasing temperature and conductivity for the *p*-type samples in Figure 13 is more like what would be expected from simple theory. The thermoelectric power of the pressed specimen of oxygen/uranium ratio 2.160 is especially interesting in that it displays a double crossover corresponding, probably, to the transitions:



The first *p*-type characteristic was quenched in from above 400 C. As the temperature was raised to about 200 C the ratio of UO_{2+x} to U_4O_{9-y} was changed until U_4O_{9-y} , *n*-type, was predominant. The ratio of the two phases changed continually with further increases of temperature, with the formation of UO_{2+x} being favored. Finally, at about 335 C, *p*-type conductivity was again predominant and the specimen was in a state similar to that originally quenched in.

Sintering Experiments

During the course of the anneal-quench experiments it was found necessary to determine precisely weight and volume changes so that the



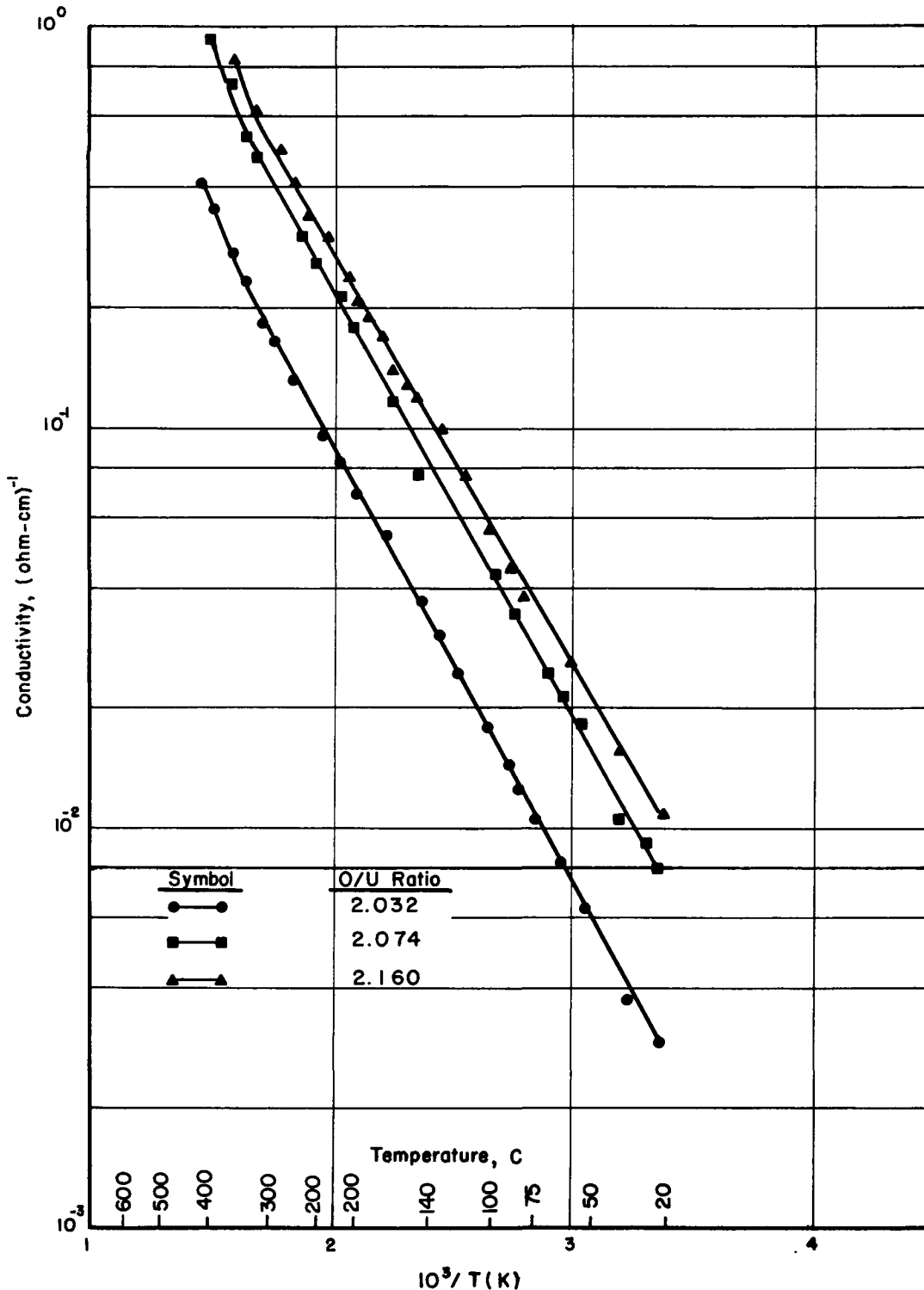


FIGURE 11. CONDUCTIVITY OF PRESSED SPECIMENS OF p-TYPE URANIUM DIOXIDE OF VARIOUS OXYGEN/URANIUM RATIOS AFTER ANNEALING AT 400 C AND QUENCHING TO ROOM TEMPERATURE

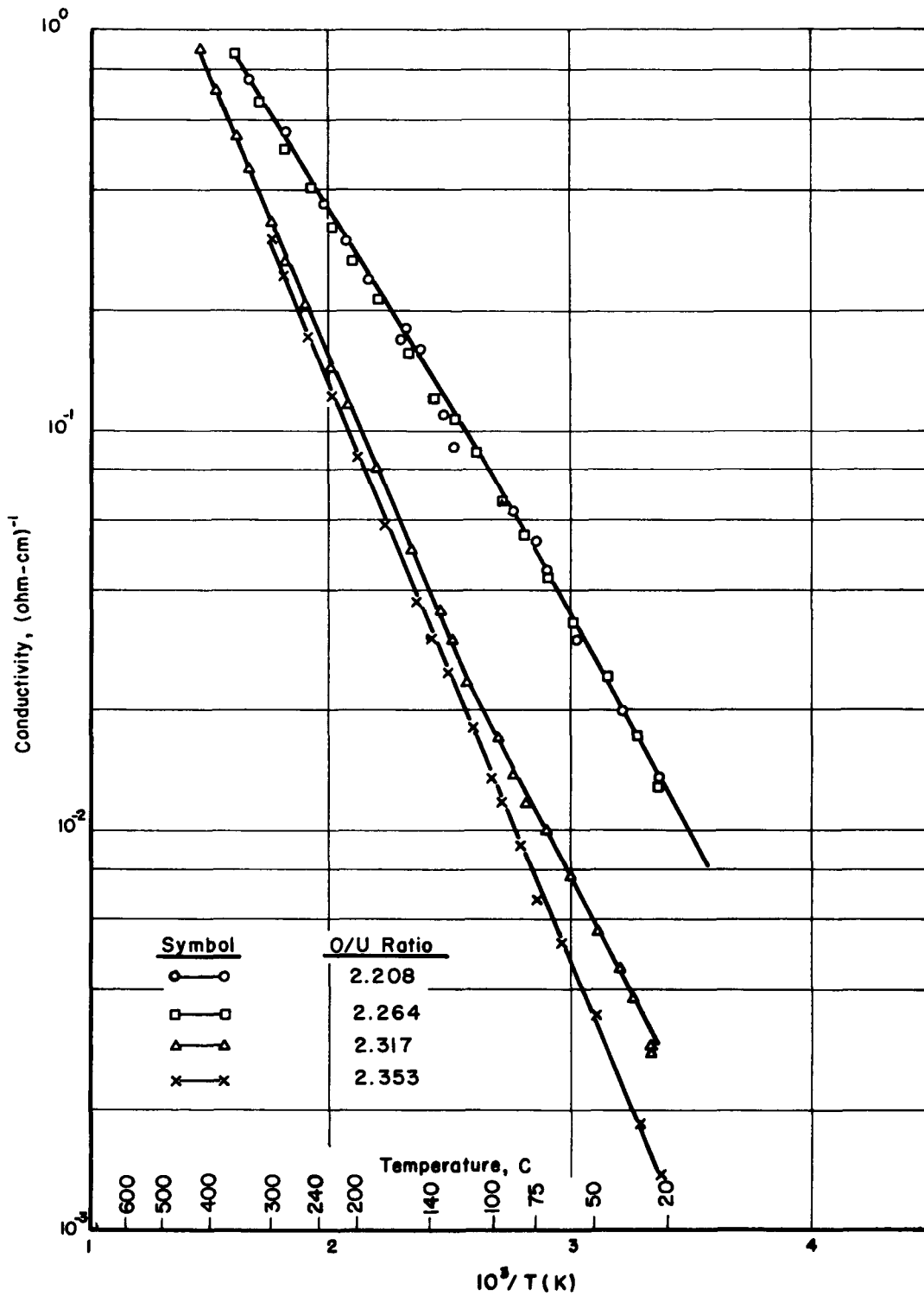


FIGURE 12. CONDUCTIVITY OF PRESSED SPECIMENS OF *n*-TYPE URANIUM DIOXIDE OF VARIOUS OXYGEN/URANIUM RATIOS AFTER ANNEALING AT 400 C AND QUENCHING TO ROOM TEMPERATURE

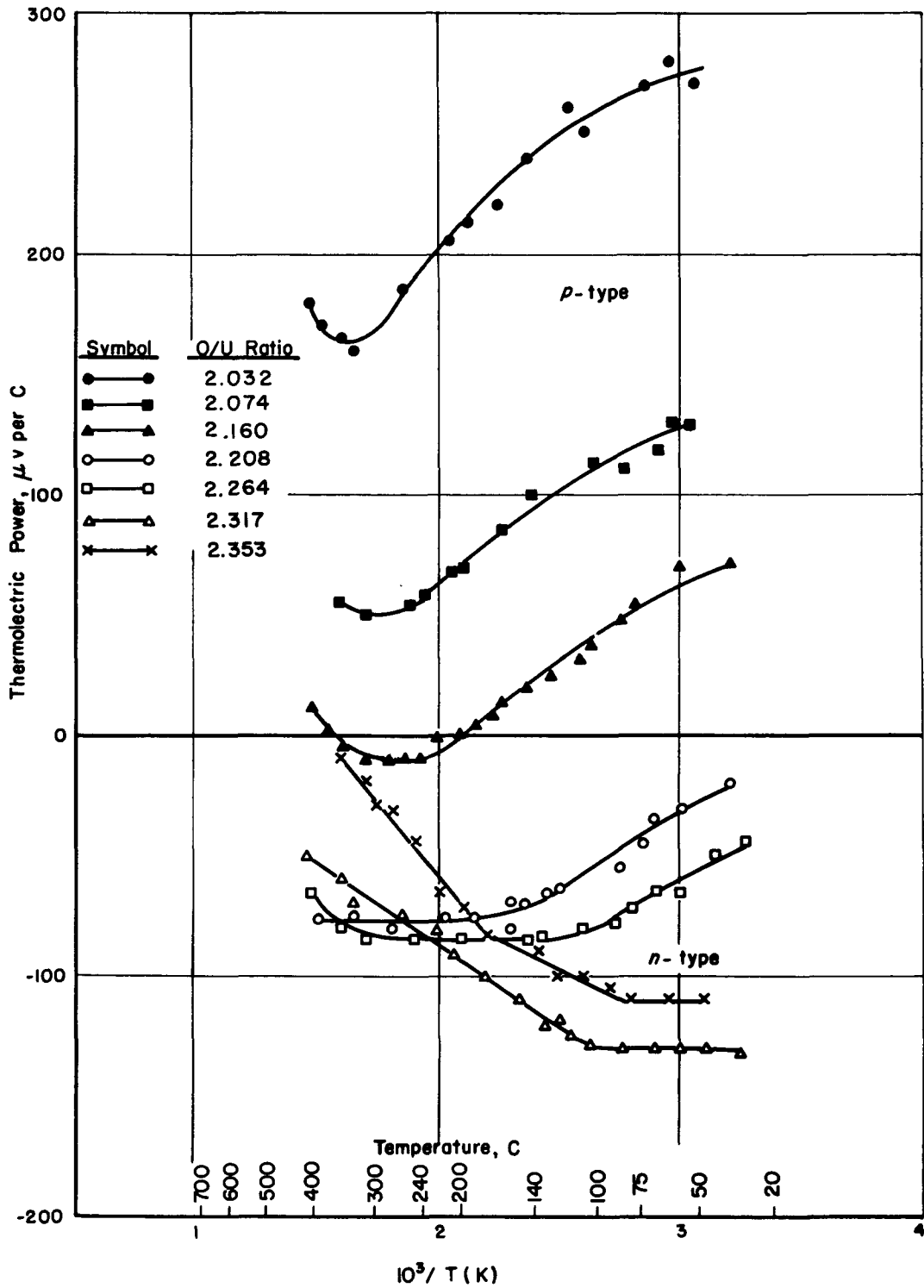
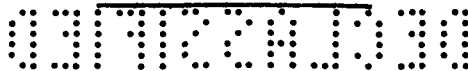


FIGURE 13. THERMOELECTRIC POWER OF PRESSED SPECIMENS OF URANIUM DIOXIDE OF VARIOUS OXYGEN/URANIUM RATIOS AFTER ANNEALING AT 400 C AND QUENCHING TO ROOM TEMPERATURE



proper density correction to the conductivity could be applied. It was observed that the volume of some of the p-type specimens decreased considerably when annealed at elevated temperatures. The volume decrease appeared to be related to the excess oxygen content, and, hence, conductivity, of the specimens. Since one of the objectives of this investigation was the correlation of the electrical properties with the sintering characteristics of uranium dioxide, it appeared desirable to further investigate this change.

Three specimens of p-type uranium dioxide were chosen for the experiments. The as-prepared oxygen/uranium ratio and room-temperature conductivity of the specimens are tabulated below:

<u>Oxygen/Uranium Ratio</u>	<u>Conductivity, (ohm-cm)⁻¹</u>
2.039	5.1×10^{-4}
2.075	1.0×10^{-3}
2.103	1.1×10^{-3}

The specimens were sealed in small Vycor capsules under a partial pressure of argon and annealed at each selected temperature for 16 hr. No attempt was made to anneal the specimens to a steady state as before. After each anneal period, the specimens were quenched, removed from the capsules and weight, volume, and conductivity measurements made. After annealing at 500 C and higher, the conductivities were as tabulated in Table 1.

Up to 600 C, no changes in volume or weight were detected. Above 600 C, some oxygen was lost from the specimens, as indicated in Table 1 by the decrease in conductivity at high temperatures. It was impossible to measure the actual loss of oxygen by weight changes, since some material was invariably lost from the samples simply by handling. The volume changes of the specimens are plotted in Figure 14. (Because of the small weight change due to handling and loss of oxygen, a plot of volume change is more significant than a plot of density change.) The percentage change of volume was calculated from the expression:

$$\text{Percentage change} = (V_T - V_0)/V_T \quad , \quad (5)$$

where

V_0 is the original volume

V_T is the volume after anneal at temperature T.

An examination of Figure 14 and Table 1 reveals an important correlation between the electrical properties and the sintering characteristics of uranium dioxide. It is clearly evident that the volume of specimens of

TABLE 1. ROOM-TEMPERATURE CONDUCTIVITIES OF UO₂ AFTER ANNEALING AT ELEVATED TEMPERATURES

Oxygen/Uranium Ratio	Conductivity, (ohm-cm) ⁻¹				
	500 C	600 C	800 C	900 C	1000 C
2.039	8.3×10^{-3}	1.8×10^{-2}	9.9×10^{-3}	9.4×10^{-3}	8.3×10^{-3}
2.075	1.2×10^{-2}	1.5×10^{-2}	1.4×10^{-2}	1.3×10^{-2}	--
2.103	1.6×10^{-2}	1.6×10^{-2}	1.5×10^{-2}	9.8×10^{-3}	9.1×10^{-3}

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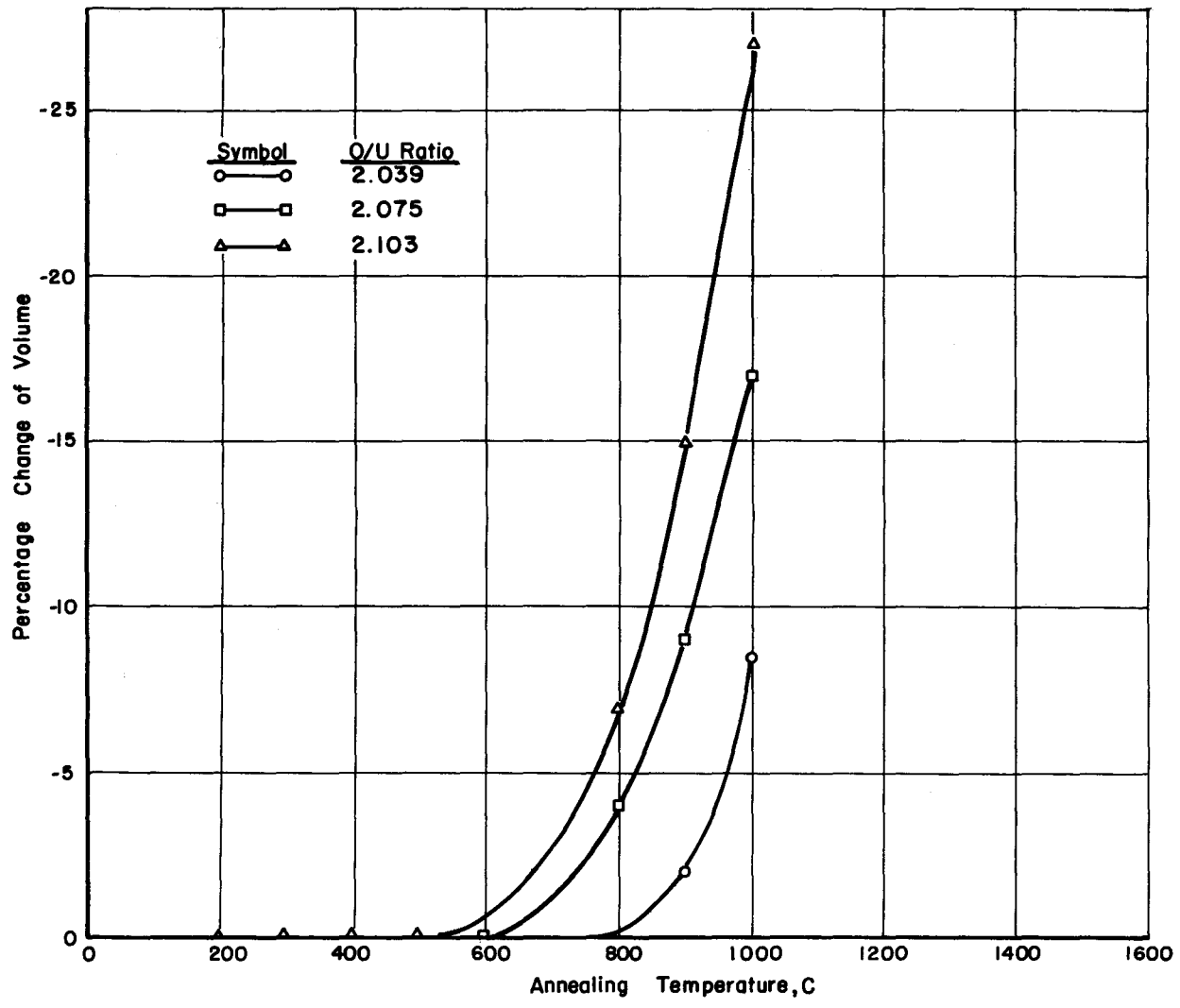


FIGURE 14. PERCENTAGE CHANGE OF VOLUME AS A FUNCTION OF ANNEALING TEMPERATURE FOR VARIOUS SPECIMENS OF p-TYPE URANIUM DIOXIDE

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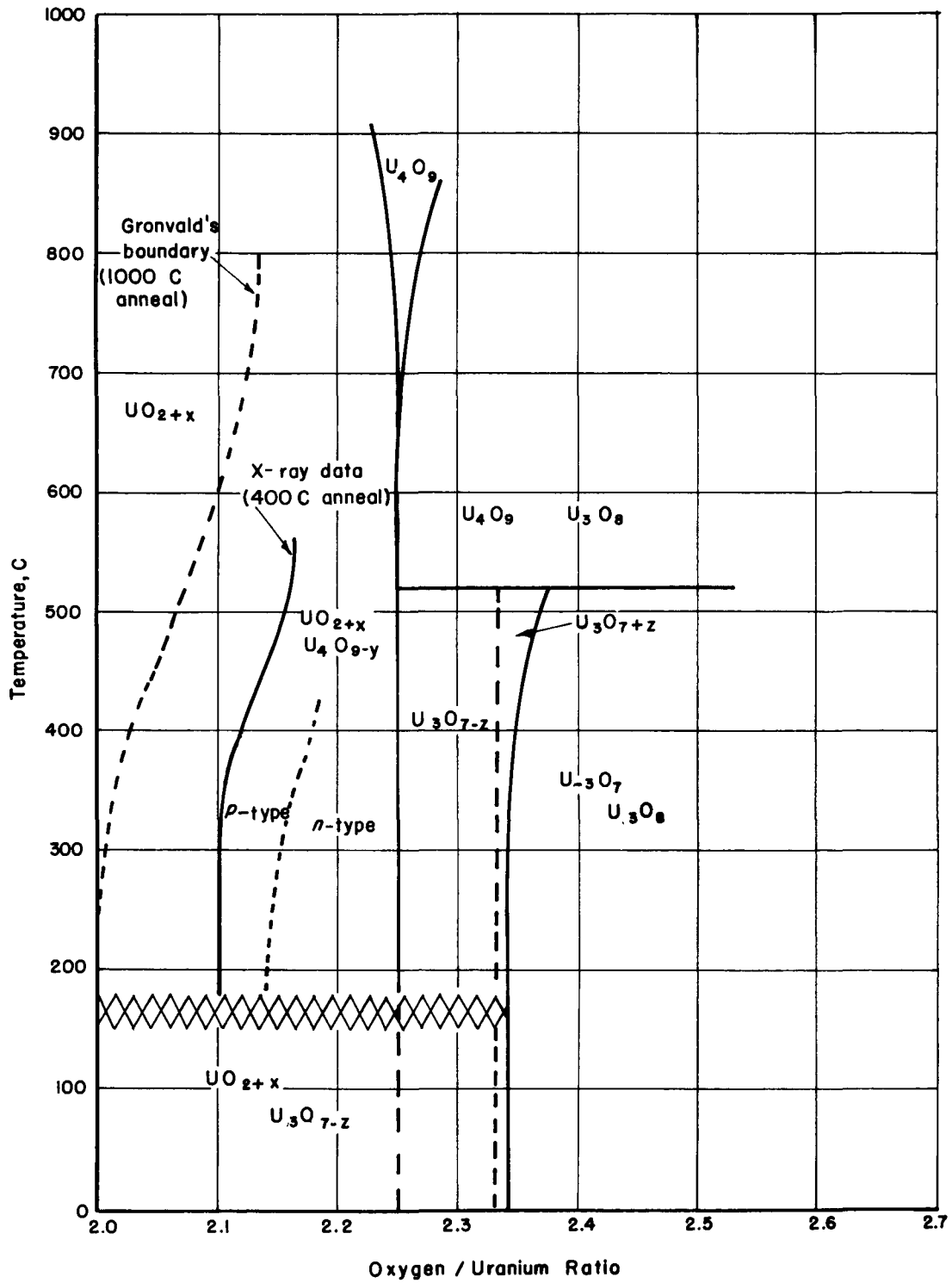


FIGURE 15. THE $UO_2-U_3O_7$ SYSTEM

- (2) A two-phase region above 180 C of $\text{UO}_2 + \text{U}_4\text{O}_9$ extends to a composition of $\text{UO}_{2.24}$. The exact representation of this region depends on the temperature and oxygen concentration. Up to about $\text{UO}_{2.14}$, the region is best represented as $\text{UO}_{2+x} + \text{U}_4\text{O}_9$; above this ratio as $\text{UO}_{2+x} + \text{U}_4\text{O}_{9-y}$. Heating a specimen above 180 C within this region results first in an ordering of many of the oxygen atoms into the body center of the unit cell; that is, the U_4O_9 structure is preferred. Increasing the temperature still further finally destroys the order, as shown in Figure 15.
- (3) At oxygen concentrations between $\text{UO}_{2.26}$ and $\text{UO}_{2.34}$ a tetragonal phase is predominant. In this structure, corresponding to the formula U_3O_7 , interstitial oxygen atoms are occupying planes perpendicular to the [001] direction of the fluorite cubic system. Indications are that this phase is stable to at least 400 C.

The study of the $\text{UO}_2\text{-U}_3\text{O}_7$ system by means of electrical measurements was limited to temperatures below 400 C because of changes in oxygen content at higher temperatures. The high-temperature data of large ratios of Figure 15 were taken from Perio's diagram.

Indications are that the equilibria of the system are not clear cut. This is especially true of the equilibria involving UO_2 and U_4O_9 . For example there is a large difference between the boundary of the two-phase region, $\text{UO}_2 + \text{U}_4\text{O}_9$, and the single-phase region, UO_2 , given by Gronvald and that obtained from Battelle X-ray data. This difference may possibly be attributed to the differences in anneal temperature, purity of materials (nitrogen content, etc.), and the precision to which the second phase can be detected. There is also a question of whether equilibrium was actually obtained during the X-ray measurements. Furthermore, the continually increasing conductivity with increasing temperature found in the anneal-quench experiments indicates a temperature-dependent oxygen solubility for which, at low temperatures, much of the excess oxygen is not incorporated in the lattice but perhaps is precipitated on the grain boundaries. Somewhat similar results have been reported for the case of excess lead in lead telluride⁽¹⁷⁾.

From the sign and relative magnitude of the conductivity one can determine whether a phase is metal excess, metal deficit, or nearly stoichiometric. Using this type of analysis, the discontinuity in electrical conductivity as a function of oxygen/uranium ratio (Figure 10) becomes the dashed line separating the p -type and n -type regions in the $\text{UO}_{2+x} + \text{U}_4\text{O}_{9-y}$ portion in Figure 15. Referring to Figure 10, the electrical conductivity increases as a function of the oxygen/uranium ratio for ratios between

2.00 and 2.07, and then decreases for ratios up to 2.14. The decrease can only be explained by assuming that part of the oxygen is going into a compound of a higher valence state of uranium. The second phase is confirmed by X-ray analysis. At a ratio of about 2.16, the conductivity becomes large, *n*-type, and decreases as the oxygen/uranium ratio is increased to 2.32. The large *n*-type conductivity at about oxygen/uranium = 2.16 indicates the predominance of a metal-excess phase which is identified as U_4O_9 by X-rays. The X-ray data also show the region to be two phase with the second phase being UO_{2+x} , the excess oxygen being indicated by a slight reduction of the lattice constant of uranium dioxide. The second phase is not in contradiction with the electrical data and may even contribute to the large values of conductivity observed. The change in slope of the *n*-type conductivity and its decrease to a very low value for an oxygen/uranium ratio at 2.32 suggest a stoichiometric compound with an oxygen/uranium ratio slightly higher than this. Obviously, this compound is U_3O_7 and its existence is confirmed by X-ray data.

Electrical measurements on the quenched specimens after prolonged aging at room temperature indicate the reversibility of the phase transitions discussed above. The conductivity of all quenched specimens decreased as a function of time when allowed to age at room temperature. Although it was possible to quench in the high-temperature phases, prolonged aging resulted in the precipitation of oxygen or the appearance of U_3O_{7-z} as indicated by the phase diagram of Figure 15.

Additional information on the phase diagram can be obtained from magnetic-susceptibility measurements. Dawson and Lister⁽¹⁸⁾ and Arrott and Goldman⁽¹⁹⁾ have determined the magnetic susceptibility of uranium oxides in the region UO_2 to U_3O_8 . Their data are plotted* in Figure 16, and should be compared with Battelle data in Figure 10. Unfortunately, Battelle does not have X-ray data, electrical measurements, and magnetic-susceptibility data on the same samples under the similar conditions, but it seems reasonable to assume that the susceptibility data for oxygen/uranium ratios between 2.00 and 2.35 were for mixtures of UO_{2+x} and U_3O_7 . However, it is interesting to note that anomalous magnetic susceptibility below 29 K as a function of the oxygen/uranium ratio as measured by Arrott and Goldman has a behavior similar to the electrical conductivity at room temperature following the anneal and quench treatment. Namely, both the susceptibility and the conductivity increase with increasing oxygen/uranium ratio for ratios between 2.00 and 2.10 and decrease with increasing oxygen/uranium ratio between 2.20 and 2.33. Collection of more data will be necessary, however, before any definite conclusions can be drawn.

*According to Perio⁽¹⁵⁾, Anderson has indicated that the starting material used by Alberman and Anderson, who were the source for the material used by Dawson and Lister, had the composition of $UO_{2.04}$, rather than $UO_{2.000}$ as stated in their paper.

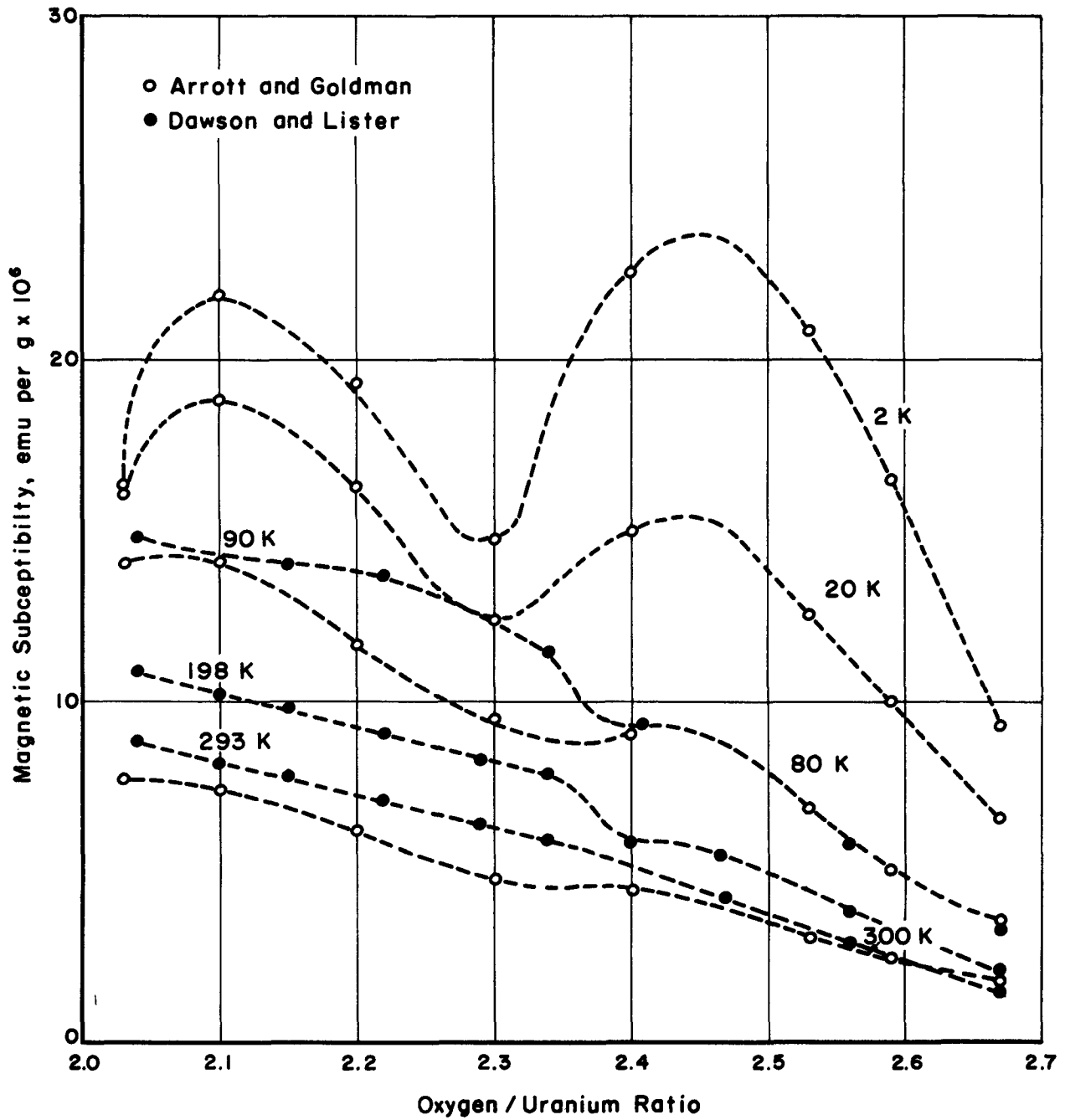


FIGURE 16. MAGNETIC SUSCEPTIBILITY AS A FUNCTION OF OXYGEN/URANIUM RATIO AT VARIOUS TEMPERATURES

Electrical Properties of Uranium Oxides

A summary of the activation energies obtained from the slope of the log of the extrinsic conductivity as a function of reciprocal-temperature curves from this investigation and from the literature is shown in Figure 17. The *p*-type (metal deficit) activation energies are in the range of 0.37 ± 0.1 ev, but apparently decrease with increasing conductivity. The lowest value of activation energy and largest room-temperature conductivity are obtained from Chiotti's data. The *n*-type (metal excess) activation energies are nearly double those of the *p*-type, but seem to decrease almost twice as fast with increasing conductivity. Calculations using reasonable values for the effective mass and mobility of the positive current carriers give good agreement with the estimated number of acceptor levels. However, similar calculations for the *n*-type conductivity indicate other factors must be taken into consideration. If the *n*-type material with an activation energy of about 0.9 ev contains both donors and acceptors (say, UO_{2+x} and U_3O_{7-z}), the effect is one of reducing the free carrier density. Since saturation value (obtained at high temperatures) of free electrons is equal to the difference between the concentration of donors and acceptors and independent of the density of acceptors, the charge-carrier density must drop off more sharply as the temperature falls if acceptor levels are present. In fact, it has been shown⁽²⁰⁾ that when the concentration of acceptors is very much greater than the density of free electrons (from donor levels) the latter changes twice as rapidly with temperature as it would if the acceptor levels were not present. Thus, the activation energy, ΔE , of the donor levels calculated using Equation (4) could be too large by a factor of 2. The large activation-energy values and their rapid decrease with increasing conductivity calculated for *n*-type material can, therefore, be explained by the above mechanism of compensation. Some of the calculations of the *p*-type activation energies may also yield values which are too high because of compensation. It is interesting to note that the value for the active oxide is low, 0.28 ev, compared with most of the others, and, therefore, if the above hypothesis is correct it would contain negligible compensation (few or no donor or metal-excess atoms).

Although Meyer⁽¹²⁾ reports UO_2 to be an amphoteric semiconductor we have not found any evidence for the existence of UO_{2-x} . Measurements on a specimen with an oxygen/uranium ratio of 1.96 indicated *p*-type conductivity; therefore, the specimen was UO_{2+x} plus a second phase. All *n*-type conductivity could be attributed to the presence of U_4O_{9-y} or U_3O_{7-z} .

The electrical properties of other compounds have been found to depend on order. Of particular interest is the behavior of the Hall coefficient of quenched specimens of Cu_3Au ⁽²¹⁾. In the ordered state the

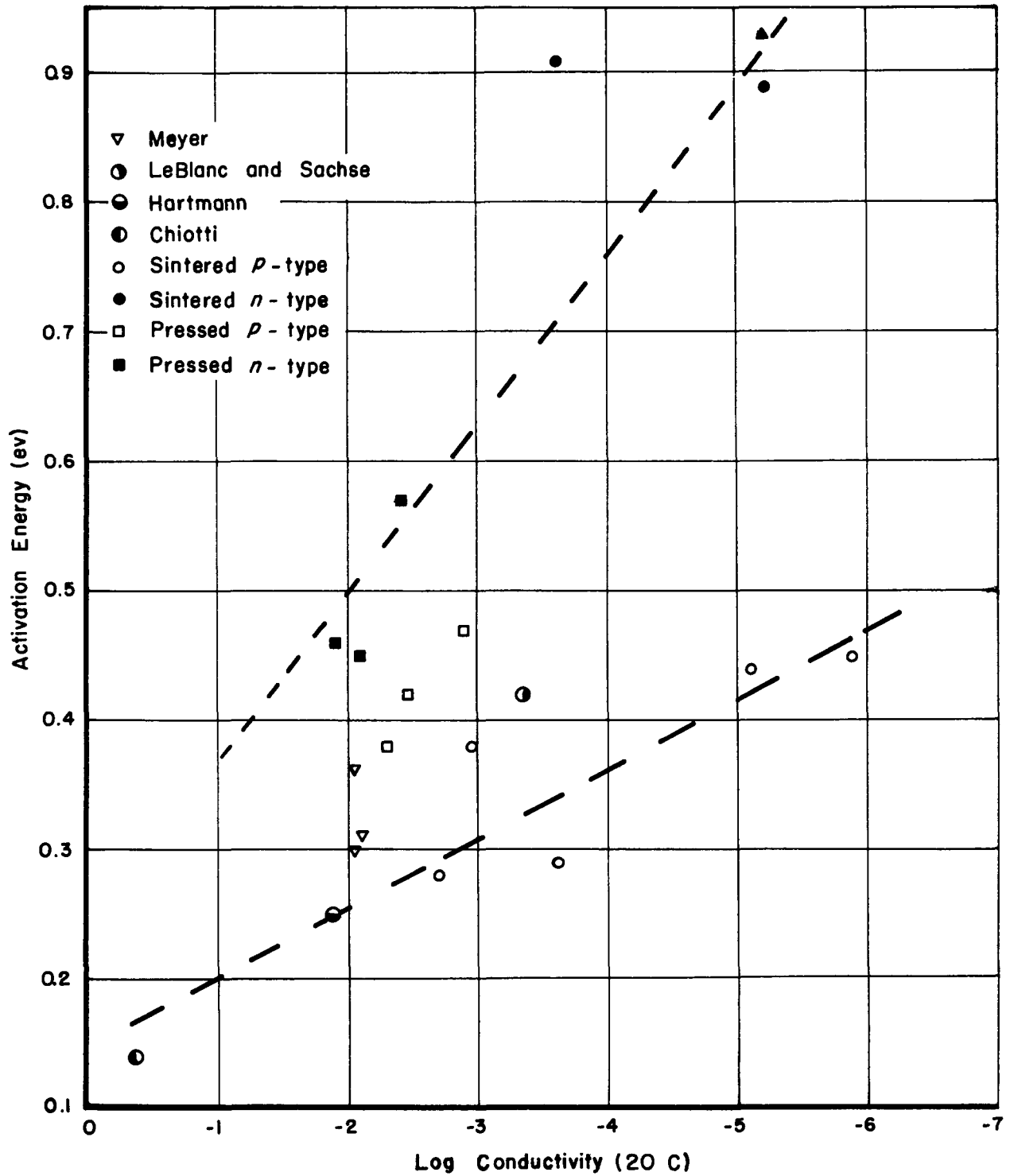


FIGURE 17. ACTIVATION ENERGY AS A FUNCTION OF LOG CONDUCTIVITY FOR VARIOUS SPECIMENS OF URANIUM DIOXIDE

Hall coefficient was positive, but became negative with increasing disorder. As in UO_2 , the change in type of conductivity indicates that the electronic-band structure changes when ordering occurs.

The anomalous behavior of the thermoelectric power of sintered specimens (that is, the increase of thermoelectric power with increasing conductivity) may be explained by the presence of U_3O_{7-z} at the lower temperatures and a decrease in its relative amount as the temperature is increased.

Sintering Characteristics of Uranium Dioxide

Sintering experiments with uranium dioxide have demonstrated a correlation between the electrical conductivity and the sintering characteristics of uranium dioxide. As these experiments were performed on excess-oxygen UO_2 , they confirm the general rule that the transport of matter during sintering is roughly proportional to the deviation from stoichiometry. However, the "doping" of UO_2 with excess oxygen to obtain UO_2 of high sintered density was proven impractical. The loss of oxygen during sintering, even in an inert atmosphere, is too rapid to allow much contribution of the excess atoms to the sintering process. The results do suggest that high-density sintered bodies could be obtained by the addition of a p-type metallic impurity to uranium dioxide. Metallic elements of the first three groups of the Periodic Table should be p-type impurities and should increase the sintered density of UO_2 .

The anomalous decrease in conductivity of sintered normal UO_2 at high temperatures, not observed in "active" UO_2 , has not been satisfactorily explained. Also, the effects of the presence of nitrogen have not been resolved as yet, and these aspects of the work deserve further consideration.

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