

# Temperature Dependence of the Elastic Constants of Thoria Specimens of Varying Porosity

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The temperature dependence of Young's and the shear modulus of 18 thoria specimens of porosities ranging from 3.7 to 39.4 percent have been measured by the dynamic resonance method. The temperature range of the measurements was from 25 to 1,300 °C. The moduli decreased with increasing temperature in general accordance with the pattern observed for other polycrystalline materials. The relative decrease in modulus with temperature for all the materials was essentially independent of porosity up to about 800 °C. Above this temperature the relative decrease in modulus for the high porosity specimens tended to be more rapid than for the low porosity specimens. Also, Poisson's ratio for any particular specimen remained constant over the entire temperature range of measurement.

## 1. Introduction

In a previous paper [1]<sup>1</sup> data were presented on the relation between the elastic constants and porosity of polycrystalline thoria specimens, at room temperature. The present paper presents data on the relation between elastic constants and temperature using representative specimens of varying porosities selected from among those used in the previous study.

Wachtman et al. [2] have already presented data on the temperature dependence of Young's modulus on a specimen of polycrystalline thoria having a porosity of 9.3 percent in the temperature range from about -180 °C to 600 °C. The present study extends these data in the following three ways:

1. Measurements were taken for specimens over a wide range of porosities (from about 4% to 40%).
2. The upper temperature limit of the data was increased, measurements being taken from 25 °C to about 1,300 °C.
3. The variation in the shear modulus as well as Young's modulus with temperature was determined.

## 2. Experiment

### 2.1. Specimens

From the previous paper it is recalled that three groups of specimens were measured and that each of these groups were divided into several subgroups of the same nominal porosity. It is also recalled that the specimens were rectangular bars about  $6 \times \frac{1}{2} \times \frac{1}{4}$  in. Since first measurements on two specimens of one subgroup (2-4-6-1 and 2-4-6-3) showed no significant difference in the relative de-

crease in modulus with temperature (and, as will be seen later, since very little difference was noted between specimens of different porosity from different subgroups), all subsequent measurements were made on one specimen from each subgroup.

TABLE 1. Porosity and elastic moduli of all the specimens used in this investigation

Specimen <sup>a</sup>	Porosity	Young's modulus	Shear modulus	Number of runs
	<i>Percent</i>	<i>Kilobars</i>	<i>Kilobars</i>	
2-4-0-24	6.95	2135	835.8	2
2-4-6-1	12.31	1834	720.5	5
2-4-6-3	12.23	1841	723.7	2
2-4-12-3	16.42	1606	634.7	3
2-4-18-2	22.00	1245	506.6	1
2-4-24-1	28.71	795.2	342.4	4
2-4-30-4	33.33	697.1	294.2	1
2-4-36-6	39.37	425.0	197.0	2
0-2-0-18	3.73	2290	893.9	2
0-2-6-6	7.87	2021	794.2	2
0-2-12-2	13.41	1583	623.7	1
0-2-18-1	18.95	1067	474.5	2
0-2-24-1	23.5	819.8	378.1	2
0-2-30-1	32.8	186.7	125.3	2
4-7-0-37	17.05	1573	626.6	1
7-13-0-37	23.61	1196	483.3	2
13-24-0-27	26.23	1033	419.0	2
24-44-0-31	26.09	996.2	405.7	2

<sup>a</sup> Specimens are designated in same way as in previous paper [1]. Numbers before and after first dash indicate the nominal range of starting particle size in microns; number after second dash indicates nominal volume percent of filler used; number following third dash indicates particular specimen of a subgroup.

Table 1 lists all the specimens measured along with the porosity and room temperature values of the elastic moduli of these specimens.

### 2.2. Method

The dynamic resonance method which was used for making these measurements as well as the associated calculations have been described previously [3,4]. These calculations include a correction for thermal expansion. The data for this quantity for ThO<sub>2</sub> were obtained from Wachtman, Scuderi,

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

and Cleek [5], who used an interferometric method and from Geller and Yavorsky [6] who used both an interferometric and a dilatometer method at the higher temperatures.

The final column in table 1 gives the number of modulus-temperature runs made on each specimen. For any set of runs for a particular specimen the fundamental flexural resonance frequency, overtones of this type of vibration (usually the first two) and the fundamental torsional resonance frequency was determined at the temperature of measurement, although not all these resonance frequencies were necessarily determined during each run. Young's modulus was computed independently from the different flexural resonance frequencies and the shear modulus from the torsional. The values of Young's modulus, computed from these different flexural frequencies at each temperature, were not averaged, but were entered as separate points in the figures. Thus, the reproducibility of the determination of Young's modulus was checked in two different ways; from the agreement of different runs and from the agreement of different resonance frequencies on a particular specimen at any given temperature. For the shear modulus, where overtones were used only occasionally, one relied mainly on agreement between separate runs as indicators of the reproducibility of the data. This reproducibility (taken as two standard deviations as determined from the scatter of the points shown in fig. 3) was estimated to be about 0.2 percent for both Young's and shear modulus, which is about the value reported for other materials using the same method [7].

One further point should be noted concerning the determination of the torsional resonance frequency at elevated temperatures. In the paper dealing with the cermets [4] it was observed that if the specimens were appropriately suspended, then torsional resonance could be obtained along with the flexural. However, it was also noted that the torsional resonance frequency died out at a lower temperature than the flexural. This was attributed to the geometry of the specimens (mainly, an insufficient width to depth ratio); and, in the later paper [7], dealing with vitreous silica, torsional responses were obtained, along with flexural, up to the highest temperature of measurement by increasing the width to depth ratio of the specimens. In the present investigation, however, the dimensions of the specimens were about the same as those of the cermets, yet torsional responses were detectable, along with the flexural, up to the highest temperatures measured. It is not surprising to find that materials such as  $\text{ThO}_2$ , primarily because of their low internal friction, will show certain detectable resonance responses under experimental conditions (such as temperature and specimen geometry) where other materials having somewhat higher internal friction do not. The upper temperature limit of the measurements was determined, as in the previous studies, [4,7] by the increase in internal friction, associated with increased thermal vibrations [4,7] and grain boundary slip [4] rendering the resonance responses undetectable.

### 3. Results and Discussion

Typical data showing the Young's modulus and shear modulus temperature relations for all the specimens measured in the 2-4  $\mu$  particle size group are shown in figures 1 and 2.

One observes the characteristic pattern previously noted with other polycrystalline materials; namely, the fairly linear decrease in modulus with temperature until some elevated temperature region is reached, in which region the modulus decreases more rapidly with increasing temperature. This more rapid decrease has been attributed to grain boundary slip [8,9,4] and is also believed to be the mechanism operating here.

It is also noted that for a particular specimen the values of Young's modulus as a function of temperature appear to be independent of the order of the resonance frequency (whether fundamental or overtones) used in their determination. As previously mentioned, it was this agreement along with the agreement of successive runs that was used to check the reproducibility of the data.

A final observation is that in comparing the different specimens for both Young's and the shear modulus, the steepest slopes in the linear portions of the curves, up to about 800 °C, appear to be associated with the highest modulus (lowest porosity) specimens. The curves of the specimens not shown follow the same pattern. They are not shown simply because it would have led to overcrowded figures.

This final observation was tested more rigorously in figure 3 in which the relative decrease in both Young's and the shear modulus, using the room temperature modulus as the reference value, is plotted as a function of temperature for all the specimens of this investigation. Each point in this graph represents an individual determination whether from successive runs or from the fundamental resonance frequency or overtones (no averaging). When plotted on this relative basis, it is seen that up to about 800 °C, the decrease in modulus with temperature appears to be independent of the porosity of the specimens and of the particular elastic modulus (whether Young's or shear) involved, within the precision of the data. Actually, a more careful analysis of the data shows that a slight porosity dependence of the relative elastic moduli with temperature does exist. However, it will be more appropriate to discuss this after a comparison of the results of this investigation with those of Wachtman et al. [2] and a consideration of the results of this investigation above 800 °C.

The fact that there is no significant difference between the relative temperature decrease of Young's modulus and the shear modulus means that Poisson's ratio for a specimen does not change with temperature. It will be shown later that whatever other changes may occur about 800 °C, this equivalence in the relative temperature decreases of Young's and the shear modulus continues, so that Poisson's ratio for a given specimen does not change with

SPECIMEN	POROSITY(%)	SYMBOL	$f_r$	NO. OF RUNS
A-2-4-0-24	6.95	● ○	1308 6942	2
B-2-4-6-3	12.23	● ○	1262 6702	2
C-2-4-12-3	16.42	● ○	1177 6280	3
D-2-4-18-2	22.00	● ○	1049 5732	1
E-2-4-24-1	28.71	● ○	7940 4357	4
F-2-4-30-4	33.33	● ○	840 2225 4585	1
G-2-4-36-6	39.37	● ○ ▲ △	602 1725 3365 5579	1

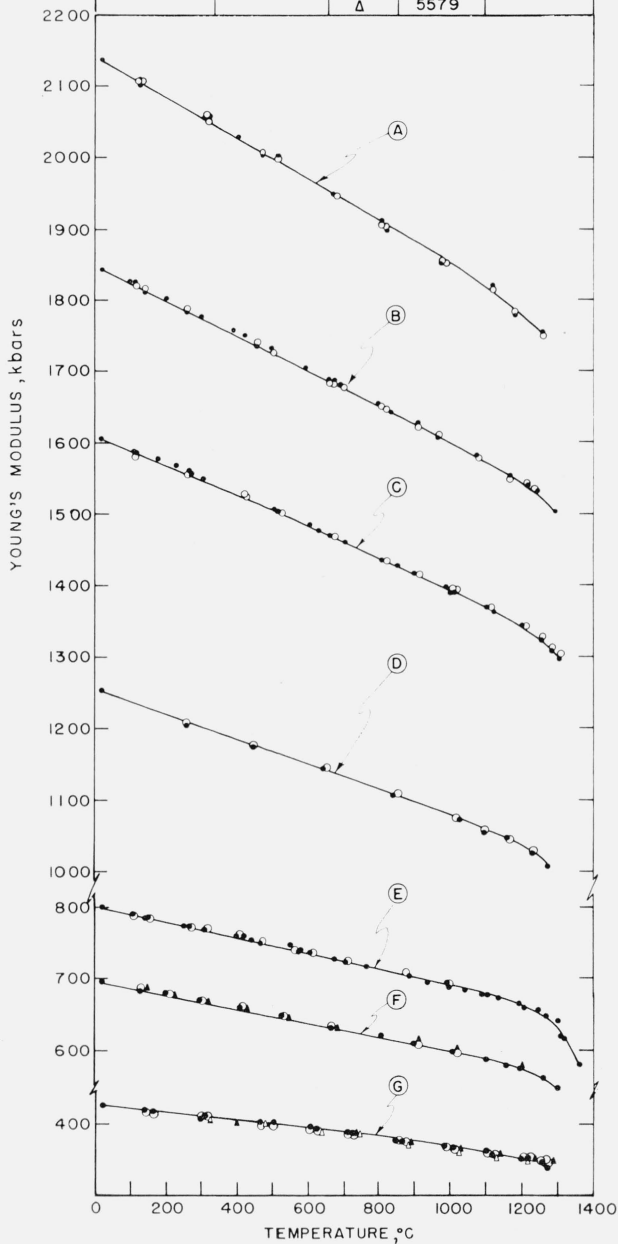


FIGURE 1. Young's modulus versus temperature for a group of  $\text{ThO}_2$  specimens of different porosity.

$f_r$  is the room temperature value of the flexural resonance frequency (fundamental or overtones) of the specimens.

SPECIMEN	POROSITY (%)	$f_r$
A-2-4-0-24	6.95	6731
B-2-4-6-3	12.23	6611
C-2-4-12-3	16.42	6250
D-2-4-18-2	22.00	5623
E-2-4-24-1	28.71	4627
F-2-4-30-4	33.33	4772
G-2-4-36-6	39.37	3721

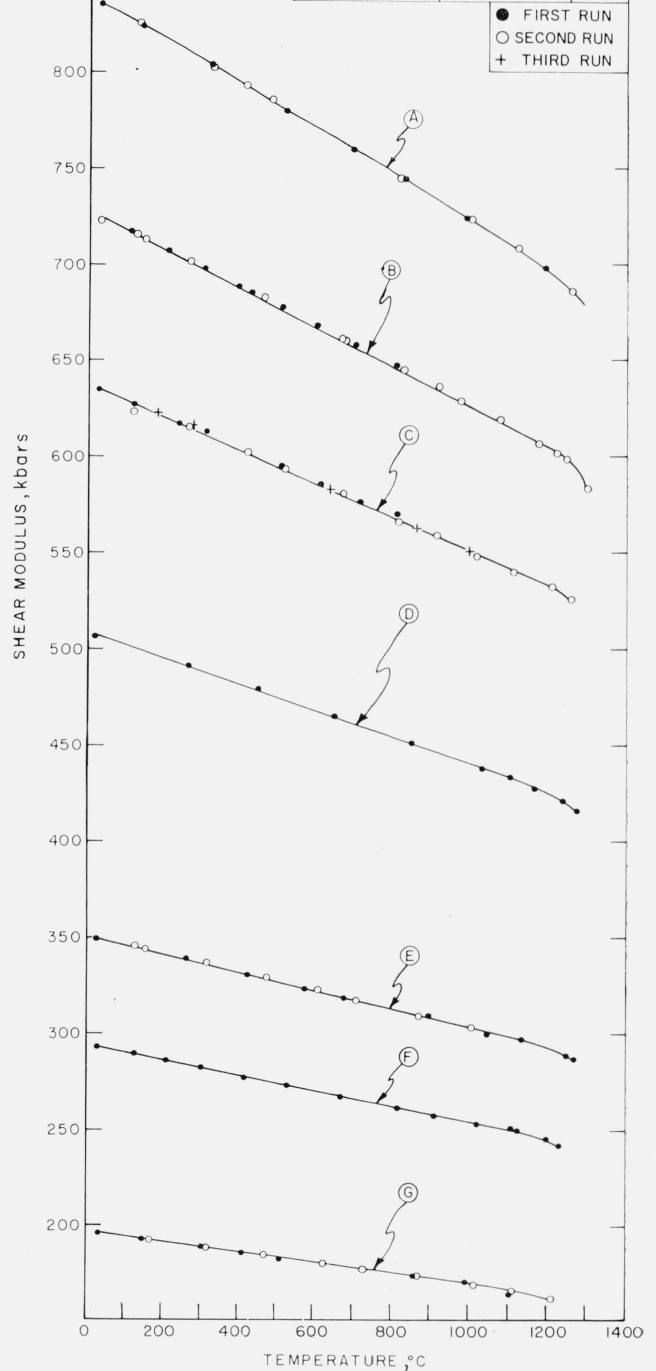


FIGURE 2. Shear modulus versus temperature for a group of  $\text{ThO}_2$  specimens of different porosity.

$f_r$  is the room temperature value of the fundamental torsional resonance frequency of the specimens.

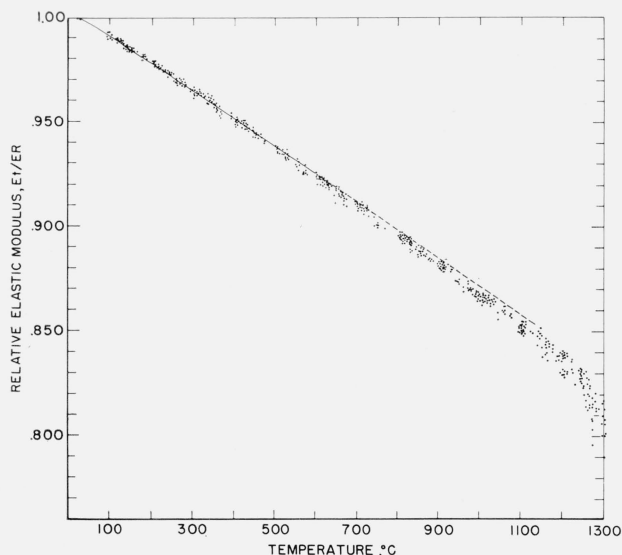


FIGURE 3. Ratio of elastic moduli at elevated temperature to those at room temperature as a function of temperature for all the specimens of this investigation.

Each point represents a single determination whether from the fundamental or overtones of flexural resonance (Young's modulus) or from torsional resonance (shear modulus). Also, the points for most specimens are based on repeated runs.

temperature over the entire temperature range under investigation. It is only because Poisson's ratio does not change with temperature that one is able to compute Young's modulus from overtones of the flexural resonance frequency as well as from the fundamental without any cross-sectional correction. Had Poisson's ratio increased with increasing temperature (as it does for some materials), then not only would the relative decrease in the shear modulus have been greater than that for Young's modulus, but the apparent (uncorrected) decrease in Young's modulus would be less the higher the overtone used for its determination [7].

The results of this investigation and the previous one [1] concerning the effects of temperature and porosity on Poisson's ratio are in contrast with those of Coble and Kingery [10] who made similar determinations on polycrystalline  $\text{Al}_2\text{O}_3$ . Coble and Kingery found Poisson's ratio to increase with increasing temperature and to remain fairly constant with porosity except for a decrease at the highest value of porosity (50%), which they stated was less than the experimental error. In this investigation and the previous one [1] with  $\text{ThO}_2$ , Poisson's ratio was found to remain constant with temperature and to decrease with increasing porosity.

The work of Wachtman et al. [2] with  $\text{ThO}_2$  has already been mentioned. It is of interest to compare their results with those obtained here in the temperature range where the two sets of data overlap (from room temperature to 600 °C). This can best be done in terms of an equation which was developed in their paper relating Young's modulus to temperature and which was found to fit the experimental data of all the specimens of their investi-

gation. These specimens consisted of several different orientations of single crystals of  $\text{Al}_2\text{O}_3$  and some polycrystalline materials including  $\text{ThO}_2$ . The equation was

$$E = E_0 - BT \exp(-T_0/T) \quad (1)$$

where  $E$  is Young's modulus at any temperature,  $T$ , in °K and  $E_0$ ,  $B$ , and  $T_0$  are experimental parameters having the following significance;  $E_0$  is Young's modulus at 0 °K,  $T_0$  is a characteristic temperature and  $B$  is the value that  $dE/dT$  approaches as  $T$  increases. These experimental parameters were determined by a least squares technique. The differences between the experimental and calculated values of  $E$  so obtained were well within the experimental precision of the measurements. These values were:  $T_0 = 181 \pm 3$  °K,  $E_0/E_r = 1.0223 \pm 0.0002$ , and  $B/E_r = (1.367 \pm 0.004) \times 10^{-4}$  per °K where the indicated uncertainty is the standard deviation.  $E_r$  is the reference or room temperature value (25 °C) of  $E$ . (Wachtman et al., presented the latter two parameters in absolute and relative terms using  $E_r$  as the reference value for the relative terms. The relative form is chosen here as more convenient for comparison with data over a wide range of porosities as presented in this study as shown in fig. 3.)

The solid line in figure 3 is the solution of eq (1) using the above constants and shows graphically the agreement of the data of their investigation with this one up to the upper temperature limit (600 °C) of their measurements. The dashed line is the solution of the same equation with the same constants extrapolated above 600 °C. It is seen that at the higher temperatures (above about 800 °C), the experimental points decrease more rapidly than the equation predicts. This is believed to be due mainly to grain boundary slip.

A further step in this same comparison consisted in fitting the Young's modulus-temperature data for all the specimens of this investigation determined from the fundamental and overtones of flexure and from repeated runs, from room temperature to 600 °C, to the same equation. This involved some 350 points. Since no measurements were made in this investigation below room temperature, the characteristic temperature,  $T_0 = 181$  °K obtained by Wachtman et al. was also assumed to hold here. The problem of obtaining the other two parameters by least squares was consequently considerably reduced in complexity. The values so obtained were,  $E_0/E_r = 1.0230 \pm 0.002$ , and  $B/E_r = (1.405 \pm 0.006) \times 10^{-4}$  per °K. The slightly higher values of standard error associated with the constants obtained here as compared with Wachtman et al., is believed to be due in part to the effect of the wire<sup>2</sup> suspension which was used in this investigation in order to be able to reach higher temperatures rather than the glass fiber used by them although the latter was a superior material up to the highest temperatures of their investigation.

<sup>2</sup> The suspension wire used here was of the same material as in the two previous studies [4, 7].



The difference in the values of the parameters themselves in this study and that of Wachtman et al., on the basis of the associated standard errors, is seen to be statistically significant, and is also believed to be due, in part, to the difference in the suspensions in the two investigations. It should be noted, however, that although significant, the difference in the effect of these two parameters on  $E$  is not large. The differences in  $B/E_r$ , the most significant constant in the temperature range of comparison, between this investigation and that of Wachtman et al., amounts to a maximum difference of about 0.2 percent in the determination of  $E$ . This figure may be taken as a measure of the accuracy of the results of this investigation since it is based on a comparison with different measurements on the same material from the same source. Because of the large number of measurements, the uncertainty due to random errors in the determination of  $E$  is effectively cancelled out.

As the temperature increases above about 800 °C, the spread in the experimental points is seen to increase. A partial explanation for this is the loss in precision in the measurements due to the increase in internal friction of the specimens associated with grain boundary slip starting in this temperature region. However, this explanation cannot be the complete one since there is very little significant loss in precision up to about 1,150 °C and even at the highest temperatures reached it is estimated that the error is increased by a factor of about 3 (from 0.2% to about 0.6%), whereas the actual scatter in the data can be seen to be much greater than this at the highest temperatures (more than 3%).

Over and above this loss in precision, a porosity dependence in the relative modulus-temperature relation develops, the more rapid decreases in the relative modulus being associated with the higher porosity specimens. This trend is illustrated in figure 4 which is an expanded version of figure 3 from 800 °C to 1,300 °C for a typical low porosity specimen (2-4-6-1, porosity 12.3%) and a high porosity specimen (2-4-36-6, porosity 39.4%). The points in the figure are also differentiated on the basis of the resonance frequencies from which they were computed. The upper curve is for the low porosity specimen and the lower curve is for the high porosity specimen.

It also appears from the figure that any possible frequency dependence on the relative change in elastic moduli cannot be distinguished above the precision of the data and within the frequency range used. However, since the highest porosity (lowest modulus) specimens have the lowest resonance frequencies while the lowest porosity (highest modulus) specimens have the highest resonance frequencies, it may be supposed that the above mentioned porosity dependence is actually a frequency dependence of the relative change in elastic moduli. That this is not the case may also be seen from inspection of figure 4. It is noted that the room temperature fundamental flexural resonance frequency of the high porosity specimen is 602 c/s, and the highest overtone of the

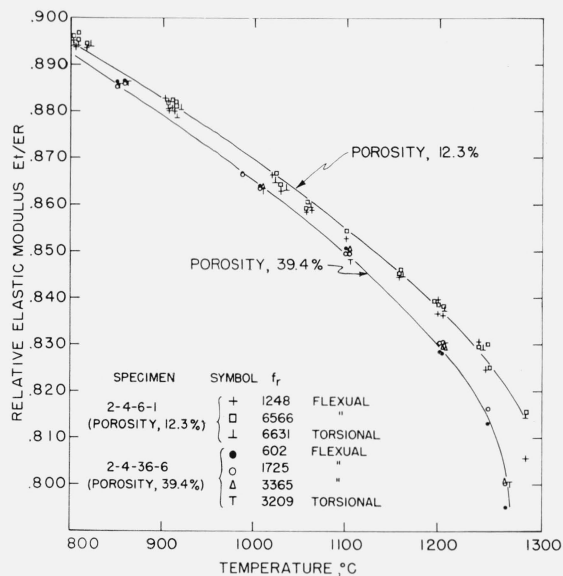


FIGURE 4. Expanded representation of figure 3 from 800 °C to 1,300 °C for two specimens, one of relatively low porosity and one of high porosity.

$f_r$  is the room temperature value of the resonance frequency. The resonance frequencies are for torsional as well as flexural modes. Both curves include data from repeated runs.

mode determined for the same specimen was 3,365 c/s. The corresponding fundamental for the low porosity specimen was 1,248 c/s and the highest overtone, 6,566 c/s. The overtone of the high porosity specimen is seen to be almost three times greater than the fundamental of the low porosity specimen, yet the relative decrease in modulus for the high porosity specimen computed from the overtone falls on the lower curve while the elastic modulus for the low porosity specimen computed from the fundamental falls on the upper curve.

This porosity dependence of the relative change in elastic moduli suggests an additional reason for the slightly higher values in the experimental parameters, especially  $B/E_r$ , and their associated standard errors for this investigation compared with that of Wachtman et al. If the divergence in the relative elastic moduli-temperature curves is unmistakable above 800 °C for specimens of different porosity, then it is reasonable to assume that the same tendency may exist to some degree below 800 °C and even below 600 °C even though not clearly noticeable above the precision of the data. Wachtman's specimen was of a relatively low porosity so that the average porosity of the specimens of this study was higher than Wachtman's. The higher average porosity for the specimens used here would result in a slightly higher value for  $B/E_r$ , and the greater range of porosities used here would lead to a larger value for the standard errors of the constants. To check this further, the following procedure was adopted. All the specimens of this investigation were divided into four sections; the first section composed of the lowest porosity specimens, the second section composed of the next higher porosity specimens and so on. Each section was then fitted

to the same equation as was previously done for all the specimens taken as a single group. If the above supposition is valid, then one would expect to find larger values for the relative slopes ( $B/E_r$ ) associated with the higher porosity specimens as well as smaller standard errors for this parameter. The results of this analysis are given in table 2 as well as the comparable results from Wachtman's data and from the specimens of this investigation taken as a whole.

TABLE 2. Comparison of the relative slope,  $B/E_r$  from Wachtman *et al.*, and from the specimens of this investigation, taken as a whole, and from sections grouped according to porosity

	Specimen	Porosity	$B/E_r(10^{-4}/^{\circ}\text{K})$		
Wachtman <i>et al.</i>	-----	9.3	$1.367 \pm 0.004^a$		
This investigation	All	3.73-39.37	$1.405 \pm .006$		
Section 1	{ 0-2-0-18 { 2-4-0-24 { 0-2-6-6	3.73 6.95 7.87	} $1.394 \pm .017$		
Section 2	{ 2-4-6-3 { 2-4-6-1 { 0-2-12-2 { 2-4-12-3 { 4-7-0-37 { 0-2-18-1	12.23 12.31 13.41 16.42 17.05 18.95		} $1.398 \pm .008$	
Section 3	{ 2-4-18-2 { 0-2-24-1 { 7-13-0-37 { 24-44-0-31 { 13-24-0-27 { 2-4-24-1	22.00 23.50 23.61 26.09 26.23 28.71			} $1.400 \pm .016$
Section 4	{ 0-2-30-1 { 2-4-30-4 { 2-4-36-6	32.80 33.33 39.37	} $1.412 \pm .011$		

<sup>a</sup> Uncertainties are standard deviations.

The difference in  $B/E_r$  between any two neighboring sections can hardly be significant in themselves since this difference is usually considerably less than the related standard errors. However, since the trend is consistent for all four sections, the higher values of  $B/E_r$  always being associated with the highest porosity specimens, the pattern seems to be above the error in the determination of the parameter. The smaller expected standard errors in  $B/E_r$  for the four sections did not develop because the advantage of a smaller range of porosities for each section was more than cancelled by the smaller number of points involved in each determination. It is also noted that Wachtman's value for  $B/E_r$  is lower even than for the section composed of specimens of lower porosity than used by him so that the difference in suspension material or some other experimental factor to account for the higher values of  $B/E_r$  obtained here is not ruled out.

Since grain boundary slip has been advanced as the reason for the more rapid decrease in modulus in certain elevated temperature regions, it may not at first be obvious why differences in porosity should be associated with differences in this more rapid decrease in modulus. One looks to see whether the grain sizes of the specimens were also different and if this, rather than differences in porosity, is

the cause of the differences in the relative decreases in modulus with temperature for these specimens. Kê [11] has already shown that the inflection in the shear modulus temperature relation associated with grain boundary slip will occur at a lower temperature (appear to decrease more rapidly) for specimens having smaller grain size. For the two specimens used for illustration in figure 4, however, no significant difference in grain size was observed, both specimens<sup>3</sup> consisting of grains of about  $10\mu$ . Nevertheless, an increase in porosity of one specimen over another of the same grain size may result in a correspondingly greater decrease in contact area between grains per unit volume. This should in turn cause a more rapid decrease in modulus due to grain boundary slip in the more porous specimen. This is believed to occur in the specimens of this investigation. An analysis of the process involved, on the basis of a rather simple model, is presented in the appendix.

The question now perhaps arises, how differences in the relative modulus-temperature slopes can be explained below  $600^{\circ}\text{C}$  where the decrease in modulus is predominantly elastic and not associated with grain boundary slip. The explanation appears to be that the temperature at which grain boundary slip is initiated is not sharply defined and a certain very small amount may occur at temperatures well below those at which it is observed in an obvious way (by an inflection in the modulus-temperature curve and an increase in internal friction.) Indeed the small, almost undetectable, differences in the relative modulus-temperature slopes below  $600^{\circ}\text{C}$  is believed to be a reflection of how slight grain boundary slip is in this temperature region.

It may also be seen from figure 4 that for a specimen of a given porosity the relative decrease in the shear modulus, based on the torsional resonance frequencies is not different from the relative decrease in Young's modulus, based on the flexural resonance frequencies. Thus, the observation made earlier, concerning the constancy of Poisson's ratio, holds up to the highest temperatures measured.

#### 4. Appendix

The problem is to show that the relative decrease in modulus,  $\Delta E/E$ , for a more porous specimen will be greater than that for a less porous specimen of the same grain size.  $\Delta E$  is the anelastic decrease in modulus associated with a rise in internal friction which is superimposed on the "normal" elastic decrease in modulus with increasing temperature and  $E$  is the reference value of modulus.

Before proceeding, it should be pointed out that it is recognized that the actual situation is undoubtedly more complex than the simple model (with associated rather restrictive assumptions) to be presented. The presentation is, nevertheless, felt to be justified; first, because it has apparently not been considered else-

<sup>3</sup> These data are part of an investigation of the microstructure of these specimens which will be presented in a future publication.

where in the literature; and, second, because it is believed that the same qualitative result would obtain on the basis of a more complex and realistic model.

We assume that a specimen at zero porosity is composed of  $n$  grains of volume,  $v$ . Then the total volume of the specimen,  $V_0 = nv$ . We further assume that all the grains are cubic in shape, having faces of area,  $s$ . The total contact area between grains  $S_0 = \frac{6sn}{2} = 3sn$ . (The factor 2 arises from the fact that two grain surfaces are required to produce one contact area between grains.)

We now assume that a single grain is removed from the interior of the specimen, then the new volume of grains,  $V_1 = nv - v = v(n-1)$  (the volume of the specimen remains  $V_0$ ) and the new contact area,  $S_1 = \frac{6sn}{2} - 6s = 3s(n-2)$ . Now  $\Delta V = V_0 - V_1$  and  $\Delta S = S_0 - S_1$ , so that dropping subscripts,

$$\frac{\Delta V}{V} = \frac{vn - v(n-1)}{vn} = \frac{1}{n}$$

and

$$\frac{\Delta S}{S} = \frac{3sn - 3s(n-2)}{3sn} = \frac{2}{n}$$

Also the porosity

$$P = \frac{\Delta V}{V} = \frac{1}{2} \frac{\Delta S}{S}. \quad (1)$$

Now it is reasonable to assume that at temperatures in which grain boundary slip is beginning (i.e., in which the associated internal friction is increasing) that  $\Delta E$  should depend upon the contact surface to volume ratio. That is,

$$\Delta E \propto \frac{S}{V}.$$

$E$  may be expressed as a function of  $P$  by

$$E = E_0(1 - \alpha P + \beta P^2) \quad (2)$$

where  $E_0$  is the modulus at zero porosity. The coefficients,  $\alpha$  and  $\beta$ , were determined by least squares in the previous paper [1] for both Young's and shear moduli for the different groups of  $\text{ThO}_2$  specimens. The average values were:  $\alpha = 2.85$  and  $\beta = 1.17$  ( $\alpha = \frac{1}{E_0} \frac{dE}{dP}$  is listed in table 5 of [1].) From equation (1)

$$V = V_0(1 - P) \quad (3)$$

and

$$S = S_0(1 - 2P) \quad (4)$$

so that

$$\frac{\Delta E}{E} = \frac{C \frac{(1-2P)}{(1-P)}}{(1-\alpha P + \beta P^2)} \quad (5)$$

where  $C = \frac{KS_0}{V_0 E_0}$ .

Substitution of the values  $\alpha = 2.85$  and  $\beta = 1.17$  in eq (5) shows that  $\Delta E/E$  will increase with increasing values of  $P$  up to  $P = 0.40$  (the highest porosity used in this investigation). Also, the rate of increase of  $\Delta E/E$  will increase as  $P$  increases. Thus, the original proposition is demonstrated.

Actually, two additional effects contribute to cause  $\Delta E/E$  to increase with increasing  $P$  more rapidly than already indicated. The first is that as  $P$  increases, the probability of removing a grain that is not completely surrounded by other grains, but already borders on a void due to previous removal of grains, increases. In such a case,  $S$  would not decrease with increasing  $P$  as rapidly as indicated by eq (4) but  $E$  and  $V$  would still change with  $P$  in the manner indicated in eqs (2) and (3). Therefore,  $\Delta E/E$  would increase with increasing  $P$  more rapidly than shown in eq (5).

The second effect is that porosity may be caused by holes within grains as well as by the removal of grains. In such a case,  $S$  would not change at all with increasing  $P$  while  $E$  and  $V$  would still decrease according to eqs (2) and (3). This would further increase  $\Delta E/E$  with increasing  $P$ .

The above result which involves specimens differing from each other in porosity, but of the same (or not significantly different) grain size may be compared with that for specimens differing from each other in grain size, but of the same porosity, and the conclusions summarized in the following manner:

In the former case, which corresponds largely to the specimens of the investigation, the decrease in  $E$  as a function of increasing  $P$  is greater than any associated change in  $\Delta E$ . Therefore,  $\Delta E/E$  for such specimens will increase with increasing  $P$ . The latter case applies to many polycrystalline metals such as those studied by Kê, in which the porosity remains constant at (or near) zero, the main variation between specimens being in the grain size. In such cases, the value of  $E$  remains constant from specimen to specimen and as  $S$  increases with decreasing grain size,  $\Delta E$ , and hence  $\Delta E/E$  increases.

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## 5. References

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