

# Is Osmium Always the Densest Metal?

## A comparison of the densities of iridium and osmium

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Having established that osmium is the densest metal at room temperature the question arises as to whether it is always the densest metal. It is shown here that at ambient pressure osmium is the densest metal at all temperatures, although there is an ambiguity below 150 K. At room temperature iridium becomes the densest metal above a pressure of 2.98 GPa, at which point the densities of the two metals are equal at  $22,750 \text{ kg m}^{-3}$ .

### Introduction

Reviews by Crabtree (1) and the present author (2–5) established that at 293.15 K (20°C) osmium is the densest metal at  $22,589 \pm 5 \text{ kg m}^{-3}$  compared to  $22,562 \pm 11 \text{ kg m}^{-3}$  for iridium, the difference of  $27 \pm 12 \text{ kg m}^{-3}$  considered as confirming this. The question then arises as to whether osmium is always the densest metal. Although it would have been desirable to consider this in terms of a full pressure-temperature-volume evaluation, limited high pressure data for iridium confines the evaluation to just two aspects – the effect of temperature at ambient pressure and the effect of pressure at room temperature.

### The Effect of Temperature at Ambient Pressure

The thermal expansion of iridium is known with precision below room temperature, satisfactory up to 2000 K and estimated above this temperature (4) whilst the thermal expansion of osmium is known only between room temperature and 1300 K and is estimated below room temperature (5). Because the room temperature thermal

expansion coefficient of iridium at  $6.47 \times 10^{-6} \text{ K}^{-1}$  is higher than the average value for osmium at  $4.99 \times 10^{-6} \text{ K}^{-1}$ , it would be expected that with the greater contraction below room temperature iridium would be the densest metal at low temperatures. However this proves not to be the case with the density of osmium at 0 K being  $22,661 \pm 11 \text{ kg m}^{-3}$  compared to a value of  $22,652 \pm 11 \text{ kg m}^{-3}$  for iridium. The difference of  $9 \pm 16 \text{ kg m}^{-3}$  indicates an ambiguity and the possibility that iridium could be the densest metal statistically. Assuming that the assigned accuracy for osmium increases linearly from  $\pm 5 \text{ kg m}^{-3}$  at 293.15 K to  $\pm 11 \text{ kg m}^{-3}$  at 0 K then the density ambiguity exists below 150 K where the density difference becomes equal at  $14 \pm 14 \text{ kg m}^{-3}$ . The variation of the density of both elements over the range from 0 to 300 K is shown in **Figure 1**. In the high temperature region there is no ambiguity with the density difference increasing to  $147 \pm 12 \text{ kg m}^{-3}$  at 1300 K, the experimental limit for osmium, whilst comparison with neighbouring elements rhodium (6) and ruthenium (7) suggests that the average thermal expansion coefficient for osmium will continue to be lower than that of iridium so that osmium will remain the densest metal in the high temperature region.

### The Effect of Pressure at Room Temperature

The effect of pressure (P) on volume (V) is given in terms of a third order Birch–Murnaghan equation of state:

$$P = 1.5 B_0 (Y^{7/3} - Y^{5/3}) [1 + 0.75 (B'_0 - 4)(Y^{2/3} - 1)] \quad (\text{i})$$

where  $Y = V_0/V$  and  $V_0$  is the volume at zero pressure,  $B_0$  is the bulk modulus and  $B'_0$  is the pressure derivative of the bulk modulus. When  $B'_0 = 4$  the equation is said to be second order.

The equation indicates that the higher the value of  $B_0$  then the less compressible would be the material and

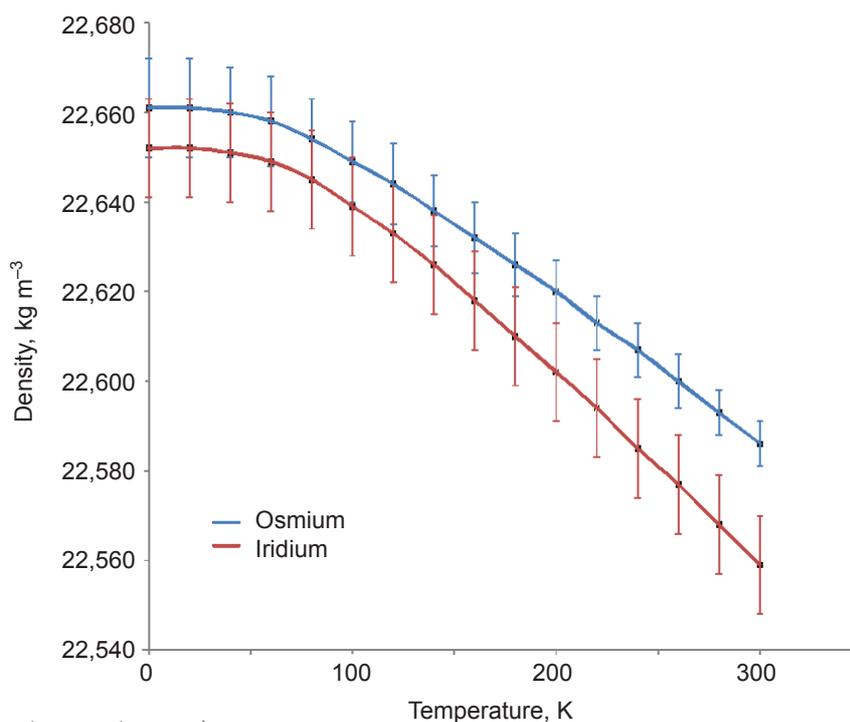


Fig. 1. Density in the low temperature region

therefore it was a complete surprise when Cynn *et al.* (8) determined the value of  $B_0$  for osmium to be 462 GPa compared to 443 GPa for diamond which appeared to overturn a long held belief that diamond was the least compressible element. This resulted in further measurements for osmium as indicated in **Table I** which suggest that the value determined by Cynn *et al.* appears to have been too high and subject to a systematic error which Liang and Fang (9) suggested was due to different quasi-hydrostatic conditions which were better determined in the later experiments. Distinction is made between determining the bulk modulus by elastic constant measurements (EC) and volume compression (VC).

The selected values are simple averages with the assigned accuracies encompassing all of the accepted values. The selected value of  $B_0$  for osmium is now less than that of diamond and therefore the latter regains its status as the least compressible element. Pantea *et al.* (14) showed that low temperature had little effect on the value of  $B_0$  for osmium with the value at 0 K being only 5 GPa greater than that at 300 K. However at high temperature Voronin *et al.* (13) showed a decrease of 58 GPa between 300 K and 1273 K.

Room temperature volume compression values for iridium are given in **Table II** with the cross-over pressures calculated from Equation (i) using selected values of  $V_0$  as  $8.5195 \pm 0.0042 \text{ cm}^3 \text{ mol}^{-1}$  for iridium (4) and  $8.4214 \pm 0.0013 \text{ cm}^3 \text{ mol}^{-1}$  for osmium (5).

Since the measurements of Cynn *et al.* (8) for osmium appear to be subject to a systematic error it is considered that the same error may apply to their measurements on iridium and that these values should not be considered further. The third order and second order equations determined from the measurements of Cerenius and Dubrovinsky (18) lead to pressure values which do not agree with each other or with the selected curve in the graphical representation. However values of  $B_0$  calculated from elastic constants measurements at 355 GPa for MacFarlane and Rayne (19) and 361 GPa for Adamesku *et al.* (20) show excellent agreement with the second order value of Cerenius and Dubrovinsky and it is considered possible that systematic errors in measurements which may have influenced the third order fit were restrained by the second order fit. The third order fit is therefore rejected. However the calculated cross-over pressure for the second order fit is well below the experimental limit of measurements at 10 GPa and therefore must initially be considered with some suspicion. The selected compressibility curve is therefore the interpretation by Gschneidner Jr. (21) of the pressure measurements of Bridgman (22) which up to 3 GPa can be represented by the equation:

$$V/V_0 = 1 - 2.775 \times 10^{-3} P - 2.64 \times 10^{-10} P^2 \quad (\text{ii})$$

where  $P$  is the pressure in GPa.

Table I. Determination of the Bulk Modulus of Osmium					
Authors	Reference	Method	B <sub>0</sub> , GPa	B' <sub>0</sub> , GPa	Notes
Cynn <i>et al.</i>	(8)	VC	462 ± 12	2.4 ± 0.5	(a)
Joshi <i>et al.</i>	(10)	VC	434	(4.0)	(b)
Kenichi	(11)	VC	395 ± 15	4.5 ± 0.5	
Occelli <i>et al.</i>	(12)	VC	411 ± 6	4.0	
Voronin <i>et al.</i>	(13)	VC	435 ± 19	3.5 ± 0.8	
Pantea <i>et al.</i>	(14)	EC	405 ± 5	–	
Pandey <i>et al.</i>	(15)	EC	411.9	–	
Armentrout and Kavner	(16)	VC	421 ± 3	(4.0)	
Chen <i>et al.</i>	(17)	VC	390 ± 6	(4.0)	
		Selected	413 ± 25	4.0 ± 0.5	

Notes to Table I

(a) Not included in the average

(b) Revision of the measurements of Cynn *et al.* (8)

Table II. Determination of the Bulk Modulus of Iridium				
Authors	Reference	B <sub>0</sub> , GPa	B' <sub>0</sub> , GPa	Cross-over Pressure, GPa
Cynn <i>et al.</i>	(8)	383 ± 14	3.1 ± 0.8	–
Cerenius and Dubrovinsky	(18)	306 ± 23	6.8 ± 1.5	1.47
		354 ± 6	(4.0)	3.04

The cross-over pressure using Equations (i) and (ii) is 2.98 GPa at a density of 22,750 kg m<sup>-3</sup> in excellent agreement with the second order value of Cerenius and Dubrovinsky. In fact the agreement of the extrapolated values of the latter agree so closely with Equation (ii) at 3 GPa that they can be considered as being representative of the volume compression values for iridium from this pressure up to the experimental limit at 65 GPa.

The average value of B<sub>0</sub> from Equation (ii) at 355 GPa (21) is in such excellent agreement with the values obtained from the elastic constant measurements of MacFarlane and Rayne (19) and Adamesku *et al.* (20) and the second order value of Cerenius and Dubrovinsky (18) that 355 ± 10 GPa can be considered as representing the value of B<sub>0</sub> for iridium in the room

temperature region. A further room temperature value of 371 GPa (actually 37,800 kgf mm<sup>-2</sup>) selected by Darling (23) is almost certainly due to a different interpretation of the measurements of Bridgman.

Taking into account the assigned accuracies of the selected B<sub>0</sub> value for osmium and iridium the cross-over pressure is considered to be accurate to 5% (±0.15 GPa). Based on this value and the density values for the individual elements then the density at the cross-over point can be considered to be accurate to ±20 kg m<sup>-3</sup>. The behaviour of the density values with pressure in the relevant region 2.5 GPa to 3.5 GPa are shown in **Figure 2** where the value for iridium at 3.5 GPa is the second order value of Cerenius and Dubrovinsky.

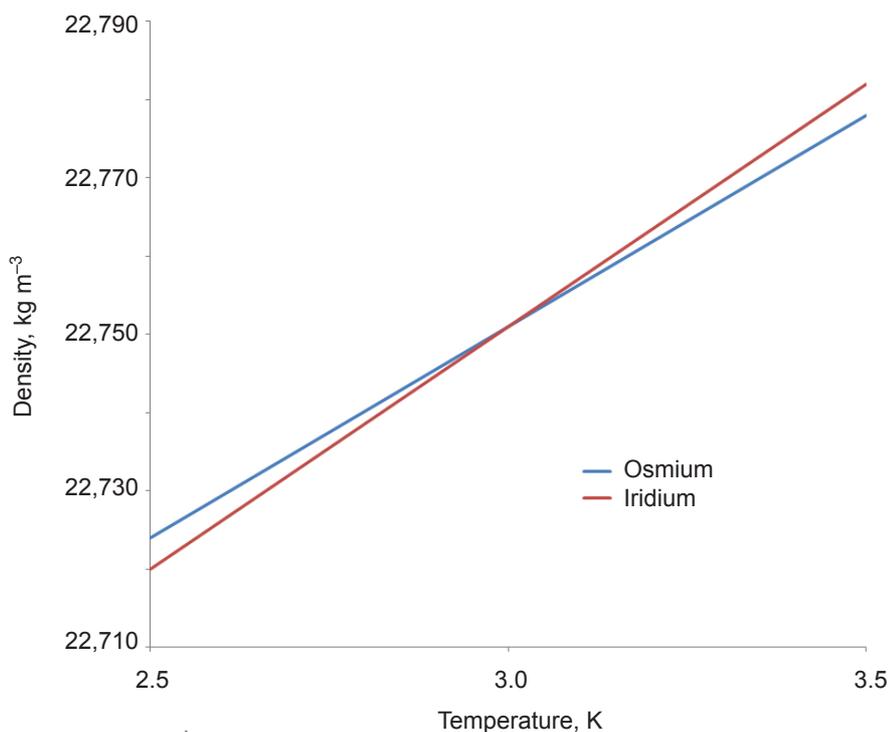


Fig. 2. Density in the cross-over region

## Conclusions

At ambient pressure it is shown that osmium appears to be the densest metal at all temperatures although there is an ambiguity below 150 K which will not be resolved until new measurements are carried out on the low temperature thermal expansion of osmium. At room temperature iridium appears to become the densest metal above a pressure of  $2.98 \pm 0.15$  GPa and a density of  $22,750 \pm 20$  kg m<sup>-3</sup>, although it is considered that further experimental determinations are definitely required. With the presently available data it is considered that representative room temperature  $B_0$  values are  $413 \pm 25$  GPa for osmium and  $355 \pm 10$  GPa for iridium.

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## The Author



John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.