

Temperature Dependence of Lattice Parameters of Alpha-Zirconium

R. A. Versaci
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Comisión
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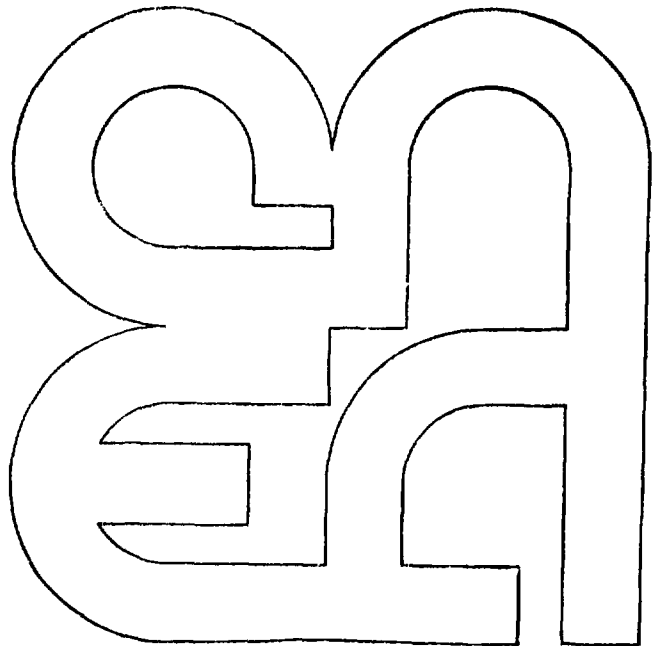
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**ZIRCONIUM-ALPHA
LATTICE PARAMETERS
TEMPERATURE DEPENDENCE
THERMAL EXPANSION
THERMAL ANALYSIS
X-RAY DIFFRACTOMETRY
HEXAGONAL LATTICES
IMPURITIES**

COMISION NACIONAL DE ENERGIA ATOMICA
DEPENDIENTE DE LA PRESIDENCIA DE LA NACION

TEMPERATURE DEPENDENCE OF
LATTICE PARAMETERS OF α -ZIRCONIUM

R.A.VERSACI AND M.IFOHORSKI

ABSTRACT

This note presents a brief review of X-Ray and thermal expansion determinations of lattice parameters for α -Zirconium. Data reported by different authors cover almost all the field of existence of the hexagonal phase of Zirconium, from temperatures as low as 4.2 K up to about 1130 K, near the $\alpha \rightarrow \beta$ transformation temperature. Polynomial expressions based on a least squares fitting of experimental data are also presented. The expressions obtained by Goldak et al. are

considered to be the most complete. The influence of impurities on the lattice parameters is also discussed.

DEPENDENCIA DE LOS PARAMETROS DE RED
DEL ZIRCONIO- α CON LA TEMPERATURA

RESUMEN

En este trabajo se presenta una revisión de las determinaciones de rayos X y expansión térmica de los parámetros de red del zirconio- α . Los datos presentados por distintos autores cubren casi todo el rango de existencia de la fase hexagonal del Zirconio, desde temperaturas tan bajas como 4.2 K hasta los 1130 K, próximas a la temperatura de transformación $\alpha \rightarrow \beta$. Se presentan también diversas expresiones polinómicas obtenidas por ajuste de cuadrados mínimos de los datos experimentales. Las expresiones obtenidas por Goldak et al. se consideran como las más completas. La influencia de impurezas en los parámetros de red es también analizada.

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I. LATTICE PARAMETERS DETERMINATIONS

The first systematic measurements of lattice parameters as a function of temperature were performed by Russell [1]. In order to obtain the coefficients of linear thermal expansion of hexagonal α -Zirconium, the author has measured its lattice parameters in the range 273 to 873 K, using X-Ray diffraction techniques. Specimens were prepared from low Hafnium, dehydrogenated Westinghouse bar. Chemical analysis of Russell's specimens, as well as those corresponding to other authors, are listed in Table I. The purity of the Zr specimens was 99,90 wt% (99,63 at%) with 3680 at ppm of impurities present in the metal.

From the experimental results the author obtained by Cohen's method [2] the following expressions for the lattice parameters \underline{a} and \underline{c} in Å units, as a function of the absolute temperature T in the range 273-873 K

$$\begin{aligned}
 a &= 3.22612 + 1.6072 \cdot 10^{-5} T + 3.6940 \cdot 10^{-9} T^2 \\
 \Delta a &= \pm 0,00086 \text{ Å} \\
 c &= 5.14105 + 1.1532 \cdot 10^{-5} T + 3.6416 \cdot 10^{-8} T^2 \\
 \Delta c &= \pm 0,00134 \text{ Å} \quad (\text{I.1})
 \end{aligned}$$

being Δa and Δc the corresponding root mean-square deviations. The axial ratio c/a also increases with temperature, as well as the distance of closest approach

$$\alpha_1 = \left(\frac{a^2}{3} + \frac{c^2}{4} \right)^{1/2}$$

From eqs. (I.1) lattice parameters at room temperature (298 K) result to be

$$a = 3.2312 \text{ \AA} \quad c = 5.1477 \text{ \AA} \quad c/a = 1.5931$$

(I 2)

Lattice parameters of α -Zirconium at room temperature were later measured by Lichter [3] in his research on Zirconium-Oxygen solid solutions. Specimens were prepared from Hafnium free Westinghouse Grade 1 Zirconium. Substantially all the hydrogen was removed by annealing at 1473 K in a high vacuum. Chemical analysis of such dehydrogenated Zirconium is given in Table I. Lattice parameters were measured by Back-Reflection X-Ray techniques using a symmetrical focussing camera. Greater accuracy of the measurements was achieved with large-grained samples, adequate temperature control during exposures, and by analytical extrapolation for the calculation of the parameters. The final reported values for Oxygen-free Zirconium are

$$\begin{array}{ll} T = 298 \text{ K} & a = 3.2316 \pm 0.0001 \text{ \AA} \\ & c = 5.1475 \pm 0.0003 \text{ \AA} \\ T = 302 \text{ K} & a = 3.2317 \pm 0.0001 \text{ \AA} \\ & c = 5.1476 \pm 0.0003 \text{ \AA} \end{array} \quad (I.3)$$

These values are in very good agreement with Russell's determinations, eqs. (I.2).

Lloyd [4] has measured the lattice parameters of α -Zirconium single crystals with a dilatation interferometer as a function of temperature from 273 to 1130 K. Since the interference technique does not give absolute values, Lichter's room temperature parameters, eqs. (I.3) were used as reference constants. Lloyd's results are probably more accurate than Russell's values, since dila-

tometer techniques are not subjected to errors due to specimen contamination during long X-Ray exposures. In addition, dilatometric measurements result from properties of the bulk, and not from surface layers as it is the case of X-Ray samples.

Douglass [5] later combined Lichter's data with Lloyd's dilatation measurements, and obtained the following expressions for the temperature dependence of the lattice parameters, valid in the interval 273-1130 K

$$\begin{aligned}
 a &= 3.22623 + 1.6626 \cdot 10^{-5} T \\
 c &= 5.12638 + 9.77181 \cdot 10^{-5} T - 1.44957 \cdot 10^{-7} T^2 + \\
 &\quad + 1.55621 \cdot 10^{-10} T^3 - 5.0722 \cdot 10^{-14} T^4
 \end{aligned}$$

(I.4)

Parameter a is then a linear function of temperature T , whereas c exhibits an increasing rate of expansion with increasing temperature.

A few years later the most systematic determination of α -Zirconium lattice parameters combining X-Ray diffraction and thermal expansion measurements, over the temperature range 4.2 to 1130 K, was performed by Goldak et al. [6]. Single crystals were isolated from large grains grown in iodide Hafnium-free Westinghouse grade I crystal-bar Zirconium. X-Ray specimens were prepared after three passes in a floating zone melting equipment. Hydrogen contents in all the crystals were less than 1 ppm by weight after a dehydrogenation treatment at 1073 K for 24 hours in a vacuum of 2×10^{-6}

Torr. The amounts of impurities present in the specimens are detailed in Table I. Lattice parameters were determined by Bond's method for single crystals of high perfection. The combined geometrical errors did not exceed 6 parts in 10^6 . The largest correction was for refraction, still a matter of discussion. The refraction corrected d values were calculated from the apparent values d' obtained from Bragg's law, by the relationship

$$d = d' \left(1 + \frac{\delta}{\sin^2 \theta} \right)$$

being

$$\delta = 4.48 \cdot 10^{-6} \eta_e \lambda_e$$

where

λ_e = X-Ray wavelength

η_e = Number of electrons / \AA^3

For the wavelength and reflections used, the corrections for the values of the parameters a and c resulted to be

$$\delta a = 7 \cdot 10^{-5} \text{\AA} \quad \delta c = 12 \cdot 10^{-5} \text{\AA}$$

Thus, to correct for refraction δa has to be added to a , and δc added to c . Goldak et al. also measured thermal expansions between room temperature and 1130 K by dilatation interferometric techniques. The lattice parameters at 273 K from the X-Ray measurements were used as the bases for converting the dilatation measurements to values of the lattice parameters. Finally, the polynomial expressions of the lattice parameters as a function of temperature in the whole interval 50 to 1130 K are

$$\begin{aligned}
 a &= 3.22849 + 1.457 \cdot 10^{-5} T + 3.37 \cdot 10^{-9} T^2 - \\
 &\quad - 1.64 \cdot 10^{-12} T^3 \\
 c &= 5.13956 + 2.562 \cdot 10^{-5} T + 1.936 \cdot 10^{-8} T^2 + \\
 &\quad + 2.45 \cdot 10^{-12} T^3
 \end{aligned}$$

(I.5)

The authors also reported the following values at $T=4.2$ K

$$\begin{array}{rcl}
 a = & 3.22945 \text{ \AA} & c = 5.14139 \text{ \AA} \\
 & 3.22947 \text{ \AA} & 5.14147 \text{ \AA}
 \end{array}$$

Couterne and Cizeron [7] used dilatometry in order to determine the principal coefficients of thermal expansion of Zr between 273 and 973 K, and calculated lattice parameters from them, using Russell's room temperature values as reference. Specimens were hot drawn polycrystalline bars whose texture was quantitatively determined. Starting material was Van Arkel Zirconium bar, see Table I for the analysis of impurities. There is no mention about Hf or interstitial impurities (C, N, O).

The values obtained by Couterne and Cizeron are lower than Russell's in almost all the temperature range. An anomalous behaviour starts near 673 K which is the temperature at which anomalous electric resistivity changes were previously noted [8]. This behaviour was explained by the authors in terms of variations of electronic structure.

Other determinations of α -Zirconium lattice parameters at room temperature were reported by different authors. Fast [9] has measured lattice constants

in a sample free of Hafnium. However, there is no mention about the amount of impurities. His values, given apparently in terms of kX units, were corrected by Russell and converted to Å units

$$a = 3.231 \text{ \AA} \quad c = 5.144 \text{ \AA}$$

The value of a is slightly lower than other reported results. Parameter c is too low to be considered. Domagala and Mc Pherson [10] obtained for "Iodide" Zirconium at 298 K

$$a = 3.236 \text{ \AA} \quad c = 5.153 \text{ \AA}$$

Skinner and Johnston [11] also determined lattice parameters of "Iodide" zirconium at room temperature and in the high temperature range 950-1164 K. Lattice parameters were calculated by Cohen's method and corrected for contamination and also for the presence of $\approx 1\% \text{ Hf}$ in the specimen. Their experimental results, expressed originally in kX units, are listed in Å units in Table II. Values at room temperature agree with previous and later results, but they seem to be high at the top end of the temperature range.

Precision lattice parameters values at room temperature were also determined by Treco [12]. The author has studied the effect of oxygen on the hexagonal phase lattice constants of zirconium. Extrapolated values for oxygen free zirconium in three different kinds of materials are listed in Table III. It could be seen that parameters of the Mg reduced material are too high. The other set of values is consistent with later reports. Swanson et al. [13] reported a value of 3.2325 Å for α -zirconium lattice parameter a .

Recently, Tiwari and Tangri [14] have determined the lattice parameters of Zr-Al solid solutions equilibrated at high temperatures and quenched in water. Since the authors found a linear decrease of parameter a with increasing Al content, the value corresponding to pure zirconium was easily obtained extrapolating their experimental values down to zero Al. They reported a value

$$a = 3.2332 \pm 0.0003 \text{ \AA}$$

Parameter c did not change so regularly with Al additions. From the authors Fig.2 a rough extrapolation down to zero Al content gives a value of

$$c = 5.147 \text{ \AA}$$

which is consistent with previously mentioned results. Analysis of interstitial impurities of their reactor grade zirconium is given in Table I.

Easton and Betterton [15] reported the following values

$$a = 3.2327 \text{ \AA} \quad c = 5.1471 \text{ \AA} \quad c/a = 1.5922$$

for the lattice parameters of α -zirconium at room temperature. These values were obtained extrapolating their results on Zr-Ga solutions down to zero Ga content.

Finally it should be mentioned that lower values

$$a = 3.230 \pm 0.002 \text{ \AA} \quad c = 5.138 \pm 0.003 \text{ \AA}$$

cited elsewhere, see for instance references [16] and [17], were taken from the earlier work of Burgers and

Jacobs [18] published in 1936. All the above mentioned results are summarized in Table IV.

II. INFLUENCE OF IMPURITIES

In order to attempt a discussion of the results reported by the above mentioned authors, the influence of different impurities on the lattice parameters will be first considered.

- Oxygen

The effect of oxygen on the hexagonal phase lattice constants of pure zirconium has been studied by different authors. As early as in 1940 De Boer and Fast [19] have shown that oxygen is taken into solid solution in large amounts, appearing to occupy interstitial positions. In later works, the hardening effect of oxygen in α -zirconium has been shown to be, at least partially, due to the lattice distortion accompanying its introduction. Treco [12] prepared a series of alloys of increasing oxygen content, starting from a pure crystal bar degassed in a high vacuum glass system. Variations of lattice parameters with oxygen can then be expressed, according to Treco, by the following linear relationships

$$a = 3.2323 + 0.0010205 \times \text{atomic percent of O}$$

$$c = 5.1479 + 0.0020008 \times \text{atomic percent of O}$$

(II.1)

Later in 1960 Lichter [3] found similar expressions, valid at 302 K

$$a = 3.23168 + 0.001099 \times \text{atomic percent of O}$$

$$c = 5.14764 + 0.002077 \times \text{atomic percent of O}$$

(II.2)

From (II.1) and (II.2) variations of lattice parameters can also be expressed as

$$\Delta a = 0.0010 \text{ \AA} / 1 \text{ at \% O}$$

$$\Delta c = 0.0020 \text{ \AA} / 1 \text{ at \% O}$$

(II.3)

- Nitrogen

According to Grozier [20] both lattice parameters of α -zirconium increase linearly with increasing nitrogen content up to the limit of solubility at room temperature (22.8 at % N). From Grozier's graphics the following expressions were obtained

$$\Delta a = 0.0020 \text{ \AA} / 1 \text{ at \% N}$$

$$\Delta c = 0.0025 \text{ \AA} / 1 \text{ at \% N}$$

Then, parameter c is affected more or less in the same way by the presence of nitrogen and oxygen. Parameter c is more dependent on N content.

- Hafnium

There are contradictory results with respect

to the effect of Hafnium on lattice parameters. According to Russell [1] the effect of 1.2 at % Hf is to decrease lattice parameter a from 3.23115 to 3.23078 Å. The same amount of Hf decreases the value of c from 5.14756 to 5.14551 Å. Then, the variations of lattice parameters per each 1 at % Hf are

$$\Delta a = - 0.0003 \text{ \AA} / 1 \text{ at \% Hf}$$

$$\Delta c = - 0.0017 \text{ \AA} / 1 \text{ at \% Hf}$$

However, according to Treco [12] both lattice parameters increase with increasing amounts of Hf. Treco's determinations in "Iodide" crystal bars with 0.014 and 1.239 at % Hf showed the following increments

$$\Delta a = 0.0009 \text{ \AA} / 1 \text{ at \% Hf}$$

$$\Delta c = 0.0014 \text{ \AA} / 1 \text{ at \% Hf}$$

Thus, the actual effect of Hf, which is a substitutional impurity in the Zr lattice, is not clear at present.

III. DISCUSSION

Fig.1 and Fig.2 show the variation with temperature T of lattice parameters a and c , respectively. The polynomial expressions proposed by Russell [1] Douglass [5] and Goldak [6] are graphically represented. Single measurements of different authors are also shown, including the unusually high values obtained by Treco [12] in 1953 for "Mg reduced" Zr sponge, and

the low values reported earlier in 1952 by Fast [9].

The curves covering the widest range of temperatures (50-1130 K) are those proposed by Goldak et al. in 1966. Douglass curves start at room temperature (293 K) and extend up to 1130 K. It could be seen in Fig.1 and Fig.2 that both series of curves are almost parallel. Douglass curve for parameter a is displaced about 0.0020 \AA towards lower values in the whole temperature range. Curves corresponding to parameter c are displaced in the same way, i.e. Douglass obtained lower values. The displacement is equal to 0.0020 \AA near room temperature and increases up to about 0.0030 \AA for high temperatures. Both set of curves could be considered as the upper (Goldak) and lower (Douglass) limits of all other results reported in the literature, except the high temperature range. At room temperature Russell's curves lie somewhere between those obtained by Goldak and Douglass. Near the upper limit of Russell's determinations (873 K) his values are coincident with Goldak. Couterne and Cizeron curves lie also between the two limiting curves at room temperature. However at temperatures higher than 600 K both a and c parameters decrease, and are the lowest reported heresofar in the high temperature range. Single measurements of a and c at room temperature reported by other authors fall also at or between the two limiting curves.

Results plotted in Fig.1 and Fig.2 could be explained only partially in terms of different amounts of interstitial or substitutional impurities. The high values of parameters a and c reported by Treco for "Mg reduced" Zr sponge are most probably

related to the high oxygen content (5660 at ppm) of the samples. Also, Goldak and Douglass limiting curves correspond to a similar content of impurities. Goldak reports 2300 at ppm of (O + N) and Douglass based his curve on Lichter's values at room temperature which were also obtained for specimens with 2300 at ppm of oxygen. Discrepancies between X-Ray data could be due to contamination of the outermost surfaces of samples during lengthy exposures, since there is no way of eliminating adsorbed gases in the top 0.03 mm diffracting surface. There is no easy way either for determining the amount of adsorbed gases present. This is not the case of dilatometric measurements, since they result from properties of the bulk, although some plastic deformation of the dilatometric samples could occur at high temperatures. Goldak showed that lattice parameters could be determined by X-Rays with an accuracy of about 1 part in 10^5 , considering both the errors in reading the corresponding diffraction peaks and the errors in the published X-Ray wavelengths. Then, according to Goldak, the main source of errors must be due to impurities or a nonuniform distribution of impurities. Even in the same specimen, Goldak found a difference between the c lattice parameters measured on opposite faces of a single crystal sheet being as large as 0.0014 \AA . The standard deviation of seven parameter determinations was 0.0001 \AA for a and 0.0006 \AA for c . Both values are an order of magnitude larger than the average error in reading an X-Ray diffraction peak. Thus, the almost constant difference between Goldak and Russell's curves has to be explained in terms of their experimental techniques.

At present, there seems to be no justification for discarding any of the two limiting curves on the basis of different amounts of impurities or heat treatments. However, if consistent values of α -Zr lattice parameters as a function of temperature are needed, Goldak's curves should be considered, since they cover the whole range over which the hexagonal phase exists.

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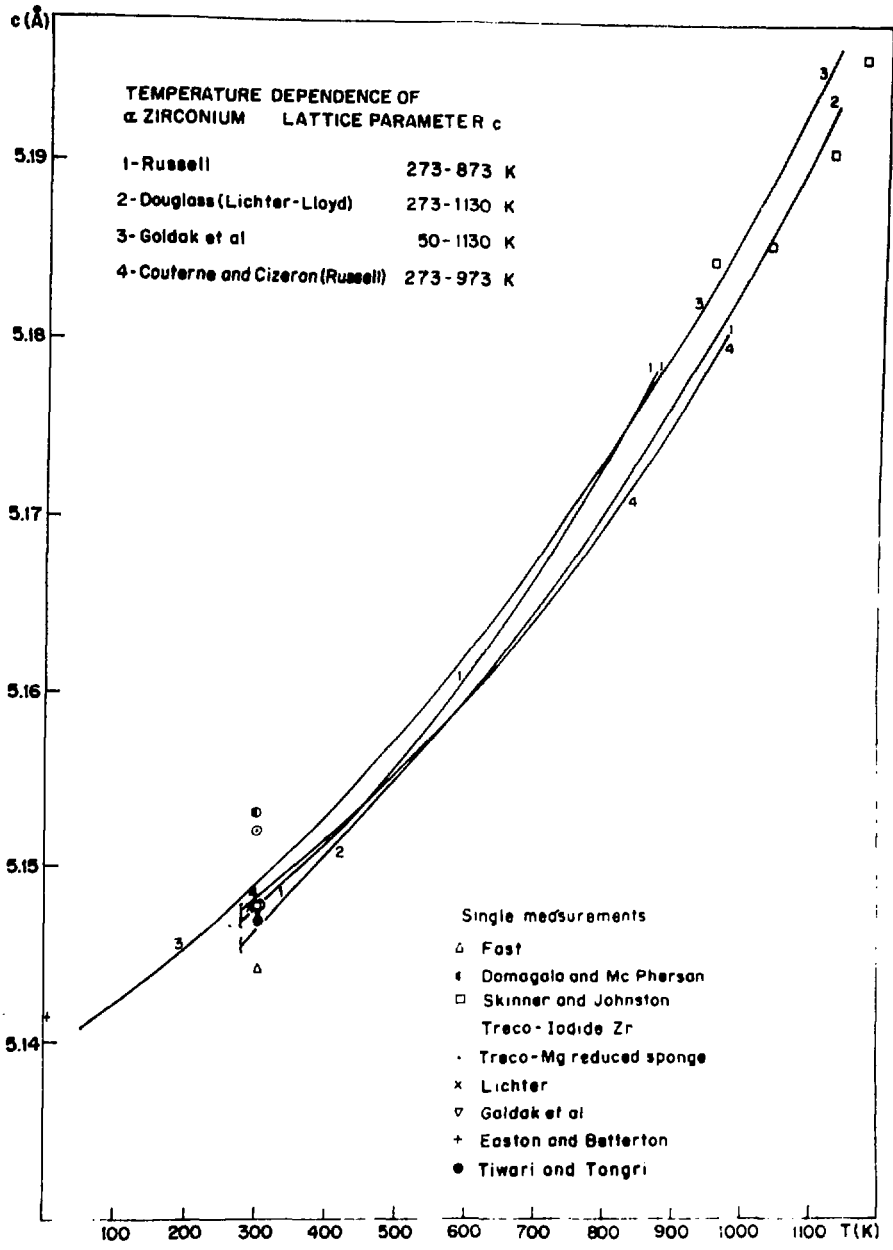


Fig.2 - Temperature Dependence of α -Zirconium Lattice Parameter c .

T A B L E I

Amount of Impurities, weight ppm (at.ppm)

Author and Reference	Interstitial Impurities											
	O	N	C	Hf	Fe	Al	Ti	Pb	Si	Cu	Ni	Cr
Russell [1]	130 (740)	5 (32)	260 (2000)	100 (50)	250	35	25	--	--	--	--	--
Lichter [3]	410 (2300)	14 (91)	150 (1150)	300 (150)	90	--	--	50	50	--	--	--
Goldak [6]	250 (1425)	150 (977)	430 (3300)	500 (250)	3-6	--	--	--	150	50	--	--
Couterne et al. [7]	--	--	--	--	500	25	--	--	25	200	115	40
	--	10 (65)	--	140 (70)	--	--	--	--	--	--	--	--
Treco [12]	1470 (8400)	--	--	140 (70)	--	--	--	--	--	--	--	--
	5660	--	--	400 (200)	--	--	--	--	--	--	--	--
Tiwari & Tangri [14]	130 (740)	37 (240)	40 (300)	--	--	--	--	--	--	--	--	--

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T A B L E I I

Values Obtained by Skinner and Johnston

<u>Temperature (K)</u>	<u>Lattice Parameters (Å)</u>	
	a	c
298	3.2331	5.1476
950	3.2459	5.1847
1032	3.2459	5.1857
1042	3.2472	5.1922
1119	3.2466	5.1909
1164	3.2479	5.1962
Error	± 0.0010	± 0.0015

T A B L E III

Values Obtained by Treco

<u>Material</u>	<u>Impurities</u>	<u>Lattice Parameters (Å)</u>	
High Purity Zr Crystal Bar	Hf 140	3.2324	5.1478
	N 10		
"Iodide" Zr	Hf 140	3.2322	5.1476
	O 1470		
Mg Reduced Zr Sponge	Hf 400	3.2445	5.1520
	O 5660		
	$\Delta a = 0.0006$	Å	
	$\Delta c = 0.0010$	Å	

T A B L E I V

Single Measurements of Lattice Parameters

Authors and References	Impurities		Lattice Parameters (Å)		T(K)
	at.ppm (O+N)	at.ppm Hf	a	c	
Fast 1952 [9]	--	--	3.231	5.144	298
Domagala & McPherson 1953 [10]	--	--	3.236	5.153	298
Skinner & Johnston 1953 [11]	--	corrected	3.2331	5.1476	298
		for Hf	3.2459	5.1847	950
			3.2479	5.1962	1164
Treco 1953 [12]	1470	140	3.2322	5.1476	298
Treco 1953 [12]	5660	400	3.2345	5.1520	298
Lichter 1960 [3]	2400	150	3.2316	5.1475	298
Goldak et al. 1966 [6]	2300	250	3.22935	5.14139	4.2
Easton and Betterton 1970 [15]	57 Oxygen	--	3.2327	5.1471	298
Tiwari & Tangri 1970 [14]	1000	--	3.2332	5.147	298