

Crystallographic Properties of Platinum

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Crystallographic and bulk properties of platinum from absolute zero to the melting point are assessed from a review of the literature covering the period 1901 to date. Selected values of thermal expansion are used to calculate the variation with temperature of length changes, lattice parameters, inter-atomic distances, atomic and molar volumes, and density. The crystallographic properties are based mainly on the precise dilatometric thermal expansion data, including corrections to account for thermal vacancy effects at the highest temperatures. Literature values are compared graphically with the selected values, and an Appendix is included to explain some of the terms used.

Platinum exists in a face-centred cubic structure (Pearson symbol cF4) up to the melting point, which is a proposed secondary fixed point on the International Temperature Scale, ITS-90, at 2041.3 K (1). High precision thermal expansion data for platinum is available up to 85 K and from 246 to 1900 K which allows the use of this metal as a thermal expansion standard above room temperature. In the temperature interval from 85 to 246 K thermal expansion values are estimated from a relationship between thermal expansion and specific heat developed by the present author from earlier Russian work (see Appendix). The close agreement between experimental length change measurements in this region and those obtained by integrating the estimated thermal expansion values gives validity to this approach to interpolation.

Only the lattice parameter at 293.15 K (20°C) has been used in deriving the crystallographic properties, all other values are based on the precision dilatometric measurements and include the thermal vacancy corrections which apply above 1300 K. The large scatter in the lattice parameter measurements, especially at high temperatures, is surprising for an element which is inert and obtained in very high purity. This scatter precludes comparison with the dilatometric data to obtain an independent estimate of the thermal vacancy parameters.

Thermal Expansion

Of the 22 sets of thermal expansion data tabulated by Touloukian and co-workers (2) in 1975, Kirby (3) considered that only those of: Holborn and Day (4) from 273 to 1273 K, Austin (5) from 273 to 1173 K, White (6) 3 to 85 and 283 K and Hahn and Kirby (7) 293 to 1900 K, as well as the more recent measurements of Edsinger, Reilly and Schooley (8) 246 to 841 K, satisfy the necessary criteria of sensitivity of method and purity of the materials used, and of these only those of Edsinger, Reilly and Schooley were

Low Temperature Thermal Expansion Data		
0–26 K:	$\alpha = 1.83531 \times 10^{-9} T + 4.86241 \times 10^{-11} T^3 + 5.06150 \times 10^{-14} T^5 - 6.06097 \times 10^{-17} T^7 \text{ K}^{-1}$	(i)
26–71 K:	$\alpha = C_p (3.84248 \times 10^{-7} - 3.38481 \times 10^{-10} T - 1.12981 \times 10^{-6} / T) \text{ K}^{-1}$	(ii)
71–272 K:	$\alpha = C_p (3.51722 \times 10^{-7} - 2.73616 \times 10^{-12} T - 5.20350 \times 10^{-7} / T) \text{ K}^{-1}$	(iii)

reported in sufficient detail to allow an unambiguous temperature scale correction (from IPTS-68 to ITS-90).

In the low temperature region the thermodynamic thermal expansion coefficient, α , is based on the measurements of White (6) and Edsinger, Reilly and Schooley (8). The derivation of Equations (ii) and (iii) is explained in the Appendix.

The values of C_p are taken from the recent review by the present author (9). Equation (i) is accurate to $\pm 3 \times 10^{-10} \text{ K}^{-1}$ and Equations (ii) and (iii) to $\pm 2 \times 10^{-8} \text{ K}^{-1}$. Although Kirby (3) used a different approach to interpolate within the range 85 to 245 K, calculated values of α^* in this region agree to within $7 \times 10^{-8} \text{ K}^{-1}$. Since Table II is given at relatively wide temperature intervals at low temperature, a knowledge of C_p is required in order to use Equations (ii) and (iii). For inter-

polation this requirement has been overcome by fitting smoothed values of α calculated from Equations (ii) and (iii) to a series of spline-fitted polynomials, Equations (iv) to (vii).

In the high temperature region selected values of α^* , defined in the Appendix, are based on the measurements of Holborn and Day (4) (to 1023 K), Austin (5) (to 873 K), Hahn and Kirby (7) and Edsinger, Reilly and Schooley (8), see Equation (viii).

Equation (viii) for α^* has an overall accuracy of $\pm 2 \times 10^{-8} \text{ K}^{-1}$ and agrees with the interpretation of the same data by Kirby (3) to within $5 \times 10^{-8} \text{ K}^{-1}$.

Because of the scatter in the lattice parameter data, Equations (i) to (ix), were used to represent both the crystallographic and bulk properties of platinum up to the melting point, with

Low Temperature Thermal Expansion Data (Spline-Fitted Equations above 25 K)	
25-40 K:	$\alpha = 8.98456 \times 10^{-6} - 1.14388 \times 10^{-6} T + 5.36960 \times 10^{-8} T^2 - 1.00997 \times 10^{-9} T^3 + 7.07395 \times 10^{-12} T^4 \text{ K}^{-1}$ (iv)
40-85 K:	$\alpha = -1.71786 \times 10^{-6} + 5.94864 \times 10^{-8} T + 2.55729 \times 10^{-9} T^2 - 4.04451 \times 10^{-11} T^3 + 1.75555 \times 10^{-13} T^4 \text{ K}^{-1}$ (v)
85-200 K:	$\alpha = -3.58576 \times 10^{-6} + 2.09166 \times 10^{-7} T - 1.50863 \times 10^{-9} T^2 + 5.23922 \times 10^{-12} T^3 - 7.09562 \times 10^{-15} T^4 \text{ K}^{-1}$ (vi)
200-277 K:	$\alpha = -2.05384 \times 10^{-5} + 4.71823 \times 10^{-7} T - 2.91766 \times 10^{-9} T^2 + 8.10650 \times 10^{-12} T^3 - 8.44311 \times 10^{-15} T^4 \text{ K}^{-1}$ (vii)
High Temperature Dilatometric Thermal Expansion	
	$\alpha^* = 7.08788 \times 10^{-6} + 1.04970 \times 10^{-8} T - 2.00846 \times 10^{-11} T^2 + 2.28200 \times 10^{-14} T^3 - 1.18453 \times 10^{-17} T^4 + 2.37348 \times 10^{-21} T^5 \text{ K}^{-1}$ (viii)
	$\delta L/L_{293.15 \text{ K}} = 7.08788 \times 10^{-6} T + 5.24850 \times 10^{-9} T^2 - 6.69487 \times 10^{-12} T^3 + 5.70500 \times 10^{-15} T^4 - 2.36906 \times 10^{-18} T^5 + 3.95580 \times 10^{-22} T^6 - 2.39745 \times 10^{-3}$ (ix)
High Temperature Lattice Parameter Thermal Expansion	
	$\delta a/a_{293.15 \text{ K}} = dL/L_{293.15 \text{ K}} - (1/3)e^{(1.32 - 17523/T)}$ (x)
	$\alpha^*_{(\text{lattice})} = \alpha^*_{(\text{dilatometric})} - (5841/T^2) e^{(1.32 - 17523/T)} \text{ K}^{-1}$ (xi)

the crystallographic properties in the high temperature range calculated from the dilatometric data by taking into account thermal vacancy effects.

Unfortunately, there are no absolute measurements of the thermal vacancy concentration, c_v (that is simultaneous measurements of dilatometric and lattice thermal expansion) but such measurements for copper (10), silver (11), gold (12) and aluminium (13) suggest a common value of $(7 \pm 2) \times 10^{-4}$ at the melting point. The enthalpy of monovacancy formation in platinum, H_v^f , is now well established as 1.51 eV (14–16) and adopting the above value of c_v leads to a value for the entropy of monovacancy formation, S_v^f , of $(1.32 \pm 0.3)k$ (k is the Boltzmann Constant), which is in excellent agreement with values of $1.3k$, calculated by Schumacher, Seeger and Härlin (17) from a re-analysis of the self-diffusion experiments of Kidson and Ross (18) and Cattaneo, Germagnoli and Grasso (19), and $1.45k$ estimated by Heigl and Sizmann (15) from results using a millisecond heat pulse technique. Therefore a value for c_v of 7×10^{-4} at the melting point is adopted for platinum, and

the lattice thermal expansion can be related to the dilatometric thermal expansion as in Equations (x) and (xi).

Lattice Parameter at 293.15 K

A combination of those values selected by Donohue (20) as well as more recent determinations were corrected from kX and ångström units to nm using conversion factors recommended in the 1986 review of the fundamental constants (21). Lattice parameters were corrected to 293.15 K using thermal expansion coefficients selected in this review.

Density values in Table II were calculated using an atomic weight of 195.078 (36) and $6.0221367 \times 10^{23} \text{ mol}^{-1}$ for Avogadro's Constant (21). Crystallographic and bulk properties, Tables II and III, respectively, would be identical below 1300 K.

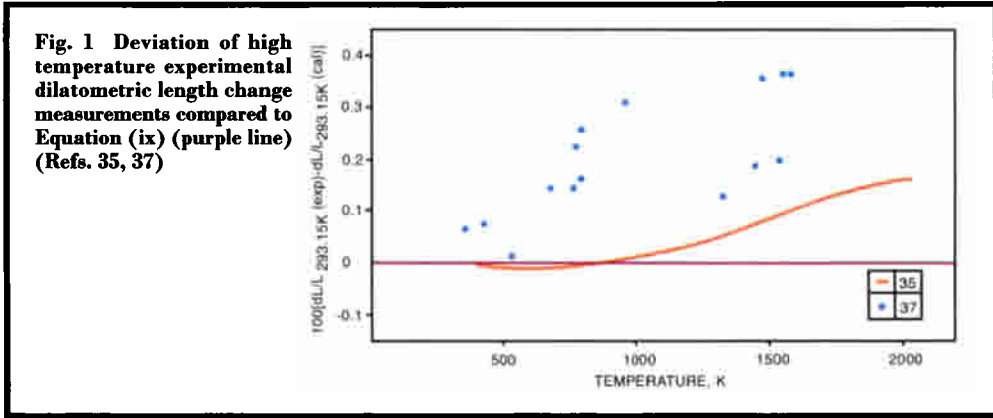
Comparison with Other Data

Figure 1 shows those dilatometric measurements which differ notably from the selected values – the measurements of Vertogradskii (37) 356–1589 K and the direct density measurements of Stankus and Khairulin (35) 293–2042 K. The

Authors	Reference	Lattice constant at 293.15 K, nm	Original temperature, K
Van Arkel	22	0.39223	rt*
Stenzel and Weerts	23	0.39232	293
Owen and Yates	24	0.39240	291
Owen and Yates	25	0.39244	288
Moeller	26	0.39226	293
Esch and Schneider	27	0.39239	rt*
Goldschmidt and Land	28	0.39242	rt*
Grube, Schneider and Esch	29	0.39238	rt*
Swanson and Tatge	30	0.39232	298
Kidron	31	0.39237	298
Evans and Fischer	32	0.39236	293
Schröder and co-workers	33	0.39234	297
Waseda, Hirata and Ohtani	34	0.39241	298
Stankus and Khairulin	35	0.39240**	293
	Selected	0.39236 ± 0.00006	

rt* is room temperature - no thermal expansion correction applied

** from direct density measurement 21445 kg m^{-3}



finer scale graph, see Figure 2, shows the dilatometric measurements of Cowder and colleagues (38) 293–1773 K and the AGARD (Advisory Group for Aerospace Research and Development) pooled data, as reported by Weisenburger (39) and 573–1173 K (five participants), Fitzer (40) 573–1273 K (average of ten participants) and Fitzer and Weisenburger

(41) 373–1873 K (five participants in all).

Not shown are the measurements of Dorsey (42) 93–293 K which, on the basis of:

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

agree with the selected values to within 0.001; and those of Scheel (43) 83–373 K, Scheel and Heuse (44) 90–289 K, Henning (45) 82–289 K,

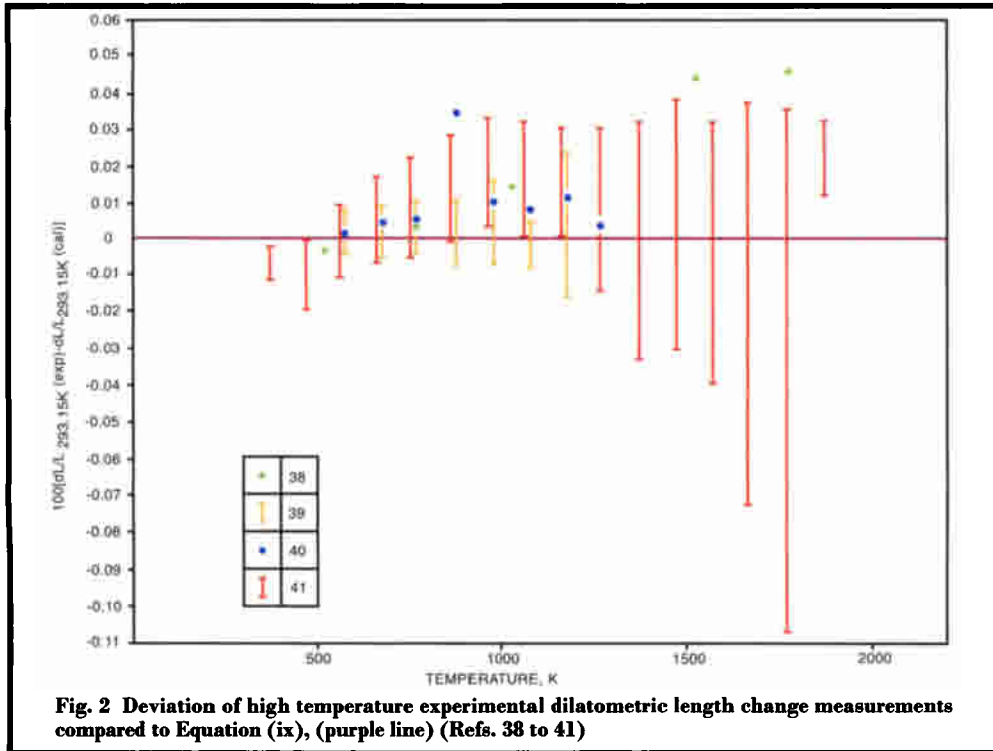


Table II
Crystallographic Properties

Temp., 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	-0.1933	0.39160	0.27690	15.013	9.041	21577
10	0.071	-0.1933	0.39160	0.27690	15.013	9.041	21577
20	0.51	-0.1930	0.39160	0.27690	15.013	9.041	21576
30	1.45	-0.1921	0.39161	0.27691	15.014	9.041	25176
40	2.61	-0.1900	0.39161	0.27691	15.015	9.042	21575
50	3.69	-0.1869	0.39163	0.27692	15.016	9.043	21573
60	4.60	-0.1827	0.39164	0.27693	15.018	9.044	21570
70	5.32	-0.1777	0.39166	0.27695	15.020	9.045	21567
80	5.89	-0.1722	0.39168	0.27696	15.023	9.047	21563
90	6.37	-0.1660	0.39171	0.27698	15.026	9.049	21559
100	6.77	-0.1595	0.39173	0.27700	15.028	9.050	21555
110	7.10	-0.1525	0.39176	0.27702	15.032	9.052	21550
120	7.37	-0.1453	0.39179	0.27704	15.035	9.054	21546
130	7.59	-0.1378	0.39182	0.27706	15.038	9.056	21541
140	7.78	-0.1301	0.39185	0.27708	15.042	9.058	21536
150	7.93	-0.1223	0.39188	0.27710	15.045	9.060	21531
160	8.07	-0.1143	0.39191	0.27712	15.049	9.063	21526
180	8.29	-0.0980	0.39198	0.27717	15.056	9.067	21515
200	8.46	-0.0812	0.39204	0.27722	15.064	9.072	21504
220	8.59	-0.0642	0.39211	0.27726	15.072	9.076	21493
240	8.70	-0.0469	0.39218	0.27731	15.079	9.081	21482
260	8.80	-0.0294	0.39224	0.27736	15.087	9.086	21471
280	8.89	-0.0117	0.39231	0.27741	15.095	9.091	21459
293.15	8.93	0	0.39236	0.27744	15.101	9.094	21452
300	8.95	0.006	0.39238	0.27746	15.103	9.095	21448
400	9.25	0.097	0.39274	0.27771	15.145	9.120	21389
500	9.48	0.191	0.39311	0.27797	15.187	9.146	21329
600	9.71	0.287	0.39349	0.27824	15.231	9.172	21268
700	9.94	0.386	0.39387	0.27851	15.276	9.199	21205
800	10.19	0.487	0.39427	0.27879	15.322	9.227	21142
900	10.47	0.591	0.39468	0.27908	15.370	9.256	21076
1000	10.77	0.698	0.39510	0.27938	15.419	9.285	21009
1100	11.10	0.808	0.39553	0.27968	15.469	9.316	20940
1200	11.43	0.921	0.39597	0.28000	15.522	9.347	20870
1300	11.77	1.038	0.39643	0.28032	15.576	9.380	20797
1400	12.11	1.159	0.39691	0.28066	15.632	9.414	20723
1500	12.48	1.284	0.39740	0.28100	15.690	9.448	20647
1600	12.86	1.412	0.39790	0.28136	15.749	9.484	20568
1700	13.31	1.545	0.39842	0.28173	15.811	9.522	20488
1800	13.86	1.683	0.39896	0.28211	15.876	9.561	20404
1900	14.58	1.827	0.39953	0.28251	15.944	9.601	20318
2000	15.57	1.981	0.40013	0.28294	16.016	9.645	20226
2041.3	16.07	2.047	0.40039	0.28312	16.047	9.664	20187

Table III Bulk Properties *				
Temperature, K	Thermal expansion, $10^6 \times \alpha, \text{K}^{-1}$	Length change, $\delta L/L \times 100$	Molar volume, $10^6 \times \text{m}^3 \text{mol}^{-1}$	Density, kg m^{-3}
1300	11.79	1.039	9.380	20797
1400	12.16	1.160	9.414	20723
1500	12.56	1.285	9.449	20646
1600	13.01	1.414	9.485	20567
1700	13.56	1.549	9.523	20485
1800	14.26	1.690	9.563	20400
1900	15.17	1.839	9.605	20310
2000	16.40	2.000	9.650	20214
2041.3	17.03	2.070	9.670	20173

* This Table would be identical to Table II below 1300 K

Nix and MacNair (45) 85–368 K, Branchereau, Navez and Perroux (46) 573 K, Amatuni and co-workers (47) 373–1273 K, and the interferometric measurements of participant no. 7 (373–1073 K) noted by Fitzer and Weisenburger (41), which all agree with the selected curve to within 0.002. The measurements of Esser and Eusterbrock (49) 273–1273 K agree to within 0.001 up to 973 K, then deviate up to 0.007 low. The single measurement of Masumoto and Kobayashi (50) at 313 K is 0.006 low.

The comparison of lattice parameters, see Figure 3, includes measurements by: Owen and Yates (25) 288–873 K, Shinoda (51) 288–1373 K, Esser, Eilander and Bungardt (52) 293–1373 K, Eisenstein (53) 1148 K, Edwards, Speiser and Johnston (54) 291–2005 K, Mauer and Bolz (55) 273–1663 K, Brand and Goldschmidt (56) 673–1607 K, Lui, Takahashi and Bassett (57) 286–701 K, Evans and Fischer (32) 293–1783 K, Schröder, Schmitz-Pranghe and Kohlhaas (33) 85–1933 K, and Waseda, Hirata and Ohtani (34) 298–2029 K. The scatter in the data, especially at high temperatures, indicates the difficulties in reaching conclusions concerning thermal vacancy effects by trying to match unrelated lattice and dilatometric measurements.

Figure 4 shows deviations of the thermal expansion coefficients reported by Valentiner and Wallot (58) 96–284 K, which are up to 3 per cent low, and those of Kraftmakher (59)

1000–1900 K which rise sharply upwards reaching 25 per cent higher than the selected value at 1900 K. The low temperature measurements of Andres (60) 2–13 K are reported in equation form, which gives a value at 10 K of $1.0 \times 10^{-8} \text{K}^{-1}$ (14 per cent) higher than the selected value.

Appendix

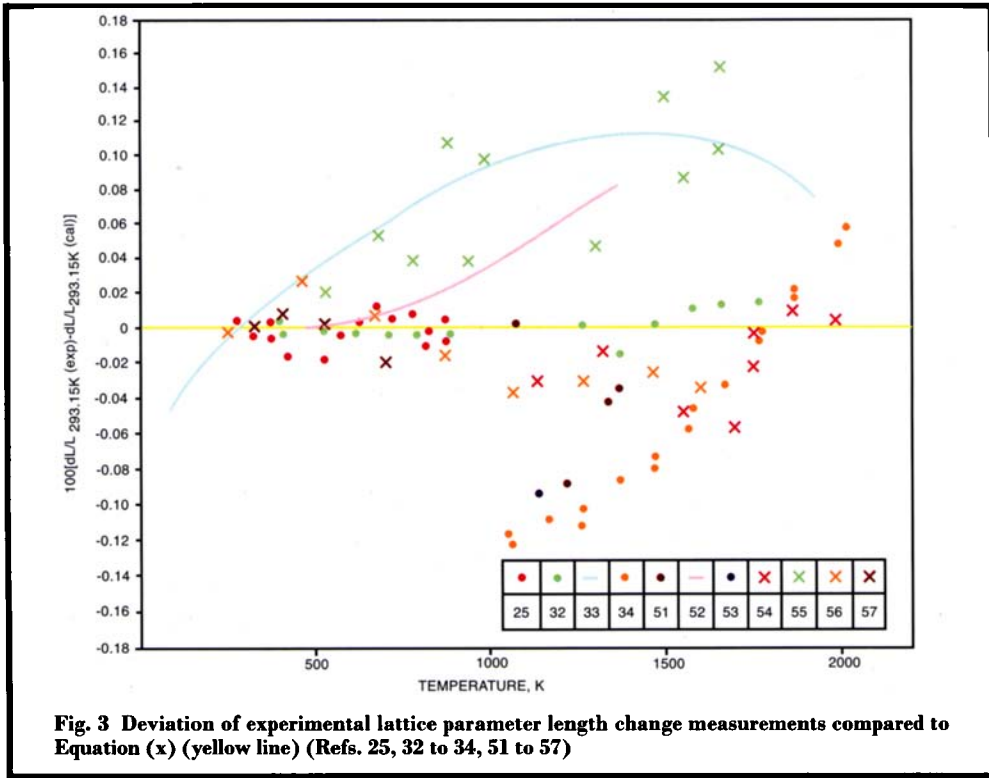
The Definition of Thermal Expansion

The thermodynamic thermal expansion coefficient, α , is the instantaneous change in length per unit length per degree or $(1/L)(\partial L/\partial T)$. In practice it is determined as a change in length over a very short temperature interval and over this length α is defined as $((L_2 - L_1)/L_1)/(T_2 - T_1)$ at the mean temperature $(T_2 + T_1)/2$. In the higher temperature region length changes are measured relative to a reference temperature such as 293.15 K (20°C) and are fitted to a polynomial as $(L_T - L_{ref})/L_{ref}$. Differentiation of this equation leads to the instantaneous thermal expansion coefficient relative to the reference temperature $\alpha^* = (1/L_{ref})(\partial L/\partial T)$; α and α^* are related by the Equation:

$$\alpha = \alpha^*/(1 + (L_T - L_{ref})/L_{ref})$$

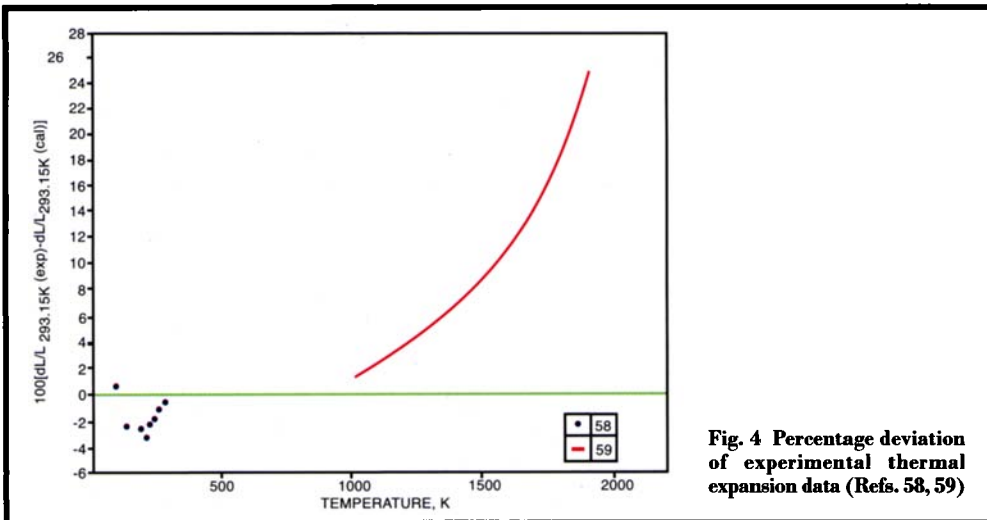
The kX Lattice Parameter Unit

The X unit (X.U.) was introduced by Seigbahn (61, 62) to be exactly equal to the milliångström unit (10^{-13}m) and is defined as being equal to



a lattice spacing of a calcite crystal. Throughout the 1930s and early 1940s X-ray wavelengths were defined in terms of this scale, and lattice spacing values were reported in 1000 X.U. (kX

units). However when the lattice spacings of different calcite crystals were shown to be variable and it was realised that the kX unit was 0.2 per cent too large because of an error in the



fundamental constants used in its original derivation, then by international agreement the kX unit was defined as being exactly equal to 1.00202 ångström units (63). Continual improvement in the determination of this ratio led in the 1986 revision of the fundamental constants (21) to a derivation that the kX unit was equivalent to $0.100207789 \pm 0.000000070$ nm on the scale in which the primary X-ray wavelength, Cu $K_{\alpha 1}$, is defined as being exactly 1537.400 X.U. All relevant lattice parameter values reported in the literature as being in kX units have been corrected using this ratio and those reported in conventional ångström units have been corrected using the ratio $0.100207789/1.00202$.

Precision Relationship between Thermal Expansion and Specific Heat

In the specific heat at constant pressure (C_p) version of the Grüneisen equation:

$$\alpha = (1/3) \Gamma C_p / B_s V$$

where α is the linear thermal expansion coefficient, Γ is the Grüneisen parameter, B_s is the adiabatic bulk modulus and V is the molar volume, α and C_p increase rapidly below room temperature, whereas Γ , B_s and V vary only slowly and can be lumped together as a weak function of temperature. Mel'nikova and co-workers (64–67) developed this relationship to:

$$\alpha = C_p (A + B T)$$

where A and B are constants and T is temperature, in order to represent the sparse thermal expansion coefficient data for the alkali metals lithium to rubidium. However the bulk of the thermal expansion data for these elements is in the form of length change measurements which are poorly represented by the constants chosen by Mel'nikova and colleagues, especially for sodium and potassium below 200 K.

An independent assessment of this equation for certain metals for which high quality thermal expansion and specific heat data is available below room temperature indicates that it gives a reasonable correlation down to about 150 K but is unsatisfactory below this temper-

ature. However it can be shown (68) that the addition of further terms to this basic equation does lead to a precision relationship between α and C_p in the form:

$$\alpha = C_p (A + BT + \sum_{n=1}^n C_n T^{-n})$$

which, when $n = 2$, leads to a fit of the thermal expansion coefficient data for aluminium and tungsten below 300 K to within $1.6 \times 10^{-8} \text{ K}^{-1}$ and $1.1 \times 10^{-8} \text{ K}^{-1}$, respectively, and for copper using either $n = 1$ or 2 to within $8 \times 10^{-9} \text{ K}^{-1}$. Therefore the behaviour of this equation suggests that it can be used for interpolation for the surprising number of metals for which high quality thermal expansion data is available only below 90 K and at room temperature. The order of the equation used depends on the quality of the available data and for platinum it is found that the best compromise is to use two equations both with $n = 1$ rather than a single equation or one of higher order.

The Thermal Vacancy Effect

The generation of thermal vacancies close to the melting point leads to a difference between macroscopic or bulk thermal expansion (dL/dT) and microscopic or lattice thermal expansion (da/dT) and this difference can be exploited in order to obtain an absolute value of the vacancy concentration parameter (c_v) as:

$$3((L_T - L_0)/L_0 - (a_T - a_0)/a_0)$$

where L_0 and a_0 are referred to a temperature at which c_v is zero but which can be assumed to be the reference temperature 293.15 K without any loss in accuracy. Considered only in terms of monovacancies and neglecting the effects of divacancies or interstitials, c_v can then be related to the entropy (S_v^f) and enthalpy (H_v^f) of vacancy formation as: $\exp(S_v^f/k - H_v^f/kT)$ where k is Boltzmann's Constant, $8.617385 \times 10^{-5} \text{ eV K}^{-1}$ (21) and T is temperature.

Therefore since the above two equations are equal, S_v^f and H_v^f can be determined by a measurement of the thermal expansion difference. Of other techniques which could be used these parameters can also be determined with a fair degree of accuracy from a combination of

electrical resistivity measurements on specimens with quenched-in vacancies and diffusion experiments (17). These measurements and a comparison with actual determinations for other

metals allow an accurate estimate of the thermal vacancy parameters for platinum even though absolute values have not yet been determined.

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Shiny Adhesive Platinum Coatings

The deposition of platinum coatings from electroplating baths onto various substrates has been written about here on previous occasions (1, 2). The use of Q-salts has been particularly successful, and finds commercial application for plating the turbine blades of jet engines, so extending the life of the blades and the time between replacements.

Now, researchers at Southampton University, England, have used platinum electroplating baths at the typical deposition temperature of 368 K, and at various potentials to examine the morphology of coatings produced on polished copper substrates (3).

They found that the morphology of the deposits depended strongly on the deposition potential. At a potential of -650 mV the deposit shows the cauliflower-like structure, typical of many high performance electroplates, and consists of many overlapping hemispheres, 0.5 to 2 μm in diameter. This coating is highly stressed, adhesion is poor and cracks are apparent; these increase as plating thickness increases.

As the potential is shifted to more negative values, such as -700 and -750 mV, which are potentials close to the peak in the current/potential response, the deposits appear shiny and highly reflective. Micrographs show very little structure, the deposits consisting of very small, tightly packed, crystallites. At the more negative potential the coatings display the strongest adhesion to the substrate and the crack density decreases. These deposits may be made at 13 mA cm^{-2} , with high current efficiency. At even more negative potentials, the morphology totally changes, structure then consists of angular grains of dimension $\sim 0.5 \mu\text{m}$; the appearance is metallic, but semi-bright, and all signs

of stress have disappeared. There are no cracks and adhesion is very good. With significant hydrogen evolution the current efficiency drops and the deposit becomes increasingly matt in appearance.

Thinner platinum layers, 0.5 to 1.2 μm thick, were also deposited. For thin deposits at potentials positive to -800 mV the deposits are highly reflecting with good adhesion to the substrate and no evidence of cracking, although any surface blemishes on the underlying copper were visible.

At a current density of 13 mA cm^{-2} and a constant potential of -750 mV, the deposition rate can reach 12.9 $\mu\text{g cm}^{-2} \text{s}^{-1}$ with high deposit quality, which is more than five times the maximum rate achieved with constant current control. At constant current control, the most similar deposition occurs at a current density of 2.5 mA cm^{-2} , corresponding to a plating rate of 2.4 $\mu\text{g cm}^{-2} \text{s}^{-1}$. The authors conclude that while it may be technically difficult to achieve constant potential deposition, nevertheless it does seem to have considerable advantages over the more usual constant current deposition, and stress- and crack-free coatings, thicker than 5 μm , can be produced. It is thus suggested that deposition at constant potential may provide a cheaper alternative for substrates which have a simple geometry.

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