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HIGH TEMPERATURE THERMAL EXPANSION OF UO_2 AND ThO_2

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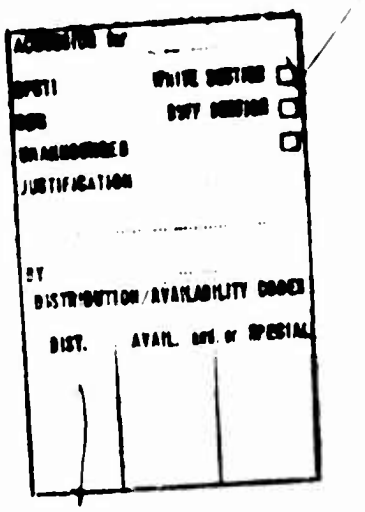

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FOREWORD

This report was prepared by the University of Cincinnati under Contract No. F33615-67-C-1565. This contract was initiated under Project No. 7360, Task No. 736005.

The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command with Mr. Freeman F. Bentley as project engineer.

This report summarizes work performed from July 1967 through July 1968. Manuscript was released in July by the author for publication as an RTD technical report.

The work was performed at the University of Cincinnati with Dr. Michael Hoch serving as the principal investigator.

This report has been reviewed and is approved.

Freeman F. Bentley
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ABSTRACT

The thermal expansion of uranium dioxide and thorium dioxide has been measured between 20 and 2100°C using high temperature x-ray diffraction techniques. The thermal expansion of UO_2 and ThO_2 as measured by x-ray diffraction is identical to that obtained by bulk expansion measurements. Because of this, and because the specific heat of UO_2 shows a rapid increase above 1700°C indicating a disorder, it must be concluded that the major structural defect is a Frenkel type disorder. This probably involves the oxygen atom moving from the tetrahedral into an empty octahedral position.

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INTRODUCTION

The importance of UO_2 and ThO_2 as fuel and fertile material in nuclear power reactors is well known. However, limited data exist in the literature on the high temperature physical properties of these materials. Thermal expansion data[1-7] on UO_2 have been obtained mostly by bulk expansion measurements using dialatometric, interferometric, or telemicroscopic techniques up to the melting point of UO_2, and by x-ray diffraction techniques[8-12] up to 900°C. Recently, Baldock, Spindler, and Baker[13] have obtained thermal expansion data using x-ray diffraction up to 2250°C. Their data are in general agreement with the bulk expansion measurements up to 1400°C; however, above this temperature Baldock, et al.[13] found that the x-ray thermal expansion was significantly lower than the bulk expansion. The reasons for this difference at higher temperatures were not clear and certain. Baldock, et al.[13] suggest a large contribution by Schottky defects. The present work was therefore undertaken to elucidate this point. For this purpose, thermal expansion measurements using high temperature x-ray diffraction techniques were carried out on UO_2 in vacuum over the temperature range 850-2100°C.

In order to check the results obtained with UO_2, thermal expansion measurements were carried out on ThO_2 using high

temperature x-ray diffraction techniques, and the results compared with those of other investigators.[14-16]

EXPERIMENTAL PROCEDURE

Equipment

The high temperature induction heated x-ray diffraction camera used in this work was the same as used by Hoch, Dean, Hwu, and Wolosin[17] and by Wyder and Hoch.[18] Temperature was measured with an L&N disappearing filament optical pyrometer.

Copper K_α radiation was used for obtaining high temperature x-ray diffraction patterns. Room temperature x-ray diffraction patterns were taken on a Norelco x-ray diffraction unit using CuK_α radiation.

An induction heated vacuum furnace was used to heat large quantities (5-10 grams) of UO_2 to elevated temperatures in a tungsten crucible to study the variation of stoichiometry with heating temperature.

Materials

The uranium dioxide powder of 99.9% purity was supplied by K & K Laboratories, Plainview, New York (Lot 31833); its average particle size was between 100 and 150 mesh. Thorium dioxide, 99.9% ThO_2, was obtained from Fairmount Chemical Company, Inc., Newark, New Jersey.

Temperature Calibration

To eliminate the error due to the emmissivity of the sample, the temperature of a black-body hole put in the place

of the x-ray diffraction sample was measured. For this purpose, a hole 0.047" in diameter by 0.063" deep was drilled into a sample of 0.15" diameter and 0.16" length. Thus the correction was evaluated under conditions identical to those when x-ray diffraction patterns were taken. For the absorption correction of the glass window, the curve developed in this laboratory was used.

Sample Preparation and Operation

The samples were pressed without any binder and were compacted into cylindrical rods of 1/16" diameter and about 3/16" length. The sample was then placed into the high temperature x-ray diffraction camera. The camera was evacuated with a mechanical fore pump and an oil diffusion pump to a vacuum of 2×10^{-5} torr. After heating to the elevated temperature, the sample was kept at this temperature for 1/2 hour before the 5-hour long exposure was taken. For each run a fresh sample was used.

Measurement of Lattice Parameters

The lattice parameters were calculated by employing the Nelson-Riley extrapolation technique.[19] The accuracy of the lattice parameter measurements in the high temperature x-ray diffraction camera is ±0.003Å; that in the Norelco room temperature camera is ±0.001Å.

EXPERIMENTAL RESULTS AND DISCUSSION

A. UO_2

The oxygen-to-uranium ratios of several UO_2 samples were determined by the oxidation method and are given in Table I. Weighed amounts of the sample were heated in air at 650°C to constant weight, and the ratios then calculated from the weight gain due to oxidation to U_3O_8. Samples 1, 2, 3, and 4 were treated in this manner; the average oxygen-to-uranium ratio of these samples was 2.067±0.002.

According to the calculation of Hoch and Furman,[20] the oxygen partial pressure above $UO_{2.07}$ is quite high (3.73×10^{-7} atm at 1244°C) and thus heating the sample should cause $UO_{2.07}$ to decompose and approach the stoichiometric composition $UO_{2.0}$ as it is heated to higher and higher temperatures. To check this, samples of $UO_{2.07}$ were heated in a vacuum of 10^{-6} torr for 5 hours to different temperatures and cooled rapidly in vacuum. Both in this measurement and in the high temperature x-ray diffraction camera, "cooling rapidly" means shutting off the induction heating power and letting the sample cool by radiation in vacuum. As the mass of the heated parts is very small, the rate of cooling is fairly rapid. The samples thus obtained were analyzed for oxygen-to-uranium ratio and the results are given as Samples 5, 6, and 7 in Table I. As can be expected after heating to high

temperatures, the oxygen-to-uranium ratio becomes lower and the sample heated to 1960°C has the stoichiometric composition.

The lattice parameter measurements on UO_2 samples over the temperature range of 850 to 2000°C are summarized in Table II. The room temperature lattice parameters of the sample as received and unheated (Run No. 1) and of the samples after heating to 925, 1244, 1542, and 1960°C in vacuum and cooling to room temperature in vacuum (Runs 6a, 8a, 13a, and 23a) are identical. This is expected because the difference in lattice parameter between $UO_{2.00}$ and $UO_{2.07}$ at room temperature is only 0.005Å.[23]

To show that the small change in stoichiometry has a negligible effect on the lattice determination of the thermal expansion coefficient, x-ray diffraction patterns were taken on two samples at 845°C and 927°C after the samples had been heated for 5 hours to 1960°C and thus had the stoichiometric composition $UO_{2.0}$. These two points are points 24 and 25 in Table II and are plotted with a different sign in Figure 1. They do not differ from the other data points.

The data in Table II were converted into percent linear expansion and plotted together with those of Conway, et al.[7] and Baldock, et al.[13] in Figure 1. As can be seen in Figure 1, the present data obtained by x-ray diffraction techniques

and those of Conway[7] obtained by bulk expansion measurements agree well over the whole experimental range, but the present data disagree with that of Baldock.[13] As the specific heat of UO_2 shows a rapid increase above 1700°C,[21] indicating some kind of lattice disorder, it must be concluded that the lattice disorder in question is of the Frenkel type. For a Frenkel type disorder the thermal expansion determined by x-ray diffraction and by bulk measurements should be equal. The Frenkel disorder which suggests itself immediately is that of an oxygen atom in a tetrahedral position moving into an empty octahedral site. This type of disorder should be present, as it is relatively easy to prepare hyper- and hypo-stoichiometric UO_2.

It is impossible to understand and explain the difference in thermal expansion measurements obtained by x-ray diffraction between Baldock, et al.[13] and this research. Baldock[13] only used two specimens whereas in this work a new sample was used for every lattice parameter measurement. The precision in Baldock's determination is greater than in the present data; however, the scatter in the thermal expansion curve in Figure 1 of Baldock's data is not smaller than the scatter of the present results. The possibility exists that the thermocouple used by Baldock[13] (W/W-26Re thermocouple) may have deteriorated during the measurements.

An error of 300°C at 2200°C in Baldock's temperature measurements would be required to bring his highest data point onto the curve of Conway.[7]

Thus, the thermal expansion of $UO_{2.0}$ is best represented by the equation given by Conway, et al.[7]

$$\% \text{ Expansion} = 6.797\times10^{-7}T + 2.896\times10^{-7}T^2 - 1.723\times10^{-2},\ T \text{ in } °C.$$

B. ThO_2

The lattice parameter measurements of ThO_2 are summarized in Table III and plotted in Figure 2 in terms of the linear thermal expansion as a function of temperature. This figure also contains the x-ray thermal expansion measurements of Aronson, et al.[14] and the bulk expansion measurements of Geller and Yavorsky[15] and Ohnysty and Rose.[16] The agreement on thermal expansion of ThO_2 among the four authors is extremely good. From the data of Ohnysty and Rose[16] the following equation is derived for the thermal expansion of ThO_2:

$$\% \text{ Expansion} = 8.383\times10^{-4}T + 0.9995\times10^{-7}T - 2.106\times10^{-2},\ T \text{ in } °C.$$

The bulk and x-ray expansion data on ThO_2 agree with each other. The only high temperature heat content data

available[22] do not show a rapid rise. Thus, the disorder in ThO_2 is not yet defined.

To compare the thermal expansions of ThO_2 and UO_2 at elevated temperatures, the ratio of their thermal expansion was plotted in Figure 3. As can be seen, above 700°C where the measurements of Conway, et al.[7] and ours were carried out, the ratio is a smooth curve somewhat concave downward. From this it can be concluded that the thermal expansion of UO_2 is quite similar to that of ThO_2.

TABLE I

Oxygen-to-Uranium Ratio of Uranium Dioxide Samples

Sample No.	Oxygen-to-uranium ratio	Treatment before analysis
1	2.068	as received
2	2.066	as received
3	2.067	as received
4	2.066	as received
5	2.000	heated for 5 hours in vacuum (10^{-6} torr) at 1960°C
6	2.012	heated for 5 hours in vacuum (10^{-6} torr) at 1542°C
7	2.042	heated for 5 hours in vacuum (10^{-6} torr) at 1046°C

TABLE II

Lattice Parameter Measurements of UO_2

Run No.	Temperature °C	Lattice Parameter Å
1	25	5.469 ± 0.003
2	1074	5.525
3	1587	5.566
4	1415	5.554
5	886	5.507
6	925	5.511
6a	25	5.468
7	1159	5.533
8	1244	5.536
8a	25	5.469
9	1472	5.558
10	1301	5.542
11	1187	5.534
12	1387	5.548
13	1542	5.565
13a	25	5.468
14	1766	5.584
15	1822	5.587
16	1921	5.595
17	1759	5.580
18	1670	5.575
19	1359	5.547
20	1018	5.522
21	1825	5.589
22	870	5.503
23	1960	5.601
23a	25	5.470
24*	845	5.507
25*	927	5.513

* Run Nos. 24 and 25 are samples heated to 1960°C in vacuum (10^{-6} torr) for 5 hours before taking x-ray diffraction patterns.

TABLE III

Lattice Parameter Measurements of ThO_2

Run No.	Temperature °C	Lattice Parameter Å
1	25	5.595 ± 0.003
2	895	5.641
3	1175	5.655
4	1280	5.661
5	1370	5.663
6	1455	5.671
7	1665	5.679
8	1805	5.692
9	1965	5.703
10	1025	5.645
11	2090	5.712
12	845	5.633
13	1750	5.687
14	2025	5.708
15	1895	5.695

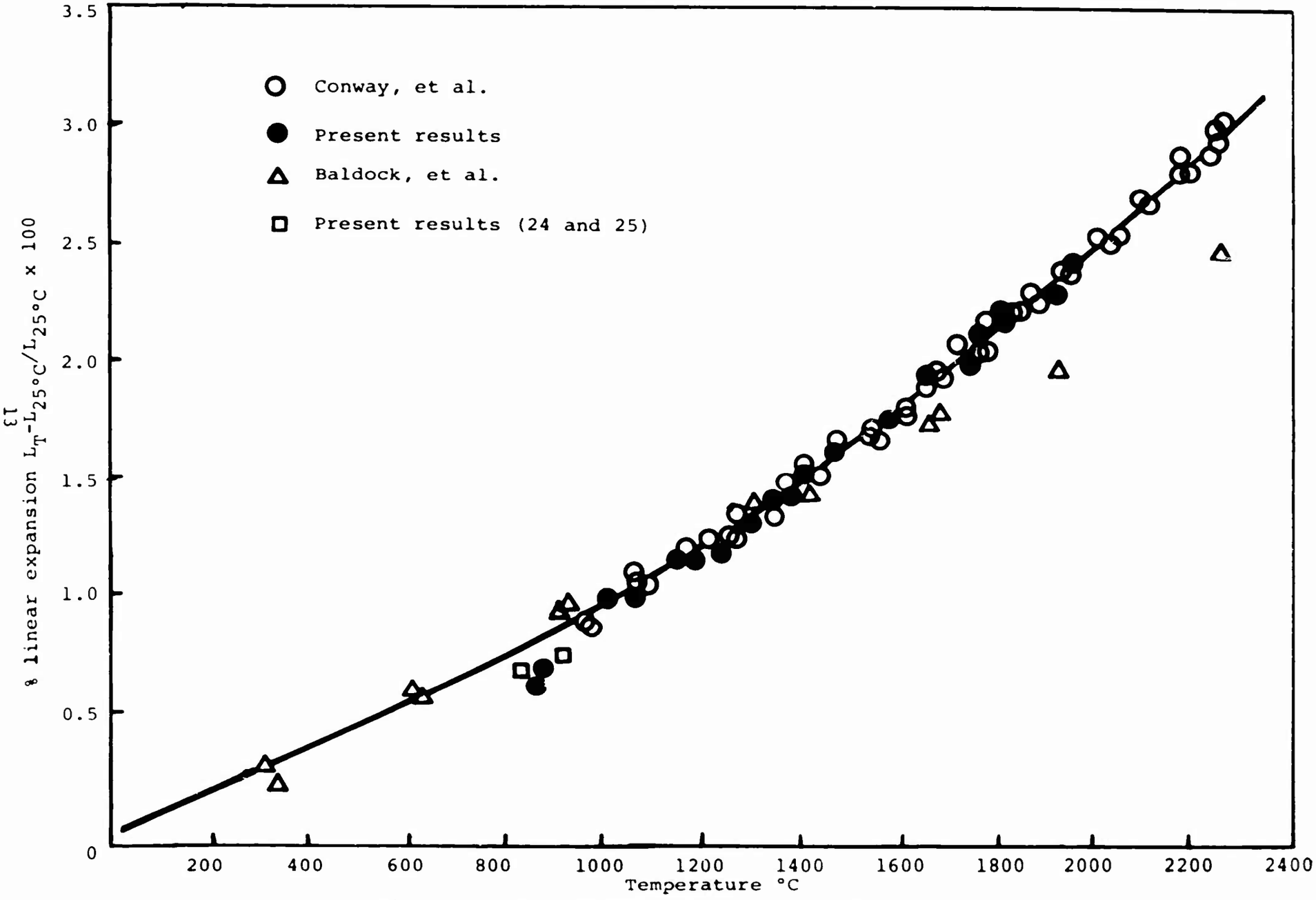

Fig. 1. Linear Thermal Expansion of UO_2

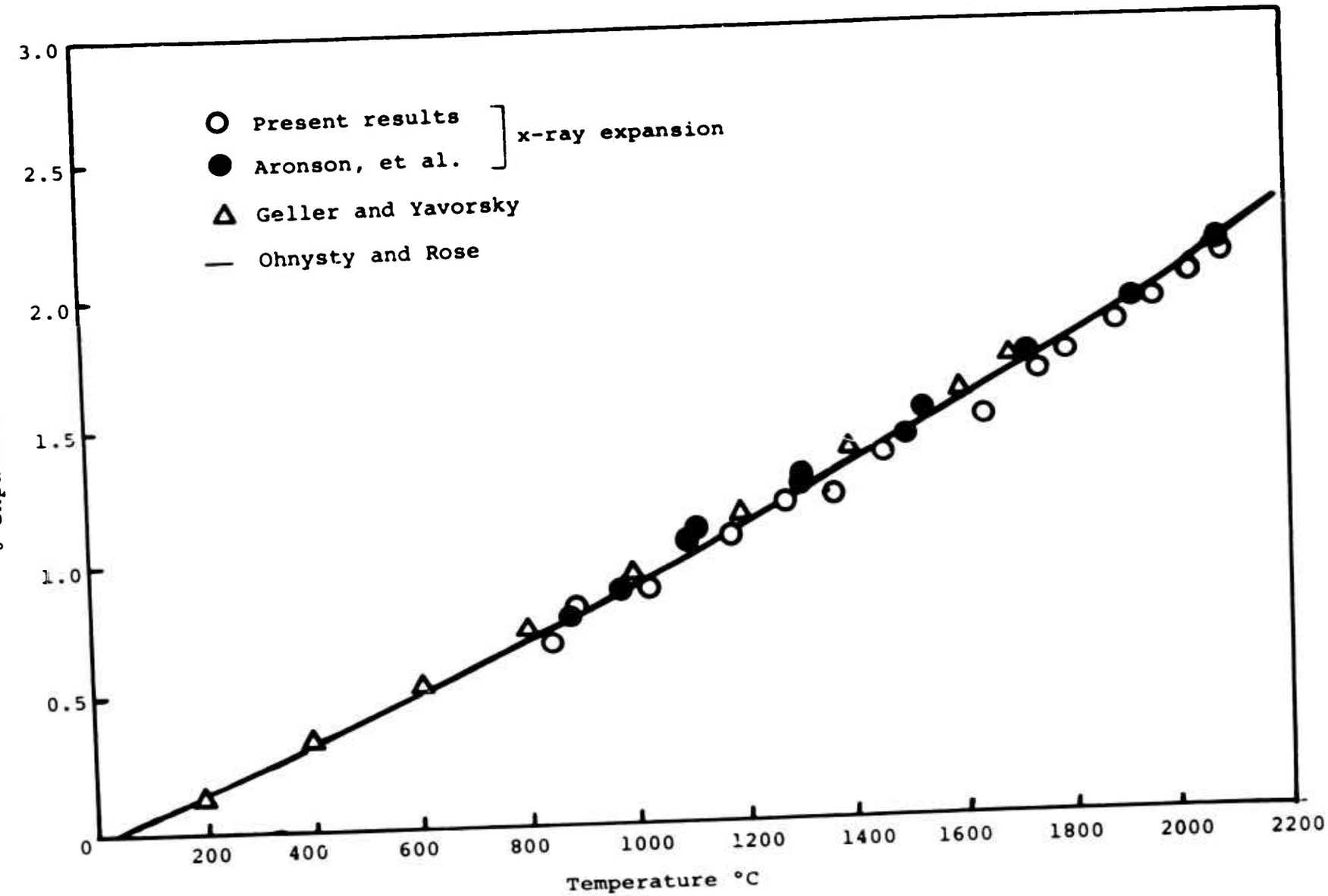

Fig. 2. Linear Thermal Expansion of ThO_2

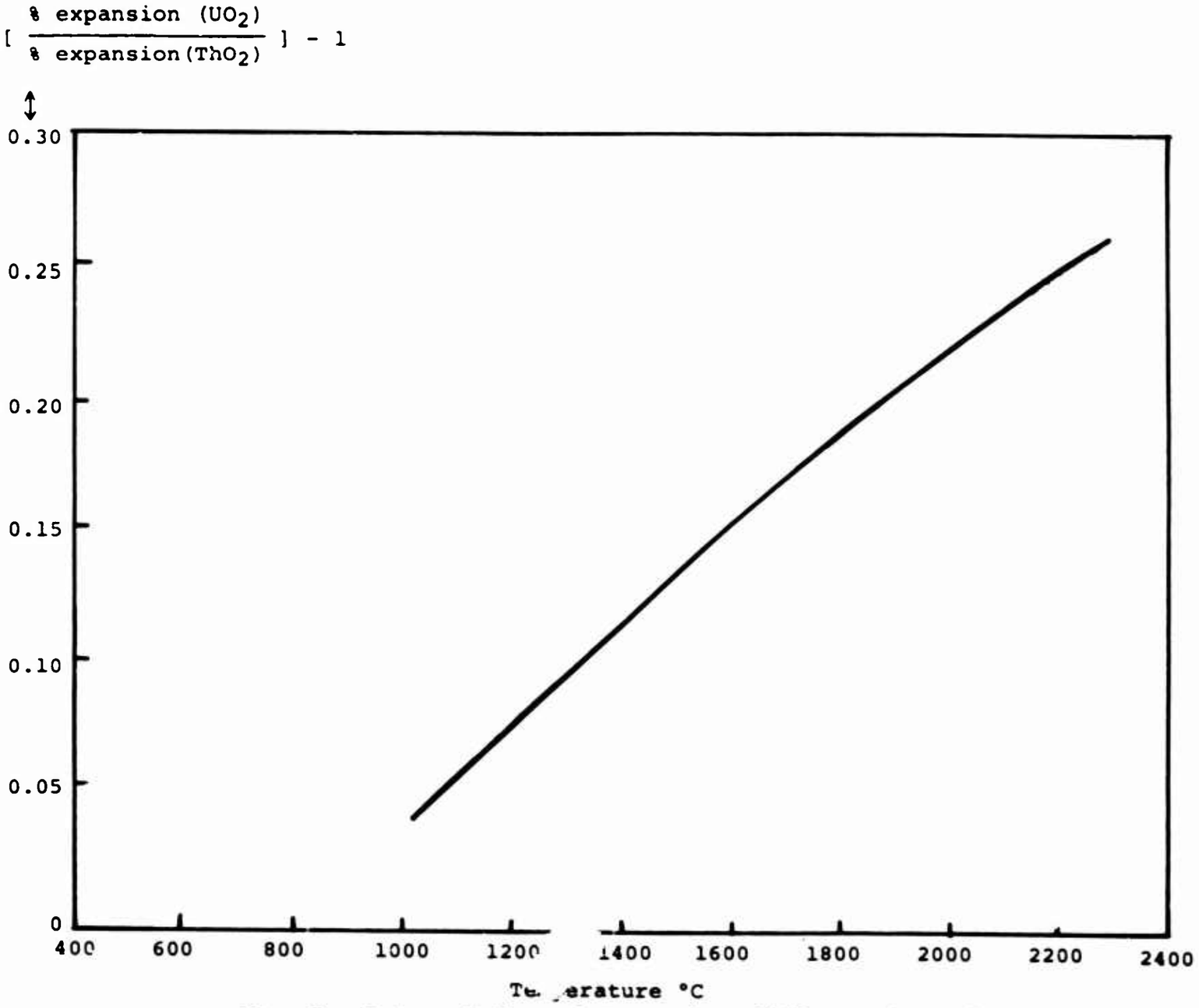

Fig. 3. Rates of Thermal Expansion of UO_2 to that of ThO_2

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