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Lattice Parameters, Thermal Expansions, and Grüneisen Coefficients of Zirconium, 4.2 to 1130°K

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The lattice parameters, atomic volume, nearest-neighbor interatomic distance, axial ratio, and coefficients of thermal expansion of zirconium are reported over the temperature range 4.2 to 1130°K. The data were obtained from single crystals, using a precision x-ray diffraction technique in the range 4.2 to 300°K and an interferometric dilatometer in the range 300 to 1130°K. Polynomial expressions, based on least-squares fitting of the data, are presented. Some of the parameters in Å are: at 4.2°K, $a=3.2294$, $c=5.1414$ ($c/a=1.5921$); at 300°K, $a=3.2331$, $c=5.1491$ ($c/a=1.5926$); at 1125°K, $a=3.2468$, $c=5.1964$ ($c/a=1.6004$). Expansion coefficients $\times 10^6$ are: at 300°K, $\alpha_a=4.99$, $\alpha_c=7.36$, $\beta=17.35$; at 1125°K, $\alpha_a=4.91$, $\alpha_c=15.14$, $\beta=24.94$. The Grüneisen coefficient is found to be essentially constant from 100 to 1130°K; the directional Grüneisen coefficients are also computed.

INTRODUCTION

This paper presents x-ray determinations of lattice parameters for zirconium over the temperature range 4.2 to 300°K and dilatometric data for the range 300 to 1130°K, near the alpha → beta transformation temperature. Polynomial expressions are fitted by the least-squares method to various lattice dimensions and properties, and Grüneisen constants are evaluated.

Data of this kind for hexagonal metals and for zirconium in particular are of perennial interest for a number of reasons. For example, there are strong correlations between the axial ratio, c/a, and the occurrence of a transformation from the *hcp* to *bcc* structure at elevated temperatures, between c/a, and the temperature dependence of the elastic constant c_{66}, and between c/a and the ratio c_{44}/c_{66}, as pointed out by Fisher and Renken.[1] It is of interest, too, that the transformation temperatures of zirconium and titanium are very similar (1135 and 1155°K, respectively) despite their large differences in atomic number (22 and 40) and atomic weight (47.90 and 91.22); also the temperature dependence of the elastic constants are quite similar for these metals and for hafnium, which also has $c/a=1.59$.

EXPERIMENTAL

Single Crystals

Single crystals were isolated from large grains grown in iodide crystal-bar zirconium (Westinghouse hafnium-free grade I) by a grain-growth treatment.[2] The specimens used in the dilatation interferometer were prepared from as-received material (see Table I for typical analyses). Those used for the x-ray measurements were prepared from the material after it had been subjected to three passes in floating-zone melting equipment. Ranges of analyses for this latter material are given in Table I also. Hydrogen contents in all the crystals were less than 1 ppm by weight because they were subjected to a dehydrogenation treatment of 1073°K for 24 h in a vacuum of at least 2×10^{-6} Torr as a final step in their preparation.

X-Ray Apparatus and Procedure

The lattice parameters were determined by Bond's method[3] for single crystals of high perfection. Reflection

Table I. Zirconium analyses (ppm by weight).

Element	Iodide crystal bar	Floating zone melted crystal bar
O	100	30 -250
C	...	90 -430
N	10	10 -150
Ag	<1	0.5- 1.0
B	<0.1	0.1- 1.0
Cr	30	3 - 20
Cu	7	1 - 50
Fe	400	3 - 6
Hf	<500	300 -500
Mg	3	8 - 20
Mn	<1	1 - 10
Na	7	4 - 10
Ni	7	3 - 20
Pb	8	1 - 20
Si	150	40 -150
Sn	<5	3 - 10

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[1] E. S. Fisher and C. J. Renken, Phys. Rev. **135**, A482 (1964).

[2] J. P. Langeron and P. Lehr, Compt. Rend. **243**, 151 (1956).

[3] W. L. Bond, Acta Cryst. **13**, 814 (1960).

angles were determined from the crystal settings (not counter settings) for high-angle reflections on one side and then on the other side of the direct beam.

Corrections for the Lorentz-polarization factor were completely negligible. Care was taken in making the axis of rotation of the diffractometer perpendicular to the x-ray beam, and the diffracting plane in the crystal parallel to the diffractometer axis. Bond's analysis shows that the error in the spacing between planes, d, can be limited to 1 part in 10^6 if the sum of these two errors is limited to 4.8′; the tests of our alignment procedure indicated that errors did not exceed 8′. Slits defined the x-ray beam to an axial divergence that limited the divergence error in d to a calculated upper limit of about 4 parts in 10^6. It is estimated that the combined geometrical errors did not exceed 6 parts in 10^6. The largest correction was for refraction; the corrected d values were calculated from the apparent values, d', which were obtained directly from Bragg's law, by using the relation

$$d = d'(1 + \delta/\sin^2\theta), \tag{1}$$

$$\delta = 4.48\times10^{-6} n_0 \lambda_0, \tag{2}$$

where n_0 is the number of electrons per Å^3 and λ_0 is the wavelength in Å. In this work the wavelengths,[4] the reflections used, and the refraction corrections were as follows:

	λ (Å)	*hkl*	θ (deg)	$d-d'$ (Å)
Ni K_{β_1}	1.50010	220	68.2	$\delta a = 7\times10^{-5}$
W L_{α_1}	1.47635	220	66.0	$\delta a = 7\times10^{-5}$
Ni K_{α_1}	1.65784	006	75.1	$\delta c = 12\times10^{-5}$
Ni K_{α_1}	1.66169	006	75.6	$\delta c = 12\times10^{-5}$

Intensities were measured with a scintillation-counter pulse-height analyzer circuit using step scanning with a time of 30 sec at each step, with stepping at 1′ intervals of angular position of the crystal, R_i. The intensity data were plotted as in Fig. 1 and the position of the mid-chord line were it intersected the peak was used to determine the reflection angle θ through the relationship:

$$\theta = (R_1 - R_2)/2 - 90°, \tag{3}$$

where R_1 and R_2 are the readings of the angular position of the crystal for reflection on the two sides of the direct beam.

Two single crystals were used for the x-ray measurements: one polished on a (11·0) plane and the other on a (00·1) plane. Care was taken in cutting and chemically polishing the crystals to leave strain-free surfaces parallel to within a degree to the reflecting plane. The quality of the surfaces was checked by Berg-Barrett[5] x-ray reflection micrographs and by the sharpness and shape (e.g., Fig. 1) of the diffraction peaks obtained on the spectrometer.

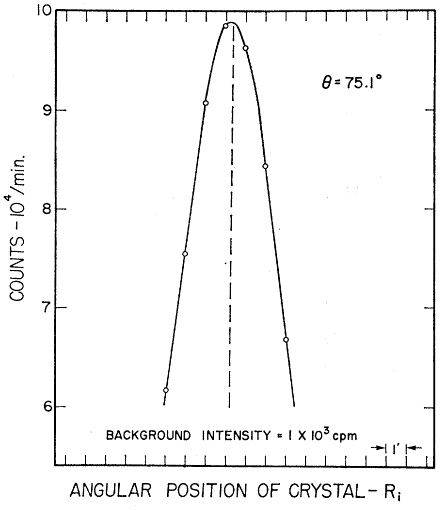

FIG. 1. (220) reflection of alpha-zirconium at 77.4°K (W L_{α_1} radiation).

The crystals were clamped with a light spring in a specimen holder of a double Dewar cryostat that enabled the temperature to be varied from 4.2 to 300°K. The specimen was surrounded by a radiation shield maintained at the temperature of the crystal. The cryostat was mounted on a spectrometer built by Societé Genevoise. The θ and 2θ circles could be read directly with an accuracy of 2″ of arc. The desired temperatures were obtained with liquid nitrogen, liquid helium, and dry ice at atmospheric pressure and nitrogen and dry ice at about 10^{-2} Torr pressure. The temperature of the crystal was measured with three copper-constantan thermocouples made from calibrated thermocouple wire. The measured temperature of the crystal when cooled with liquid nitrogen or dry ice at atmospheric pressure was within 0.05°K of the temperature expected.

Dilatation Measurements

Thermal expansion between room temperature and 1130°K was measured by a dilatation interferometry technique similar to the one described by Merritt.[6] This method is based upon interference patterns that are created by reflection of light from two optically flat surfaces separated by samples of the material under investigation. By observing the sequential number of the interference fringe n in coincidence with a reference mark and the corresponding temperature T in a vacuum environment and knowing the wavelength of the illuminating light λ plus the original length of the samples L_0 the thermal expansion at the temperature $(\Delta L)_T$ can be calculated according to the relationship:

$$(\Delta L)_T = n\lambda/2L_0. \tag{4}$$

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[4] Y. Canchois and H. Hulubei, *Longuers d'Onde des Emission X et des Discontinuities d'Absorption X* (Hermann & Cie., Paris, 1947).

[5] C. S. Barrett, Trans. AIME **161**, 15 (1945).

[6] G. E. Merritt, J. Res. Natl. Bur. Std. (U. S.) **10**, 59 (1933).

TABLE II. Measured values of a and c lattice parameters for alpha-zirconium. (to correct for refraction add 7×10^{-5} Å to a and 12×10^{-5} Å to c.)

Temperature °K	a Lattice parameter (Å) Ni K_{β_1}	a Lattice parameter (Å) W L_{α_1}	Temperature °K	c Lattice parameter (Å) Ni K_{α_1}	c Lattice parameter (Å) Ni K_{α_2}
297.3	3.23310	3.23307	300.3	5.14897	5.14893
292.0	3.23302	3.23296	196.6	5.14502	5.14504
195.2	3.23138	3.23137	196.2	5.14509	5.14516
194.9	3.23128	3.23126	194.6	5.14500	5.14511
77.4	3.22970	3.22975	154.3	5.14382	5.14386
77.4	3.22977	3.22972	77.4	5.14173	5.14173
51.0	3.22945	3.22944	47.2	5.14140	5.14143
4.2	3.22943	3.22935	4.2	5.14139	5.14143
4.2	3.22947	3.22937	4.2	5.14144	5.14147

Two sets of three single crystals each were prepared in the form of truncated pyramids: One set had the directions of testing normal to (00·1) planes within 0.5°, and the other set was normal to {10·0} planes. The weight and height (~6 mm) of each crystal were measured before and after testing to the nearest 10^{-4} g and the nearest 0.025 mm at a known temperature.

Dilatation measurements were made in a Gaertner interferometer, which used mercury-vapor green light for illumination, $\lambda=5461$ Å. The quartz optical flats and the specimens were contained in a copper "bucket" and heated in a furnace that was maintained at vacuums in the range 5×10^{-5} to 5×10^{-7} Torr. Electrical power to the furnace was controlled by a motor-driven cam, which rotated a variable autotransformer. Approximately 4.5 h were required to bring the interferometer assembly from room temperature to 1130°K. Temperatures were determined by a chromel-alumel thermocouple bead placed as close as possible to the specimens and in contact with the upper surface of the lower optical flat.

The primary error in the measurements was associated with the inherent temperature differential between the thermocouple bead and the specimens, which resulted from performing the tests under dynamic conditions. Since the heating program for the furnace and the physical arrangement of the interferometer assembly were reproducible, this temperature differential was evaluated by calibration runs with a platinum specimen, and appropriate corrections were applied to the temperatures measured during the experiments on zirconium. At room temperature the correction for calibration of the thermocouple was less than 1°K. As the temperature was increased, the differential between the observed temperature and the specimen true temperature rose rapidly, as would be expected for a vacuum furnace where the primary mode of heat transfer at low temperatures is by conduction, and reached a maximum of approximately 12.5°K at about 370°K. Further heating caused the differential to decrease to zero at about 620°K, and above this temperature, where heating by radiation becomes more effective, the differential was 1°K or less.

Data Treatment

Polynomial equations of the type

$$Y_T=k_0+k_1T+k_2T^2+\cdots+k_pT^p, \tag{5}$$

where Y_T represents the dimension at temperature T, the k_i's are constants, and p is the order of the polynomial, were fitted separately to both types of experimental results by the least-square method. Equations were determined for p equal to 1 through 7. The best fit in each case was selected as the equation that gave the last appreciable decrease in standard deviation. The resulting equations then were evaluated at 25° intervals to yield a_T and c_T in the 50 to 300°K range from the x-ray measurements and in the 275 to 1130°K rang from the dilatation measurements. 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. The axial ratio c_T/a_T, volume per atom V_T/atom, and the distance of closest approach between atoms D_T, in turn, were computed at each 25° interval. The relationships for calculating the last two dimensions were:

$$V_T/\text{atom}=(\sqrt{3}/4)a_T^2c_T, \tag{6}$$

$$D_T=(a_T^2/3+c_T^2/4)^{1/2}. \tag{7}$$

Equations then were fitted to the computed dimensions as well as the lattice parameters to give expressions for the different factors in the 50 to 1130°K range.

Equations for the expansion coefficients, α_a, α_b, and β were determined for a_T, c_T, and V_T/ atom by fitting values of $\ln Y_T$ to polynomial equations of the type

$$\ln Y_T=k_0'+k_1'T+k_2'T^2+\cdots+k_p'T^p. \tag{8}$$

Differentiation of such equations gave

$$\alpha_Y=(1/Y)(dY/dT=k_1'+2k_2'+\cdots pk_p'T^{(p-1)}, \tag{9}$$

RESULTS

X-Ray Measurements

The experimental results are listed in Table II. No significant change was detected in either of the lattice parameters below 50°K; therefore, the polynomial expressions were evaluated only for the range above 50°K and are not applicable below this range. Least-squares fitting of the data, not corrected for refraction, yielded the following values:

$$\begin{aligned}a_T=3.2303\,0&-48.6\times10^{-6}T+919.8\times10^{-9}T^2\\&-6971.1\times10^{-12}T^3+28\,294.0\times10^{-15}T^4\\&-57\,620.6\times10^{-18}T^5+46\,196.7\times10^{-21}T^6,\end{aligned}$$

$$\begin{aligned}c_T=5.1415\,1&-18.4\times10^{-6}T+395.5\times10^{-9}T^2\\&-1658.8\times10^{-12}T^3+3626.5\times10^{-15}T^4\\&-2974.4\times10^{-18}T^5.\end{aligned}$$

Values calculated from these equations did not differ by more than 1 part in 30 000 from measured values.

TABLE III. Coefficients for polynomial equations that express dimensions or properties of the alpha-zirconium lattice as functions of temperatures (50 to 1130°K).

Dimension or property	k_0	$k_1 \times 10^6$	$k_2 \times 10^9$	$k_3 \times 10^{12}$
a_T	3.22849	14.57	3.37	−1.64
c_T	5.13956	25.62	19.36	2.45
c_T/a_T	1.59194	0.74	4.35	1.52
$D_T = (a_T^2/3 + c_T^2/4)^{1/2}$	3.17461	15.31	8.96	4.56
$(V/\text{atom})_T = (\sqrt{3}/4) a_T^2 c_T$	23.19662	325.03	137.34	−11.26
$a_T/a_{4.2^\circ K}$	0.99972	4.51	1.04	−0.51
$c_T/c_{T4.2^\circ K}$	0.99964	4.98	3.76	0.48
$V_T/V_{4.2^\circ K}$	0.99907	14.00	5.92	−0.48
	$k_1' \times 10^6$	$2k_2' \times 10^9$	$3k_3' \times 10^{12}$	
$\alpha_a = (1/a_T) da_T/dT$	4.51	2.07	−1.53	...
$\alpha_c = (1/c_T) dc_T/dT$	5.02	7.40	1.42	...
$\beta = (1/V_T) dV_T/dT$	14.03	11.59	−1.68	...

Dilatation Measurements

Each of the two sets of single crystals were tested seven times for expansion between approximately 290 to 1130°K. Height and weight measurements of each crystal after the tests agreed with the corresponding measurements before the tests within the limits of accuracy. Since the crystals were tested several times without significant weight or dimensional changes and since no systematic drifts of the expansion curves were observed with successive runs, it was concluded that the vacuum furnace provided good protection of the samples against contamination by gaseous impurities, and that the samples were not deformed by creep at the higher temperatures as a result of the load applied by the upper optical flat.

The polynomial equations that best fit the experimental results were as follows:

$$(a_T - a_{273^\circ K})/a_{273^\circ K} = -1.435 \times 10^{-3} + 5.14 \times 10^{-6} T$$

and

$$(c_T - c_{273^\circ K}/)c_{273^\circ K} = -3.554 \times 10^{-3} + 17.63 \times 10^{-6} T - 25.93 \times 10^{-9} T^2 + 29.25 \times 10^{-12} T^3 - 9.86 \times 10^{-15} T^4.$$

Combined Data

The coefficients for the polynomial equations that best fit the various dimensions and properties of the alpha-zirconium lattice as functions of temperature in the range 50 to 1130°K, are given in Table III. Evaluations of these equations at selected temperatures are tabulated in Table IV. Some of the factors are plotted versus temperature in Figs. 2 and 3.

The thermal-expansion coefficient for the *a* axis is approximately constant from 100 to 1130°K, while that for the *c* axis increases linearly in this range (Fig. 3); thus, the *c*/*a* ratio increases with temperature.

TABLE IV. Evaluations of polynomial equations that express dimensions or properties of alpha-zirconium as functions of temperatures between 50 and 1130°K.

Temperature (°K)	a_T (Å)	c_T (Å)	c_T/a_T	D_T (Å)	$(V/\text{atom})_T$ (Å^3)	$\alpha_a \times 10^6$ (1/°K)	$\alpha_c \times 10^6$ (1/°K)	$\beta \times 10^6$ (1/°K)
4.2	3.22940	5.14143	1.5921	3.17565	23.2182			
50	3.22922	5.14089	1.5920	3.17540	23.2132	4.61	5.39	14.60
75	3.22960	5.14159	1.5920	3.17581	23.2218	4.66	5.58	14.89
100	3.22998	5.14232	1.5921	3.17623	23.2305	4.70	5.77	15.17
125	3.23036	5.14307	1.5921	3.17666	23.2394	4.74	5.96	15.45
150	3.23074	5.14385	1.5922	3.17711	23.2484	4.79	6.16	15.73
175	3.23113	5.14465	1.5922	3.17757	23.2576	4.83	6.35	16.00
200	3.23152	5.14548	1.5923	3.17803	23.2670	4.86	6.55	16.28
250	3.23232	5.14721	1.5924	3.17900	23.2863	4.93	6.96	16.82
300	3.23312	5.14905	1.5926	3.18002	23.3062	4.99	7.36	17.35
350	3.23393	5.15100	1.5928	3.18109	23.3267	5.05	7.78	17.88
400	3.23475	5.15306	1.5930	3.18220	23.3479	5.09	8.20	18.39
450	3.23558	5.15523	1.5933	3.18336	23.3697	5.13	8.63	18.90
500	3.23641	5.15752	1.5936	3.18456	23.3921	5.16	9.07	19.40
600	3.23809	5.16243	1.5943	3.18712	23.4386	5.20	9.97	20.38
700	3.23978	5.16782	1.5951	3.18988	23.4876	5.21	10.89	21.32
800	3.24146	5.17370	1.5961	3.19283	23.5388	5.19	11.84	22.22
900	3.24314	5.18008	1.5972	3.19598	23.5922	5.14	12.82	23.10
1000	3.24479	5.18699	1.5986	3.19934	23.6477	5.05	13.83	23.94
1100	3.24642	5.19443	1.6000	3.20290	23.7053	4.94	14.87	24.74
1125	3.24682	5.19637	1.6004	3.20383	23.7201	4.91	15.14	24.94

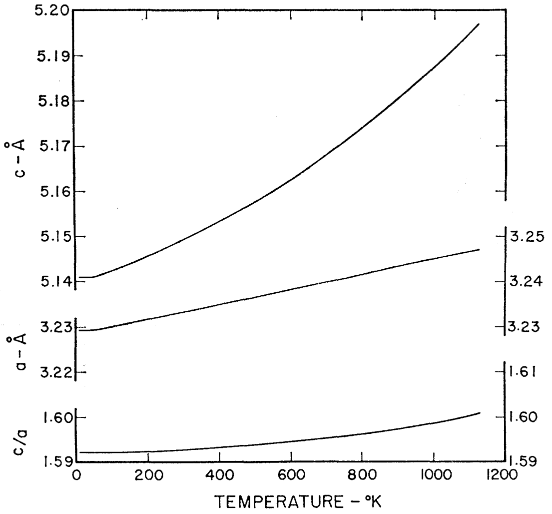

FIG. 2. Lattice dimensions of alpha-zirconium between 4.2 and 1130°K.

DISCUSSION

Lattice Parameters and Expansion Coefficients of Zirconium

The difference between lattice parameters obtained with different wavelengths is small. For example, in Table II, the root-mean-square average difference between c parameters obtained at each temperature with Ni K_{α_1} and Ni K_{α_2} radiation is 3.3 parts in 10^6, using all nine pairs of c parameters. For the a parameter, using Ni K_{β_1} and W L_{α_1}, the root-mean-square average difference is 5.6 parts in 10^6, using the nine pairs of a parameters. This shows that the sum of the reading errors plus the difference between errors in the published wavelengths is about 1 part in 10^5.

The main difficulty in determining precise lattice parameters in zirconium is caused by variations in lattice parameters due to impurities. Even in a single crystal of the highest purity zirconium available, Table V shows that the difference between the c lattice parameter measured on opposite faces of a crystal 3-mm thick were as large as 0.0014 Å, and the standard deviation or seven c parameters measured at room temperature was 0.0006 Å. This is an order of magnitude larger than the average error in reading a peak. The variations in lattice parameter made it necessary to take all measurements from the same area of the crystal. This was accomplished by adjusting the cryostat to compensate for its thermal expansion and by careful centering of the crystal face on the diffractometer axis.

TABLE V. Variation of lattice parameters of zirconium at room temperature caused by nonuniform distribution of impurities.

Crystal	a (Å)	c (Å)
a	3.23338	5.14756
a	3.23302	5.14762
a	3.23306	5.14763
a	3.23297	5.14753
a	3.23276	5.14749
b	3.23310	5.14897
b	3.23307	5.14893
average	3.2331±0.0001	5.1480±0.0006

TABLE VI. Published lattice parameters of zirconium.

Material	Temperature (°K)	a (Å)	c (Å)	Source
"Iodide" Zr	298	3.236	5.153	Domagala and McPherson[a] (1953)
"Iodide" Zr	298	3.2321	5.1475	Treco[b] (1953)
"Mg reduced" Zr	298	3.2344	5.1519	Treco[b] (1953)
Estimate for oxygen-free Zr	298	3.2322	5.1477	Treco[b] (1953)
"Iodide" Zr	298	3.2330	5.1475	Skinner and Johnston[c] (1953)
"Iodide" Zr	292	3.2318	5.1483	Russell[d] (1954)
Oxygen-free "Iodide" Zr	298	3.2316	5.1475	Lichter[e] (1960)
"Iodide" Zr single crystals	298	3.2331	5.1480	Present work

[a] Reference 11.
[b] Reference 7.
[c] Reference 8.
[d] Reference 9.
[e] Reference 10.

The lattice parameters determined in this investigation are in reasonable agreement (≈1 part in 3000) with the published values of Treco,[7] Skinner and Johnston,[8] Russell,[9] and Lichter[10] (Table VI). Treco's values for "Mg-reduced" Zr and Domagala and McPherson's[11] values for "iodide" Zr, however, are

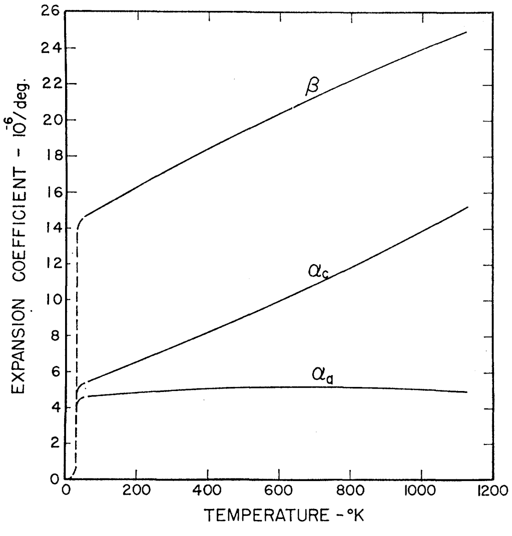

FIG. 3. Expansion coefficients of alpha-zirconium between 4.2 and 1130°K.

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[7] R. M. Treco, Trans. AIME **197**, 344 (1953).

[8] G. B. Skinner and H. L. Johnston, J. Chem. Phys. **21**, 1383 (1953).

[9] R. B. Russell, Trans. AIME **200**, 1045 (1954).

[10] B. D. Lichter, Trans. AIME **218**, 1015 (1960).

[11] R. F. Domagala and D. J. McPherson, U. S. Atomic Energy Commission Publication No. COO-181, 1953 (unpublished).

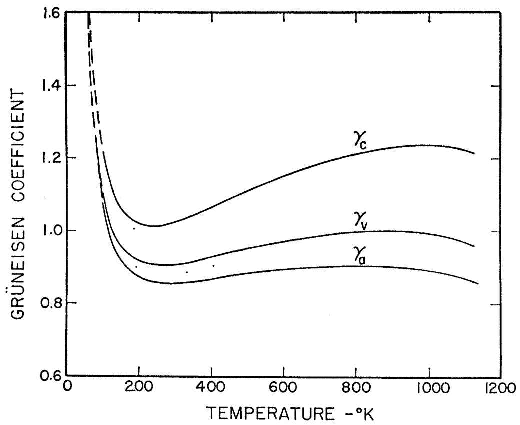

FIG. 4. Grüneisen coefficients for alpha-zirconium.

significantly larger, particularly the c parameter. These discrepancies probably are due to real differences in lattice parameters caused by impurities in the samples used by different experimenters. Indeed, Table V shows differences of 2 parts in 10^4 in the c parameter in two crystals prepared from the same material.

The results for the thermal expansion coefficients between 300°K and 1130°K along the two principal crystallographic directions do not vary markedly from the data reported previously by Skinner and Johnston[8] and by Russell,[9] particularly for the c direction (Table VII).[12–14] Somewhat larger coefficients were found by these workers for the a direction. The discrepancies can be explained on the basis of contamination, which could occur in the outermost surfaces of samples during lengthy x-ray exposures at elevated temperatures, to yield larger values of the lattice parameters. The only previously reported expansion data below room temperature are for polycrystalline material.[15] The present results for the expansion in the two principal directions bracket these data and, therefore, are in qualitative agreement with them.

TABLE VII. Published expansion coefficients of zirconium.[a]

Temperature range (°K)	$\alpha_a \times 10^6$ (1/°K)	$\alpha_c \times 10^6$ (1/°K)	Source
273–373	14.3	2.5	unknown chemistry—Shinoda[b] (1934)
298–573	4.5	10.3	1.5% Hf—Mechlin[c] (1951)
298–473	4.7	7.9	Hf-free—Adenstedt and Brocklehurst[d] (1952)
298–1143	5.5	10.8	2% Hf—Skinner and Johnston[e] (1953)
298–973	6.43	11.23	Hf-free—Russell[f] (1954)
298	5.65	6.46	Hf-free—Russell[f] (1954)
300–1100	5.15	11.03	Hf-free—present work
300	4.99	7.36	Hf-free—present work

[a] All of the previously reported expansion coefficients were obtained from x-ray measurements of the lattice parameters at various temperatures.
[b] Reference 12.
[c] Reference 13.
[d] Reference 14.
[e] Reference 8.
[f] Reference 9.

Grüneisen Coefficients

The value of the volume Grüneisen coefficient γ_V[16] was calculated as a function of temperature (Fig. 4) from the equation

$$\gamma_V = \beta V / C_p \chi_a , \tag{10}$$

where β is the volume-expansion coefficient, V is the specific volume, C_p is the specific heat at constant pressure, and χ_a is the adiabatic volume compressibility. Values of C_p were obtained by combining the data of Skinner and Johnston[17] and Scott.[18] Compressibilities were obtained from the work of Fisher and Renken,[1] and the other two variables were from the present work. The most striking feature is that γ_V is essentially constant, 0.95±0.05, from 100°K ($\approx 0.3\theta_D$) to 1130°K ($\approx 0.4\theta_D$). It must be emphasized that γ_V was calculated entirely from experimental data taken at temperature without extrapolation. At low temperatures the uncertainty in the coefficients of thermal expansion do not permit a meaningful calculation of γ_V from this data.

Directional Grüneisen coefficients, γ_a and γ_c, were calculated from the tensor form of the relationship[19] according to the following equations:

$$\begin{aligned} (V/C_p)\alpha_a &= (s_{11}+s_{12})\gamma_a + s_{13}\gamma_c , \\ (V/C_p)\alpha_c &= 2s_{13}\gamma_a + s_{33}\gamma_c , \end{aligned} \tag{11}$$

where the s_{ij}'s were the elastic compliance moduli from the data of Fisher and Renken.[1] The values for the directional γ's are shown in Fig. 4: 1.12±0.11 in the c direction and 0.87±0.03 in the a direction between 100 and 1130°K.

In addition, the various γ's were calculated using lattice specific heat $C_p - C_e$, with two different electronic specific heat C_e corrections.[20,21] It can be argued, however, that the electronic-specific-heat correction should not be applied to the specific heat without applying a similar correction to the coefficient of thermal expansion. Unless zirconium has a most exceptional density of states curve, the available data indicate that the electronic contribution to the coefficient of thermal expansion is perhaps four orders of magnitude less

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than the phonon contribution, above $0.3\theta_D$. Therefore, it can be argued that the electronic contribution to the thermal expansion is negligible. If the lattice specific heat is used, the γ's vary more with temperature, but the shapes of the curves remain the same. If the C_e correction is based upon the work of Kneip *et at.*,[20] $\gamma_V=1.01\pm0.08$, $\gamma_a=0.94\pm0.05$, and $\gamma_c=1.20\pm0.16$ between 100 and 1130°K. If it is based upon Shimizu and Kalsuki's data,[21] $\gamma_V=1.08\pm0.15$, $\gamma_a=1.00\pm0.11$, and $\gamma_c=1.29\pm0.25$ in the same temperature range.

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Empirical Fermi-Surface Parameters for W and Mo†

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Torsion measurements have been made of the de Haas–van Alpen effect in tungsten and molybdenum. The results of these measurements are extremal cross-section areas of the Fermi surface and their corresponding cyclotron effective masses. These data are shown to be qualitatively interpretable in terms of orbits assigned to the various sheets of a Fermi-surface topology proposed by Lomer. A semiquantitative Fermi-surface model based on the Lomer topology is constructed and is shown to be compatible with the compensation of carriers, the connectivity of surfaces, the total surface area, the extremal dimensions, and the cyclotron effective masses reported by other investigators.

I. INTRODUCTION

THE band structure of the chromium-group metals tungsten and molybdenum is of considerable experimental and theoretical interest. Measurements of the anomalous skin effect[1] indicate that the total Fermi-surface area is much less than that for a valence-six nearly-free-electron model. Measurements of the magnetoresistance[2,3] indicate that the Fermi surface is both closed and compensated. Other experiments have determined extremal dimensions,[4,5] extremal cross-sectional areas,[6,7] and cyclotron effective masses[8,9] of the Fermi-surface sheets, often in considerable detail.

A model for the topology of the Fermi surface of the chromium-group metals which is in qualitative agreement with a majority of the above experimental results was first proposed by Lomer.[10] This model was based on

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