# Selected Values of the
## Crystallographic Properties
## of the Elements

J O H N   W .   A R B L A S T E R

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# Preface

A unique and comprehensive review on the crystallographic properties of all of the elements. A general reference book for metallurgists and crystallographers. The book evaluates the crystallographic properties of all of the elements at ambient pressure in order to provide a base line for high pressure studies.

The book presents lattice parameters of the elements as a function of temperature. It also provides related properties, for example, thermal expansion coefficients, molar volumes and densities. This book is the first to include this data for all of the elements; it condenses all of the data in to a single volume with special attention given to ensure that the selected values correspond to the latest values of atomic weights and the fundamental constants.

The author, John Arblaster, spent his career as a metallurgical chemist analysing a wide variety of ferrous and non-ferrous metals and alloys in a number of commercial laboratories. He first became interested in crystallography in order to solve the dispute over whether osmium or iridium was the densest metal in the room temperature region. He showed, by proper application of up to date input data, that it was in fact osmium. He then produced comprehensive reviews on the crystallographic properties of the six platinum group of metals and has now extended this work to all of the elements. Background notes relating to this book can be obtained from the author at the e-mail address: jwarblaster@yahoo.co.uk

# Contents

The Elements

## A. INTRODUCTION

The main purpose of this book is to evaluate the crystallographic properties of all of the elements at ambient pressure in order to provide a base line for high pressure studies. The exception is of course helium which cannot be obtained as a solid at ambient pressure and is therefore considered on a temperature-pressure-volume basis. Allotropic modifications are considered for boron, carbon, oxygen, phosphorus, sulfur and selenium and separate isotopic evaluations are given for hydrogen, helium, lithium, boron, carbon, nitrogen, neon and silicon.

Compilations on the thermodynamic properties of the elements at the U.S. Bureau of Mines were introduced in 1934 (Kelley 1960) but the first comprehensive review on all of the elements appears to be that of Stull and Sinke 1956. However, until the present evaluation there does not appear to have been a similar detailed review on the crystallographic properties of the elements, although various aspects of such a review were contained in three *tours de force*, on the thermal expansion of the metallic elements by Touloukian et al. 1975, on the non-metallic elements by Touloukian et al. 1977, and on the crystal structures of the elements by Donohue 1974. Not only did Touloukian et al. 1975, 1977 contain extensive bibliographies but they also included a significant amount of data which was originally given only in the form of graphs. They also gave representative equations, graphs and tables of both selected values and original thermal expansion and length change values. Although new data has resulted in many of the equations becoming obsolete there are still several which cannot be improved upon and have been accepted in the present publication with full acknowledgement. Donohue 1974 also included an extensive bibliography and, especially for the room temperature region, included all of the reported lattice parameter measurements available for each element. Values already rejected by Donohue 1974 were not included in the present evaluation. Although published over forty years ago, many of the room temperature lattice parameter values selected by Donohue 1974 are very close to values selected here once wavelength corrections are taken into account. A further very useful service provided in the review of Donohue 1974 was the correct description of axis sequencing for anisotropic structures which eliminated much confusion that had existed in the literature.

Other reviews included tables of thermal expansion for many elements by Kirby at al 1972 but without references. Goldak et al. 1966 reviewed the crystallographic properties of alpha zirconium, and Lloyd and Barrett 1966 reviewed alpha uranium. Wang and Reeber 1998 selected thermal expansion values for the body-centered cubic refractory metals vanadium, niobium, tantalum, molybdenum and tungsten, Reeber and Wang 1996a diamond, Reeber and Wang 1996b silicon and germanium, Wang and Reeber 1996 copper and Wang and Reeber 2000 aluminum. Lu et al. 2005 reviewed the thermal expansion of several metallic elements but appeared ultimately to have relied on the thermal expansion values given by Kirby et al. 1972 and Touloukian et al. 1975, as did Zhang et al. 2013 who carried out an assessment of the thermal expansion coefficients for forty two pure metals using a Debye-Grüneisen model.

## B. NOTATION

T = Temperature in kelvins

t = Temperature in degrees Celsius

RT = Room temperature

$\alpha$ = Thermodynamic thermal expansion coefficient in units of $K^{-1}$

$\alpha^*$ = Thermal expansion coefficient relative to 293.15 K in units of $K^{-1}$

$\varepsilon_T = (l_T - l_{293.15\,K})/\, l_{293.15\,K}$

$\varepsilon_0 = (l_T - l_{0\,K})/\, l_{0\,K}$

$L_T = 1 + \varepsilon_T$ or $1 + \varepsilon_0$

$\alpha_m = \varepsilon_T\, / \,(T - 293.15\ K)$

$100\Delta\varepsilon = 100\varepsilon_T$ experimental $- \,100\varepsilon_T$ calculated or $100\varepsilon_0$ experimental $- \,100\varepsilon_0$ calculated

For anisotropic structures $\varepsilon_T$ avr $= (V_T/V_{293.15})^{\frac{1}{3}} - 1$ where $V_T$ is the molar volume of the phase at temperature T and $V_{293.15}$ is the molar volume of the reference phase at 293.15 K. For anisotropic structures based on a baseline of 0 K then $\varepsilon_0$ avr $= (V_T/V_0)^{\frac{1}{3}} - 1$ where $V_0$ is the molar volume of the reference phase at 0 K.


## C. CONSTANTS

### C1. Reporting of Accuracy

A short hand method is adopted, i.e. 236.42 (2) is used to represent 236.42 ± 0.02 while 2.364 (4) x $10^{10}$ is used to represent (2.364 ± 0.004) x $10^{10}$ and 21.2 (1.2) is used to represent 21.2 ± 1.2

### C2. Avogadro Constant

This is required to calculate molar volumes and densities. The accepted value is that selected by Mohr et al. 2016a, 2016b for the 2014 CODATA fundamental physical constants: $N_A = 6.022140857$ (74) x $10^{23}$ $mol^{-1}$. At the level of accuracy given no molar volume or density values would be affected by correcting to the 2017 CODATA value of $N_A = 6.02214076$ x $10^{23}$ $mol^{-1}$ exactly (Newell et al. 2018)

### C3. Atomic Weights

Atomic weights are required to calculate density values from lattice parameter data. However, it is unfortunate that for the 2009 atomic weights ten elements, hydrogen, lithium, boron, carbon, nitrogen, oxygen, silicon, sulfur, chlorine and thallium, were no

longer given as single atomic weight values but only as a range of extreme values (Wieser and Coplen 2011). This is a highly unsatisfactory situation since the actual extreme values represent only a small fraction of the total and therefore cannot be considered as being fully representative of these elements. However, it was noted that in the graphical representations of the isotopic ratios that the 2007 atomic weights (Wieser and Berglund 2009) with their assigned accuracies would be representative of the vast majority of any materials likely to be encountered. Therefore, these values were used to calculate the density values. For the 2011 atomic weights (Wieser et al. 2013) only bromine and magnesium were treated in this manner and therefore the 2009 atomic weights were used for these elements. No further corrections of this type were included in the 2013 atomic weights (Meija et al. 2016) or in the 2015 atomic weights (CIAAW 2015) but were included for argon and lead in the 2017 atomic weights (Meija 2017). For the elements with no stable or very long lived isotopes, as well as for individual stable isotopes such as deuterium, helium 3, lithium 6 and 7, boron 10 and 11, carbon 13, nitrogen 15, neon 20 and 22 and silicon 28, atomic masses were selected from the review by Wang et al. 2017.

### C4. The Effect of Ambient Pressure on Selected Molar Volume and Density Values

Molar volume and density values calculated from lattice parameter measurements are necessarily those values obtained in a vacuum. However, at the level of accuracy assigned to these values the differences from values that would be obtained at ambient pressure (atmospheric pressure) are entirely negligible and the quoted values could be considered as equally applying in both vacuum and ambient pressure conditions. The density values selected for beta rhombohedral boron, alpha white phosphorus and germanium are based on directly determined ambient pressure values. An exception would be the ultra precision lattice parameter measurements for silicon 28 except that all values associated with silicon 28 experiments are determined in vacuum conditions. A further exception is of course helium where all values are subject to pressure and temperature effects.

### C5. Wavelength Scales

The traditional value for the conversion factor from kX to ångstroms at 1.00202 has long been superseded as indicated by the 2014 CODATA fundamental physical constants conversion factors for the primary X-ray wavelength standards (Mohr et al. 2016a, 2016b).

| Wavelength | Definition | Conversion Factor | Equivalent Value nm |
|---|---|---|---|
| Cu K$\alpha_1$ | 1.537400 kX | 0.100207697 (28) | 0.154059313 (43) |
| Mo K$\alpha_1$ | 0.707831 kX | 0.100209952 (53) | 0.070931711 (38) |
| W K$\alpha_1$ | 0.2090100 Å* | 0.100001495 (90) | 0.020901312 (19) |

Values given in kX units without wavelength standards were converted to nm using the above conversion factor for Cu K$\alpha_1$ while values given in ångstroms without wavelength standards were converted using the default ratio 0.100207697/1.00202. Bearden 1964 carried out a review of wavelengths where published values were adjusted so as to be

equivalent to the Mo Kα₁ definition of 707.831 x units. On this scale, Cu Kα₁ is equal to 1537.370 x units. Bearden 1967 returned to using Cu Kα₁ with the above definition 1537.400 x units. Therefore, all of the values given in Bearden 1964 which were related to Cu Kα₁ were converted to nm using the ratio 0.100207697 x 1.537400/1537.370 which is 1.00209652 x $10^{-4}$ which was used to construct the table of wavelength standards below, except for Cu Kα₂ which Bearden 1964 originally selected as 1541.198 x units which should have converted to 1.544398 Å* but was instead given as 1.544390 Å* which is equivalent to the value 1541.1905 x units which is used as a basis below. The only exception is MoKα₂ which is directly related to MoKα₁. The value of Kα is defined as being equal to (2 Kα₁ + Kα₂)/3.

| Element | Kα₁ nm | Kα₂ nm | Kα nm | Kβ nm |
|---|---|---|---|---|
| V | 0.250361 | 0.250744 | 0.250489 | 0.228445 |
| Cr | 0.228975 | 0.2293653 | 0.229105 | 0.208491 |
| Mn | 0.2101863 | 0.210583 | 0.204064 | 0.198025 |
| Fe | 0.1936082 | 0.1940020 | 0.1937395 | 0.175665 |
| Co | 0.1789002 | 0.1792887 | 0.1790297 | 0.162082 |
| Ni | 0.1657944 | 0.1661781 | 0.1659229 | 0.1500166 |
| Cu | Defined | 0.1544422 | 0.1541869 | 0.1392247 |
| Mo | Defined | 0.0713607 | 0.0710747 | - |

**C6. Reference Temperatures**

Although absolute zero would be the ideal fundamental reference temperature, difficulties still exist for several elements in obtaining low temperature measurements and in view of this the adoption of absolute zero is still not ideal although required for those elements which are either liquid or gaseous at 293.15 K. However, room temperature represents a pivotal point for thermal expansion measurements with traditionally a switch from low temperature thermal expansion coefficient measurements to high temperature length change measurements. For thermal expansion a reference temperature of 293.15 K (20°C) was adopted by the International Committee for Weights and Measures in 1931 (Doiron 2007).

**C7. Crystal Geometry – Volumes of the Unit Cell**

Cubic: $V = a^3$

Tetragonal: $V = a^2 c$

Orthorhombic: $V = abc$

Hexagonal: $V = (\sqrt{3}/2)\, a^2 c$

Rhombohedral: $V = a^3 \sqrt{(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$

Monoclinic: $V = abc \sin\beta$

Triclinic: $V = abc \sqrt{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha \cos\beta \cos\gamma)}$

## C8. Pearson Designations for the 14 Bravais Lattices

| Bravais lattice | Pearson Symbol |
|---|---|
| Cubic – primitive | cP |
| Cubic – body-centered | cI |
| Cubic – all face-centered | cF |
| Tetragonal – primitive | tP |
| Tetragonal – body-centered | tI |
| Orthorhombic - primitive | oP |
| Orthorhombic – one-face-centered | oS |
| Orthorhombic – body-centered | oI |
| Orthorhombic – all face-centered | oF |
| Hexagonal – primitive | hP |
| Rhombohedral – rhombohedral | hR |
| Monoclinic – primitive | mP |
| Monoclinic – one face-centered | mS |
| Triclinic - primitive | aP |

The number following the Pearson symbol is the number of atoms in the unit cell.

## D. THE RHOMBOHEDRAL – HEXAGONAL CONVERSION EQUATIONS

Elements crystallizing in the rhombohedral (hR) structure are also given in terms of an equivalent hexagonal (hP) structure because this facilitates the representation of thermal expansion data.

*Rhombohedral and hexagonal conversion equations*

$a_r$ and $\alpha$ represent the rhombohedral lattice spacing and inclusive angle while $a_h$ and $c_h$ represent the equivalent hexagonal lattice spacings

$$a_r^2 = a_h^2 / 3 + c_h^2 / 9; \quad \sin (\alpha / 2) = a_h / (2\, a_r)$$

$$a_h = 2\, a_r \sin (\alpha/2); \quad c_h = a_r \sqrt{(3 + 6 \cos \alpha)}$$

## E. REPRESENTATION OF THERMAL EXPANSION DATA

While high temperature thermal expansion data can usually be represented by simple linear or polynomial equations, low temperature data tends to behave in a more complex manner but can also be represented by a series of high order polynomials if sufficient high quality data is available. However, if the data is more limited then the approach suggested in Appendix A is adopted in which thermodynamic thermal expansion ($\alpha$) and specific heat ($C_p$) data were related to a high degree of correlation by means of the equation:

$$\alpha = C_p(A + B\,T + C/\,T) \tag{A}$$

Where A, B and C are constants.

When, instead of thermal expansion coefficients only limited length change values ($L_T$) were available below room temperature, then these were combined with values of absolute enthalpy ($H_T - H_0$) in the equation also suggested in Appendix A:

$$\ln(L_T) = (H_T - H_0)(D + E\,T + F/\,T) + G \tag{B}$$

Where D, E, F and G are constants.

Differentiation of equation B lead to thermal expansion:

$$\alpha = D\,C_p + E[C_p\,T + (H_T - H_0)] + F[C_p/\,T - (H_T - H_0)/\,T^2] \tag{C}$$

### F. GRAPHICAL DATA

Although a significant amount of data originally reported in the form of graphs was given as actual length change values by Touloukian et al. 1975, 1977 it is unfortunate that data subsequently continued to be reported in this form. It is considered that the accuracy of the graphs can be read to 0.5 mm of the original graphical scale and although the graphs can be expanded electronically to any size it is then reliant on the expertise in creating the graphs in the first place and this remains as a chief source of systematic errors. In order to smooth out estimates from the graphs, readings were fitted to straight lines or polynomials. The philosophy of reporting data only in graphical form is extraordinary because it diminishes the great effort in trying to obtain the best possible values experimentally.

### G. ACKNOWLEDGEMENTS

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