# Atomic-environment classification of the chemical elements

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## Abstract

Of the 103 known chemical elements, 96 crystallize in 52 different crystal structures. Included in these 52 structures are those which are stable under normal (298 K, 100 kPa) conditions (NC) as well as high or low temperature (HT/LT) and high pressure (HP) conditions, but with the O-, N-, and C-stabilized structures excluded as well as structures observed in thin films.

Of the 275 experimentally found and reported element modifications, 95% can be classified with just seven different atomic environment types (AETs), all belonging to the single-environment type. A single-environment type encompasses all structures in which all atoms present in the structure have the same AET.

The seven AETs observed are the octahedron, the cubo-octahedron, the twinned cubo-octahedron and the rhombic dodecahedron for metals, and the dumb-bell, the double link and the tetrahedron for non-metals.

With modified structural stability diagrams (SSDs) we show that under normal conditions the elements are simply separated into different AET domains. With the HT/LT and HP crystal structure data included in our SSDs, we predict for 31 elements the AET modification (so far unknown) to be found under HP or HT/LT conditions, based on our SSD-AET domains.

Finally, our investigation includes a comprehensive, critically evaluated crystallographic data set for all element modifications as well as a recommended atomic volume table. These volumes are calculated from the unit cell volume divided by the number of atoms per unit cell.

## 1. Introduction

In this paper we present a classification of the chemical elements according to the atomic environments as realized in the solid state. We observed that the 96 elements crystallize in 52 different structure types, including the modifications formed under normal (298 K, 100 kPa) conditions (NC) as well as those formed under high pressure (HP) and high or low temperature (HT/LT) conditions. Apart from the modifications excluded already, we also excluded the boron structure types because they are very complex structures and it is probably better to described them as structure types built up from clusters of boron atoms. For example, the $hR12$ B structure type can be described as a close packing of boron clusters, each cluster being an icosahedron formed by 12 boron atoms (with no central atom, which is in contrast to our AETs). From ref. 1 we know that other boron structures can be described in terms of boron clusters with up to 156 atoms.

From these experimental facts it can be concluded that the common idea that bonding in the elements is simple is incorrect. The bonding situation in the elements is in fact very complicated, almost as complicated as in intermetallic compounds, where we often have a mixture of metallic, covalent and ionic bonding and where it is very difficult to predict proportions.

The electrical conductivities of the elements [2] give the possibility of dividing them into metals and non-metals (see Table 1). We define the elements with an electrical conductivity greater than $10^4 \ \Omega^{-1} \ cm^{-1}$ as metals and those with a conductivity of $10^4 \ \Omega^{-1} \ cm^{-1}$ or less as non-metals (indicated by a bold frame in Table 1). It is interesting that all metals have a conductivity in the range between $10^5$ and $10^7 \ \Omega^{-1} \ cm^{-1}$, Ag being the best and Pu the worst conductor, compared with the non-metals where the conductivities range from $10^4$ to $10^{-22} \ \Omega^{-1} \ cm^{-1}$.

Assuming pure metallic bonding in metals, the situation from the structural point of view is very simple: positive cores surrounded by a "cloud" of non-directional free-conducting electrons will result in either a cubic or hexagonal close-packed (c.c.p. or h.c.p.) structure in which each coordinating atom lies exactly the same distance from the central atom.

King [3] pointed out that the structures of non-metals are governed by the number of available s- and p-

TABLE 1. The electrical conductivities ($10^4$ $\Omega^{-1}$ cm$^{-1}$) of the elements (273–293 K) in periodic system representation. The non-metals are indicated by a bold frame.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li 10.7 | Be 15.2 | | | | | | | | | | | B $1\cdot10^{-4}$ | C $7.7\cdot10^4$ | N | O | F | Ne |
| Na 21.1 | Mg 25.0 | | | | | | | | | | | Al 38.2 | Si $10^2$-$10^5$ | P $10^{-15}$ | S $5\cdot10^{-22}$ | Cl | Ar |
| K 15 | Ca 25 | Sc 1.57 | Ti 2.28 | V 5.5 | Cr 7.7 | Mn 0.39 | Fe 10 | Co 15.4 | Ni 13.3 | Cu 58.8 | Zn 16.4 | Ga 7.35 | Ge $1.54\cdot10^0$ | As 3 | Se $1.25\cdot10^1$ | Br | Kr |
| Rb 7.9 | Sr 5.0 | Y 1.54 | Zr 2 | Nb 6.25 | Mo 20 | Tc 5.9 | Ru 13.3 | Rh 19.6 | Pd 7.7 | Ag 62 | Cd 13.3 | In 11.9 | Sn 8.85 | Sb 2.56 | Te $6.25\cdot10^2$ | I $7.7\cdot10^{-14}$ | Xe |
| Cs 4.81 | Ba 1.67 | La 1.77 | Hf 2.5 | Ta 7.15 | W 20 | Re 5 | Os 11.1 | Ir 20.4 | Pt 10.2 | Au 43.5 | Hg 1.04 | Tl 6.65 | Pb 5.27 | Bi 0.92 | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

| Ce 1.33 | Pr 1.42 | Nd 1.56 | Pm 1.00 | Sm 0.99 | Eu 1.23 | Gd 0.70 | Tb 0.86 | Dy 1.11 | Ho 1.11 | Er 1.18 | Tm 1.11 | Yb 3.7 | Lu 1.47 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th 5.26 | Pa | U 3.1 | Np | Pu 0.69 | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

electrons following the empirical Hume-Rothery "valence electrons equals $8 - N$" rule, where $N$ is the group number. The inert gases in group VIII thus have no valence electrons for bonding, so that when these elements condense to solids at low temperature, they crystallize in close-packed structures, the atoms being held together (in contrast to metals) by van der Waals forces. The halogens (group VII) are composed of dumb-bells (diatomic molecules) with just one valence electron. At low temperatures in the condensed state these molecules are also held together by van der Waals forces.

Elements of group VI are composed of double links: the "central" atom forms with two neighbouring atoms a non-linear molecule. These two single-covalent linkages form strongly bonded chains or rings, the chains or rings again being held together by van der Waals forces in the solid state. Like the above-mentioned boron atoms, the elements of this group can be described as cluster structures, e.g. the sulphur double links lead to sulphur clusters (rings) with seven or eight sulphur atoms. The structure type $oF128$ S consists of 16 $S_8$ rings and the structure types $mP28$ S and $mP56$ S consist of four and eight $S_7$ rings respectively.

Group V non-metals, with three electrons available, form tetrahedral molecules (without a central atom) when bonded to a "loose" triangle, while group IV non-metals form tetrahedra (with a central atom) with their four electrons available.

Section 2 gives the general idea of the atomic environment approach and describes the method and terminology used.

In Section 3 we give the results of our analysis of the modifications stable under NC (298 K, 100 kPa).

In Section 4 the results of our analysis of the HP and HT/LT modifications are given and it is shown that changes in the atomic environments can follow specific sequences during polymorphic transformations.

In Section 5 the NC modifications are classified in modified structure stability diagrams (SSDs) [4]; these SSDs have proven to be very successful in separating the structure types of intermetallic compounds [5–7]. In a separate discussion the HP and HT/LT modifications are included in the SSDs.

Section 6 contains a complete table of critically evaluated crystallographic data for all experimentally known element modifications as well as a complete data set of atomic volumes calculated from the unit cell volume. The results are discussed together with metallic, covalent and ionic radii which have been derived from intermetallic compounds with predominantly metallic, covalent or ionic bonds. In contrast to the experimentally determined or derived atomic volumes (radii), we compare these with the pseudopotential radii as calculated by Zunger [8].

## 2. The atomic environment approach

Before we introduce our atomic environment approach, we have to mention that in addition to the definition given below, which is familiar to many crystallographers, there exists another approach to describe the local environment of an atom, namely the Voronoi (also known as the Wigner–Seitz or Dirichlet) polyhedron construction which is most often used by physicists.

### 2.1. Atomic environment type (AET)

The aim of the concept described in the following is to define each atomic environment (AE) as clearly as possible so that we will ultimately be able to group them into distinct AETs.

First we define the maximum-gap rule, which is based on the method proposed by Brunner and Schwarzenbach [9], where all interatomic distances between an atom and its neighbours are plotted in a next-neighbour histogram (NNH). In the NNH the height of the bars is proportional to the number of neighbours ($n$) and it is convenient to express all distances ($d$) relative to the shortest distance ($d_{min}$). In most cases a clear maximum gap is revealed. The AE or coordination polyhedron is constructed with the atoms to the left of this gap. Figures 1(a)–1(c) show the NNHs of the cubo-octahedron (c.c.p. or $cF4$ Cu type), the twinned cubo-octahedron (h.c.p. or $hP2$ Mg type) and the rhombic dodecahedron ($cI2$ W type) respectively. Also given

in Fig. 1 are drawings of the AEs together with their polyhedron codes (explained below) and coordination numbers (CNs).

This maximum-gap rule, however, leads in a few cases to incorrect AEs. These incorrect AEs can have, for example, more than the central atom enclosed or be AEs with atoms lying on one or more faces of the coordinating polyhedron.

For these incorrect environments we define another rule: the maximum-convex-volume rule. In this rule a coordination polyhedron is defined as the maximum convex volume around only one central atom enclosed by convex faces with all coordinating atoms lying at the intersections of at least three faces. In those cases where two (or more) equal or practically equal maximum gaps were observed in an NNH, we kept the number of different AETs in a structure type as small as possible. In the structures of the p-elements we observed irregular atomic environments (IAETs). These are AEs which, unlike AETs, cannot be described as convex volumes, *e.g.* the dumb-bell, the double link and the triangle.

### 2.2. Polyhedron code

The AETs are characterized by a polyhedron code [10] based on the number of triangles, squares, pentagons, hexagons, etc. that join each other in the different vertices (coordinating atoms). The code gives the number of equivalent vertices with the number of faces in the above-mentioned sequence as an exponent. For example, polyhedron 11-a in Fig. 2 has nine vertices adjoining two triangles and two squares and two vertices adjoining no triangles and three squares. Its code therefore is $9^{2.2}2^{0.3}$ with $CN = 11$.

### 2.3. Coordination type

In our classification, structure types belong to a certain coordination type when they have the same number and kinds of AETs. In the simplest case, with just one kind of AET, the atomic-environment type is equal to the coordination type.

### 2.4. Single-environment type

A crystal structure with all atoms (point sets) having the same AET is called a single-environment type. This means that each atom in the unit cell is chemically identical in terms of the elements.

### 2.5. Two- and poly-environmental types

Structures having two or more different AETs belong to the two- or poly-environment types. This means for

a)

$d_{min} = .255$ nm

max. gap

$d/d_{min}$

cF4 Cu

CN=12     code: $12^{2.2}$ (c)

cubic closed
packing (ccp)

Cubooctahedron (12–b)

b)

$d_{min} = .319$ nm

max. gap

$d/d_{min}$

hP2 Mg

CN=12     code: $12^{2.2}$ (h)

hexagonal closed
packing (hcp)

twinned cuboctahedron (12–d)

c)

$d_{min} = .274$ nm

max. gap

$d/d_{min}$

cl2 W

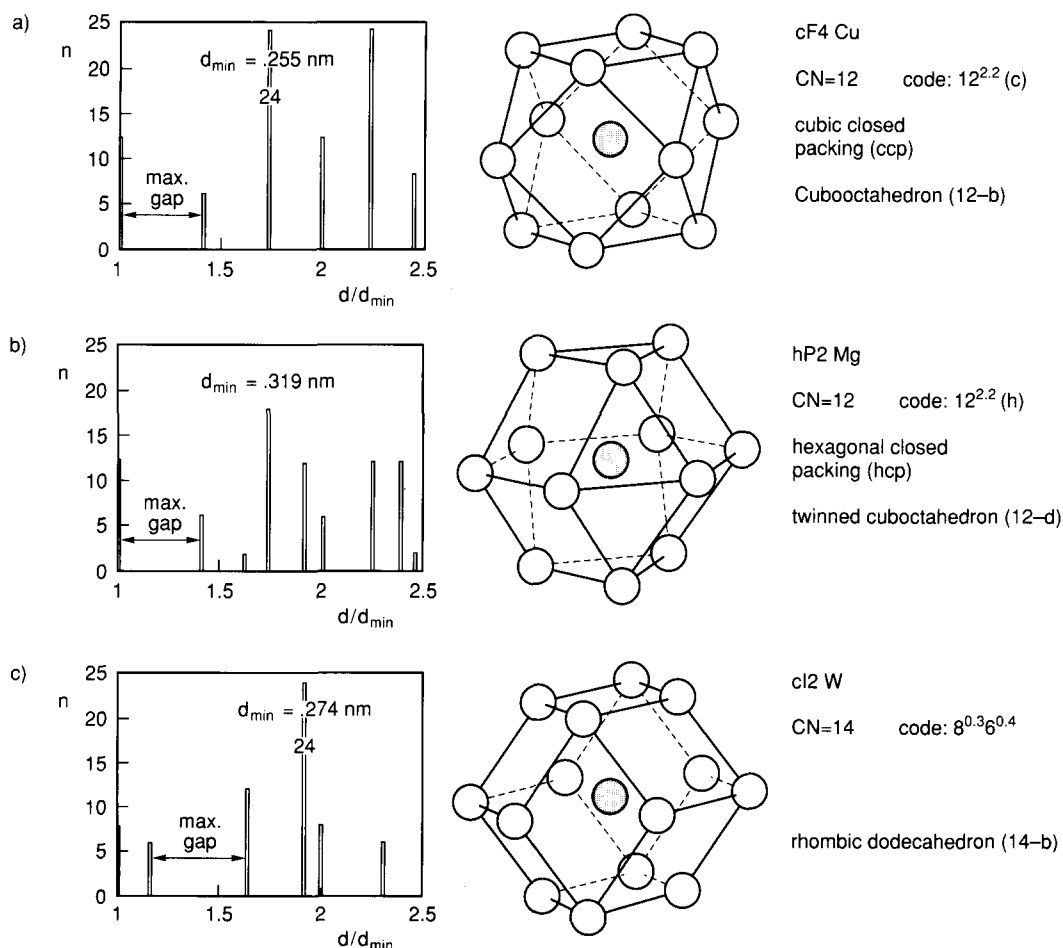CN=14     code: $8^{0.3}6^{0.4}$

rhombic dodecahedron (14–b)

Fig. 1. The atomic environments as they are realized in (a) c.c.p., (b) h.c.p. and (c) b.c.c. structures. The realized coordination polyhedra (AETs) are the cubo-octahedron, the twinned cubo-octahedron and the rhombic dodecahedron respectively.

the elements that we have two or more different atomic positions in the structure type. This is of course only possible when we have a different bonding situation for each atomic position.

The lattice symmetry and space group of a compound are important for certain physical properties, but for crystal chemistry they are less important. A minor change in the position of the atoms in a crystal structure can reduce its symmetry (and space group), although the resulting deformation of the atomic environment may be negligible so that the AET does not change.

For intermetallic phases with cubic and rhombohedral structure types [11, 12] we could reduce the number of different structure types significantly by grouping them into coordination types with the same or similar AETs.

We will show that a similar simplification can be achieved with the 52 crystal structures types in which the elements crystallize. Crystal structures with the same or similar AETs have a common feature and are

therefore grouped as a coordination type. The structure types belonging to the same coordination type have only minor differences and one could call a polymorphic transformation from one structure to another structure within a coordination type a second-order transformation. For example, cF4 SZn and hP4 SZn, both structures belonging to the single-environment type, have the tetrahedron as an AET. The cohesive energy difference between the two modifications must be much smaller when compared with a transformation which involves a change in the AET. This energy difference will be significantly higher when the CN is also changing than when only the AET changes but the CN remains the same.

Much more complex is the situation in the structure types with two, three or more different AETs and it is difficult to speculate about the cohesive energy difference between structure types belonging to a single-environment type and those belonging to a two- or poly-environment type.
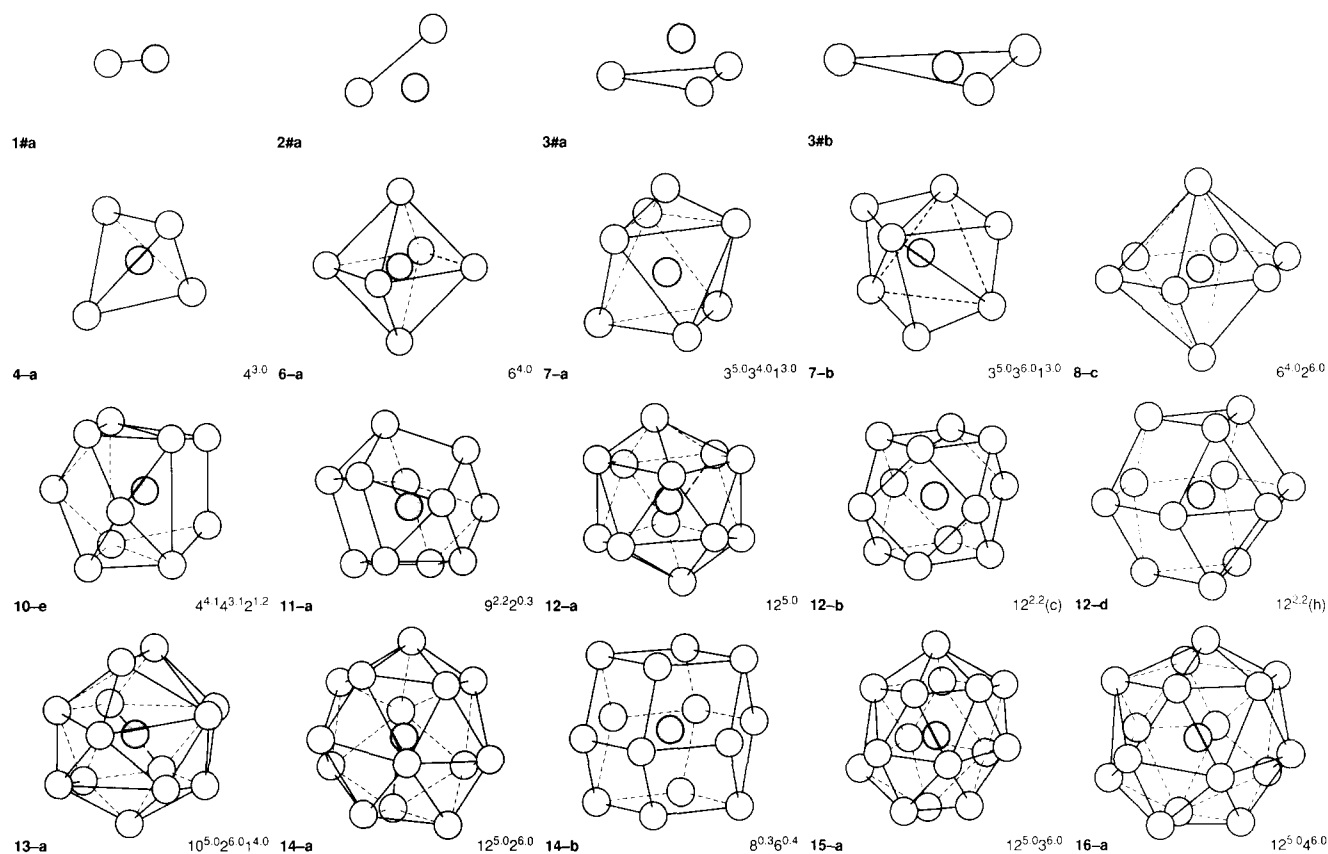
Fig. 2. The atomic environments as they are realized under NC, HT/LT and HP conditions in the modifications of the elements with their label (coordination numbers are incorporated in the label) and the polyhedron code.

## 3. Atomic environment classification under normal conditions

In Table 2 we give the 52 structure types in which the element modifications crystallize under NC, HP and HT/LT conditions. Table 2 lists the structure types (alphabetically ordered) and we give for each type the Pearson symbol, the space group, the Wyckoff letter and the coordinates of the atoms. In addition, we give for each point set the label of the AET (the CN is incorporated in our label), the number of different AETs and the elements crystallizing in this structure type. Figure 2 shows drawings of AETs found in the element structures together with their codes and labels, the latter being used throughout the paper to specify a certain AET.

The labels of the AETs are a combination of the CN and a character as explained in ref. 12, where we have analyzed the rhombohedral "intermetallic" structure types.

In Table 3 we present all modifications in the periodic table representation, the structure types being given by a number (first column of Table 2). The position of those numbers in the element boxes indicates whether

the structure type was observed under NC, HP or HT/LT conditions, as demonstrated in the inset.

When we look at the metal element structures (as defined in Section 1; see Table 1) from the AET point of view and assume a simple bonding situation in pure metals (in contrast to the intermetallic compounds which have metallic, covalent and ionic bonds), we expect, as already explained in Section 1, either a cubo-octahedron or a twinned cubo-octahedron as an AE.

Assuming pure non-directional metallic bonding, crystal structures with AETs having two different distances, e.g. as the rhombic dodecahedron (see Fig. 1(c)), should not occur. In this AET the first eight neighbouring atoms have an interatomic distance which is 15% shorter than the next six neighbouring atoms, although all 14 atoms clearly belong to the first coordination sphere.

Even harder to understand would be structures belonging to the two- or poly-environment types, because this would point in these cases to directional or ionic bonding and exclude purely non-directional metallic bonding.

Accepting the validity of the empirical "valence electrons equals $8 - N$" rule for non-metals, this will mean that from the AET point of view only the following AETs are available:

TABLE 2. The structure types in which the elements crystallize, ordered alphabetically.

| No. | Structure type/PS | Space group | Wyckoff notation | Atomic Coordinates X | Y | Z | AET | No. of AET's | Elements crystallizing in this structure type |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Am/mP4 | P2$_1$/m | 2a | 0 | 0 | 0 | 14–b | 1 | Am (HP) |
| | | | 2e | 0.380 | 1/4 | 0.275 | 14–b | | |
| 2 | As/hR2 | R3̄m | 6c | 0 | 0 | 0.2271 | 6–a | 1 | As,Bi,P(HP),Sb,Te(HP) |
| 3 | Be/oP4 | P2$_1$2$_1$2 | 4c | 0.67 | 0.82 | 0.70 | 11–a | 1 | Be(HP) |
| 4 | Bi/mC4 | C2/m | 4i | 0.250 | 0 | 0.125 | 6–a | 1 | Bi(HP) |
| 5 | BiIn/hP1 | P6/mmm | 1a | 0 | 0 | 0 | 8–c | 1 | Si(HP) |
| 6 | C/hP4 | P6$_3$/mmc | 2b | 0 | 0 | 1/4 | 3#b | 1 | C |
| | | | 2c | 1/3 | 2/3 | 1/4 | 3#b | | |
| 7 | C/cF8 | Fd3̄m | 8a | 0 | 0 | 0 | 4–a | 1 | C,Ge,Si,Sn |
| 8 | Cf/aP4 | P1̄ | 1a | 0 | 0 | 0 | 12–b | 1 | Cf(HP) |
| | | | 1c | 0 | 1/2 | 0 | 12–b | | |
| | | | 2i | 0.572 | 0.259 | 0.433 | 12–b | | |
| 9 | Cl$_2$/oC8 | Cmca | 8f | 0 | 0.13 | 0.10 | 1#a | 1 | Cl$_2$Br$_2$,I |
| 10 | CrFe/tP30 | P4$_2$/mnm | 2a | 0 | 0 | 0 | 12–a | 3 | U(HT) |
| | | | 4f | 0.3986 | 0.3986 | 0 | 15–a | | |
| | | | 8i | 0.4635 | 0.1312 | 0 | 14–a | | |
| | | | 8i | 0.7393 | 0.0661 | 0 | 12–a | | |
| | | | 8j | 0.1827 | 0.1827 | 0.2520 | 14–a | | |
| 11 | Cs/tP8 | P4$_2$/mbc | 8h | 0.073 | 0.250 | 0 | 14–b | 1 | Cs(HP) |
| 12 | Cu/cF4 | Fm3̄m | 4a | 0 | 0 | 0 | 12–b | 1 | Ac,Ag,Al,Am(HT),Am(HP),Ar,Au,Bk(HP), Bk(HT)Ca,Ce(HT),Ce(HP),Cf(HT),Cm(HP), Cm(HT),Co(HT),Cs(HP),Cu,Eu,Fe(HT),H$_2$(LT), He,Ir,K(HP),Kr,La(HT)La(HP),Li(HP),Mn(HT), Nd(HP),Ne,Ni,Pa(HT),Pb,Pd,Pr(HT),Pr(HP), Pt,Pu(HT),Rh,Si(HP),Sr,Th,Tl(HT),Xe,Yb |
| 13 | F$_2$/mC8 | C2/c | | | | | 1#a | 1 | F$_2$ |
| 14 | Ga/oC4 | Cmcm | 4c | 0 | 0.133 | 1/4 | 10–e | 1 | Ga |
| 15 | Ga/oC8 | Cmca | 8f | 0 | 0.1525 | 0.0785 | 7–a | 1 | Ga |
| 16 | Ga/cI12 | I4̄3d | 12a | 3/8 | 0 | 1/4 | 12–b | 1 | Ga(HP) |
| 17 | Ge/tP12 | P4$_3$2$_1$2 | 4a | 0.0912 | 0.0912 | 0 | 4–a | 1 | Ge(HP) |
| | | | 8b | 0.1730 | 0.3784 | 0.2486 | 4–a | | |
| 18 | Hg/hR1 | R3̄m | 3a | 0 | 0 | 0 | 12–b | 1 | Hg,Po(HT),Te(HP) |
| 19 | In/tI2 | I4/mmm | 2a | 0 | 0 | 0 | 12–b | 1 | Ce(HP),Ga(HP),In,Pu(HT),Sc(HP),Sn |
| 20 | La/hP4 | P6$_3$/mmc | 2a | 0 | 0 | 0 | 12–b | 2 | Am,Bk,Ce,Cf,Cm,Gd(HT/HP),La,Nd,Pm,Pr, Si,Sm(HP) |
| | | | 2c | 1/3 | 2/3 | 1/4 | 12–d | | |
| 21 | Mg/hP2 | P6$_3$/mmc | 2c | 1/3 | 2/3 | 1/4 | 12–d | 1 | Al(HP),Ar,Ba(HP),Be,Ca(HT),Cd,Ce(HP),Cf, Co,Dy,Er,Eu(HP),Fe(HP),H$_2$(LT),Hf,He,Ho, Li(LT), Lu,Mg,N$_2$(LT),Na(LT),Os,Pb(HP), Re,Ru,Sb(HP),Sc,Si(HP),Sm(HT),Sr(HT), Tb,Tc,Ti,Tl,Tm,Y,Yb(LT),Yb(HT),Yb(HP), Zn,Zr |
| 22 | Mn/cP20 | P4$_1$32 | 8c | 0.061 | 0.061 | 0.061 | 12–a | 1 | Mn(HT) |
| | | | 12d | 1/8 | 0.206 | 0.457 | 14–a | | |
| 23 | Mn/cI58 | I4̄3m | 2a | 0 | 0 | 0 | 16–a | 3 | Mn |
| | | | 8c | 0.317 | 0.317 | 0.317 | 16–a | | |
| | | | 24g | 0.356 | 0.356 | 0.042 | 13–a | | |
| | | | 24g | 0.089 | 0.089 | 0.278 | 12–a | | |
| 24 | N$_2$/hP24 | P6$_3$/mmc | 24l | 0.2096 | 0.5429 | 0.8053 | 1#a | 1 | N$_2$(LT/HP) |
| 25 | N$_2$/hR16 | R3̄c | 12c | 0 | 0 | 0.0495 | 1#a | 1 | N$_2$(LT/HP) |
| | | | 36f | 0.2731 | 0.2127 | 0.2828 | 1#a | | |
| 26 | N$_2$/cP64 | Pm3̄n | 16i | 0.042 | 0.042 | 0.042 | 1#a | 1 | N$_2$ (LT/HP) |
| | | | 48f | 0.239 | 0.531 | 0.080 | 1#a | | |
| 27 | NbS$_2$/hP6 | P6$_3$/mmc | 2b | 0 | 0 | 1/4 | 12–b | 2 | Tb(HP) |
| | | | 4f | 1/3 | 2/3 | 0.125 | 12–d | | |

(continued)

TABLE 2. (continued)

| No. | Structure type/PS | Space group | Wyckoff notation | Atomic Coordinates X | Y | Z | AET | No. of AET's | Elements crystallizing in this structure type |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 28 | Np/oP8 | Pnma | 4c | 0.036 | 1/4 | 0.208 | 14–b | 2 | Np |
|  |  |  | 4c | 0.319 | 1/4 | 0.842 | 16–a |  |  |
| 29 | Np/tP4 | P42₁2 | 2a | 0 | 0 | 0 | 14–b | 1 | Np(HT),Sc(HP) |
|  |  |  | 2c | 0 | 1/2 | 0.625 | 14–b |  |  |
| 30 | O₂/cP16 | Pm3̄n |  |  |  |  | 1#a | 1 | F₂,O₂ |
| 31 | O₂/hR2 | R3̄m | 6c | 0 | 0 | 0.0577 | 1#a | 1 | O₂(LT/HP) |
| 32 | P/oC8 | Cmca | 8f | 0 | 0.098 | 0.910 | 3#a | 1 | As(HT),P |
| 33 | Pa/tI2 | I4/mmm | 2a | 0 | 0 | 0 | 14–b | 1 | Hg(LT),Pa,Sn(HP) |
| 34 | Po/cP1 | Pm3̄m | 1a | 0 | 0 | 0 | 6–a | 1 | Bi(HP),Ca(HP),P(HP),Po,Sb(HP) |
| 35 | Pr/hP6 | P3₁21 | 6c | 0.280 | 0.280 | 0.772 | 3#a | 1 | Pr(HP) |
| 36 | Pu/mP16 | P2₁/m | 8 * 2e |  |  |  | Complex |  | Pu |
| 37 | Pu/mC34 | C2/m | 2a,4h,3 * 4i,2 * 8j |  |  |  | Complex |  | Pu(HT) |
| 38 | S/mP28 | P2₁/c | 7 * 4e |  |  |  | 7 * 2#a | 1 | S |
| 39 | S₅Se₃/mP32 | P2/c | 8 * 4g |  |  |  | 8 * 2#a | 1 | S |
| 40 | S/mP56 | P2₁/c | 14 * 4e |  |  |  | 14 * 2#a | 1 | S(HT) |
| 41 | Sb/mP4 | P2₁/m | 2e | 0.74 | 1/4 | 0.08 | 16–a | 2 | Bi(HP),Sb(HP) |
|  |  |  | 2e | 0.34 | 1/4 | 0.40 | 7–b |  |  |
| 42 | Se/mP32 | P2₁/c | 8 * 4e |  |  |  | 8 * 2#a | 1 | Se |
| 43 | Se/mP64 | P2₁/c | 16 * 4e |  |  |  | 16 * 2#a | 1 | Se |
| 44 | Se/hP3 | P3₁21 | 3a | 0.217 | 0 | 1/3 | 2#a | 1 | Se,Te |
| 45 | Se/hR6 | R3̄ | 18f | 0.1602 | 0.2023 | 0.1205 | 2#a | 1 | Se(HT) |
| 46 | Sm/hR3 | R3̄m | 3a | 0 | 0 | 0 | 12–b | 2 | Dy(HP),Gd(HP),Ho(HP),Li(LT),Lu(HP), |
|  |  |  | 6c | 0 | 0 | 0.2220 | 12–d |  | Na(LT),Sm,Tb(HP),Tm(HP) |
| 47 | Sn/tI4 | I4₁/amd | 4a | 0 | 0 | 0 | 6–a | 1 | Ge(HP),Si(HP),Sn |
| 48 | Si/cI16 | Ia3̄ | 16c | 0.1003 | 0.1003 | 0.1003 | 4–a | 1 | Ge(HT/HP),Si |
| 49 | Te/mP4 | P2₁ | 2a | 0.25 | 0.23 | 0.48 | 14–b | 2 | Te(HP) |
|  |  |  | 2a | 0.48 | 0.00 | 0.02 | 12–b |  |  |
| 50 | U/oC4 | Cmcm | 4c | 0 | 0.105 | 1/4 | 12–d | 1 | Am(HP),Bk(HP),Ce(HP),Cf(HP),Cm(HP), Dy(LT),U |
| 51 | U/tP30 | P4₂nm | 2a | 0 | 0 | 0.66 | 12–a | 3 | U |
|  |  |  | 4c | 0.11 | 0.11 | 0.23 | 15–a |  |  |
|  |  |  | 4c | 0.32 | 0.32 | 0.00 | 14–a |  |  |
|  |  |  | 4c | 0.68 | 0.68 | 0.50 | 14–a |  |  |
|  |  |  | 8d | 0.56 | 0.24 | 0.25 | 12–a |  |  |
|  |  |  | 8d | 0.38 | 0.04 | 0.20 | 14–a |  |  |
| 52 | W/cI2 | Im3m | 2a | 0 | 0 | 0 | 14–b | 1 | Ba,Be(HT),Bi(HP),Ca(HP)Ca(HT),Ce(HT), Cr,Cs,Dy(HT),Er(HT),Eu,Fe,Fe(HT),Gd(HT), He,Hf(HT),Ho(HT),K,La(HT),Li,Lu(HT), Mg(HP),Mn(HT),Mo,Na,Nb,Nd(HT),Np(HT), Pa(HT),Pr(HT),Pu(HT),Ra,Rb,Sc(HT), Sn(HP),Sr(HP),Ta,Tb(HT),Th(HT),Ti(HT), Tl(HT),Tm(HT),U(HT),V,W,Y(HT),Yb(HT) |

| Group no. | No. of valence electrons available | Available AET (see Fig. 2) | Non-metals |
|-----|-----|-----|-----|
| VIII | 0 | Cubo-octahedron (12-b) or twinned cubo-octahedron (12-d) | He, Ne, Ar, Kr, Xe, Rn |
| VII | 1 | Dumb-bell (1≠a) | F, Cl, Br, I, At |
| VI | 2 | Double link (2≠a) | O, S, Se, Te |
| V | 3 | Triangle (3≠a or 3≠b) | N, P |
| IV | 4 | Tetrahedron (4-a) | C, Si, Ge |

Looking at the experimental available for NC (see Table 4), we can confirm that our expectation holds for 70 elements, metals as well as non-metals. We observe four exceptions.

TABLE 3. The structure types in which the elements crystallize, presented in a periodic system representation with the HP and HT/LT modifications included (see inset). The numbers in the boxes refer to column 1 of Table 2.

The periodic system representation (inset legend): Chemical element, HT modification (left), HP modification (right), NC modification (bottom).

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **H** 21 / 12 | | | | | | | | | | | | | | | | | **He** 52 21 12 |
| **Li** 21 / 46 52 12 | **Be** 52 21 3 | | | | | | | | | | | **B** | **C** 6/7 | **N** 26 25 24 21 | **O** 30 31 | **F** 13 30 | **Ne** 12 |
| **Na** 46 / 21 52 | **Mg** 21 52 | | | | | | | | | | | **Al** 12 21 | **Si** 12 / 20 21 / 48 5 / 7 47 | **P** 34 / 32 2 | **S** 39 / 40 38 | **Cl** 9 | **Ar** 12 |
| **K** 52 12 | **Ca** 52 34 / 21 12 52 | **Sc** 29 / 52 21 19 | **Ti** 52 21 | **V** 52 | **Cr** 52 | **Mn** 12 52 / 22 23 | **Fe** 52 / 12 52 21 | **Co** 12 21 | **Ni** 12 | **Cu** 12 | **Zn** 21 | **Ga** 19 / 15 16 | **Ge** 48 / 17 / 7 47 | **As** 32 2 | **Se** 43 42 / 45 44 | **Br** 9 | **Kr** 12 |
| **Rb** 52 | **Sr** 21 12 52 | **Y** 52 21 | **Zr** 21 | **Nb** 52 | **Mo** 52 | **Tc** 21 | **Ru** 21 | **Rh** 12 | **Pd** 12 | **Ag** 12 | **Cd** 21 | **In** 19 | **Sn** 47 / 19 52 / 7 33 | **Sb** 41 / 21 / 2 34 | **Te** 18 / 49 / 44 2 | **I** 9 | **Xe** 12 |
| **Cs** 11 / 52 12 | **Ba** 52 21 | **La** 52 / 12 20 12 | **Hf** 52 21 | **Ta** 52 | **W** 52 | **Re** 21 | **Os** 21 | **Ir** 12 | **Pt** 12 | **Au** 12 | **Hg** 33 18 | **Tl** 12 / 52 21 | **Pb** 12 21 | **Bi** 52 41 34 / 2 4 | **Po** 18 34 | **At** (9) | **Rn** (12) |
| **Fr** | **Ra** 52 | **Ac** 12 | | | | | | | | | | | | | | | |

| **Ce** 19 21 / 52 50 / 12 20 12 | **Pr** 52 35 / 12 20 12 | **Nd** 52 20 12 | **Pm** 20 | **Sm** 21 46 20 | **Eu** 12 / 52 21 | **Gd** 20 / 52 21 46 | **Tb** 52 27 / 50 21 46 | **Dy** 52 / 50 21 46 | **Ho** 52 21 46 | **Er** 52 21 | **Tm** 52 21 46 | **Yb** 52 / 21 12 21 | **Lu** 52 21 46 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Th** 52 12 | **Pa** 52 / 12 33 | **U** 52 51 / 10 50 | **Np** 52 / 29 28 | **Pu** 52 19 12 / 37 36 | **Am** 50 / 12 20 12 | **Cm** 1 / 12 20 12 | **Bk** 50 / 12 20 12 | **Cf** 50 / 21 50 / 12 20 8 | **Es** | **Fm** | **Md** | **No** | **Lr** |

(a) Sixteen metals have under NC the $cI2$ W type of structure, which corresponds to the rhombic dodecahedron as an AET. Nine of these elements (V, Nb, Ta, Cr, Mo, W, K, Rb and Ra) also have no other modification under HT or HP conditions. Hence this AET is very stable and more favourable than the cubic or hexagonal closed-packed AETs, which is, according to Young [13], imposed by a smooth repulsive inter-atomic potential. Alternatively, the Madelung electrostatic energy favours the rhombic dodecahedron as an AET.

(b) About half the f-elements crystallize in the $hP4$ La or $hR3$ Sm type of structure, both belonging to the two-environment type, having the c.c.p. and h.c.p. AETs. It is interesting that out of all the possible two-environment types these metals realize exactly the ones which represent a combination of the cubic and hexagonal closed-packed AETs. The cohesive energy difference between these two AETs must be close to zero. Thus in a first-order approximation this special case of a two-environment type can be considered as a single-environment type found in the f-elements where the number of s-electrons is constant.

(c) Ga, Mn, Np, Pu and U have very unusual complex structures, the modifications of these elements crystallizing in single- to poly-environment types. Therefore these elements must have a significantly large proportion of directional bonding, because such complex structures cannot be formed with isotropic metallic bonding. These structures are very different from all previously discussed structures and it will take some time before such complex structures can be fully understood.

TABLE 4. The atomic environment types (AETs) found in the crystal structures of the elements under normal conditions (298 K, 100 kPa). The elements marked with an asterisk are given for non-normal conditions.

| H * 12-b | | | | | | | | | | | | | | | | | He * 12-b |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li 14-b | Be 12-d | | | | | | | | | | | B Cluster structure | C 4-a | N * 1#a | O * 1#a | F * 1#a | Ne * 12-b |
| Na 14-b | Mg 12-d | | | | | | | | | | | Al 12-b | Si 4-a | P 3#a | S 2#a | Cl * 1#a | Ar * 12-b |
| K 14-b | Ca 12-b | Sc 12-d | Ti 12-d | V 14-b | Cr 14-b | Mn Complex | Fe 14-b | Co 12-d | Ni 12-b | Cu 12-b | Zn 12-d | Ga 7-a | Ge 4-a | As 6-a | Se 2#a | Br * 1#a | Kr * 12-b |
| Rb 14-b | Sr 12-b | Y 12-d | Zr 12-d | Nb 14-b | Mo 14-b | Tc 12-d | Ru 12-d | Rh 12-b | Pd 12-b | Ag 12-b | Cd 12-d | In 12-b | Sn 4-a 6-a 12-b | Sb 6-a | Te 2#a | I 1#a | Xe * 12-b |
| Cs 14-b | Ba 14-b | La 12-b 12-d | Hf 12-d | Ta 14-b | W 14-b | Re 12-d | Os 12-d | Ir 12-b | Pt 12-b | Au 12-b | Hg 12-b | Tl 12-d | Pb 12-b | Bi 6-a | Po 6-a | At 1#a | Rn * 12-b |
| Fr | Ra 14-b | Ac 12-b | | | | | | | | | | | | | | | |

| Ce 12-b 12-d | Pr 12-b 12-d | Nd 12-b 12-d | Pm 12-b 12-d | Sm 12-b 12-d | Eu 12-b 14-b | Gd 12-d | Tb 12-d | Dy 12-d | Ho 12-d | Er 12-d | Tm 12-d | Yb 12-b | Lu 12-d |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th 12-b | Pa 14-b | U 12-d or complex | Np 14-b 16-a | Pu Complex | Am 12-b 12-d | Cm 12-b 12-d | Bk 12-b 12-d | Cf 12-b 12-d | Es | Fm | Md | No | Lr |

(d) As, Sb, Bi and Sn, which all belong, according to their electrical conductivity (see Table 1), to the metals, have an octahedron (6-a) as an AET. This is only understandable if there is some directional covalent bonding between the atoms.

Summarizing the crystal structures of the elements under NC from the AET point of view shows that the metals crystallize (except Ga, Mn, Np, Pu and U) in one of the following four AETs: the octahedron, the cubo-octahedron, the twinned cubo-octahedron or the rhombic dodecahedron. The non-metal structures crystallize in structure types having either a dumb-bell, a double link, a triangle or a tetrahedron as an AET.

Looking at Table 3 reveals that tI2 In, hR1 Hg and oC4 U do not fit the general structural trend, but when we look at the realized AEs they fit nicely (see Table 4).

## 4. Atomic environment classification for normal as well as high pressure and high temperature conditions

Including all HP and HT modifications leads to the 19 different AETs shown in Fig. 2, covering the co-ordination numbers 1–16, omitting only 5 and 9. All realized polyhedra are highly symmetrical and have also been found in the intermetallic structures types [11, 12, 14]. Classifying the 52 structure types into single-, two-, three- and poly-environment types respectively leads to the following results (see Table 5):

TABLE 5. Classification of the structure types grouped into single-, two- and poly-environment types.

| No. | Pearson symbol | Structure type | No. of elements | No. of point sets | Coordination number(s) | 1#a | 2#a | 3#a | 3#b | 4-a | 6-a | 7-a | 7-b | 8-c | 10-e | 11-a | 12-a | 12-b | 12-d | 13-a | 14-a | 14-b | 15-a | 16-a |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | mC8 | $F_2$ | 1 |  | 1 | X | | | | | | | | | | | | | | | | | | |
| 9 | oC8 | $Cl_2$ | 3 | 1 | 1 | X | | | | | | | | | | | | | | | | | | |
| 24 | hP24 | $N_2$ | 1 | 1 | 1 | X | | | | | | | | | | | | | | | | | | |
| 31 | hR2 | $O_2$ | 1 | 1 | 1 | X | | | | | | | | | | | | | | | | | | |
| 25 | hR16 | $N_2$ | 1 | 2 | 1 | X | | | | | | | | | | | | | | | | | | |
| 30 | cP16 | $O_2$ | 2 | | 1 | X | | | | | | | | | | | | | | | | | | |
| 26 | cP64 | $N_2$ | 1 | 2 | 1 | X | | | | | | | | | | | | | | | | | | |
| 38 | mP28 | S | 1 | 7 | 2 | | X | | | | | | | | | | | | | | | | | |
| 39 | mP32 | $S_5Se_3$ | 1 | 8 | 2 | | X | | | | | | | | | | | | | | | | | |
| 42 | mP32 | Se | 1 | 8 | 2 | | X | | | | | | | | | | | | | | | | | |
| 40 | mP56 | S | 1 | 14 | 2 | | X | | | | | | | | | | | | | | | | | |
| 43 | mP64 | Se | 1 | 16 | 2 | | X | | | | | | | | | | | | | | | | | |
| 44 | hP3 | Se | 2 | 1 | 2 | | X | | | | | | | | | | | | | | | | | |
| 45 | hR6 | Se | 1 | 1 | 2 | | X | | | | | | | | | | | | | | | | | |
| 32 | oC8 | P | 2 | 1 | 3 | | | X | | | | | | | | | | | | | | | | |
| 35 | hP6 | Pr | 1 | 1 | 3 | | | X | | | | | | | | | | | | | | | | |
| 6 | hP4 | C | 1 | 2 | 3 | | | | X | | | | | | | | | | | | | | | |
| 17 | tP12 | Ge | 1 | 2 | 4 | | | | | X | | | | | | | | | | | | | | |
| 48 | cI16 | Si | 2 | 1 | 4 | | | | | X | | | | | | | | | | | | | | |
| 7 | cF8 | C | 4 | 1 | 4 | | | | | X | | | | | | | | | | | | | | |
| 4 | mC4 | Bi | 1 | 1 | 6 | | | | | | X | | | | | | | | | | | | | |
| 47 | tI4 | Sn | 3 | 1 | 6 | | | | | | X | | | | | | | | | | | | | |
| 2 | hR2 | As | 5 | 1 | 6 | | | | | | X | | | | | | | | | | | | | |
| 34 | cP1 | Po | 5 | 1 | 6 | | | | | | X | | | | | | | | | | | | | |
| 15 | oC8 | Ga | 1 | 1 | 7 | | | | | | | X | | | | | | | | | | | | |
| 5 | hP1 | BiIn | 1 | 1 | 8 | | | | | | | | | X | | | | | | | | | | |
| 14 | oC4 | Ga | 1 | 1 | 10 | | | | | | | | | | X | | | | | | | | | |
| 3 | oP4 | Be | 1 | 1 | 11 | | | | | | | | | | | X | | | | | | | | |
| 8 | aP4 | Cf | 1 | 3 | 12 | | | | | | | | | | | | X | | | | | | | |
| 19 | tI2 | In | 6 | 1 | 12 | | | | | | | | | | | | X | | | | | | | |
| 18 | hR1 | Hg | 3 | 1 | 12 | | | | | | | | | | | | X | | | | | | | |
| 16 | cI12 | Ga | 1 | 1 | 12 | | | | | | | | | | | | X | | | | | | | |
| 12 | cF4 | Cu | 46 | 1 | 12 | | | | | | | | | | | | X | | | | | | | |
| 50 | oC4 | U | 7 | 1 | 12 | | | | | | | | | | | | | X | | | | | | |
| 21 | hP2 | Mg | 44 | 1 | 12 | | | | | | | | | | | | | X | | | | | | |
| 1 | mP4 | Am | 1 | 2 | 14 | | | | | | | | | | | | | | | | | X | | |
| 29 | tP4 | Np | 2 | 2 | 14 | | | | | | | | | | | | | | | | | X | | |
| 11 | tP8 | Cs | 1 | 1 | 14 | | | | | | | | | | | | | | | | | X | | |
| 33 | tI2 | Pa | 3 | 1 | 14 | | | | | | | | | | | | | | | | | X | | |
| 52 | cI2 | W | 47 | 1 | 14 | | | | | | | | | | | | | | | | | X | | |
| 41 | mP4 | Sb | 2 | 2 | 7/16 | | | | | | | X | | | | | | | | | | | | X |
| 20 | hP4 | La | 12 | 2 | 12/12 | | | | | | | | | | | | X | X | | | | | | |
| 27 | hP6 | $NbS_2$ | 1 | 2 | 12/12 | | | | | | | | | | | | X | X | | | | | | |
| 46 | hR3 | Sm | 9 | 2 | 12/12 | | | | | | | | | | | | | X | X | | | | | |
| 22 | cP20 | Mn | 1 | 2 | 12/14 | | | | | | | | | | | | X | | | | X | | | |
| 49 | mP4 | Te | 1 | 2 | 12/14 | | | | | | | | | | | | | X | | | | X | | |
| 28 | oP8 | Np | 1 | 2 | 14/16 | | | | | | | | | | | | | | | | | X | | X |
| 23 | cI58 | Mn | 1 | 4 | 12/13/16 | | | | | | | | | | | | X | | | X | | | | X |
| 10 | tP30 | CrFe | 1 | 5 | 12/14/15 | | | | | | | | | | | | X | | | | X | | X | |
| 51 | tP30 | U | 1 | 6 | 12/14/15 | | | | | | | | | | | | X | | | | X | X | X | |
| 36 | mP16 | Pu | 1 | 8 | 12/14/16 | | | | | | | | | | | | | | X | | X | X | | X |
| 37 | mC34 | Pu | 1 | 7 | 12/13/14/15 | | | | | | | | | | | | | X | | X | X | X | X | |

13 single-environment types, five two-environment types, three three-environment types and one poly-environment type.

We can see, for example, that the following five structure types have the rhombic dodecahedron as an AET and therefore belong to the same coordination type: *mP*4 Am, *tP*4 Np, *tP*8 Cs, *tI*2 Pa and *cI*2 W.

It is clear that these structure types vary considerably with respect to their symmetry, but in the atomic environments realized they differ only slightly. Although the simplification summarized in Table 5 does not seem to be the most obvious one, it should be borne in mind that most "exotic" environment types have only one representative.

The "exotic" types are the following coordination types: *oC*8 Ga (7-a), *oC*4 Ga (10-e), *hP*1 BiIn (Si, 8-c), *oP*4 Be (11-a), *mP*4 Sb (7-b + 16-a), *cP*20 Mn (12-a + 14-a), *mP*4 Te (12-b + 14-b), *oP*8 Np (14-b + 16-a), *cI*58 Mn (12-a + 13-a + 16-a), *tP*30 CrFe (U, 12-a + 14-a + 15-a), *tP*30 U (12-a + 14-a + 15-a), *mC*34 Pu and *mP*16 Pu (both poly).

The exceptions, *hP*4 La and *hR*3 Sm, have already been discussed. They belong to the two-environment type with the cubo-octahedron and the twinned cubo-octahedron as AETs and they can be considered as a special case of a single-environment type.

If we neglect the 13 above-mentioned special modifications, we are left with the nine main single-environment types. In these nine single-environment types the following AETs are observed: the dumb-bell (CN1 1#a), the double link (CN2 2#a), the triangle (CN3 3#a + 3#b) and the tetrahedron (CN4 4-a) are found in non-metals; the octahedron (CN6 6-a), the cubo-octahedron (CN12 12-b), the twinned cubo-octahedron (CN12 12-d) and the rhombic dodecahedron (CN14 14-b) are found in metals.

Excluding the structure types with only one representative, we can simplify the structures of the elements with nine different AETs (nine different coordination types), including 260 out of 275 modifications. In these nine AETs, with the exception of the rhombic dodecahedron, the central atoms have just one kind of neighbouring atom at identical distances from the central atom. All other AETs, mostly observed in one modification, have non-equal distances within the coordination sphere, which indicates that those structures are either very exotic or their description is wrong.

We analyzed the influence of high pressure and high temperature on the AETs by looking at the known polymorphic transitions. Figure 3 shows (a) the polymorphic transformation schemes for eight AETs within the single-environment types, (b) two schemes for the two-environment types and (c) two schemes for the three-environment types. It is interesting that with increasing pressure as well as temperature all AETs
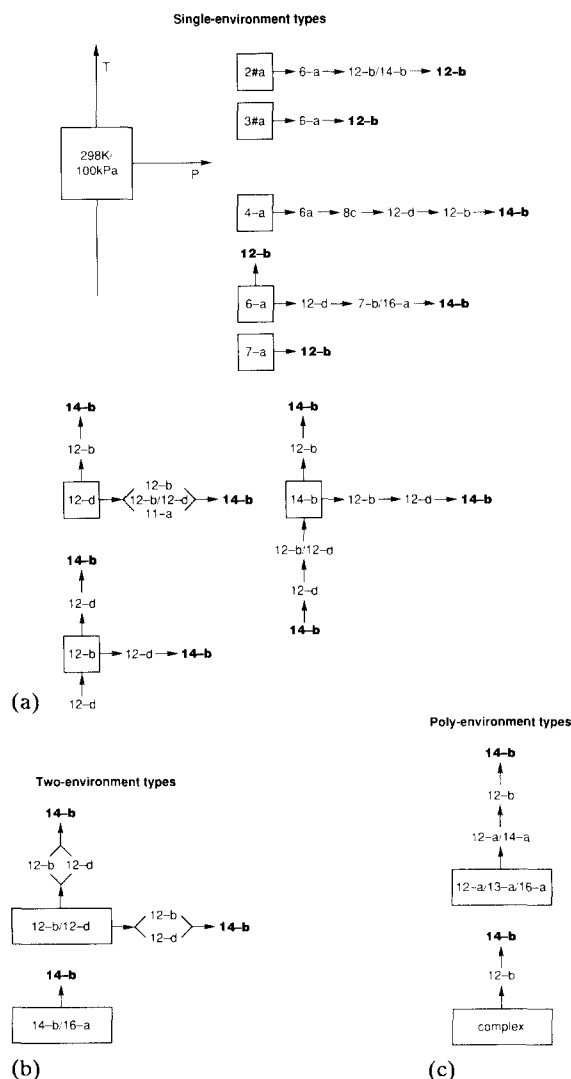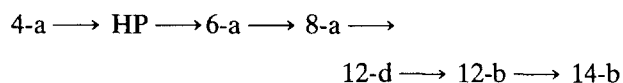


Fig. 3. The atomic environment type transformation schemes as a function of HP or HT for the (a) single-, (b) two- and (c) poly-environment types. The labels used refer to Fig. 2.

transform into one of the AETs only observed for metals (12-b, 12-d or 14-b).

These results are confirmed by Young [13], who also stated that with increasing pressure covalent bonds are destabilized and the elements of the top right-hand corner of the periodic table evolve towards close-packed structures.

As an example we take the transformation scheme of the tetrahedron (CN4 with label 4-a):

$$4\text{-a} \longrightarrow \text{HP} \longrightarrow 6\text{-a} \longrightarrow 8\text{-a} \longrightarrow$$

$$12\text{-d} \longrightarrow 12\text{-b} \longrightarrow 14\text{-b}$$

An element normally having the tetrahedron as an AET will change according to the experimentally known polymorphic modifications with increasing pressure to 14-b in the sequence as given. Some of the elements having a tetrahedron as an AET under NC do not

TABLE 6. Atomic environment types (AETs) observed in the element modifications in periodic system representation.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **H**<br>12-b<br>12-d | | | | | | | | | | | | | | | | | **He**<br>12-b<br>12-d<br>14-b |
| **Li**<br>12-b<br>12-d<br>14-b | **Be**<br>11-a<br>12-d<br>14-b | | | | | | | | | | | **B**<br>3#b<br>4-a | **C**<br>1#a | **N**<br>1#a | **O**<br>1#a | **F**<br>1#a | **Ne**<br>12-b |
| **Na**<br>12-b<br>12-d<br>14-b | **Mg**<br>12-d<br>14-b | | | | | | | | | | | **Al**<br>12-b<br>12-d | **Si**<br>4-a<br>6-a<br>8-c<br>12-b<br>12-d<br>14-b | **P**<br>3#a<br>6-a | **S**<br>2#a | **Cl**<br>1#a | **Ar**<br>12-b<br>12-d |
| **K**<br>12-b<br>14-b | **Ca**<br>6-a<br>12-b<br>12-d<br>14-b | **Sc**<br>12-b<br>12-d<br>14-b | **Ti**<br>12-d<br>14-b | **V**<br>14-b | **Cr**<br>14-b | **Mn**<br>Complex | **Fe**<br>12-b<br>12-d<br>14-b | **Co**<br>12-b<br>12-d | **Ni**<br>12-b | **Cu**<br>12-b | **Zn**<br>12-d | **Ga**<br>7-a<br>12-b | **Ge**<br>4-a<br>6-a | **As**<br>3#a<br>6-a | **Se**<br>2#a | **Br**<br>1#a | **Kr**<br>12-b |
| **Rb**<br>14-b | **Sr**<br>12-b<br>12-d<br>14-b | **Y**<br>12-d<br>14-b | **Zr**<br>12-d | **Nb**<br>14-b | **Mo**<br>14-b | **Tc**<br>12-d | **Ru**<br>12-d | **Rh**<br>12-b | **Pd**<br>12-b | **Ag**<br>12-b | **Cd**<br>12-d | **In**<br>12-b | **Sn**<br>4-a<br>6-a<br>12-b<br>14-b | **Sb**<br>6-a<br>7-b<br>12-d<br>16-a | **Te**<br>2#a<br>6-a<br>12-b<br>14-b | **I**<br>1#a | **Xe**<br>12-b |
| **Cs**<br>12-b<br>14-b | **Ba**<br>12-d<br>14-b | **La**<br>12-b<br>12-d<br>14-b | **Hf**<br>12-d<br>14-b | **Ta**<br>14-b | **W**<br>14-b | **Re**<br>12-d | **Os**<br>12-d | **Ir**<br>12-b | **Pt**<br>12-b | **Au**<br>12-b | **Hg**<br>12-b<br>14-b | **Tl**<br>12-b<br>12-d<br>14-b | **Pb**<br>12-b<br>12-d | **Bi**<br>6-a<br>7-b<br>14-b<br>16-a | **Po**<br>6-a<br>12-b | **At**<br>1#a | **Rn**<br>12-b |
| **Fr** | **Ra**<br>14-b | **Ac**<br>12-b | | | | | | | | | | | | | | | |

| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-b<br>12-d<br>14-b | 3#a<br>12-b<br>12-d<br>14-b | 12-b<br>12-d | 12-b<br>12-d | 12-b<br>12-d | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b | 12-b<br>12-d<br>14-b |

| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12-b<br>14-b | 12-b<br>14-b | 12-a<br>12-d<br>14-a<br>14-b<br>15-a | 14-b<br>16-a | 12-a<br>12-b<br>13-a<br>14-b<br>15-a<br>16-a | 12-b<br>12-d<br>14-b | 12-b<br>12-d | 12-b<br>12-d | 12-b<br>12-d | | | | | |

follow this sequence but change directly into an AET with a higher CN.

Table 6 shows, in periodic system representation, all AETs found for each element in its different modifications. Here it is nicely demonstrated that with the exception of the p-elements C, N, O, As, P, S and Se and the halides (mainly with the AETs 1#a (dumb-bell) and 2#a (double link)), all have either 12-d, 12-b or 14-b as an AET. For 1#a and 2#a there has until now been no polymorphic transformation scheme, but as mentioned before, structures having these AETs are probably better described in terms of cluster environments. From this observation it seems to be a safe prediction that those elements will have no modifications with either 12-d, 12-b or 14-b as an AET. The periodic table shows a clear tendency for the p-elements with a high group number and a low quantum number to have $CN \leqslant 6$.

An explanation for the fact that the AET 14-b is much preferred at HT is given by Young [13] in terms of the higher entropy of the b.c.c. ($cI2$ W type) phase, given a sufficiently "soft" interaction potential. The "softness" of the interaction potential is approximately determined by the Gruneisen parameter $\gamma$.

## 5. Modified structure stability diagrams (SSDs) for the elements

SSDs have been very successful in separating the structure types of binary intermetallic compounds at
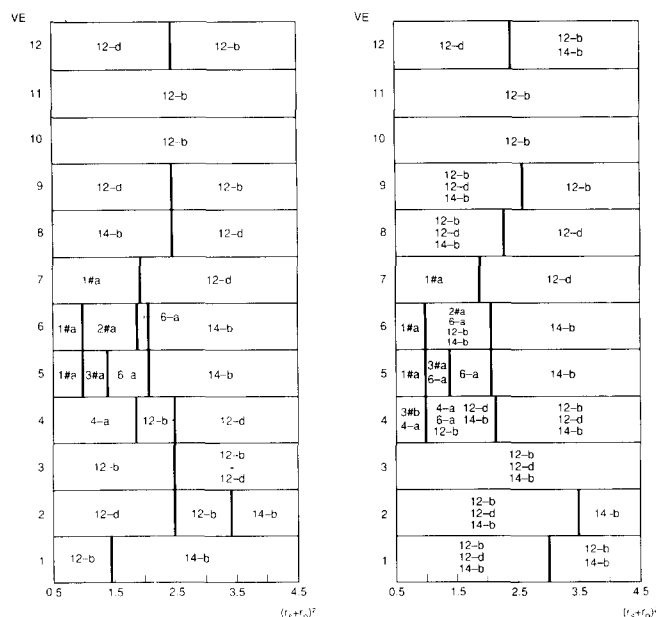
Fig. 4. The structure stability diagrams (SSDs) with AET stability domains (a) for the NC modifications and (b) with the HP and HT/LT modifications included. The labels used refer to Fig. 2.

constant stoichiometric ratios, e.g. AB, $AB_2$, etc. [5, 6]. Recently it was possible, by introducing the concentration as a variable, to extend the SSD for separating ternary and quaternary single-environment types [4]. In the approach with constant stoichiometric ratio the structure types could be separated, while in the approach with a variable concentration it was possible to separate different AET domains in the SSD. The axes normally used in the SSD are the sum of the valence electrons (VE), the differences between Zunger's pseudopotential radii $((r_s+r_p)^Z)$ and the difference in Martynov and Batsanov's [15] electronegativity $(X^{M\&B})$ of the constituent elements or their analogous concentration-dependent expressions.

For the elements the differences mentioned are zero. Therefore we modified the SSD by using only the tabulated values of VE, $(r_s+r_p)^Z$ and $X^{M\&B}$. Since the

electronegativity $(X^{M\&B})$ had no separation effect in the SSD, it seems to be irrelevant for the structure of the elements. Figure 4(a) shows the results for the element structures under NC. We observe a simple separation for all elements governed by VE and $(r_s+r_p)^Z$ only.

Including the HP and HT/LT modifications in our SSD, as we did in Fig. 4(b), made the interpretation only slightly more difficult. Again, it is possible to separate AET stability domains in the SSD. There are areas where definitely only one AET is stable for one of the modifications and others where three or four different AETs are stable for one of the modifications. We can use the observed separation in the AET stability domains for predicting the structure (AETs) of hitherto unknown HP and HT modifications. In Table 7 our predicted coordination types are given. We left out that AETs which are realized in only one representative because we think that it is not very sensible to base predictions on structures which occur just once.

## 6. Recommended atomic volumes

This section gives a complete, critically evaluated set of crystallographic data for the elements. Included in our list are the data of 275 modifications observed for the 96 elements as published in refs. 16 and 17. All modifications stable under NC as well as HP and HT/LT conditions, metastable modifications, modifications stabilized by oxygen, nitrogen or carbon atoms and modifications observed in thin film experiments are included. The minimum requirement for a modification to be included in Table 8 is that at least the structure type has to be known (refined or assigned) as well as the unit cell dimensions.

In Table 8 under the headings "Temperature" and "Pressure" the temperatures and pressures are given at which the unit cell dimensions have been determined. A blank space is given for all cases where no explicit measuring conditions were published in the paper. Under the heading "Comments" we give, wherever

TABLE 7. Predicted atomic environment types (AETs) for HP or HT/LT modifications of some elements based on SSD-AET domains (cf. Fig. 4(b)).

| Coordination type | Atomic environment type | Predicted high temperature and/or high pressure modifications |
|---|---|---|
| double link | 2#a | Po |
| tetrahedron | 4-a | Pb |
| octahedron | 6-a | Pb, S, Se |
| cubo-octahedron | 12-b | Ba, Be, Er, Fr, Ge, Hf, Mg, Rb, S, Se, Ti, U, Y, Zr |
| twinned cubo-octahedron | 12-d | Ac, Ga, Ge, In, Pa, Pu, Sn, Th |
| rhombic dodecahedron | 14-b | Ac, Al, Bk, Cf, Cm, Co, Fr, Ga, Ge, H, In, Pb, Pm, Po, S, Se, Sm, Zr |

TABLE 8. All element modifications listed alphabetically, with the data critically evaluated.

| | Temperature [K] | Pressure [GPa] | Pearson symbol | Structure type | Unit-cell dimension(s) a [nm] | b [nm] | c [nm] | β [°] | Atomic volume [10⁻²nm³] | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| Ac | | | cF4 | Cu | 0.5670(6) | | | | 4.557 | |
| Ag | 298 | | cF4 | Cu | 0.408626(4) | | | | 1.706 | (5N) |
| Al | 296 | | cF4 | Cu | 0.404950(12) | | | | 1.660 | (5N) |
| Al | | >20.5 | hP2 | Mg | 0.2693 | | 0.4398 | | 1.381 | HP |
| Am | 293 | | hP4 | La | 0.34681(8) | | 1.1241(3) | | 2.927 | stable below 1347K,5.2GPa |
| Am | | | cF4 | Cu | 0.4894(5) | | | | 2.930 | HT stable above 873K |
| Am | | 7.8 | cF4 | Cu | 0.4656(1) | | | | 2.523 | HP stable above 5.2GPa |
| Am | | 12.5 | mP4 | Am | 0.3025(5) | 1.1887(19) | 0.2830(5) | 106.11 | 2.444 | HP |
| Am | | 15.2 | oC4 | U | 0.3063(4) | 0.5968(10) | 0.5169(8) | | 2.362 | HP stable above 15GPa |
| Ar | 83.65 | | cF4 | Cu | 0.5316 | | | | 3.756 | LT |
| Ar | 83.6 | | hP2 | Mg | 0.3760 | | 0.6141 | | 3.760 | LT |
| As | 296 | | hR2 | As | 0.37598(3) | | 1.0547(2) | | 2.152 | (4N) |
| As | | | oC8 | P | 0.362 | 1.085 | 0.448 | | 2.243 | HT stable above 721K |
| Au | 298 | | cF4 | Cu | 0.407894(5) | | | | 1.697 | (5N) |
| B | | | hR105 | B | 1.096(5) | | 2.389(9) | | 0.789 | (5N) |
| B | | | hR12 | B | 0.491 | | 1.257 | | 0.729 | LT stable below 1373K |
| B | | | tP196 | B | 1.0061(5) | | 1.4210(5) | | 0.734 | |
| B | | | tP50 | B | 0.875(2) | | 0.5075(1) | | 0.777 | |
| Ba | 298 | | cI2 | W | 0.5013(5) | | | | 6.299 | (99.3%) |
| Ba | | 6.2 | hP2 | Mg | 0.3901 | | 0.6154 | | 4.055 | HP stable above 5.9GPa |
| Ba | | | cF4 | Cu | 0.605(2) | | | | 5.536 | metastable |
| Be | 293 | | hP2 | Mg | 0.22858(2) | | 0.35843(3) | | 0.811 | (3N); stable below 1527K, 28GPa |
| Be | 1527 | | cI2 | W | 0.25515 | | | | 0.831 | (99.96%); HT stable above 1527K |
| Be | | 28.3 | oP4 | Be | 0.2168 | 0.3755 | 0.3416 | | 0.695 | HP stable above 28.3GPa |
| Bi | 298 | | hR2 | As | 0.45460(5) | | 1.1862(1) | | 3.538 | |
| Bi | | 0.26 | mC4 | Bi | 0.6674(2) | 0.6117(2) | 0.3304(2) | 110.33 | 3.162 | |
| Bi | 298 | 2.5 | cP1 | Po | 0.3177(9) | | | | 3.207 | HP |
| Bi | | 3.55 | mP4 | Sb | 0.665 | 0.420 | 0.465 | 85.33 | 3.236 | HP |
| Bi | | 9 | cI2 | W | 0.3800(5) | | | | 2.744 | HP |
| Bk | | | hP4 | La | 0.3428(3) | | 1.1075(1) | | 2.818 | LP stable below 8GPa |
| Bk | | | cF4 | Cu | 0.4997(4) | | | | 3.112 | HT stable above 1250K |
| Bk | | | cF4 | Cu | 0.481(1) | | | | 2.782 | HP stable between 8-22GPa |
| Bk | | 45.9 | oC4 | U | 0.2317 | 0.5584 | 0.4480 | | 1.449 | HP |
| Br | 265.75 | | oC8 | Cl₂ | 0.668 | 0.449 | 0.874 | | 3.277 | LT |
| C | 296 | | hP4 | C | 0.2464(2) | | 0.6711(4) | | 0.882 | |
| C | 298 | | cF8 | C | 0.3566986(3) | | | | 1.135 | HP stable above 60GPa |
| Ca | 299 | | cF4 | Cu | 0.55884(2) | | | | 4.363 | LT stable below 617K |
| Ca | 688 | | hP2 | Mg | 0.400(2) | | 0.650(2) | | 4.503 | (99.8%); HT stable 617-883K |
| Ca | 888 | | cI2 | W | 0.4488(5) | | | | 4.520 | (99.8%); HT stable above 883K |
| Ca | | 26.5 | cI2 | W | 0.3559 | | | | 2.254 | HP |
| Ca | | 39 | cP1 | Po | 0.2615(2) | | | | 1.788 | HP |
| Cd | 294 | | hP2 | Mg | 0.2972(8) | | 0.5605(4) | | 2.144 | (6N) |
| Ce | | | hP4 | La | 0.36810 | | 1.1857 | | 3.478 | |
| Ce | | | cF4 | Cu | 0.51612(5) | | | | 3.437 | HT stable above 334K |
| Ce | 1030 | | cI2 | W | 0.412 | | | | 3.497 | HT |
| Ce | | 1.5 | cF4 | Cu | 0.482 | | | | 2.800 | HP stable above 0.7GPa |
| Ce | | 5.8 | oC4 | U | 0.3049 | 0.5998 | 0.5215 | | 2.384 | HP stable between 5.1-9.5GPa |
| Ce | | 6.5 | hP2 | Mg | 0.316(1) | | 0.520(2) | | 2.248 | (3N); HP stable above 5GPa |
| Ce | | 30.4 | tI2 | In | 0.2827(4) | | 0.4777(12) | | 1.909 | HP stable above 12.5GPa |
| Cf | | | hP4 | La | 0.3380(2) | | 1.1025(2) | | 2.727 | coexists with hP4 La with a=0.4002nm, c=1.2803nm |
| Cf | | | hP2 | Mg | 0.3988(4) | | 0.6887(8) | | 4.743 | |
| Cf | | 46.6 | oC4 | U | 0.2313 | 0.5526 | 0.4472 | | 1.429 | HP |
| Cf | | | cF4 | Cu | 0.5743(6) | | | | 4.735 | HT? |
| Cf | | | aP4 | Cf | 0.3307 | 0.7412 | 0.2793 | 89.1/85.2/85.7 | 1.700 | HP |
| Cl | | | oC8 | Cl₂ | 0.624 | 0.448 | 0.826 | | 2.886 | LT |
| Cm | 293 | | hP4 | La | 0.3496(3) | | 1.1331(5) | | 2.998 | LP stable below 23GPa |
| Cm | | | cF4 | Cu | 0.493(1) | | | | 2.996 | HP stable between 23-43GPa |
| Cm | | 455 | cF4 | Cu | 0.5039(1) | | | | 3.199 | HT; two phase sample |
| Cm | | | oC4 | U | 0.2436 | 0.5810 | 0.4515 | | 1.598 | HP stable above 43GPa |
| Co | | | hP2 | Mg | 0.25071(3) | | 0.40695(5) | | 1.108 | (5N); LT stable below 673K |
| Co | 793 | | cF4 | Cu | 0.35688 | | | | 1.136 | (99.92%); HT stable above 673K |
| Co | | | hP46 | Co | 0.8288 | | 1.0542 | | 1.363 | (3N); metastable; C-stabilized |
| Cr | 290 | | cI2 | W | 0.28844 | | | | 1.200 | (99.95%) |
| Cr | | | tI2 | Cr | 0.2882 | | 0.2887 | | 1.199 | HP |
| Cr | | | cP8 | Cr₃Si | 0.460 | | | | 1.217 | thin films |
| Cs | | | cI2 | W | 0.6141(7) | | | | 11.579 | |
| Cs | | | cF4 | Cu | 0.6465(15) | | | | 6.755 | HP |
| Cs | 300 | 4.25 | cF4 | Cu | 0.5800(7) | | | | 4.878 | HP stable between 4.22-4.27GPa |
| Cs | 300 | 4.1 | cF4 | Cu | 0.5984(11) | | | | 5.357 | HP stable between 2.37-4.22GPa |
| Cs | | 18.2 | tP8 | Cs | 0.6506(4) | | 0.5627(5) | | 2.977 | HP stable above 10GPa |
| Cu | | | cF4 | Cu | 0.361491 | | | | 1.181 | (5N) |
| Dy | | | hP2 | Mg | 0.35903(2) | | 0.56475(2) | | 3.152 | (99.8%) |
| Dy | | | cF4 | Cu | 0.518(5) | | | | 3.475 | thin films |
| Dy | | | cI2 | W | 0.398(2) | | | | 3.152 | HT |
| Dy | 86 | | oC4 | U | 0.3595 | 0.6184 | 0.5678 | | 3.156 | presumably oC4 U-type |
| Dy | | 7.5 | hR3 | Sm | 0.334(1) | | 2.45(1) | | 2.630 | HP stable above 4.8GPa |
| Er | | | hP2 | Mg | 0.35588(3) | | 0.55874(3) | | 3.064 | (99.8%) |

TABLE 8. (*continued*)

| | Temperature [K] | Pressure [GPa] | Pearson symbol | Structure type | Unit–cell dimension(s) | | | | | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | a [nm] | b [nm] | c [nm] | β [°] | Atomic volume [10⁻²nm³] | |
| Er | | | cl2 | W | 0.394(2) | | | | 3.058 | HT |
| Er | | | cF4 | Cu | 0.509(5) | | | | 3.297 | thin films |
| Eu | | | cF4 | Cu | 0.4580(2) | | | | 2.402 | |
| Eu | | | cl2 | W | 0.4583 | | | | 4.813 | (99.98%); LP stable below 11GPa |
| Eu | | 13.0 | hP2 | Mg | 0.3398 | | 0.5385 | | 2.693 | (99.98%); HP stable above 13GPa |
| Eu | | 15.1 | hP2 | Mg | 0.3407(3) | | 0.5450(5) | | 2.739 | HP stable above 15 GPa |
| Eu | | 20 | hP2 | Mg | 0.3273 | | 0.5083 | 102.17 | 2.358 | (99.98%); HP stable above 19.9GPa |
| F | 45.4 | | mC8 | F₂ | 0.550 | 0.338 | 0.728 | | 1.654 | LT |
| F | 53.33 | | cP16 | O₂ | 0.667 | | | | 1.855 | LT |
| Fe | 293 | | cl2 | W | 0.28665 | | | | 1.178 | (99.97%); LT stable below 1183K |
| Fe | | 12.7 | hP2 | Mg | 0.2473 | | 0.3962 | | 1.049 | HP stable above 8.3GPa |
| Fe | 1349 | | cF4 | Cu | 0.36599 | | | | 1.225 | HT stable above 1183K |
| Fe | 1663 | | cl2 | W | 0.29315 | | | | 1.260 | (99.97%); HT stable above 1663K |
| Ga | 291 | | oC8 | Ga | 0.45167(1) | 0.76448(2) | 0.45107(1) | | 1.947 | |
| Ga | 313 | 2.6 | cl12 | Ga | 0.5951(5) | | | | 1.756 | HP |
| Ga | 298 | 2.8 | tl2 | In | 0.2813(3) | | 0.4452(5) | | 1.762 | HP |
| Ga | 191 | | hR22 | Ga | 0.9087(6) | | 1.702(1) | 92.03 | 1.844 | metastable |
| Ga | 248 | | mC4 | Ga | 0.2766(8) | 0.8053(24) | 0.3332(10) | | 2.133 | metastable |
| Ga | 257 | | oC4 | Ga | 0.290(3) | 0.813(3) | 0.317(3) | | 1.869 | metastable |
| Ga | | | oC40 | Ga | 1.0593(2) | 1.3523(3) | 0.5203(1) | | 1.863 | metastable |
| Gd | | | hP2 | Mg | 0.36360(9) | | 0.57826(6) | | 3.310 | (99.7%) |
| Gd | | | cl2 | W | 0.405(2) | | | | 3.322 | HT stable above 1508K |
| Gd | | 3.5 | hR3 | Sm | 0.349(1) | | 2.56(1) | | 3.000 | HP stable above 2.5GPa |
| Gd | 573 | 7.5 | hP4 | La | 0.3402 | | 1.1047 | | 2.768 | (3N); HP |
| Gd | | | cF4 | Cu | 0.540(5) | | | | 3.937 | thin films |
| Ge | 296 | | cF8 | C | 0.565752(17) | | | | 2.264 | (7N); LP stable below 10.5GPa |
| Ge | | 12 | tl4 | Sn | 0.49585 | | 0.27463 | | 1.688 | HP stable above 10.5GPa |
| Ge | | 10.8 | tP12 | Ge | 0.58017 | | 0.66257 | | 1.859 | HP stable above 12GPa |
| Ge | | | cl16 | Si | 0.692(1) | | | | 2.071 | HP/HT |
| Ge | | | hP4 | SZn | 0.394(5) | | 0.655(5) | | 2.201 | metastable |
| H | 1.1 | | cF4 | Cu | 0.5338 | | | | 1.902 | LT |
| H | 13.66 | | hP2 | Mg | 0.3776 | | 0.6162 | | 3.805 | LT |
| He | 15 | 0.125 | cF4 | Cu | 0.4240 | | | | 1.906 | |
| He | 4.06 | | hP2 | Mg | 0.3555 | | 0.5798 | | 3.173 | |
| He | 1.53 | 0.03 | cl2 | W | 0.4110 | | | | 3.472 | |
| Hf | 298 | | hP2 | Mg | 0.3198 | | 0.5061 | | 2.241 | LT stable below 2050K |
| Hf | 2073 | | cl2 | W | 0.3615 | | | | 2.362 | HT stable above 2050K |
| Hg | 227 | | hR1 | Hg | 0.3460 | | 0.6702 | | 2.316 | |
| Hg | | | hP6 | Hg | 0.454(2) | | 0.774(2) | | 2.303 | LT stable below 118K; As–stabilized |
| Hg | 79 | | tl2 | Pa | 0.3995 | | 0.2825 | | 2.255 | LT/HP |
| Ho | | | hP2 | Mg | 0.35773(1) | | 0.56158(2) | | 3.112 | (99.4%) |
| Ho | | | cl2 | W | 0.396(2) | | | | 3.105 | HT |
| Ho | | 8.5 | hR3 | Sm | 0.334(1) | | 2.41(1) | | 2.587 | HP stable above 7.0GPa |
| Ho | | | cF4 | Cu | 0.515(5) | | | | 3.415 | thin films |
| I | | | oC8 | Cl₂ | 0.72697 | 0.47903 | 0.97942 | | 4.263 | |
| In | | | tl2 | In | 0.32530(1) | | 0.49455(2) | | 2.617 | (6N) |
| Ir | 297 | | cF4 | Cu | 0.38385 | | | | 1.414 | (99.97%) |
| K | 301 | | cl2 | W | 0.533017(34) | | | | 7.572 | (99.95%) |
| K | | 12.4 | cF4 | Cu | 0.5148 | | | | 3.411 | HP stable above 12GPa |
| Kr | 115.61 | | cF4 | Cu | 0.5810 | | | | 4.903 | LT |
| La | | | hP4 | La | 0.3770(2) | | 1.2159(8) | | 3.741 | (99.8%); LT stable below 533K |
| La | | | cF4 | Cu | 0.5291(5) | | | | 3.703 | HT stable between 673–1123K |
| La | 1160 | | cl2 | W | 0.426 | | | | 3.866 | HT stable above 1113K |
| La | 298 | 2.0 | cF4 | Cu | 0.517 | | | | 3.455 | HP |
| Li | 298 | | cl2 | W | 0.351004(41) | | | | 2.162 | (99.8%) |
| Li | 20 | | hR3 | Sm | 0.30978(5) | | 2.2734(5) | | 2.099 | (4N); LT stable below 20K |
| Li | 78 | | hP2 | Mg | 0.3111 | | 0.5093 | | 2.465 | two phase sample |
| Li | | 8.0 | cF4 | Cu | 0.3900(3) | | | | 1.483 | HP stable above 6.9GPa |
| Lu | | | hP2 | Mg | 0.35031(4) | | 0.55509(4) | | 2.950 | (3N) |
| Lu | | | cl2 | W | 0.390(2) | | | | 2.966 | HT |
| Lu | 296 | 23 | hR3 | Sm | 0.3176(6) | | 2.177(4) | | 2.113 | HP stable above 23.0GPa |
| Mg | 298 | | hP2 | Mg | 0.320944 | | 0.521076 | | 2.324 | (99.94%) |
| Mg | | 58 | cl2 | W | 0.29530(20) | | | | 1.288 | HP stable above 50GPa |
| Mn | 293 | | cl58 | Mn | 0.8910(3) | | | | 1.220 | (99.87%); LT stable below 993K |
| Mn | 1008 | | cP20 | Mn | 0.6482 | | | | 1.362 | (99.87%); HT stable above 993K |
| Mn | 1352 | | cF4 | Cu | 0.3860 | | | | 1.438 | HT stable above 1352K |
| Mn | 1416 | | cl2 | W | 0.3080 | | | | 1.461 | HT stable above 1416K |
| Mo | | | cl2 | W | 0.314700(1) | | | | 1.558 | (99.994%) |
| N | 296 | 2.51 | hP2 | Mg | 0.3629(4) | | 0.5890(10) | | 3.359 | LT/HP |
| N | 110 | 6.2 | hP24 | N₂ | 0.8119(2) | | 1.1332(11) | | 2.695 | LT/HP |
| N | 110 | 7.8 | hR16 | N₂ | 0.8020(12) | | 1.1104(29) | | 1.289 | LT/HP |
| N | 299 | 4.9 | cP64 | N₂ | 0.6164(1) | | | | 0.366 | LT/HP |
| Na | 298 | | cl2 | W | 0.42820(5) | | | | 3.926 | |
| Na | 5 | | hP2 | Mg | 0.3767 | | 0.6154 | | 3.782 | LT stable below 36K |
| Na | 20 | | hR3 | Sm | 0.376586(8) | | 2.76531(2) | | 3.774 | martensitic phase |
| Nb | 295 | | cl2 | W | 0.33063(2) | | | | 1.807 | (99.995%) |
| Nd | | | hP4 | La | 0.36579(3) | | 1.17992(5) | | 3.418 | (99.8%) |
| Nd | 1156 | | cl2 | W | 0.413 | | | | 3.522 | HT stable above 1156K |

(*continued*)

TABLE 8. (continued)

| | Temperature [K] | Pressure [GPa] | Pearson symbol | Structure type | a [nm] | b [nm] | c [nm] | β [°] | Atomic volume [10⁻²nm³] | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| Nd | 573 | 5.5 | cF4 | Cu | 0.4917 | | | | 2.972 | (3N); HP/HT |
| Ne | 29.41 | | cF4 | Cu | 0.4462 | | | | 2.221 | LT |
| Ni | | | cF4 | Cu | 0.35232 | | | | 1.093 | (99.997%) |
| Ni | | | hP2 | Mg | 0.2622 | | 0.4321 | | 1.287 | thin films; O-stabilized |
| Np | 293 | | oP8 | Np | 0.6663(3) | 0.4723(1) | 0.4887(2) | | 1.922 | |
| Np | 586 | | tP4 | Np | 0.4897(2) | | 0.3388(2) | | 2.031 | HT stable between 551–803K |
| Np | 849 | | cI2 | W | 0.352 | | | | 2.181 | HT stable above 849K |
| O | 54.21 | | cP16 | O₂ | 0.683 | | | | 1.991 | LT stable below 54.21K |
| O | 299 | 5.5 | hR2 | O₂ | 0.28467(2) | | 1.02249(8) | | 1.196 | HP |
| O | 23 | | mC4 | O₂ | 0.5403(5) | 0.3429(3) | 0.5086(5) | 132.53 | 1.736 | LT |
| O | 297 | 9.6 | oF8 | O₂ | 0.42151(6) | 0.29567(4) | 0.66897(17) | | 1.042 | HP |
| Os | 291 | | hP2 | Mg | 0.27304(5) | | 0.43099(5) | | 1.391 | (99.8%) |
| P | | | oC8 | P | 0.33136(1) | 1.0478(5) | 0.43763(1) | | 1.899 | |
| P | | 9 | hR2 | As | 0.339 | | 0.864 | | 1.433 | (5N); HP stable between 5.3–9.8GPa |
| P | | 25 | cP1 | Po | 0.229 | | | | 1.201 | HP stable above 10GPa |
| Pa | | | tI2 | Pa | 0.3932(3) | | 0.3238(3) | | 2.503 | |
| Pa | | | cF4 | Cu | 0.5031(2) | | | | 3.184 | HT |
| Pa | 1443 | | cI2 | W | 0.381 | | | | 2.766 | HT stable above 1443K |
| Pb | 298 | | cF4 | Cu | 0.49508(4) | | | | 3.034 | (5N) |
| Pb | 298 | 13.9 | hP2 | Mg | 0.3265(4) | | 0.5387(7) | | 2.487 | (5N); HP stable above 13GPa |
| Pd | 293 | | cF4 | Cu | 0.38874(1) | | | | 1.469 | (99.993%) |
| Pm | | | hP4 | La | 0.365 | | 1.165 | | 3.360 | |
| Po | | | cP1 | Po | 0.3345(2) | | | | 3.743 | LT stable below 348K |
| Po | | | hR1 | Hg | 0.5079(5) | | 0.4916(5) | | 3.661 | HT stable above 348K |
| Pr | | | hP4 | La | 0.36725(7) | | 1.18354(12) | | 3.456 | (3N) |
| Pr | 1094 | | cI2 | W | 0.413 | | | | 3.522 | HT |
| Pr | 293 | | cF4 | Cu | 0.5186 | | | | 3.487 | HT |
| Pr | 298 | 4.0 | cF4 | Cu | 0.488 | | | | 2.905 | HP |
| Pr | | 14.4 | hP6 | Pr | 0.3240 | | 1.5762 | | 2.388 | HP stable above 14.4GPa |
| Pt | 298 | | cF4 | Cu | 0.39242 | | | | 1.511 | (3N) |
| Pu | 294 | | mP16 | Pu | 0.6183(1) | 0.4822(1) | 1.0963(1) | 101.79 | 2.000 | (3N); LT stable below 395K |
| Pu | 366 | | mC34 | Pu | 1.1830 | 1.0449 | 0.9227 | 138.65 | 2.216 | HT stable between 395–479K |
| Pu | 508 | | oF8 | Pu | 0.31587(4) | 0.57682(4) | 1.0162(2) | | 2.314 | (99.85%); HT stable between 486–585K |
| Pu | 653 | | cF4 | Cu | 0.46347 | | | | 2.489 | (99.97%); HT stable between 592–724K |
| Pu | 750 | | tI2 | In | 0.3339(3) | | 0.4446(7) | | 2.479 | (99.97%); HT stable between 724–758K |
| Pu | 773 | | cI2 | W | 0.36375 | | | | 2.407 | HT; stable above 724K |
| Ra | | | cI2 | W | 0.5148(15) | | | | 6.822 | |
| Rb | | | cI2 | W | 0.5585 | | | | 9.284 | |
| Re | | | hP2 | Mg | 0.2760 | | 0.4458 | | 1.470 | (4N) |
| Rh | | | cF4 | Cu | 0.37956(3) | | | | 1.367 | (4N) |
| Ru | | | hP2 | Mg | 0.27059(3) | | 0.42816(2) | | 1.357 | (4N) |
| S | | | oF128 | S | 1.0437(10) | 1.2845(10) | 2.4369(10) | | 2.552 | LT stable below 368.5K |
| S | | | mP32 | S₅Se₃ | 0.8442(30) | 1.3025(10) | 0.9356(50) | 124.98 | 2.634 | |
| S | | | hR6 | Se | 1.09 | | 0.427 | | 2.441 | |
| S | 163 | | mP56 | S | 1.5096(5) | 0.5998(7) | 2.0951(5) | 133.91 | 2.440 | |
| S | | | mP28 | S | 0.9680(3) | 0.7641(2) | 0.9409(2) | 102.08 | 2.430 | |
| Sb | | | hR2 | As | 0.4297 | | 1.1244 | | 2.997 | (5N); LP stable below 6 GPa |
| Sb | | 7 | cP1 | Po | 0.2986(9) | | | | 2.662 | HP stable between 6–7.5GPa |
| Sb | 423 | 11.5 | mP4 | Sb | 0.5752 | 0.3914 | 0.4452 | 85.35 | 2.498 | HP stable above 8GPa |
| Sb | | 9.0 | hP2 | Mg | 0.3369 | | 0.533 | | 2.620 | HP stable above 8.5GPa |
| Sb | | | hP2 | Mg | 0.333 | | 0.523 | | 2.511 | thin films; metastable |
| Sb | | | tI2 | In | 0.301 | | 0.496 | | 2.247 | thin films; metastable |
| Sb | | | cF4 | Cu | 0.461 | | | | 2.449 | thin films; metastsble |
| Sc | | | hP2 | Mg | 0,33090(1) | | 0.52733(1) | | 2.500 | (99.6%) |
| Sc | 1610 | | cI2 | W | 0.4541 | | | | 4.682 | HT stable above 1610K |
| Sc | | 26.0 | tI2 | In | 0.3758(11) | | 0.4761(32) | | 3.362 | HP stable above 19.0GPa |
| Sc | | 33.5 | tP4 | Np | 0.473(2) | | 0.318(1) | | 1.779 | HP stable above 20GPa |
| Sc | | | cF4 | Cu | 0.476(1) | | | | 2.696 | thin films; H-stabilized |
| Se | | | hP3 | Se | 0.4366 | | 0.4955 | | 2.727 | (5N) |
| Se | | | mP32 | Se | 0.931 | 0.807 | 1.285 | 93.13 | 3.013 | |
| Se | | | mP64 | Se | 1.5018(1) | 1.4713(1) | 0.8789(1) | 93.61 | 3.028 | |
| Se | | | hR6 | Se | 1.1362(1) | | 0.4429(8) | | 2.751 | LT stable below 378K |
| Se | | | cP1 | Po | 0.2982(3) | | | | 6.314 | (99.98%); metastable |
| Si | 303 | | cF8 | C | 0.54306 | | | | 2.002 | (6N) |
| Si | | | tI4 | Sn | 0.4686 | | 0.2585 | | 1.416 | HP stable above 13GPa |
| Si | | 20 | hP1 | BiIn | 0.2527 | | 0.2373 | | 1.312 | HP stable between 16–35GPa |
| Si | | 43 | hP2 | Mg | 0.2444 | | 0.4152 | | 1.074 | HP stable above 43GPa |
| Si | | 87 | cF4 | Cu | 0.334(10) | | | | 0.932 | HP stable above 78GPa |
| Si | | >0.0016 | hP4 | La | 0.380 | | 0.628 | | 1.963 | recovered from HP experiment |
| Si | | | cI16 | Si | 0.6636(5) | | | | 1.826 | |
| Sm | 273 | | hR3 | Sm | 0.36280 | | 2.6194 | | 3.318 | (99.8%); LT stable below 980K |
| Sm | 980 | | hP2 | Mg | 0.3644(5) | | 0.5876(5) | | 3.379 | HT stable above 980K |
| Sm | | | hP4 | La | 0.3618(5) | | 1.166(1) | | 3.305 | HP/HT stable around 4GPa/573K |
| Sn | 298 | | tI4 | Sn | 0.58317(2) | | 0.31813(2) | | 2.705 | (4N) |
| Sn | 293 | | cF8 | C | 0.64892(1) | | | | 6.832 | (4N) |

TABLE 8. (continued)

| | Temperature [K] | Pressure [GPa] | Pearson symbol | Structure type | Unit-cell dimension(s) | | | | Atomic volume [10⁻²nm³] | Comments |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | a [nm] | b [nm] | c [nm] | β [°] | | |
| Sn | | | tl2 | In | 0.31815(2) | | 0.58313(2) | | 2.951 | |
| Sn | | 24.5 | tl2 | Pa | 0.3519 | | 0.3271 | | 2.096 | HP stable between 11.8–41.8GPa |
| Sn | | 53 | cl2 | W | 0.3287 | | | | 1.776 | HP stable above 50GPa |
| Sr | 298 | | cF4 | Cu | 0.60849(5) | | | | 5.632 | (99.5%); LT stable below 488K |
| Sr | 498 | | hP2 | Mg | 0.428(2) | | 0.705(2) | | 5.592 | (99.5%); HT stable between 486–875K |
| Sr | 901 | | cl2 | W | 0.487(2) | | | | 5.775 | (99.5%); HT stable above 875K |
| Ta | 299 | | cl2 | W | 0.330256(5) | | | | 1.801 | |
| Tb | 300 | | hP2 | Mg | 0.36092 | | 0.56966 | | 3.213 | (99.5%); HT stable above 223K |
| Tb | | | cl2 | W | 0.402(2) | | | | 3.248 | HT |
| Tb | 298 | | hR3 | Sm | 0.3568(7) | | 2.581(5) | | 3.162 | (99.8%); HP stable above 2.5GPa |
| Tb | | 28.8 | hP6 | NbS₂ | 0.3068(4) | | 1.487(2) | | 1.424 | HP stable between 28–32GPa |
| Tb | | | cF4 | Cu | 0.520(5) | | | | 3.515 | thin films |
| Tb | 220 | | oC4 | U | 0.3605 | 0.6244 | 0.5706 | | 3.211 | presumably oC4 U–type |
| Tc | | | hP2 | Mg | 0.2740 | | 0.4398 | | 1.430 | |
| Te | 293 | | hP3 | Se | 0.4456(1) | | 0.5921(2) | | 3.394 | (5N) |
| Te | | 3 | hR2 | As | 0.4208 | | 1.2036 | | 3.076 | HP stable above 1.5GPa |
| Te | | 4.5 | mP4 | Te | 0.3104(5) | 0.7513(10) | 0.4760(9) | 92.71 | 2.772 | HP |
| Te | | 11.5 | hR1 | Hg | 0.4603 | | 0.3822 | | 2.338 | HP stable above 7.0GPa |
| Th | 298 | | cF4 | Cu | 0.5089(1) | | | | 3.295 | (99.8%); LT stable below 1673K |
| Th | 1723 | | cl2 | W | 0.411(1) | | | | 3.472 | (99.8%); HT stable above 1673K |
| Ti | 293 | | hP2 | Mg | 0.29503(6) | | 0.46810(2) | | 1.764 | (99.93%); LT stable below 1153K |
| Ti | 1193 | | cl2 | W | 0.33112 | | | | 1.706 | (99.93%); HT stable above 1153K |
| Ti | 298 | 4 | hP3 | AlB₂ | 0.46 | | 0.282 | | 1.723 | C–stabilized |
| Tl | 291 | | hP2 | Mg | 0.34496(2) | | 0.55137(4) | | 2.841 | LT stable below 503K |
| Tl | 535 | | cl2 | W | 0.3874(1) | | | | 2.907 | (99.995%); HT stable above 503K |
| Tl | 517 | | cF4 | Cu | 0.4889(5) | | | | 2.922 | HT |
| Tm | | | hP2 | Mg | 0.35375(1) | | 0.55546(4) | | 3.010 | (3N) |
| Tm | | | cl2 | W | 0.392(2) | | | | 3.012 | HT |
| Tm | | 11.6 | hR3 | Sm | 0.3327(5) | | 2.348(4) | | 2.501 | HP stable above 11.6GPa |
| Tm | | | cF4 | Cu | 0.506(5) | | | | 3.239 | thin films |
| U | 298 | | oC4 | U | 0.28535 | 0.58648 | 0.49543 | | 2.073 | LT stable below 935K |
| U | 955 | | tP30 | CrFe | 1.07589 | | 0.56531 | | 2.181 | HT stable between 935–1045K |
| U | 1073 | | cl2 | W | 0.3532 | | | | 2.203 | HT stable above 1003K |
| U | | | tP30 | U | 1.052 | | 0.557 | | 2.055 | |
| V | 300 | | cl2 | W | 0.30309 | | | | 1.392 | (99.74%) |
| W | 298 | | cl2 | W | 0.31652 | | | | 1.586 | (3N) |
| Xe | 161.24 | | cF4 | Cu | 0.6350 | | | | 6.401 | LT stable below 161.24K |
| Y | 298 | | hP2 | Mg | 0.36515(2) | | 0.57474(4) | | 3.318 | (3N) |
| Y | 1751 | | cl2 | W | 0.407 | | | | 3.371 | HT stable above 1751K |
| Y | | | cF4 | Cu | 0.583(2) | | | | 4.954 | thin films |
| Yb | | | cF4 | Cu | 0.54862(4) | | | | 4.128 | (3N) |
| Yb | 296 | | hP2 | Mg | 0.38799 | | 0.63859 | | 4.163 | (3N); LT stable below 270K |
| Yb | 1047 | | cl2 | W | 0.444 | | | | 4.377 | HT |
| Yb | | 34.0 | hP2 | Mg | 0.3015 | | 0.4823 | | 1.899 | (99.98%); HP stable above 30.9GPa |
| Zn | 295 | | hP2 | Mg | 0.266469(2) | | 0.494616(4) | | 1.521 | (5N) |
| Zr | | | hP2 | Mg | 0.323178 | | 0.514831 | | 2.328 | (99.995%) |
| Zr | | | hP3 | AlB₂ | 0.5036 | | 0.3109 | | 2.276 | recovered from HP experiment |
| Zr | | | cl2 | W | 0.3568(5) | | | | 2.271 | metastable |

available, the purity of the elements as well as their stability range.

The recommended atomic volumes from our analysis are given in Table 9 in a periodic table representation. These atomic volumes are calculated by dividing the unit cell volume by the number of atoms in the unit cell for the modification stable under normal conditions or closest to these conditions. Figure 5(a) shows our recommended atomic volumes in a property vs. atomic number plot with the atoms sorted as in the periodic table. For comparison we also give the metallic radii (for $CN = 12$) of Teatum et al. (ref. 1, p. 151) in Fig. 5(b), the covalent radii according to Pauling (ref. 2,

p. 98) in Fig. 5(c) and the ionic radii according to Kordes (ref. 2, p. 98) in Fig. 5(d). These radii are all derived from interatomic distances in intermetallic compounds with predominantly metallic, covalent or ionic bonding.

It is obvious that the general pattern for our atomic volumes is very similar to that of the metallic and covalent radii. The trend along the same period as well as along the same group deviates only in minor details. The behaviour of the ionic radii from Kordes for the s- and the $d^3$- to $d^{10}$-elements is also similar to our pattern, while for the $d^{10}$- to $d^{12}$- and the p-elements it differs significantly, especially along the period. We

TABLE 9. The recommended atomic volumes ($10^{-2}$ nm$^3$) of the elements under normal conditions (198 K, 100 kPa). The elements marked with an asterisk are given for non-normal conditions.

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H* 1.902 | | | | | | | | | | | | | | | | | He* 1.906 |
| Li 2.162 | Be 0.811 | | | | | | | | | | | B 0.789 | C 0.882 | N* 1.289 | O* 1.736 | F* 1.855 | Ne* 2.221 |
| Na 3.926 | Mg 2.324 | | | | | | | | | | | Al 1.660 | Si 2.002 | P 1.899 | S 2.552 | Cl* 2.886 | Ar* 3.756 |
| K 7.572 | Ca 4.363 | Sc 2.500 | Ti 1.764 | V 1.392 | Cr 1.200 | Mn 1.220 | Fe 1.178 | Co 1.108 | Ni 1.093 | Cu 1.181 | Zn 1.521 | Ga 1.947 | Ge 2.264 | As 2.152 | Se 2.727 | Br* 3.277 | Kr* 4.903 |
| Rb 9.284 | Sr 5.632 | Y 3.318 | Zr 2.328 | Nb 1.807 | Mo 1.558 | Tc 1.430 | Ru 1.357 | Rh 1.367 | Pd 1.469 | Ag 1.706 | Cd 2.144 | In 2.617 | Sn 2.705 | Sb 2.997 | Te 3.394 | I 4.263 | Xe* 6.401 |
| Cs 11.579 | Ba 6.299 | La 3.741 | Hf 2.241 | Ta 1.801 | W 1.586 | Re 1.470 | Os 1.391 | Ir 1.414 | Pt 1.511 | Au 1.697 | Hg 2.316 | Tl 2.841 | Pb 3.034 | Bi 3.538 | Po 3.743 | At (5.75) | Rn* (8.25) |
| Fr (13) | Ra 6.822 | Ac 4.557 | | | | | | | | | | | | | | | |

| Ce 3.478 | Pr 3.456 | Nd 3.418 | Pm 3.360 | Sm 3.318 | Eu 4.813 | Gd 3.310 | Tb 3.213 | Dy 3.152 | Ho 3.112 | Er 3.064 | Tm 3.010 | Yb 4.128 | Lu 2.950 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Th 3.295 | Pa 2.503 | U 2.073 | Np 1.922 | Pu 2.000 | Am 2.927 | Cm 2.998 | Bk 2.818 | Cf 2.727 | Es | Fm | Md | No | Lr |

observe a doubling of the radii for the d$^{11}$- and d$^{12}$- elements and a clear decrease in the ionic radii for the p-elements with increasing group number.

.. Using one of the above-mentioned radii in the SSD for intermetallic compounds, however, was not successful. Only the introduction of the pseudopotential radii $(r_s + r_p)^Z$ of Zunger led to the complete separation of the structure types into AET domains. These radii are derived from a model in which the valence and core atoms are considered separately. The pseudo-potential reproduces only the valence charge density of the solid. This type of potential can be used to determine the orbital-dependent radii, e.g. the radii are different for s-, p- and d-electrons. Figure 5(e) shows the pseudopotential radii sum $(r_s + r_p)^Z$ of Zunger. Its general trend is analogous to the ionic radii of Kordes if the d$^{11}$-, d$^{12}$- and p-elements are shifted by approximately 0.4 to a lower value and the total plot is adjusted by a scale factor.

## 7. Conclusions

It is shown in this paper that the AET approach simplifies the structural effects found for the chemical elements. Furthermore, it can be seen that the single-environment types are greatly preferred by the chemical elements under NC. Under HT/LT or HP conditions even the few two- and poly-environment types stable under NC will transform into a single-environment type.
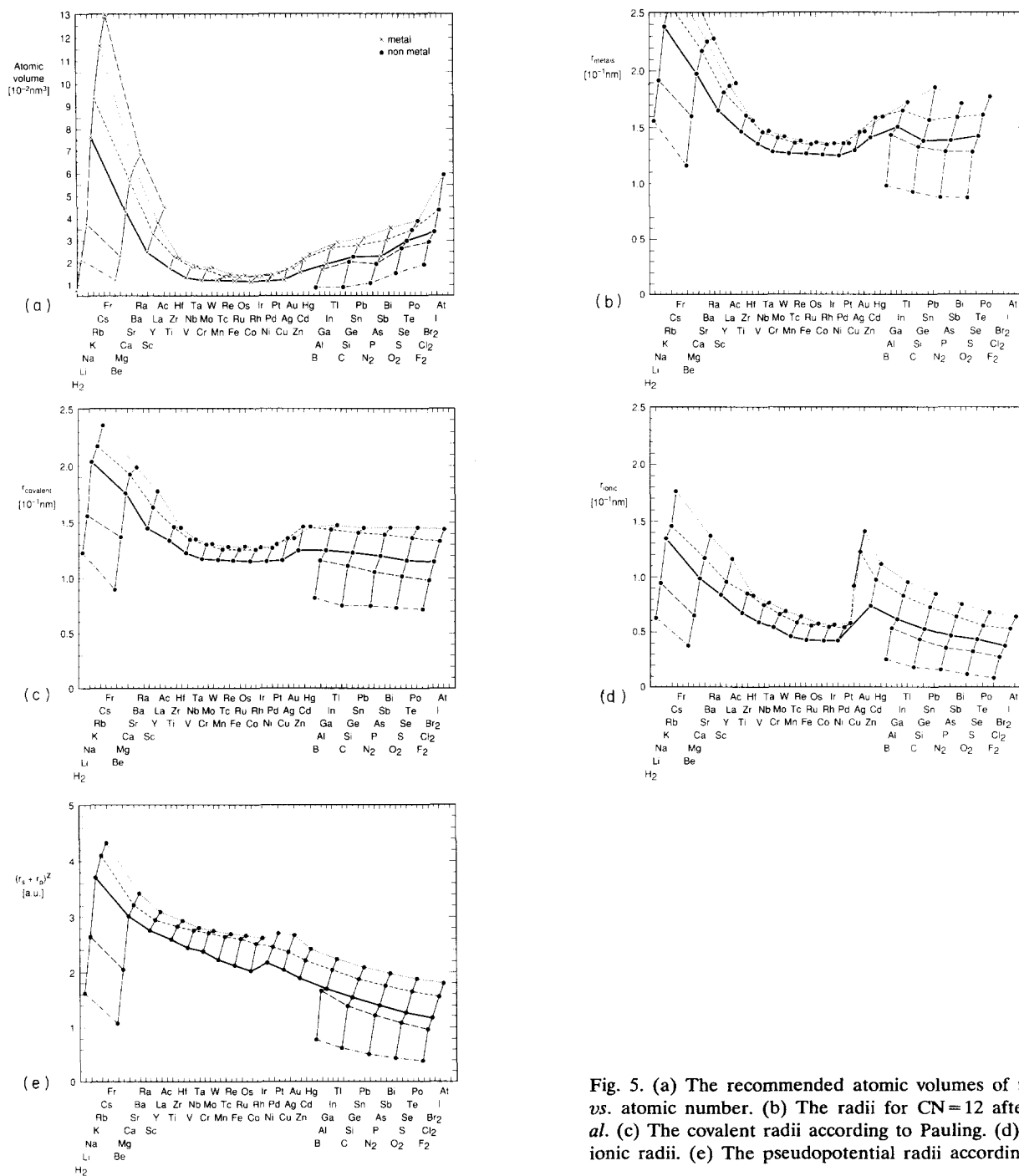
Fig. 5. (a) The recommended atomic volumes of the elements vs. atomic number. (b) The radii for CN = 12 after Teatum et al. (c) The covalent radii according to Pauling. (d) The Kordes ionic radii. (e) The pseudopotential radii according to Zunger.

A similar observation was made by Eliseev [18], who investigated the point-set symmetry of the elements.

If we combine the modified SSD with the atomic environment transformation scheme, it is possible to predict potential element modifications. Our work also reveals nicely the "exotic" element structures, all having AETs with non-equal distances. Such structures either have a very complex bonding situation or the models are not correct.

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