

Crystallographic Properties of Rhodium

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The crystallographic properties of rhodium at temperatures from absolute zero to its melting point are assessed following a review of the literature published during the period 1915 to date. Selected values of thermal expansion coefficients and length change measurements have been used to calculate the variations with temperature of lattice parameters, interatomic distances, atomic and molar volumes and density. Literature values are compared graphically with the selected values.

Rhodium exists in a face-centred cubic structure (Pearson symbol cF4) at temperatures up to its melting point, which is a proposed secondary fixed point on the International Temperature Scale, ITS-90, at 2236 K (1). In the low temperature region high precision thermal expansion data are only available up to 85

K and at 283 K. Interpolation in the region 85 to 283 K is estimated from a relationship between thermal expansion and specific heat, as explained in a previous review on platinum (2).

The adoption of this procedure for rhodium is justified on the grounds that the equation leads

Low Temperature Thermal Expansion Data		
0–29 K:	$\alpha = 2.10040 \times 10^{-9} T + 9.38048 \times 10^{-13} T^2 + 1.49885 \times 10^{-14} T^3 - 5.37107 \times 10^{-18} T^7 K^{-1}$	(i)
29–293 K:	$\alpha = C_p (3.34487 \times 10^{-7} + 3.07676 \times 10^{-11} T - 8.09712 \times 10^{-7}/T) K^{-1}$	(ii)
Low Temperature Thermal Expansion Data (Spline-Fitted Equations above 28 K)		
28–43 K:	$\alpha = 1.42465 \times 10^{-6} - 1.49903 \times 10^{-7} T + 5.42200 \times 10^{-9} T^2 - 6.61429 \times 10^{-11} T^3 + 3.88252 \times 10^{-13} T^4 K^{-1}$	(iii)
43–73 K:	$\alpha = 3.00727 \times 10^{-6} - 2.74766 \times 10^{-7} T + 8.55939 \times 10^{-9} T^2 - 8.91803 \times 10^{-11} T^3 + 3.34747 \times 10^{-13} T^4 K^{-1}$	(iv)
73–129 K:	$\alpha = -3.68548 \times 10^{-6} + 1.16152 \times 10^{-7} T - 1.16331 \times 10^{-10} T^2 - 2.76292 \times 10^{-12} T^3 + 9.75521 \times 10^{-15} T^4 K^{-1}$	(v)
129–223 K:	$\alpha = -5.48931 \times 10^{-6} + 1.84281 \times 10^{-7} T - 1.06785 \times 10^{-9} T^2 + 3.06789 \times 10^{-12} T^3 - 3.48862 \times 10^{-15} T^4 K^{-1}$	(vi)
223–293 K:	$\alpha = 2.18328 \times 10^{-6} + 4.28844 \times 10^{-8} T - 8.37574 \times 10^{-11} T^2 + 4.65408 \times 10^{-15} T^3 + 1.06597 \times 10^{-16} T^4 K^{-1}$	(vii)

High Temperature Thermal Expansion Data

$$\delta a/a_{293.15\text{ K}} = -2.30544 \times 10^{-3} + 7.24305 \times 10^{-6} T + 2.22307 \times 10^{-9} T^2 - 4.24678 \times 10^{-13} T^3 + 2.43319 \times 10^{-16} T^4 \quad (\text{viii})$$

$$\alpha^* = 7.24305 \times 10^{-6} + 4.44614 \times 10^{-9} T - 1.274034 \times 10^{-12} T^2 + 9.73276 \times 10^{-16} T^3 \text{ K}^{-1} \quad (\text{ix})$$

to a close agreement with the length change measurements of Erling (3) in this region (see the section entitled "Comparison with Other Data", below). In the high temperature region crystallographic properties are based entirely on lattice parameter measurements.

Thermal Expansion

Low Temperature Region

In the low temperature region the thermodynamic thermal expansion coefficient, α , is based on the measurements made by White and Pawlowicz (4) at 3–85 K and 283 K, except for the value at 283 K which was revised by White (5) to $(8.40 \pm 0.10) \times 10^{-6} \text{ K}^{-1}$. The thermal expansion coefficients were represented by Equations (i) and (ii) where the second equation is derived as described in the review on platinum (2) using specific heat measurements

tabulated by Furukawa, Reilly and Gallagher (6), which were incorporated into an assessment of the thermodynamic properties of rhodium by the present author (7).

Equation (i) is accurate to $4 \times 10^{-10} \text{ K}^{-1}$, while Equation (ii) is accurate to $2 \times 10^{-8} \text{ K}^{-1}$ below 85 K but decreasing to $1 \times 10^{-7} \text{ K}^{-1}$ at 283 K. Equation (ii) was extrapolated to the reference temperature 293.15 K. Because the use of this Equation would require a knowledge of the specific heat values, it can also be represented by a series of spline-fitted polynomials, Equations (iii) to (vii), which agree with Equation (ii) to within $1 \times 10^{-9} \text{ K}^{-1}$.

High Temperature Region

In the high temperature region selected values are based on a close agreement between the lattice parameter measurements of Ross and

Table I
Values of Lattice Constants from the Literature

Authors	Reference	Lattice constant, nm at 293.15 K	Original temperature, K
Owen and Iball	12	0.38034	289.7
Owen and Yates	13	0.38036	291
Swanson, Fuyat and Ugrinic	14	0.38032	298
Anderson and Hume-Rothery	15	0.38033	293
Černohorsky	16	0.38038	294.7
Ross and Hume-Rothery	8	0.38033	295.8
Pawar	17	0.38034	301
Singh	18	0.38033	303
Schröder et al	9	0.38030	299
	Selected	0.38034 ± 0.00002	

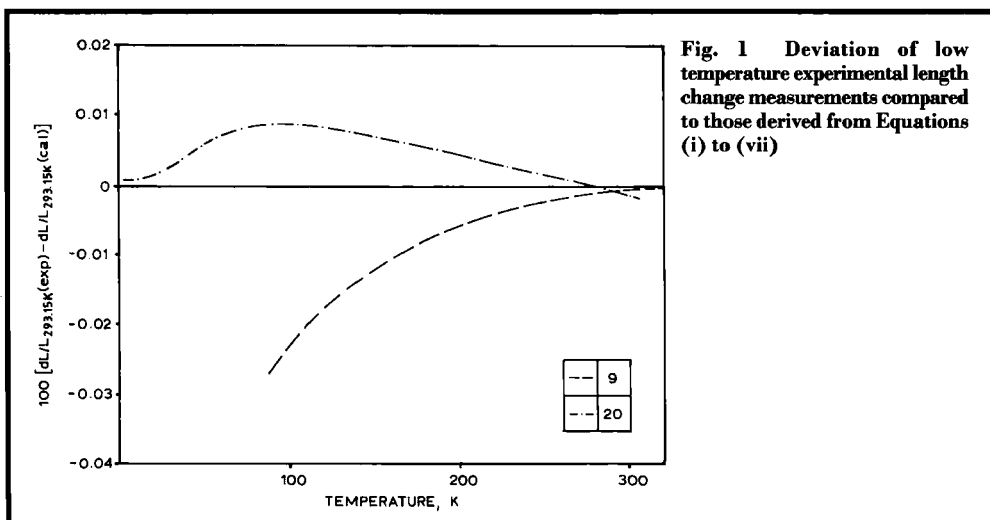


Fig. 1 Deviation of low temperature experimental length change measurements compared to those derived from Equations (i) to (vii)

Hume-Rothery (8) at 296 to 2223 K (but specifically the high precision measurements 296 to 1168 K) and those of Schröder, Schmitz-Pranghe and Kohlhaas (9) at 87 to 1942 K which were joined with the low temperature data and fitted to Equation (viii) with its derivative,

the thermal expansion coefficient relative to 293.15 K, α^* , being represented by Equation (ix). These equations representing the crystallographic data were extrapolated to the melting point of rhodium. A comparison between experimental and calculated values shows that

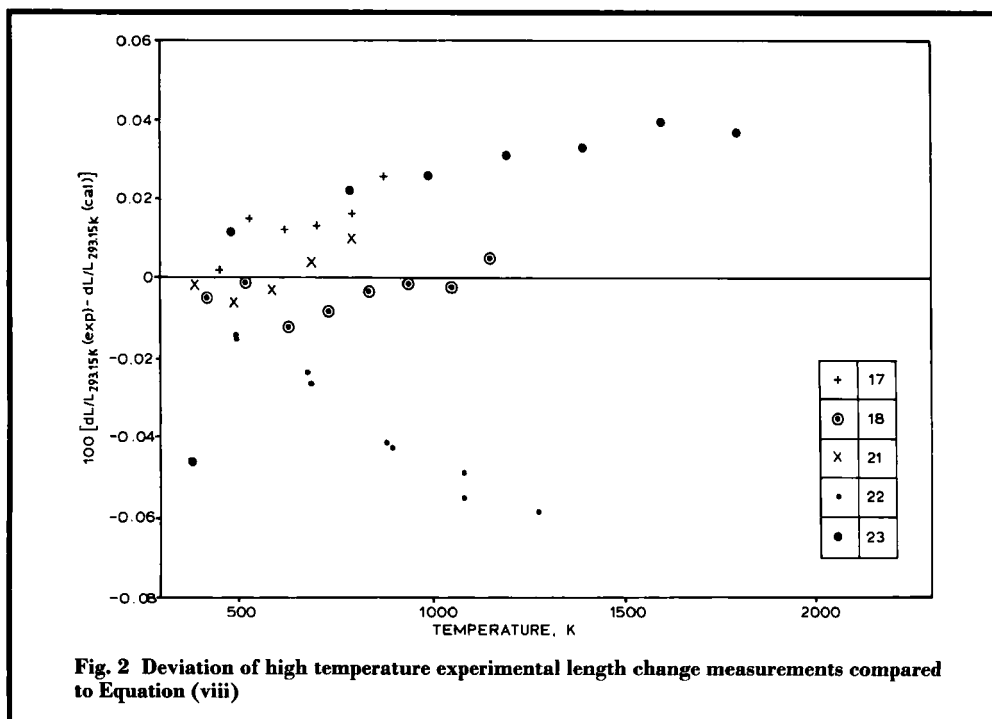


Fig. 2 Deviation of high temperature experimental length change measurements compared to Equation (viii)

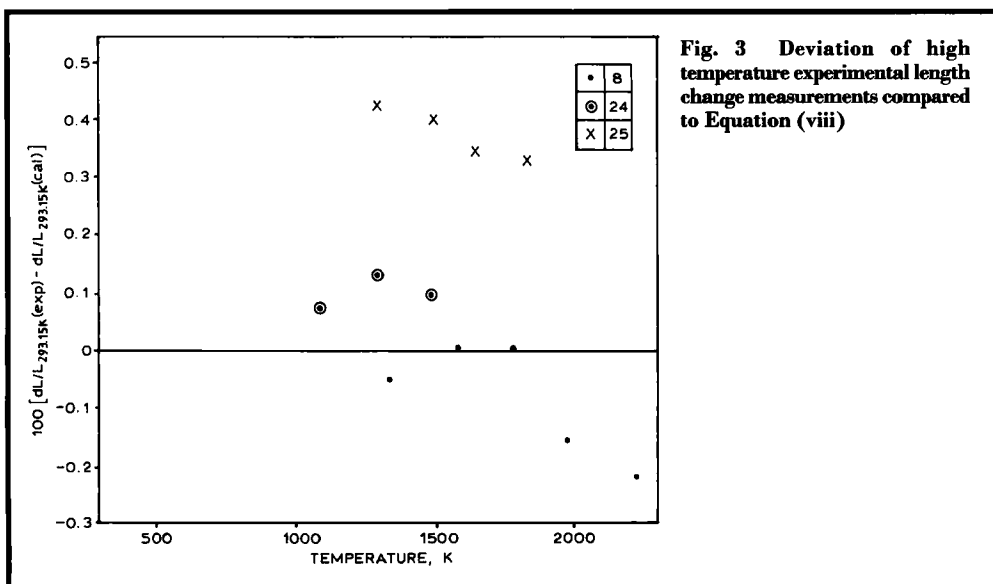


Fig. 3 Deviation of high temperature experimental length change measurements compared to Equation (viii)

Equation (viii) has an overall accuracy of 0.002 when considered in terms of the relationship: $100[\delta L/L_{293.15\text{ K}}(\text{experimental}) - \delta L/L_{293.15\text{ K}}(\text{calculated})]$.

Lattice Parameter at 293.15 K

In Table I are shown a combination of the values selected by Donohue (10) as well as more recent determinations both of which were corrected from kX and ångström units to nm using conversion factors recommended in the 1986 revision of the fundamental constants (11). Lattice parameter values were corrected to 293.15 K using thermal expansion coefficients selected in this review.

The values of molar volume and density in Table II were calculated using an atomic weight of 102.90550 (19) and an Avogadro's Constant of $6.0221367 \times 10^{23} \text{ mol}^{-1}$ (11).

Comparison with Other Data

On the basis of the relationship:

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

Figure 1 shows the deviation of the low temperature length change measurements made by Laquer (20) at 0–300 K and the measurements below 300 K of Schröder, Schmitz-Pranghe and Kohlhaas (9) taken at 87–1942 K. Not shown

are the measurements of Erling (3) at 58–273 K which agree with the selected values to within 0.001. On the same basis, Figure 2 shows the deviations of the dilatometric measurements made by Swanger (21) at 293–773 K, Holzmann (22) 293–1269 K and Ebert (23) 373–1773 K, and the lattice parameter measurements of Pawar (17) 301–860 K and Singh (18) 303–1138 K.

Figure 3, which is a coarser version of Figure 2, shows the deviation of the lattice parameter measurements of Raub, Beeskow and Menzel (24) 293–1473 K (results shown graphically only), the higher temperature measurements of Ross and Hume-Rothery (8) in the range 1323–2223 K (results shown graphically only) and the extraordinary deviant measurements of Bale (25) at 298–1819 K, shown only graphically with actual values being given by Touloukian and colleagues (26) – the expanded lattice found in these measurements may be due to severe oxygen contamination (27). Figure 4 shows the percentage deviation of the thermal expansion coefficients of Valentiner and Wallot (28) 96–287 K, which are 5 per cent lower to 6 per cent higher than the selected values, and the high temperature measurements of Glazov (29) 1200–2000 K which are 4 per cent lower

Table II
Crystallographic Properties

Temperature, K	Thermal expansion, $10^6 \times \alpha$, K^{-1}	Length change, $\Delta a/a$ $\times 100$	Lattice parameter, nm	Inter- atomic distance, nm	Atomic volume, 10^3 $\times nm^3$	Molar volume, $10^6 \times m^3$ mol^{-1}	Density, $kg m^{-3}$
0	0	-0.1603	0.37973	0.26851	13.689	8.244	12483
10	0.023	-0.1603	0.37973	0.26851	13.689	8.244	12483
20	0.091	-0.1603	0.37973	0.26851	13.689	8.244	12483
30	0.34	-0.1601	0.37973	0.26851	13.689	8.244	12483
40	0.86	-0.1595	0.37973	0.26851	13.689	8.244	12483
50	1.61	-0.1583	0.37974	0.26852	13.690	8.244	12482
60	2.41	-0.1563	0.37975	0.26852	13.690	8.245	12482
70	3.16	-0.1535	0.37976	0.26853	13.692	8.245	12481
80	3.85	-0.1500	0.37977	0.26854	13.693	8.246	12479
90	4.45	-0.1458	0.37979	0.26855	13.695	8.247	12478
100	4.98	-0.1411	0.37980	0.26856	13.697	8.248	12476
110	5.43	-0.1359	0.37982	0.26858	13.699	8.250	12474
120	5.83	-0.1303	0.37984	0.26859	13.701	8.251	12472
130	6.16	-0.1243	0.37987	0.26861	13.704	8.253	12470
140	6.46	-0.1180	0.37989	0.26862	13.706	8.254	12467
150	6.71	-0.1114	0.37992	0.26864	13.709	8.256	12465
160	6.94	-0.1046	0.37994	0.26866	13.712	8.257	12462
180	7.32	-0.0903	0.38000	0.26870	13.718	8.261	12457
200	7.61	-0.0754	0.38005	0.26874	13.724	8.265	12451
220	7.86	-0.0599	0.38011	0.26878	13.730	8.268	12446
240	8.07	-0.0440	0.38017	0.26882	13.737	8.272	12440
260	8.24	-0.0277	0.38023	0.26887	13.743	8.276	12433
280	8.38	-0.0111	0.38030	0.26891	13.750	8.281	12427
293.15	8.46	0	0.38034	0.26894	13.755	8.283	12423
300	8.48	0.006	0.38036	0.26896	13.757	8.285	12421
400	8.87	0.093	0.38069	0.26919	13.793	8.306	12389
500	9.25	0.183	0.38104	0.26943	13.831	8.329	12355
600	9.64	0.278	0.38140	0.26969	13.870	8.353	12320
700	10.03	0.377	0.38177	0.26995	13.911	8.377	12284
800	10.43	0.479	0.38216	0.27023	13.954	8.403	12246
900	10.86	0.586	0.38257	0.27052	13.998	8.430	12207
1000	11.31	0.698	0.38299	0.27082	14.045	8.458	12167
1100	11.79	0.814	0.38344	0.27113	14.094	8.487	12125
1200	12.31	0.936	0.38390	0.27146	14.145	8.518	12081
1300	12.87	1.063	0.38438	0.27180	14.198	8.550	12035
1400	13.48	1.196	0.38489	0.27216	14.254	8.584	11988
1500	14.14	1.336	0.38542	0.27253	14.314	8.620	11938
1600	14.86	1.483	0.38598	0.27293	14.376	8.657	11886
1700	15.64	1.638	0.38657	0.27335	14.442	8.697	11832
1800	16.50	1.801	0.38719	0.27379	14.512	8.739	11775
1900	17.42	1.974	0.38785	0.27425	14.586	8.784	11716
2000	18.43	2.157	0.38854	0.27474	14.664	8.831	11653
2100	19.52	2.351	0.38928	0.27526	14.748	8.881	11587
2200	20.69	2.557	0.39006	0.27582	14.837	8.935	11517
2236	21.14	2.634	0.39036	0.27602	14.871	8.955	11491

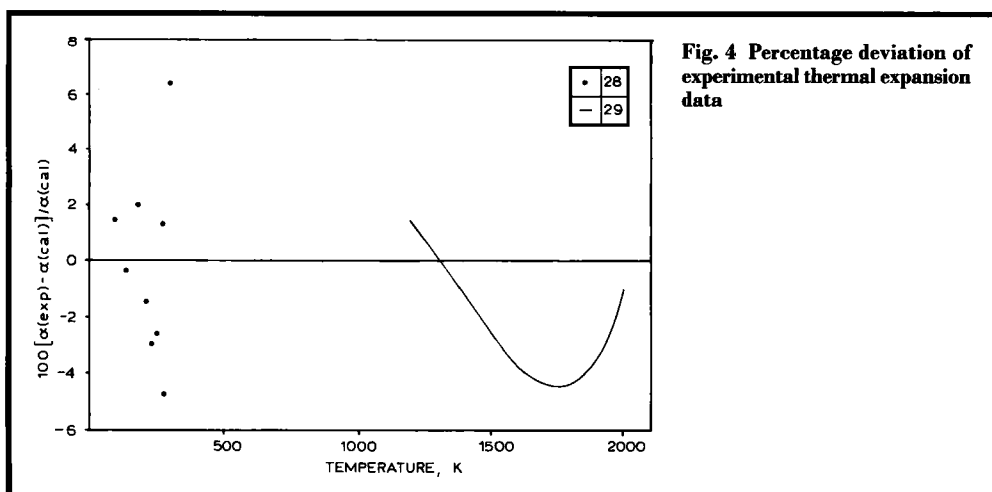


Fig. 4 Percentage deviation of experimental thermal expansion data

to 1 per cent higher. Since selected values of the thermal expansion coefficient in the high temperature region are derived from the length

change measurements then the agreement with the values of Glazov must be considered to be reasonable.

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Crystallographic Properties of Platinum

In the January 1997 issue of *Platinum Metals Review*, on page 18, in Figure 4, the percentage deviation of experimental thermal expansion data, the label on the vertical axis should have been $100[\alpha(\text{exp}) - \alpha(\text{cal})]/\alpha(\text{cal})$.