

Structural Principles

The Elements	1-9
Symmetry	10-25
Sphere Packings	26-32
Atomic and Ionic Sizes	33-40
Structural Chemistry	41-62

Understanding fundamental principles of atomic structure is a crucial aspect of solid-state chemistry. Structure is controlled by interatomic bonding forces, which influence electronic structure and thereby affects the physical and chemical behavior of materials. Since the electron densities of free atoms are spherically symmetric, many solid-state structures are described by sphere packings. On the other hand, chemists typically view structures as networks of chemical bonds. These two complementary perspectives provide useful information to generate structural comparisons and relationships because the structures of crystals are well developed. Symmetry also plays a significant role when describing and classifying solid-state structures.

READING: A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed., pp. 3-37.

The Elements

READING: A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed., pp. 1274-1286.

(1) There are 118 known elements as of 2020. Of these, 21 (At, Fr, Fm-Og) have not been obtained in sufficient quantities to identify condensed phases, although the characteristics of astatine and francium have been extrapolated from earlier members of their respective groups. Ground state structures occur close to 0 K, at which the elements would all be solids. Most elements retain their ground state structures at ambient conditions of temperature and pressure because 300 K and 1 atm correspond, respectively, to ~ 2.5 kJ/mol and ~ 0.1 J/cm³. Of the 97 structurally characterized elements at 300 K and 1 atm, 13 are no longer solids: two are liquids (Br₂ and Hg) and eleven are gases (six noble gases He, Ne, Ar, Kr, Xe, Rn, and five diatomic species H₂, F₂, Cl₂, N₂, O₂).

Melting and Vaporization: Some general trends concerning the strengths of interatomic interactions emerge by examining changes of state for the elements as temperature increases from 300 K. The periodic table provides an effective visual display of these changes. However, the lay-out of the periodic table adopted herein differs from the traditional arrangement in two specific ways: (i) H is placed above the halogens because it behaves as a nonmetal; and (ii) Lu and Lr respectively replace La and Ac because Lu and Lr have filled valence *f* orbitals and the elements immediately following Lu and Lr begin filling their valence *d* orbitals in the free atom.

At the following temperatures above 300 K, the following changes of state take place:

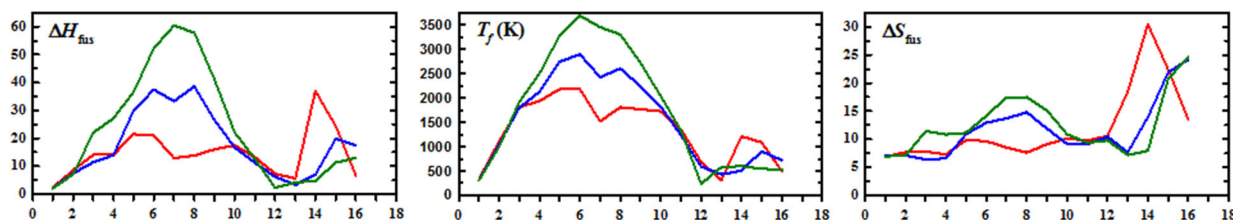
- 500 K: The halogens Br₂ and I₂ are vapors. All alkali metals Li–Fr, the post-transition group 13 metals Ga and In, as well as the nonmetals P, S, and Se are liquids.
- 1000 K: The gaseous elements now include the heavier alkali metals Rb and Cs, as well as Hg and As. The alkaline earth metals Mg, Ba, Ra, the post-transition metals and semimetals Zn, Cd, Al, Tl, Sn, Pb, Sb, Bi, Te, and Po, as well as the actinide metals Np and Pu are liquids.
- 1500 K: The *s*-valent metals Na, K, and Mg, as well as Zn, Cd, Te, and Po are vapors. The transuranium element Es is predicted to evaporate but it has not been observed. The

alkaline earth and noble metals Ca, Sr, Cu, Ag, Au, as well as the early lanthanide elements and many actinides are liquids.

2000 K: Gases include all alkali metals, most alkaline earth metals except Be and Ra, all elements to the right of group 14, all group 12 elements, as well as Eu, Yb, and Cf. Elements remaining as solids include B, C, V, Cr, groups 4-9 metals, Pt, and Th.

2500 K: Only 10 elements are solids - C and the refractory metals of the 5th and 6th periods Nb, Mo, Ru, Hf–Ir. Among the remaining elements, 44 are liquids and 43 are gases.

This examination of changes of state with temperature reveals that the strongest interatomic interactions occur in the middle of the lighter *p*-block and the middle of the heavier *d*-block elements, because they remain solids for the highest temperatures. Therefore, factors such as the number of valence electrons per atom, atomic radii, and the characteristics of core and valence electronic states significantly influence the strengths of interatomic interactions required to maintain the solid state.



Melting data for the elements of the fourth (K–Se; red), fifth (Rb–Te; blue), and sixth (Cs, Ba, Lu–Po; green) periods. (Left) Heats of fusion in kJ/mol; (middle) normal melting points in K; (right) entropies of fusion in J/mol·K.

The figures above show thermodynamic data for melting of the 4th, 5th, and 6th period elements as a function of group number. The heats of fusion and normal melting points are lowest for groups 1 and 12. These *n*th period elements have gas phase electronic configurations of [core](*ns*)¹ and [core][(*n*–1)*d*]¹⁰(*ns*)². Since their valence electronic subshells are nearly empty or filled, the interatomic interactions are weakest for the period. On the other hand, maximum values occur near the middle of the *d*-block elements around the group 6 elements Cr, Mo, and W where optimum metal-metal bonding occurs. The corresponding values of these characteristics for the *p*-block elements also exhibit maxima near the middle groups 14 and 15, with subtleties arising from presumable relativistic effects. The entropies of fusion for the *d*-block elements vary modestly with group number between ~5 and ~15 J/mol·K, whereas they are more variable for the *p*-block elements in these periods.

(2) Temperature and Pressure Effects: Most solids are studied at ~298 K and atmospheric pressure (~1 atm = 101.3 kPa), but structural changes and other interesting solid-state phenomena can occur by changing temperature, pressure, or both. The pressure-temperature phase diagram of iron illustrates such behavior. On increasing temperature at ambient pressure, Fe shows three phase transitions in the solid state before melting at 1808 K: (1) at 1043 K, ferromagnetic ordering transforms to paramagnetic behavior while keeping the body-centered cubic structure (α -Fe, BCC); (2) at 1173 K, structural change from BCC to cubic close packed (γ -Fe, CCP); and (3) at 1660 K, structural change from CCP to BCC (δ -Fe). As temperature increases, the molar volume increases and density decreases, which is typical behavior for most solids called thermal expansion. Also, the occurrence of the BCC structure just prior to melting is another common phenomenon observed for many metallic elements. When compared to close packed structures

like CCP, BCC packing has a lower coordination number for each atom, so when thermal fluctuations become large as temperature increases, the entropy of the BCC phase increases significantly.¹ On the other hand, as pressure increases at ambient temperature, the BCC α -form changes to hexagonally close packed (ϵ -Fe, HCP) at ~ 13 GPa, with a corresponding decrease in molar volume and increase in density. A triple point, at which α -, γ -, and ϵ -Fe coexist, occurs at ~ 10.4 GPa and 757 K.² There is another triple point where the two solids γ -, δ -, and liquid Fe coexist. Thus, depending on temperature and pressure, iron adopts all three typical close packed structures exhibited by metallic elements. Furthermore, as instrumental technology improves, then solid-state chemists can investigate materials over wider ranges of temperature and pressure.

(3) Structural Periodic Table: The solid-state structures of the chemical elements demonstrate how electronic structure fundamentally influences trends in atomic structure. Certain features of atoms that are significant in this regard include:

- *Numbers of valence electrons* dictate the filling of energy bands in the electronic structure of the solid;
- *Effective nuclear charges* influence the relative atomic orbital energies of the various shells and subshells;
- *Core electrons* and their *atomic orbitals* impact atomic sizes and how effectively valence orbitals overlap with orbitals on adjacent atoms; and
- *Virtual orbitals*, which are the low-lying unoccupied atomic orbitals, can become stabilized and partially occupied in condensed phase structures.

In the solid state, whether at ambient conditions or just below normal melting points, all elements form crystalline solids,³ which are summarized in the following periodic table:

																H <i>hP4</i>	He <i>hP2</i>
Li <i>cI2</i>	Be <i>hP2</i>											B <i>hR12</i>	C <i>hP4</i>	N <i>hP4</i>	O <i>cP16</i>	F <i>cP16</i>	Ne <i>cF4</i>
Na <i>cI2</i>	Mg <i>hP2</i>											Al <i>cF4</i>	Si <i>cF8</i>	P <i>oS8</i>	S <i>oF128</i>	Cl <i>oS8</i>	Ar <i>cF4</i>
K <i>cI2</i>	Ca <i>cF4</i>	Sc <i>hP2</i>	Ti <i>hP2</i>	V <i>cI2</i>	Cr <i>cI2</i>	Mn <i>cI58</i>	Fe <i>cI2</i>	Co <i>hP2</i>	Ni <i>cF4</i>	Cu <i>cF4</i>	Zn <i>hP2</i>	Ga <i>oS8</i>	Ge <i>cF8</i>	As <i>hR2</i>	Se <i>hP3</i>	Br <i>oS8</i>	Kr <i>cF4</i>
Rb <i>cI2</i>	Sr <i>cF4</i>	Y <i>hP2</i>	Zr <i>hP2</i>	Nb <i>cI2</i>	Mo <i>cI2</i>	Tc <i>hP2</i>	Ru <i>hP2</i>	Rh <i>cF4</i>	Pd <i>cF4</i>	Ag <i>cF4</i>	Cd <i>hP2</i>	In <i>tI2</i>	Sn <i>tI4</i>	Sb <i>hR2</i>	Te <i>hP3</i>	I <i>oS8</i>	Xe <i>cF4</i>
Cs <i>cI2</i>	Ba <i>cI2</i>	Lu <i>hP2</i>	Hf <i>hP2</i>	Ta <i>cI2</i>	W <i>cI2</i>	Re <i>hP2</i>	Os <i>hP2</i>	Ir <i>cF4</i>	Pt <i>cF4</i>	Au <i>cF4</i>	Hg <i>hR1</i>	Tl <i>hP2</i>	Pb <i>cF4</i>	Bi <i>hR2</i>	Po <i>cP1</i>	At <i>cF4</i>	Rn <i>cF4</i>
Fr <i>cI2</i>	Ra <i>cI2</i>	Lr <i>hP2</i>	Rf <i>hP2</i>	Db <i>cI2</i>	Sg <i>cI2</i>	Bh <i>hP2</i>	Hs <i>hP2</i>	Mt <i>cF4</i>	Ds <i>cI2</i>	Rg <i>cI2</i>	Cn <i>hP2</i>	Nh <i>hP2</i>	Fl <i>cF4</i>	Mc <i>cF4</i>	Lv <i>cF4</i>	Ts <i>cF4</i>	Og <i>cF4</i>

Lanthanides:	La <i>hP4</i>	Ce <i>hP4</i>	Pr <i>hP4</i>	Nd <i>hP4</i>	Pm <i>hP4</i>	Sm <i>hR3</i>	Eu <i>cI2</i>	Gd <i>hP2</i>	Tb <i>hP2</i>	Dy <i>hP2</i>	Ho <i>hP2</i>	Er <i>hP2</i>	Tm <i>hP2</i>	Yb <i>cF4</i>
Actinides:	Ac <i>cF4</i>	Th <i>cF4</i>	Pa <i>tI2</i>	U <i>oS4</i>	Np <i>oS8</i>	Pu <i>mP16</i>	Am <i>hP4</i>	Cm <i>hP4</i>	Bk <i>hP4</i>	Cf <i>hP4</i>	Es <i>cF4</i>	Fm <i>cF4</i>	Md <i>cF4</i>	No <i>cF4</i>

¹ See also S. Alexander, J. McTague, *Phys. Rev. Lett.* **1978**, *41*, 702-705.

² D.A. Young, *Phase Diagrams of the Elements*, University of California Press, Berkeley, 1991.

³ J. Donohue, *The Structures of the Elements*, R.E. Krieger Publishing Co., Malabar, FL, 1982.

The structures of the 21 shaded elements have not been experimentally studied as of 2020. Each element includes its Pearson symbol, which specifies the symmetry and complexity for a crystalline structure. Each Pearson symbol has three parts: (1) a lower case letter designating the crystal class (a = triclinic or anorthic, c = cubic, h = hexagonal or rhombohedral, m = monoclinic, o = orthorhombic, t = tetragonal); (2) a capital letter designating lattice type (F = face-centered, I = body-centered, P = primitive, R = rhombohedral, S = base- or side-centered); and (3) a number designating the number of atoms in one unit cell, which is the fundamental repeating unit of the crystalline solid.

The vast majority of elemental solid-state structures are simple with 2 or 4 atoms in the unit cell. Metals tend to be densely packed arrangements of atoms and are described using sphere packings. Nonmetals adopt less dense structures and are represented by nets, in which the points are atoms linked by covalent bonds (lines).

(4) In the solid state, most *metals* and all *noble gas elements* adopt one of the following four densely packed structure types:

- (a) Hexagonally close packed (HCP; $hP2$) occurs for 21 elements. The ideal c/a ratio of the two distinct unit cell lengths is 1.63. Elements from groups 2 (Be, Mg), 3 (Sc, Y), 4 (Ti, Zr, Hf), 7 (Tc, Re), 8 (Ru, Os), 9 (Co), 13 (Tl), 18 (He), and the lanthanides (Gd-Tm, Lu). Distorted HCP versions are observed for Zn and Cd.
- (b) Cubic close packed (CCP = FCC, face-centered cubic; $cF4$) also occurs for 21 elements from groups 2 (Ca, Sr), 9 (Rh, Ir), 10 (Ni, Pd, Pt), 11 (Cu, Ag, Au), 13 (Al), 14 (Pb), 18 (Ne-Rn), as well as the lanthanide Yb and three actinides (Ac, Th, Es). Distorted CCP versions are observed for In and Hg.
- (c) Mixtures of HCP and CCP arrangements ($hP4$ or $hR3$; $hP4$ = double hexagonal close packed, which is a 1:1 mixture of HCP and CCP) occur for 10 lanthanide and actinide elements (La-Sm, Am-Cf).
- (d) Body-centered cubic (BCC; $cI2$), which is less densely packed than HCP and CCP, is found for 15 elements from groups 1 (Li-Cs), 2 (Ba, Ra), 5 (V, Nb, Ta), 6 (Cr, Mo, W), 8 (Fe), and one lanthanide (Eu). A distorted BCC version exists for Pa.

The five metallic elements Mn, Ga, U, Np, and Pu exhibit distinctive structures that lie between dense sphere packings and network structures.

The subtleties of the structural variations among the metals arise from changes in the occupied and low-lying unoccupied (virtual) orbitals of each element as a function of period and group. The crystal structures of At and most of the 7th period elements (Fr, Fm-Og) remain experimentally unknown, although electronic structure theory has been applied to predict the structures of At,⁴ Fr,⁵ and the 6d metals.⁶ Many of the predicted 6d metal structures follow their 5d group analogues.

(5) *d-Block Elements*: Most of the transition metals adopt the common close packed structure types HCP, FCC = CCP, or BCC. The HCP structures for elements from groups 3, 4, 7, 8 as well as Co have nearly ideal c/a ratios of 1.58-1.62. The corresponding c/a ratios for the distorted HCP structures of Zn and Cd are, respectively, 1.86 and 1.89, so that these elements have significant 2-dimensional bonding character.⁷ On the other hand, α -Hg (Pearson symbol $hR1$) is more closely

⁴ A. Hermann, R. Hoffmann, N.W. Ashcroft, *Phys. Rev. Lett.* **2013**, *111*, 116404

⁵ A. P. Koufos, D. A. Papaconstantopoulos, *Int. J. Quant. Chem.* **2013**, *113*, 2070-2077.

⁶ J. Gyanchandani, S. K. Sikka, *Phys. Rev. B* **2011**, *83*, 172101; A. Östlin, L. Vitos, *Phys. Rev. B* **2011**, *84*, 113104.

⁷ U. Häussermann, S.I. Simak, *Phys. Rev. B* **2001**, *64*, 245114.

related to CCP and retains 3-dimensional bonding character. The CCP-type unit cell is compressed along its body diagonal, which is the c -axis of the unit cell.

The $4d$ and $5d$ elements follow the structural trend HCP-BCC-HCP-FCC across each period, a trend that correlates with the extent of filling the valence d -bands with electrons. In the $3d$ series, Mn, Fe, and Co adopt different structures than expected from their corresponding $4d$ and $5d$ group analogues. These structural differences are related to the itinerant magnetic properties of these $3d$ elements associated with their valence electrons. In particular, the BCC-HCP-FCC sequence of the ferromagnetic metals Fe, Co and Ni matches the structural sequence in the $4d$ and $5d$ series from groups 5,6 (BCC), groups 7,8 (HCP), and groups 9,10 (CCP). The spontaneous magnetization of Fe, Co, and Ni arises by breaking the degeneracy of spin-up and spin-down electronic energy states leading to unequal numbers of spin-up (majority spin) and spin-down (minority spin) valence electrons per atom. Since these electrons also engage in chemical bonding, the solid-state elemental structures are controlled by the extent of filling the minority spin d -bands.

Unlike all other transition metals, the structure of α -Mn is quite complex, with four chemically distinctive Mn sites yielding a total of 58 atoms in the cubic unit cell.⁸ Its complexity is rationalized as arising from two conflicting tendencies for a half-filled d -band: maximizing metal-metal bonding and maximizing the number of unpaired electrons according to Hund's rule.⁹ On increasing temperature, α -Mn transforms into a somewhat less complex cubic β -form⁸ with 20 atoms in the unit cell, then into FCC and BCC before melting at a lower temperature than its neighboring elements Cr and Fe. The enhanced stability of the ground state electronic configuration of the Mn atom $[\text{Ar}](4s)^2(3d)^5$ and the large effective nuclear charge for the $3d$ electrons rationalize, in part, the melting behavior of Mn. Among the other $3d$ elements at higher temperatures and before melting occurs, Sc-Fe are BCC whereas Co-Cu are FCC.

(6) f -Block Elements: The lanthanide ($4f$) and actinide ($5f$) metals show distinctive structural chemistry that can be related, in part, to the ground state electronic configurations of the atoms. For the lanthanides, the $4f$ orbitals are contracted and pseudo core-like, arising from an exceptionally large effective nuclear charge because there are no other core-level f orbitals for these atoms. As a result, bonding in these metals occurs through overlapping $5d$ and $6s$ orbitals. The later lanthanides Gd-Tm and Lu are HCP, like the other Group 3 metals Sc and Y; Yb is CCP; and the earlier metals adopt mixed HCP/CCP alternatives. La-Pm are DHCP (double hexagonal close packed = 50% HCP, 50% CCP) and Sm is 67% HCP, 33% CCP. The observed structural variation can be rationalized by subtle changes in the occupation of the valence $5d$ bands of these metals across the series.¹⁰ Furthermore, the melting points of the lanthanides generally increase across the series except for Ce, Eu, and Yb, whose values are noticeably lower than their neighboring elements. Eu and Yb behave as divalent metals because they have, respectively, a half-filled and completely filled $4f$ subshell, whereas Ce shows both trivalent and tetravalent behavior. Near room temperature, Ce, like Th of the actinides, is FCC.¹¹ Just before melting, the lanthanides La-Ho and Yb become BCC; in addition, the earlier metals La-Nd are FCC before transforming to BCC.

The actinide elements, on the other hand, show exceptional structural diversity, especially U, Np, and Pu. Unlike the $4f$ orbitals of the lanthanide metals, the $5f$ orbitals of the actinides are more diffuse and can engage in significant interatomic overlap so that they influence the formation of

⁸ V. Sliwko, P. Mohn, K. Schwarz, *J. Phys.: Condens. Matter*, **1994**, *6*, 6557-6564.

⁹ D. Hobbs, J. Hafner, D. Spišák, *Phys. Rev. B* **2003**, *B68*, 014407.

¹⁰ J.C. Duthie, D.G. Pettifor, *Phys. Rev. Lett.* **1977**, *38*, 564-567.

¹¹ B. Johansson, W. Luo, S. Li, R. Ahuja, *Sci. Rep.* **2014**, *4*, 06398.

more complex structures than HCP, FCC, or BCC. However, a thorough understanding of the role of $5f$ orbitals on structure and bonding in the actinides is not entirely clear because the energies of the $7s$, $7p$, $6d$, and $5f$ orbitals are relatively close to each other.¹² At ambient temperature and pressure, Ac, Th, and Es are FCC, Pa is distorted BCC, and Am-Cf are DHCP. The structures of α -U, α -Np, and α -Pu are also densely packed, but they have lower crystalline symmetry than either cubic (like FCC) or hexagonal (like HCP). Furthermore, U, Np, and Pu undergo various structural transitions with increasing temperature, culminating in BCC before melting. The melting points of Np and Pu are especially low. Pu is extraordinary by undergoing five solid-solid transformations with increasing temperature before melting at 914 K:¹³

Pu	Pearson Symbol	Structure	Density (g/cm ³)	Temperature Range (K)
α	<i>mP16</i>	Monoclinic	19.86	–395
β	<i>mS34</i>	Face-centered monoclinic	17.70	395–473
γ	<i>oF8</i>	Face-centered orthorhombic	17.14	473–583
δ	<i>cF4</i>	Face-centered cubic	15.92	583–724
δ'	<i>tI2</i>	Body-centered tetragonal	16.00	724–758
ϵ	<i>cI2</i>	Body-centered cubic	16.51	758–914
L		Liquid	16.65	914–

The molar volume of Pu increases substantially by 24.8% from α -Pu (*mP16*) at ambient temperature to δ -Pu (*cP4*; FCC) at 583 K. Above 583 K to 758 K, δ - and δ' -Pu (*tI2*) show decreasing molar volume, an effect called “negative thermal expansion” that is an unusual phenomenon for solids.¹⁴

(7) *p*-Block Elements: Main group elements in the *p*-block are mostly semimetallic, semiconducting, or insulating, and their structures are better described using networks of chemical bonds rather than sphere packings of atoms. In depictions of these network structures, the lines usually represent the strongest covalent interactions, whereas the weaker van der Waals contacts that are important for condensation into solids or liquids are not included. The connectivity of atoms follows the octet or $8-N$ rule (N = number of valence electrons), and, for most cases, this connectivity matches the number of two-center, two-electron bonds. However, if an interatomic covalent interaction involves both σ - and π -type orbital overlaps, then the connectivity and the number of two-electron bonds will differ, as observed for graphene and graphite. π -Bonding is important for the 2nd period elements C, N, and O because their valence $2p$ electrons experience a large effective nuclear charge.

According to the octet rule, the group 14 elements ($N = 4$), also called the tetrelides, will form four-connected nets. Si and Ge adopt the diamond structure, which is a 3-dimensional cubic framework of tetrahedrally coordinated atoms. At ambient conditions, metallic β -Sn (white tin) has a distorted diamond structure with four shorter (3.016 Å) and two longer (3.175 Å) distances. Below 286 K, β -Sn transforms to semiconducting α -Sn (gray tin) with the diamond-type structure and a Sn–Sn nearest neighbor distance of 2.81 Å. The thermodynamically favorable form of carbon is graphite, which contains planar, honeycomb-like nets of three-connected carbon atoms bonded together by σ and π bonds; graphene is the two-dimensional single layered material. Interactions between adjacent graphene sheets are relatively weak so that graphite exists in

¹² B. Johansson, *Hyperfine Interactions*, **2000**, 128, 41-66.

¹³ *Los Alamos Science*, No. 26, 1982 (<https://la-science.lanl.gov/lascience26.shtml>).

¹⁴ K. Takenaka, *Sci. Technol. Adv. Mater.* **2012**, 13, 013001.

different stacking variations. Two common variants are *2H* and *3R*. *2H*-graphite has two kinds of C atoms in each honeycomb plane: one C atom weakly interacts with two C atoms in the graphene planes above and below, whereas the second C atom does not. In *3R*-graphite every C atom weakly interacts with one C atom in one neighboring graphene sheet, either above or below. The diamond-form of carbon is metastable at ambient conditions, but there is a large kinetic barrier to convert diamond into graphite. The C–C distance in 4-connected diamond is somewhat longer (1.54 Å) than the C–C distance in 3-connected graphite (1.42-1.43 Å).

(8) The pnictides P, As, Sb, and Bi ($N = 5$) adopt three-bonded nets that form puckered honeycomb layers. The local coordination at each atom is trigonal pyramidal, so that each atom engages in three two-center σ -bonds and has one lone pair. There are three somewhat longer distances to a neighboring layer. For example, the near neighbor As–As distances in α -As are 3×2.516 Å and 3×3.121 Å. As a result, the coordination environment of each 3+3 bonded atom is a distorted octahedron.

The chalcogenides S, Se, and Te ($N = 6$) form two-bonded networks that are trigonal spiral chains for Se and Te and 8-membered rings for sulfur. In the structures of Se and Te, the local coordination is a distorted octahedron, as in the pnictide elements, but with two short covalent bonds and four longer contacts. For example, these contacts in α -Se are 2×2.373 Å and 4×3.436 Å. α -Po adopts a simple cubic structure (*cP1*) in which each atom is ideally octahedrally coordinated.

The halogens Cl, Br, and I ($N = 7$) form molecular solids that are distorted CCP arrangements of diatomic (one-bonded) molecules. Given the importance of π -bonding for nitrogen and oxygen, solid N_2 and O_2 also involve packings of diatomic molecules with multiple bonds rather than 3- or 2-connected extended networks.

(9) The group 13 elements B, Al, Ga, In, and Tl are particularly idiosyncratic because each element has its own structure! The metals Al and Tl adopt traditional CCP and HCP structures and In is a slightly distorted CCP arrangement.¹⁵ On the other hand, the structures of B and Ga suggest more localized covalent bonds, while also retaining some delocalized bonding as a result of these elements having just 3 valence electrons. The structure of gallium consists of layers of distorted densely packed atoms that are held together by the shortest Ga–Ga bonds (ca. 2.45 Å), so that each Ga atom is 7-coordinate.¹⁶ On the other hand, semiconducting α -B contains B_{12} icosahedra that are connected to each other by six two-center, two-electron bonds and six three-center, two-electron bonds. According to Wade's rules for deltahedral clusters, 26 valence electrons are necessary for optimal bonding within each B_{12} icosahedral cluster. As a result, each B_{12} icosahedron is assigned 36 valence electrons or 3 valence electrons per B atom, so that the structure of α -B is well suited to optimize intra- and inter-icosahedral chemical bonding and account for its semiconducting behavior.

¹⁵ U. Häussermann, S.I. Simak, R. Ahuja, B. Johansson, S. Lidin, *Angew. Chem. Int. Ed.* **1999**, 38, 2017-2020.

¹⁶ U. Häussermann, S.I. Simak, I.A. Abrikosov, S. Lidin, *Chem. Eur. J.* **2006**, 3, 904-911.