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Crystallographic Properties of Osmium

Assessment of properties from absolute zero to 1300 K

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Wombourne, West Midlands, UK Email: jwarblaster@yahoo.co.uk The crystallographic properties of osmium at temperatures from absolute zero to the experimental limit at 1300 K are assessed following a review of the literature published between 1935 and to date. Selected values of the thermal expansion coefficients and measurements of length changes due to thermal expansion have been used to calculate the variation with temperature of the lattice parameters, interatomic distances, atomic and molar volumes and densities. The data is presented in the form of Equations and Tables. The density of osmium at 293.15 K is 22,589 kg m⁻³.

This is the seventh in a series of papers in this Journal on the crystallographic properties of the platinum group metals (pgms), following two papers on platinum (1,2) and one each on rhodium (3), iridium (4), palladium (5) and ruthenium (6). Like ruthenium, osmium exists in a hexagonal close-packed (hcp) structure (Pearson symbol *hP*2) up to the melting point estimated by the present author to be 3400 ± 50 K (7) for the pure metal. The actual published values of 3318 ± 30 K by Knapton *et al.* (8) were for metal of only about 99.7% purity and of 3283 ± 10 K by Douglass and Adams (9) for metal of 99.5% purity.

The thermal expansion is represented by three sets of lattice parameter measurements: those of Owen and Roberts (10, 11) (from 293 K to 873 K) and Schröder *et al.* (12) (from 289 K to 1287 K) in the high-temperature region and those of Finkel' *et al.* (13) (from 79 K to 300 K) in the low-temperature region. The latter measurements were only shown graphically and by incorrect equations with the actual data points as length change values being given by Touloukian *et al.* (14). As shown below the latter measurements are incompatible with the high-temperature data so the high- and low-temperature data were initially treated separately.

Thermal Expansion High-Temperature Region

Length change values derived from the lattice parameter measurements of Owen and Roberts (10, 11) and Schröder *et al.* (12) agree satisfactorily and are represented by Equations (i) and (ii) for the *a*-axis

and *c*-axis respectively. On the basis $\pm 100\delta L/L_{293.15}$ this leads to standard deviations of ± 0.004 and ± 0.002 respectively. The selected values were extended to a rounded temperature of 1300 K.

Low-Temperature Region

The measurements of Finkel' *et al.* (13) as given by Touloukian *et al.* (14) (**Figure 1**) were fitted to smooth Equations (iii) and (iv). The incompatibility of these measurements with the high-temperature data can be shown by deriving thermal expansion coefficients from these equations at 293.15 K as $\alpha_a = 5.8 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_c = 8.8 \times 10^{-6} \text{ K}^{-1}$. These values are notably higher than those calculated from Equations (i) and (ii) and as given in **Tables I** and **II**. In spite of the high purity claimed for the metal used in the experiments of Finkel' *et al.*, the *c*-axis lattice parameter value of 0.43174 nm

at 293.15 K is notably lower than all other values given in **Table III** suggesting that these measurements must be treated with a certain degree of suspicion. Because it does not appear to be possible to reconcile the highand low-temperature data the measurements of Finkel' *et al.* were rejected.

In order to extrapolate below room temperature the procedure given in Appendix A was adopted. This utilises specific heat values selected by the present author (15) as expanded in Appendix C, leading to Equations (vii) and (viii) which were extrapolated in order to represent thermal expansion from 0 K to 293.15 K. Because there are two axes, the values of low-temperature specific heat as given in Appendix C can be substituted into the Equations, removing the need to develop a relatively large number of complimentary spline-fitted polynomial equations to



Fig. 1. Differences between the measurements of Finkel' et al. (13) as given by Touloukian et al. (14) and the selected values

Table I

Crystallographic Properties of Osmium

Temperature, K	Thermal expansion coefficient, α_a , 10 ⁻⁶ K ⁻¹	Thermal expansion coefficient, α_c , 10 ⁻⁶ K ⁻¹	Thermal expansion coefficient, α _{avr} , 10 ⁻⁶ K ^{-1 a}	Length change, δa/a _{293.15 K} × 100, %	Length change, δ c/c _{293.15 K} × 100, %	Length change, δavr/ avr _{293.15 K} × 100, %
0 ^b	0	0	0	-0.100	-0.119	-0.106
10	0.035	0.035	0.035	-0.100	-0.119	-0.106
20	0.15	0.15	0.15	-0.100	-0.119	-0.106
30	0.49	0.51	0.49	-0.100	-0.118	-0.106

(Continued)

Temperature,	Thermal	Thermal	Thermal	Length	Length	Length
К	expansion	expansion	expansion	change,	change,	change,
	coefficient,	coefficient,	coefficient,	δ а/а_{293.15 К}	δ с/с_{293.15 К}	δ avr /
	α _a, 10⁻⁶ K⁻¹	α _c, 10⁻⁶ K⁻¹	$\alpha_{\sf avr}$, 10 ⁻⁶	× 100, %	× 100, %	avr _{293.15 K}
			K ^{-1 a}			× 100, %
40	1.04	1.10	1.06	-0.099	-0.118	-0.105
50	1.62	1.78	1.70	-0.098	-0.116	-0.104
60	2.25	2.43	2.31	-0.096	-0.114	-0.102
70	2.72	2.97	2.81	-0.094	-0.111	-0.099
80	3.11	3.42	3.21	-0.090	-0.108	-0.096
90	3.41	3.79	3.54	-0.087	-0.104	-0.093
100	3.64	4.08	3.79	-0.084	-0.101	-0.089
110	3.82	4.31	3.98	-0.080	-0.096	-0.085
120	3.96	4.50	4.14	-0.076	-0.092	-0.081
130	4.07	4.67	4.27	-0.072	-0.087	-0.077
140	4.16	4.81	4.38	-0.068	-0.083	-0.073
150	4.24	4.93	4.47	-0.064	-0.078	-0.068
160	4.29	5.02	4.53	-0.059	-0.073	-0.064
170	4.33	5.10	4.59	-0.055	-0.068	-0.059
180	4.37	5.19	4.64	-0.051	-0.063	-0.055
190	4.41	5.26	4.69	-0.046	-0.057	-0.050
200	4.43	5.33	4.73	-0.042	-0.052	-0.045
210	4.45	5.40	4.76	-0.038	-0.047	-0.041
220	4.47	5.45	4.80	-0.033	-0.041	-0.036
230	4.49	5.51	4.83	-0.029	-0.036	-0.031
240	4.50	5.57	4.86	-0.024	-0.030	-0.026
250	4.52	5.63	4.89	-0.020	-0.025	-0.021
260	4.53	5.68	4.91	-0.015	-0.019	-0.016
270	4.54	5.73	4.94	-0.011	-0.013	-0.011
280	4.55	5.78	4.96	-0.006	-0.008	-0.007
290	4.56	5.83	4.98	-0.001	-0.002	-0.002
293.15	4.57	5.85	4.99	0	0	0
300	4.57	5.87	5.00	0.003	0.004	0.003
400	4.60	6.28	5.16	0.049	0.065	0.054
500	4.63	6.68	5.32	0.095	0.130	0.107
600	4.66	7.09	5.47	0.142	0.199	0.161
700	4.69	7.49	5.63	0.189	0.272	0.216
800	4.73	7.89	5.78	0.236	0.349	0.273
900	4.76	8.30	5.94	0.283	0.430	0.332
1000	4.79	8.70	6.09	0.331	0.516	0.393
1100	4.82	9.10	6.25	0.379	0.605	0.455
1200	4.85	9.49	6.40	0.428	0.699	0.518
1300	4.88	9.89	6.55	0.477	0.796	0.583

Table I (Continued)

^a avr = average

^b Since all values below 293.15 K are estimated they are given in italics

Ta	b	e	Ш.
		-	

Further Crystallographic Properties of Osmium

Temperature,	Lattice	Lattice	c/a ratio	Interatomic	Atomic	Molar	Density,
К	parameter,	parameter,		distance,	volume,	volume,	kg m⁻³
	<i>a</i> , nm ^a	<i>c,</i> nm		<i>d</i> 1, nm	10 ⁻³ nm ³	10 ⁻⁶ m ³	
						mol ⁻¹	
Ob	0.27315	0.43148	1.5797	0.26723	13.939	8.395	22661
10	0.27315	0.43148	1.5797	0.26723	13.939	8.395	22661
20	0.27315	0.43148	1.5797	0.26723	13.940	8.395	22661
30	0.27315	0.43148	1.5797	0.26723	13.940	8.395	22661
40	0.27315	0.43148	1.5797	0.26723	13.940	8.395	22660
50	0.27315	0.43149	1.5797	0.26724	13.941	8.395	22659
60	0.27316	0.43150	1.5797	0.26724	13.941	8.396	22658
70	0.27316	0.43151	1.5797	0.26725	13.942	8.396	22656
80	0.27317	0.43152	1.5797	0.26726	13.944	8.397	22654
90	0.27318	0.43154	1.5797	0.26727	13.945	8.398	22652
100	0.27319	0.43156	1.5797	0.26728	13.947	8.399	22649
110	0.27320	0.43157	1.5797	0.26729	13.948	8.400	22647
120	0.27321	0.43159	1.5797	0.26731	13.950	8.401	22644
130	0.27322	0.43161	1.5797	0.26731	13.952	8.402	22641
140	0.27323	0.43163	1.5797	0.26732	13.954	8.403	22638
150	0.27325	0.43165	1.5797	0.26734	13.955	8.404	22635
160	0.27326	0.43168	1.5797	0.26735	13.957	8.405	22632
170	0.27327	0.43170	1.5797	0.26736	13.959	8.406	22629
180	0.27328	0.43172	1.5798	0.26738	13.961	8.408	22626
190	0.27329	0.43175	1.5798	0.26739	13.962	8.409	22623
200	0.27331	0.43176	1.5798	0.26740	13.965	8.410	22620
210	0.27332	0.43179	1.5798	0.26742	13.967	8.411	22616
220	0.27333	0.43181	1.5798	0.26743	13.969	8.412	22613
230	0.27334	0.43183	1.5798	0.26744	13.971	8.414	22610
240	0.27335	0.43186	1.5799	0.26746	13.973	8.415	22607
250	0.27337	0.43188	1.5799	0.26747	13.975	8.416	22603
260	0.27338	0.43191	1.5799	0.26748	13.977	8.417	22600
270	0.27339	0.43193	1.5799	0.26750	13.979	8.419	22596
280	0.27340	0.43196	1.5799	0.26751	13.981	8.420	22593
290	0.27341	0.43198	1.5799	0.26753	13.983	8.421	22590
293.15	0.27342	0.43199	1.5800	0.26753	13.984	8.421	22589
300	0.27343	0.43201	1.5800	0.26754	13.986	8.422	22586
400	0.27355	0.43227	1.5802	0.26769	14.007	8.435	22552
500	0.27368	0.43255	1.5805	0.26785	14.029	8.448	22517
600	0.27381	0.43285	1.5808	0.26801	14.052	8.462	22480
700	0.27394	0.43316	1.5813	0.26818	14.075	8.476	22443
800	0.27406	0.43350	1.5817	0.26836	14.099	8.491	22404
900	0.27419	0.43385	1.5823	0.26855	14.124	8.506	22365

(Continued)

Table II (Continued)								
Temperature,	Lattice	Lattice	c/a ratio	Interatomic	Atomic	Molar	Density,	
К	parameter,	parameter,		distance,	volume,	volume,	kg m⁻³	
	<i>a</i> , nm ^a	<i>c,</i> nm		<i>d</i> 1, nm	10 ⁻³ nm ³	10 ⁻⁶ m ³		
						mol ⁻¹		
1000	0.27433	0.43422	1.5829	0.26874	14.149	8.521	22325	
1100	0.27446	0.43460	1.5835	0.26894	14.176	8.537	22284	
1200	0.27459	0.43501	1.5842	0.26915	14.203	8.553	22241	
1300	0.27472	0.43543	1.5850	0.26936	14.230	8.570	22198	

a a = d2

^b Since all values below 293.15 K are estimated they are given in italics

Table III

Lattice Parameter Values at 293.15 K^a

Authors (Year)	Reference	Original temperature, K	Original units	Lattice parameters, a, corrected to 293.15 K, nm	Lattice parameters, c, corrected to 293.15 K, nm	Notes
Owen <i>et al.</i> (1935)	(20)	291	kX	0.27361	0.43189	(a)
Owen and Roberts (1936)	(10)	291	kX	0.27357	0.43191	(a)
Owen and Roberts (1937)	(11)	293	kX	0.27355	0.43194	(a)
Finkel' <i>et al.</i> (1971)	(13)	293	Å	0.27346	0.43174	(a), (b)
Rudman (1965)	(21)	rt ^b	Å	0.27341	0.43188	(c)
Swanson <i>et al.</i> (1955)	(22)	299	Å	0.27342	0.43198	
Mueller and Heaton (1961)	(23)	rt	Å	0.27345	0.43200	
Taylor <i>et al.</i> (1961, 1962)	(24, 25)	296	Å	0.27342	0.43201	
Schröder <i>et al.</i> (1972)	(12)	289	Å	0.27340	0.43198	

 $^{\rm a}$ Selected values for the present paper 0.27342 \pm 0.00002 and 0.43199 \pm 0.00002

^b rt = room temperature

Notes to Table III

(a) For information only – not included in the average

(b) Lattice parameter values given by Touloukian et al. (14)

(c) The *c*-axis value was not included in the average

correspond to Equations (vii) and (viii). On the basis of the expression:

 $100 \times (\delta L/L_{293.15 \text{ K (experimental)}} - \delta L/L_{293.15 \text{ K (calculated)}})$

where $\delta L/L_{293.15 \text{ K}}$ (experimental) are the experimental length change values relative to 293.15 K as calculated from Equations (iii) and (iv) and $\delta L/L_{293.15 \text{ K}}$ (calculated) are the relative length change values as given in **Table I**, the measurements of Finkel' *et al.* for the *a*-axis over the range 80 K to 240 K show a bias of 0.005 to 0.006 lower than the selected values. For the *c*-axis at 80 K the difference is 0.029 lower with a trend to agree with the selected values with increasing temperature.

The Lattice Parameter at 293.15 K

The values of the lattice parameters, *a* and *c*, given in **Table III** represent a combination of those values selected by Donohue (16) and more recent measurements. Values originally given in kX units were converted to nanometres using the 2010 International Council for Science: Committee on Data for Science and Technology (CODATA) Fundamental Constants (17, 18) conversion factor for CuK α_1 , which is 0.100207697 ± 0.000000028. Values given in

angstroms (Å) were converted using the default ratio 0.100207697/1.00202 where the latter value represents the old conversion factor from kX units to Å. Lattice parameter values were corrected to 293.15 K using the values of the thermal expansion coefficient selected in the present review. Density values given in Tables I and II were calculated using the currently accepted atomic weight of 190.23 ± 0.03 (19) and an Avogadro constant $(N_{\rm A})$ of $(6.02214129 \pm 0.0000027) \times 10^{23} \,\mathrm{mol}^{-1}(17, 18)$. From the lattice parameter values at 293.15 K selected in **Table III** as: $a = 0.27342 \pm 0.00002$ nm and c = 0.43199 \pm 0.00002 nm, the derived selected density is 22,589 \pm 5 kg m⁻³ and the molar volume is $(8.4214 \pm 0.0013) \times$ 10⁻⁶ m³ mol⁻¹. The difference from the density value for iridium, $22,562 \pm 11 \text{ kg m}^{-3}$ (4), at $27 \pm 12 \text{ kg m}^{-3}$ is considered to be the proof that osmium is the densest metal at room temperature and pressure.

In **Tables I** and **II** the interatomic distance $d1 = (a^2/3 + c^2/4)^{\frac{1}{2}}$ and d2 = a. The atomic volume is $(\sqrt{3} \ a^2 \ c)/4$ and the molar volume is calculated as $N_A \ (\sqrt{3} \ a^2 \ c)/4$, equivalent to atomic weight divided by density. Thermal expansion $\alpha_{avr} = (2 \ \alpha_a + \alpha_c)/3$ and length change $\delta avr/avr_{293.15 \text{ K}} = (2 \ \delta a/a_{293.15 \text{ K}} + \delta c/c_{293.15 \text{ K}})/3$ (avr = average).

High-Temperature Thermal Expansion Equations for Osmium (293.15 K to 1300	К)
$\delta a/a_{293.15} \!=\! -1.32379 \times 10^{-3} + 4.46595 \times 10^{-6} T + 1.69909 \times 10^{-10} T^{2}$	(i)
$\delta c/c_{293.15} = -1.53749 \times 10^{-3} + 4.64427 \times 10^{-6} T + 2.04826 \times 10^{-9} T^2$	(ii)
Equations Representing the Thermal Expansion Data of Finkel' <i>et al.</i> (13) (79 K to 300 K)	
$\delta a/a_{293.15} = -1.22081 \times 10^{-3} + 3.13600 \times 10^{-6} T + 1.37670 \times 10^{-9} T^2 + 7.27143 \times 10^{-12} T^3$	(iii)
$\delta c/c_{293.15} = -1.71224 \times 10^{-3} + 3.88446 \times 10^{-6} T + 3.26721 \times 10^{-9} T^2 + 1.16202 \times 10^{-11} T^3$	(iv)
$\alpha_{\rm a} \left({\rm K}^{-1} \right) = C_p \left(-3.14503 \times 10^{-8} + 6.95814 \times 10^{-10} T + 1.86500 \times 10^{-5} / T \right)$	(v)
$\alpha_{\rm c} ({\rm K}^{-1}) = C_p (-7.35814 \times 10^{-8} + 1.16358 \times 10^{-9} T + 2.62261 \times 10^{-5} / T)$	(vi)
Low-Temperature Thermal Expansion Equations for Osmium (0 K to 293.15 K)	
$\alpha_{\rm a} ({\rm K}^{-1}) = C_p (1.58546 \times 10^{-7} + 1.09521 \times 10^{-11} T + 6.88982 \times 10^{-6} / T)$	(vii)
$\alpha_{\rm c} ({\rm K}^{-1}) = C_p (1.71988 \times 10^{-7} + 1.41412 \times 10^{-10} T + 6.95413 \times 10^{-6} / T)$	(viii)
High-Temperature Specific Heat Equation (240 K to 3400 K)	um ⁹ (1)
$C_{\rm p}$ (J mol ⁻⁺ K ⁻⁺) = 26.1938 + 2.64636 × 10 ⁻⁺ T + 1.15788 × 10 ⁻⁺ T ⁺ + 1.599912 × 10 ⁻¹⁰ T ⁻³ - 150378/	I ~ (1X)

Summary

The number of measurements of the thermal expansion data for osmium is very limited and although the two high-temperature sets of lattice parameter measurements show satisfactory agreement, their usefulness only applies from room temperature to about 1300 K. The low-temperature lattice parameter measurements appear to be

completely incompatible with the high-temperature data and were therefore rejected. Instead a novel approach was used to obtain values in the lowtemperature region that agreed with the hightemperature data. Clearly the thermal expansion situation for osmium is unsatisfactory and new measurements are required at both low- and hightemperatures.

Appendix A

Representative Equations for Extrapolation Below 293.15 K

Equations (i) and (ii) are considered to be confined within the experimental limits of 289 K to 1287 K except for an extrapolation to a rounded maximum of 1300 K. Therefore in order to extrapolate beyond these limits a thermodynamic relationship is required such as that proposed by the present author to represent a correlation and interpolation of low-temperature thermal expansion data (1). In this case the relationship was evaluated in the high-temperature region and extrapolated to the low-temperature region. Equations (i) and (ii) were differentiated in order to obtain values of α^* , the thermal expansion coefficient relative to 293.15 K, with thermodynamic thermal expansion coefficients calculated as $\alpha = \alpha^*/(1 + \delta L/L_{293.15 \text{ K}})$. Selected values of α at 293.15 K and in the range 300 K to 700 K at 50 K intervals were then combined with high-temperature specific heat values calculated from Equation (ix) to derive Equations (vii) and (viii). These were then extrapolated to the low-temperature region using the specific heat values given in Appendix C. The range 293.15 K to 700 K was selected since this gave a satisfactory agreement between the derived experimental and calculated values. Length change values corresponding to Equations (vii) and (viii) were obtained by three-point integration.

Appendix B

The Quality of the Density Value for Osmium at 0 K

In view of the novel approach used to estimate the low-temperature properties and the relatively large extrapolation used, an independent estimate of the density at 0 K would be considered as a test of the quality of the procedure used. Such a value can be obtained from the rejected measurements of Finkel' *et al.* (13) as given by Touloukian *et al.* (14). Equations (iii) and (iv) are considered as being confined within their experimental limits of 80 K to 293.15 K and therefore in order to extrapolate beyond these limits a similar approach to that used in Appendix A was applied. This approach led to Equations (v) and (vi) which are applicable between the limits 80 K to 293.15 K and these were extrapolated to 0 K using the specific heat values given in Appendix C. Three-point integration was used to derive values at 0 K of $100 \ \delta a/a_{293.15} = -0.107$ and $100 \ \delta c/c_{293.15} = -0.153$ so that the derived density value is thus 22,672 kg m⁻³ which is surprisingly only 11 kg m⁻³ (0.05%) greater than the selected value. It is possible therefore that the true density could lie between these two values although based on the selected value it is considered that the density at 0 K can best be represented as 22,661 ± 11 kg m⁻³.

Appendix C

Specific Heat Values for Osmium

Because of the large number of spline fitted equations that would be required to conform to both Equations (vii) and (viii), a different approach has been used for the non-cubic metals in that specific heat values are directly applied to these equations. However this would require that the table of low-temperature specific heat values originally given by the present author (15) has to be more comprehensive and the revised table is given as **Table IV**. In the high-temperature region Equation (ix) represents the specific heat essentially from 240 K to the melting point and is obtained by differentiating the selected enthalpy equation given by the present author (15). Selected values derived from Equation (ix) are given in **Table V**.

Temperature,	Specific heat,	Temperature,	Specific heat,	Temperature,	Specific heat,
К	J mol ^{−1} K	К	J mol ^{−1} K	К	J mol ⁻¹ K
10	0.0417	90	14.448	210	22.928
15	0.116	100	15.939	220	23.163
20	0.290	110	17.182	230	23.441
25	0.636	120	18.231	240	23.715
30	1.252	130	19.132	250	23.929
35	2.104	140	19.912	260	24.119
40	3.139	150	20.577	270	24.290
45	4.322	160	21.085	280	24.444
50	5.604	170	21.533	290	24.584
60	8.205	180	21.975	293.15	24.625
70	10.563	190	22.377	298.15	24.688
80	12.661	200	22.695	300	24.711

Table IV Low-Temperature Specific Heat Values for Osmium

Table V

Selected High-temperature Specific Heat Values for Osmium

Temperature,	Specific heat,	Temperature,	Specific heat,	Temperature,	Specific heat,
К	J mol ^{–1} K	К	J mol ^{−1} K	К	J mol ^{−1} K
293.15	24.625	500	26.034	800	26.994
298.15	24.688	550	26.219	900	27.301
300	24.711	600	26.386	1000	27.626
350	25.208	650	26.543	1100	27.975
400	25.555	700	26.694	1200	28.351
450	25.819	750	26.844	1300	28.757

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