

Sphere Packings

The types of interactions holding atoms or ions together in solids include *ionic*, *van der Waals*, *metallic*, and *covalent* bonding. The first three bonding forces are isotropic, depending just on interatomic or interionic distances, whereas covalent bonding forces are anisotropic. In the solid state, strong anisotropic bonding forces give rise to networks, cages, and polymers in which the atoms have low coordination numbers. The isotropic forces, on the other hand, lead to densely packed atoms or ions with larger coordination numbers and more uniform coordination environments. If atoms and ions are considered to be spherically shaped, then many structures of metals and ionic salts are based upon sphere packings.

READING: A.F. Wells, *Structural Inorganic Chemistry*, 5th Ed., pp. 141-161.

(26) In two-dimensions, the densest packing of identical spheres has hexagonal symmetry and is periodic adopting the 2-d plane group $p6mm$. Each sphere is surrounded equidistantly by six other spheres. The unit cell, which contains exactly one sphere, is a rhombus with sides equal to the distance between the centers of two adjacent spheres and interior angles of 120° and 60° . The centers of every sphere sit at the unit cell corners. To prepare for descriptions of three-dimensional sphere packings, these sites are designated

$$"A" = (00), (10), (01), (11), (\bar{1}0), (0\bar{1}), (\bar{1}\bar{1}), \dots$$

Inside each unit cell, there are two special points located at the centers of two triangles:

$$"B" = \left(\frac{2}{3}\frac{1}{3}\right), \left(\frac{5}{3}\frac{1}{3}\right), \left(\frac{2}{3}\frac{4}{3}\right), \left(\frac{5}{3}\frac{4}{3}\right), \left(\frac{1}{3}\frac{1}{3}\right), \left(\frac{2}{3}\frac{2}{3}\right), \left(\frac{1}{3}\frac{2}{3}\right), \dots \text{ and}$$

$$"C" = \left(\frac{1}{3}\frac{2}{3}\right), \left(\frac{4}{3}\frac{2}{3}\right), \left(\frac{1}{3}\frac{5}{3}\right), \left(\frac{4}{3}\frac{5}{3}\right), \left(\frac{2}{3}\frac{2}{3}\right), \left(\frac{1}{3}\frac{1}{3}\right), \left(\frac{2}{3}\frac{1}{3}\right), \dots$$

Sites **B** and **C** correspond to depressions formed by three touching spheres in the **A**-layer. Therefore, a plane of spheres occupying the **B** sites has its depressions at **A** and **C**; a plane of spheres occupying the **C** sites has its depressions at **A** and **B**. This 2-d periodic arrangement of spheres has a *packing efficiency* η of 90.7%, which is the fraction of space occupied by the spheres and is an important characteristic of sphere packings. If the radius of a sphere is R_6 (subscript 6 = coordination number) and the side of the unit cell is denoted as a , then $a = 2R_6$ and the packing efficiency equals the area of one spherical cross-section divided by the area of the unit cell:

$$\eta = \frac{\pi R_6^2}{a^2 \sin 120^\circ} = \frac{\pi}{2\sqrt{3}} = 0.907.$$

Close packings of equal spheres in 3-d are formed by stacking these hexagonal 2-d planes on each other. Densest 3-d sphere packings start with a layer of spheres in the **A** positions and require the adjacent layer to be placed either over the **B** sites or the **C** sites. So, two adjacent close packed sphere planes can be designated as "**AB**", "**AC**", "**BA**", "**BC**", "**CA**", or "**CB**". Differences emerge when placing a third layer on a two-layer slab because there are two possibilities. In particular, by starting with **AB**, then a third closed packed layer added on the **B**-side can sit over either the **A** or the **C** sites. Continuing these two choices of stacking lead to two fundamental 3-d periodic sphere packings:

Hexagonally close packed (HCP) = ... **ABABAB** ..., which has a 2-layer repeating unit; and

Cubic close packed (CCP) = ... **ABCABC** ..., which has a 3-layer repeating unit.

(27) *3-d Close Packings*: The numbers of planes per repeating unit for HCP and CCP arrangements can be viewed by projecting the structures perpendicular to the stacking direction.

Using the "**ABC**" notation derived from the positions in the 2-d unit cell, HCP = $\cdots \mathbf{AB} \cdots$ and CCP = $\cdots \mathbf{ABC} \cdots$. In each case, only the minimum number of layers per repeating unit are given; i.e., $\cdots \mathbf{ABABAB} \cdots$ is shortened simply to $\cdots \mathbf{AB} \cdots$ for HCP.

Another notation for 3-d close packings of spheres is the *Jagodzinski symbol*, which assigns to each layer the designation "h" or "c", according to how its neighboring layers are arranged. An "h" layer is any of the following underlined layers:

$$h: \cdots \underline{\mathbf{BAB}} \cdots, \cdots \underline{\mathbf{CAC}} \cdots, \cdots \underline{\mathbf{ABA}} \cdots, \cdots \underline{\mathbf{CBC}} \cdots, \cdots \underline{\mathbf{ACA}} \cdots, \text{ or } \cdots \underline{\mathbf{BCB}} \cdots,$$

which have the same near-neighbor environment as any sphere in HCP. On the other hand, a "c" layer is any of the following underlined layers:

$$c: \cdots \underline{\mathbf{BAC}} \cdots, \cdots \underline{\mathbf{CAB}} \cdots, \cdots \underline{\mathbf{ABC}} \cdots, \cdots \underline{\mathbf{CBA}} \cdots, \cdots \underline{\mathbf{ACB}} \cdots, \text{ or } \cdots \underline{\mathbf{BCA}} \cdots,$$

which have the same near-neighbor environment for any sphere in CCP. Thus, the 2-layer HCP sequence $\cdots \mathbf{AB} \cdots$ is $\cdots hh \cdots$ for each layer specified, and this is condensed to $\cdots h \cdots$. Likewise, the 3-layer CCP sequence $\cdots \mathbf{ABC} \cdots$ is $\cdots ccc \cdots$, which simplifies to $\cdots c \cdots$. Therefore, for every 3-d close packing of spheres, the "**ABC**" notation identifies the number of layers per repeating unit and the Jagodzinski symbol reveals the relative fractions of different coordination environments.

The coordination number for a given sphere in both HCP and CCP is 12, with 6 spheres in the same close packed plane, 3 spheres in the plane above, and 3 spheres in the plane below, but the two arrangements have different shapes. In CCP, the coordination polyhedron is a cuboctahedron and has point symmetry $O_h = m\bar{3}m$; in HCP, the polyhedron is a triangular orthobicupola, which has point symmetry $D_{3h} = \bar{6}m2$.

The unit cells for HCP and CCP of equally sized spheres have specific geometrical characteristics. For the hexagonal unit cell of HCP,

a = separation between two spheres, and

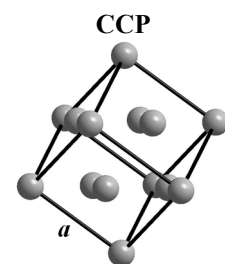
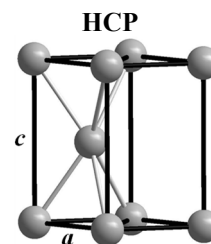
c = separation between every second close packed plane.

As the figure to the right shows, $c = 2 \times$ height of a regular tetrahedron with a base of side a . From geometrical relationships for a tetrahedron,

$$c = 2(\sqrt{2/3})a = (\sqrt{8/3})a = 1.633a$$

The value 1.633 corresponds to the ideal c/a ratio for HCP sphere packing. The space group for HCP is $P6_3/mmc$, and the two spheres in the unit cell are assigned to the Wyckoff $2c$ sites $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$. For CCP, the unit cell is cubic, the space group is $Fm\bar{3}m$, and the spheres are assigned to Wyckoff $4a$ sites $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, and $(0, \frac{1}{2}, \frac{1}{2})$ so that CCP is also called face-centered cubic (FCC) packing. If a = lattice constant of the cubic cell, then the distance between adjacent spheres is $a/\sqrt{2}$ and the repeating distance of 3 close packed planes is $\sqrt{3}a$, which is the body-diagonal of the FCC unit cell.

(28) There are, in principle, an infinite number of 3-d periodic close packings of spheres constructed via mixtures of HCP and CCP environments around the spheres. Such mixed HCP/CCP packings are observed for some of the lanthanide and actinide elements. For example, the structure of α -La involves 4 layers of close packed spheres in the stacking sequence $\cdots \mathbf{ABAC} \cdots$. The corresponding Jagodzinski symbol is $\cdots hc \cdots$ or $\cdots ch \cdots$ (these two symbols are equivalent; in the "**ABC**" notation, **red** = h, **blue** = c), which indicates that 50% of the atoms are surrounded in a HCP-type environment and the other 50% are surrounded in a CCP-type



environment. The crystallographic structure of α -La is $P6_3/mmc$, $a = 3.77 \text{ \AA}$, $c = 12.159 \text{ \AA}$, with two different sets of La atom sites: $2a$ (0, 0, 0) and (0, 0, $\frac{1}{2}$), point group $\bar{3}m = \mathcal{D}_{3d}$ are the CCP-type sites; and $2c$ ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{3}{4}$), point group $\bar{6}m2 = \mathcal{D}_{3h}$ are the HCP-type sites. The experimental c/a ratio is 3.225, which is very close to the ideal value of $2\sqrt{8/3} = 3.226$.

Another mixed HCP/CCP packing occurs for α -Sm, which has the stacking sequence $\dots hhc \dots$. Using this Jagodzinski symbol, the "ABC" sequence is $\dots ABACBCB \dots$, which indicates that there are 9 close packed planes in the repeating unit. The crystallographic structure of α -Sm is $R\bar{3}m$, $a = 3.621 \text{ \AA}$, $c = 26.25 \text{ \AA}$, with two different sets of Sm atom sites: $3a$ (0, 0, 0), point group $\bar{3}m = \mathcal{D}_{3d}$ are the CCP-type sites and $6c$ (0, 0, 0.2222), point group $3m = \mathcal{C}_{3v}$ are the HCP-type sites. The experimental c/a ratio is 7.249, which is slightly smaller than the ideal value of $(9/2)\sqrt{8/3} = 7.348$.

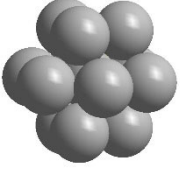
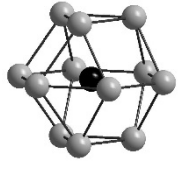
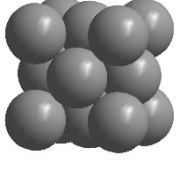
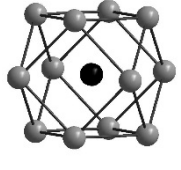
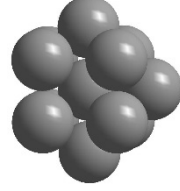
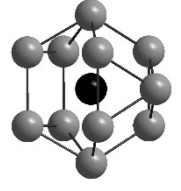
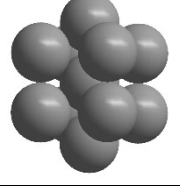
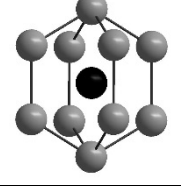
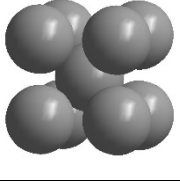
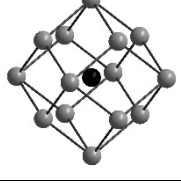
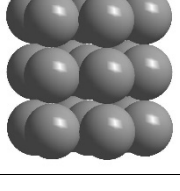
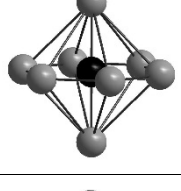
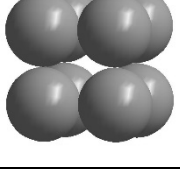
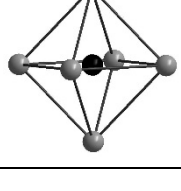
Close packings of spheres can be distinguished by the number of close packed (CP) layers for the repeating unit. However, even if this number is specified, there can be different sequences of HCP- and CCP-type environments. HCP and CCP are the only options for 2 and 3 CP layers per cell, respectively. As the number of CP layers per cell increases, the number of different options steadily increases. The solutions to this problem up to 8 CP layers per repeating unit are as follows:

# CP Layers / Cell	"ABC" Notation	Jagodzinski Symbol	HCP / CCP
2	$\dots AB \dots$	$\dots h \dots$	100% HCP
3	$\dots ABC \dots$	$\dots c \dots$	100% CCP
4	$\dots ABAC \dots$	$\dots hc \dots$	50% HCP / 50% CCP
5	$\dots ABACB \dots$	$\dots hhccc \dots$	40% HCP / 60% CCP
6	$\dots ABABCBCB \dots$	$\dots hhhchc \dots$	67% HCP / 33% CCP
	$\dots ABCACB \dots$	$\dots hcc \dots$	33% HCP / 67% CCP
7	$\dots ABABACB \dots$	$\dots hhhhccc \dots$	57% HCP / 43% CCP
	$\dots ABACBCB \dots$	$\dots hcchhc \dots$	57% HCP / 43% CCP
	$\dots ABCACB \dots$	$\dots hcccchc \dots$	29% HCP / 71% CCP
8	$\dots ABABACBCB \dots$	$\dots hhhhhchc \dots$	75% HCP / 25% CCP
	$\dots ABABCBCB \dots$	$\dots hhhc \dots$	75% HCP / 25% CCP
	$\dots ABABCACB \dots$	$\dots hhhcchcc \dots$	50% HCP / 50% CCP
	$\dots ABACBCB \dots$	$\dots hhchcchc \dots$	50% HCP / 50% CCP
	$\dots ABACBACB \dots$	$\dots hhcccccc \dots$	25% HCP / 75% CCP
	$\dots ABCACB \dots$	$\dots hccc \dots$	25% HCP / 75% CCP

(29) Packing Efficiencies: Sphere packings in 3-d space are characterized by their packing efficiencies η and the coordination environments surrounding each sphere. Packing efficiency represents the fraction of space occupied by spheres that are just touching. The coordination environment identifies the number and spatial arrangement of neighboring spheres that just touch a central sphere.

The densest possible 3-d packing of spheres occurs for a single tetrahedron, for which 77.96% of the tetrahedral volume formed by the centers of 4 touching spheres is filled by the spherical sections. However, since the dihedral angle between two faces of a tetrahedron is 70.5288° , which

is not an integral factor of 360° , 3-d space *cannot be filled with only regular tetrahedra*. Therefore, any 3-d sphere packing will have a packing efficiency lower than 0.7796. Here are 7 important 3-d packings of equal spheres with radii R_{CN} (CN = coordination number):

Name	Sphere Packing	Space Group	η	CN	Environment	Characteristics
Hexagonal Close Packing (HCP)		$P6_3/mmc$	0.7405 $(\pi/3\sqrt{2})$	12		<ul style="list-style-type: none"> $R_{12} = a/2$ $\cdots AB \cdots$ stacking $c/a = \sqrt{8/3} = 1.63$ Spheres at $2c$ sites
Cubic Close Packing (CCP)		$Fm\bar{3}m$	0.7405 $(\pi/3\sqrt{2})$	12		<ul style="list-style-type: none"> $R_{12} = a/2\sqrt{2}$ $\cdots ABC \cdots$ stacking Spheres at $4a$ sites and touch along face-diagonals
Tetragonal Close Packing (TCP)		$P4_2/mnm$	0.7187	11		<ul style="list-style-type: none"> $R_{11} = a/2$ Distortion of HCP $c/a = 0.5858$ Spheres at $4f$ sites ($x = 0.2929$)
Body-Centered Tetragonal (BCT)		$I4/mmm$	0.6981 $(2\pi/9)$	10		<ul style="list-style-type: none"> $R_{10} = c/2$ Distortion of BCC $c/a = \sqrt{2/3} = 0.816$ Spheres at $2a$ sites
Body-Centered Cubic (BCC)		$Im\bar{3}m$	0.6802 $(\sqrt{3}\pi/8)$	8 +6		<ul style="list-style-type: none"> $R_8 = \sqrt{3}a/4$ Spheres at $2a$ sites and touch along body-diagonals
Simple Hexagonal (SH)		$P6/mmm$	0.6046 $(\pi/3\sqrt{3})$	8		<ul style="list-style-type: none"> $R_8 = a/2 = c/2$ $\cdots AA \cdots$ stacking Spheres at $1a$ sites and touch along edges
Simple Cubic (SC)		$Pm\bar{3}m$	0.5236 $(\pi/6)$	6		<ul style="list-style-type: none"> $R_6 = a/2$ Spheres at $1a$ sites and touch along edges

In general, as the coordination number decreases, the efficiency of the sphere packing also decreases. If the packing efficiency of a sphere packing lies below 50%, this structural perspective becomes less favorable, and a “network” perspective of nodes (atoms) and linkages (bonds) is preferred. Now, every sphere packing listed in the table is periodic in 3-d space. Therefore, the packing efficiency η is calculated by the volumes of spheres falling exactly within one unit cell divided by the volume of the unit cell. For example, in BCC packing, the unit cell is cubic with side a and contains two spheres that touch along the body-diagonal. The nearest neighbor coordination number is 8, so that the distance between the centers of two adjacent spheres is $2R_8 = \sqrt{3}a/2$. Using this relationship, the packing efficiency for BCC packing is:

$$\eta_{\text{BCC}} = \frac{2V_{\text{sphere}}}{V_{\text{cell}}} = \frac{2(4\pi R_8^3/3)}{a^3} = \frac{8\pi R_8^3/3}{(4R_8/\sqrt{3})^3} = \frac{\sqrt{3}\pi}{8} = 0.6802.$$

Although BCC sphere packing shows nearest neighbor 8-coordination, there are 6 additional spheres located outside each square face of the cube that are ~15% farther from the central sphere than the nearest neighbor contacts. Therefore, BCC packing is often described as 8+6-coordinate.

The periodic HCP, CCP, and all HCP/CCP mixtures fill 74.05% of 3-d space, and is the densest packing of spheres according to the Kepler conjecture, which was proved in 1998.^{24,25} The tetragonal close packing (TCP) arrangement with coordination number 11 occurs in the anion packing of rutile-type structures (like CrO₂ discussed in slide 23).²⁶ O’Keeffe has shown that TCP packing can arise from a continuous distortion of 12-coordinate HCP so that dense packed 11-coordinate sphere packings can be arbitrarily close to HCP and, thereby, more dense than TCP (consider this conclusion with the transition in CaCl₂ mentioned in slide 25). The space group of these other 11-coordinate sphere packings is $Pn\bar{m}$, which is the highest symmetry subgroup of both $P6_3/mmc$ (for HCP) and $P4_2/mnm$ (for TCP).²⁷

(30) Amorphous Metals and Defects: The number of possible dense sphere packings rapidly expands when more than single sized spheres are allowed. In particular, dense packings of metal atoms with different sizes can have profound physical properties. For example, Liquidmetal® consists of five differently sized atoms, Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5} (the stoichiometric subscripts add to 100), that pack efficiently but not in a crystalline manner with long-range order. It is an example of a “metallic glass”. A result of this particular mixture and arrangement of differently sized spheres is restricted vibrational amplitudes and motions of the component atoms when the solid is subjected to a sudden force.

DEMONSTRATION:²⁸ A comparison between bouncing a metal ball from a crystalline Al surface and the amorphous (glassy) surface of Liquidmetal®. The Al surface dissipates most of the kinetic energy transferred from the ball bearing during the impulse, because ordered domains of Al atoms can move more easily from one low energy configuration to another upon the force of the impact. As a result, the ball’s bounce dampens quickly. In the metallic glass, domains of atoms on and near the surface do not move readily on impact and cannot dissipate the energy as effectively. Therefore, the ball bearing retains its energy over a longer time period and sustains its bounces higher and longer than on the crystalline Al surface.

²⁴ T.C. Hales, *Annals Math. 2nd Series*, **2005**, 162, 1065-1185.

²⁵ See also “Kepler Conjecture” at Wolfram MathWorld, <https://mathworld.wolfram.com/KeplerConjecture.html>.

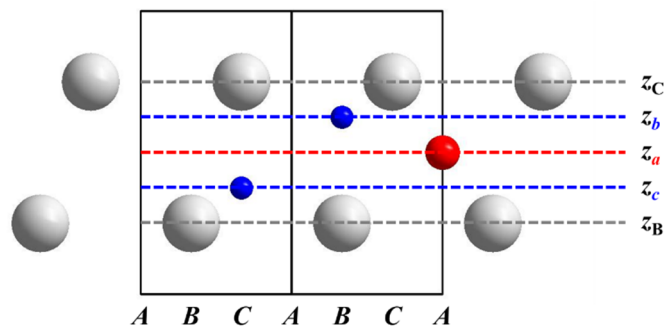
²⁶ W.H. Baur, *Mater. Res. Bull.*, **1981**, 16, 339-345.

²⁷ M. O’Keeffe, *Mater. Res. Bull.* **1984**, 19, 1433-1436.

²⁸ “Atomic Trampoline” Demonstration at <https://chemistry.beloit.edu/edetc/supplies/amorphous/index.html>.

Defects in crystalline close packings also play important roles in the properties of solids. Entropy essentially requires that the idealized models of crystalline (ordered) close packings are disrupted by various “mistakes” in the repeating pattern of atomic spheres. A clever model of a realistic depiction of close packed atoms may be created by a bubble raft,²⁹ which was first conceived by William Bragg, who was one of the “fathers” of X-ray diffraction. When equally sized bubbles form and aggregate into a 2-d raft, close packed regions (domains) are evident, but they are disrupted by vacancies (missing bubbles), point defects (surroundings with 5 or 7 nearest neighbors), line defects (misaligned segments of close packings), and interstitials (smaller bubbles encaged by the normal ones). Such imperfections readily occur in all naturally occurring solids and influence mechanical, electronic, magnetic, and chemical properties of condensed matter.

(31) Interstitial Sites: The space between two close packed planes of spheres can be completely divided into *octahedral* and *tetrahedral* voids or “holes”. One unit cell of this slab contains 2 spheres (1 sphere for each plane), 1 octahedral void, and 2 tetrahedral voids. One set of tetrahedra has a vertex pointing upward; the other set has a vertex pointing downward. Now, if $n+1$ close packed layers are stacked to give a 3-d close packing of spheres, then there are n octahedral voids and $2n$ tetrahedral voids in the unit cell. In the limit as $n \rightarrow \infty$, the ratio of octahedra to number of close packed planes $n/(n+1)$ is 1, and the ratio of tetrahedra to the number of close packed planes $2n/(n+1)$ is 2. Thus, in any 3-d close packing of spheres, there are *1 octahedral void* and *2 tetrahedral voids per close packed sphere* (atom).



Octahedral voids:

$$x_a = 0, y_a = 0, \\ z_a = \frac{1}{2} z_B + \frac{1}{2} z_C$$

Tetrahedral voids:

$$x_b = \frac{2}{3}, y_b = \frac{1}{3}, \\ z_b = \frac{1}{4} z_B + \frac{3}{4} z_C \\ x_c = \frac{1}{3}, y_c = \frac{2}{3}, \\ z_c = \frac{3}{4} z_B + \frac{1}{4} z_C$$

If the close packed spheres are assigned to the “B” and “C” sites of the unit cell, then the centers of octahedra occur at “a” sites and the centers of tetrahedra occur at “b” and “c” sites (lower case letters specify the interstitial site projections). The idealized fractional coordinates for these sites are presented above. Within a **BC**-slab of close packed spheres, octahedra share edges, tetrahedra of one sort (either vertices pointing up or down) share vertices, tetrahedra of different sorts share edges, and octahedra and tetrahedra share faces. Along the stacking direction, the octahedra and tetrahedra share different features depending on the type of packing. For HCP stacking, octahedra share opposite faces and tetrahedra share faces and vertices. For CCP stacking, octahedra share vertices and tetrahedra share edges and vertices. Using the “ABC” notation for close packing, the sequences of octahedral and tetrahedral holes are as follows:

	Octahedral Voids	Tetrahedral Voids
HCP	... A c B c A b a B a b ...
	... B a C a B c b C b c ...
	... C b A b C a c A c a ...

	Octahedral Voids	Tetrahedral Voids
CCP	... A c B a C b A b a B c b C a c ...
	... B a C b A c B c b C a c A b a ...
	... C b A c B a C a c A b a B c b ...

²⁹ <http://www.doitpoms.ac.uk/tlplib/dislocations/index.php>, *Introduction to Dislocations*, University of Cambridge.

If atoms occupy these voids to form extended structures, they tend to avoid occupying adjacent face-sharing tetrahedra and, to lesser extents, adjacent face-sharing octahedra, edge-sharing tetrahedra or edge-sharing octahedra unless there are reasons to expect chemical bonding between the elements in these sites. The rationale for this structure-building principle is geometrical because the centers of adjacent face-sharing tetrahedra and octahedra are usually much smaller than allowed for acceptable interatomic or interionic distances.

(32) *Interstitial Sites and Radius Ratios:* If atoms or ions (X) forming 3-d close packings are treated as hard spheres, then there are specific sizes for spherical atoms or ions (M) that can effectively occupy the octahedral and tetrahedral void spaces. If the size of M is too small for the interstitial site, then M will “rattle around” in the structure; if the size of M is too large, M will push the X atoms or ions apart and lower the overall packing efficiency. Both of these effects tend to destabilize structures. Therefore, the optimal size of M varies with the type of coordination polyhedron formed by ligands X around M.

If M and X are hard spheres with corresponding radii R_M and R_X , then optimal radius ratios R_M/R_X increase as the coordination number of M by X increases. One geometrical constraint for radius ratios R_M/R_X is to allow contact among the ligands X. Under this constraint, $R_M = 0.225R_X$ for tetrahedral coordination and $R_M = 0.414R_X$ for octahedral coordination. The different 12-coordinate polyhedra seen in HCP and CCP have $R_M = R_X$, whereas the icosahedron would prefer a central atom M with a radius that is approximately 10% smaller than the ligands X. Such size arguments have been cited to rationalize the stabilities of observed structures based on their constituent atoms or ions, but these arguments ignore other factors such as valence electron counts and electronegativity differences between the constituents. Nevertheless, examining size relationships for sets of compounds can be illustrative. This can be accomplished by constructing *structure maps*, which use two (or more) numerical characteristics of compounds as the basis for coordinate axes of a graph and each compound is represented by a point on the graph.

As an example, consider a structure map for 1:1 MX octet compounds using the radii R_M and R_X of each component as the coordinate axes. Common examples of such compounds with a total of 8 valence electrons per MX formula unit include ZnO-, ZnS-, NaCl-, and CsCl-types. In this map, each MX compound corresponds to a point (R_X, R_M). These different octet structure types differ in the coordination of the metal atoms: the Zn ions in ZnO and ZnS are tetrahedrally coordinated (CN = 4) by O or S ions; the Na ions in NaCl are octahedrally coordinated (CN = 6) by Cl ions; and the Cs ions in CsCl are cubically coordinated (CN = 8) by Cl ions. If lines are drawn to specify the optimal radius ratios for these coordination polyhedra, then the different structure types clearly do not follow a strict radius ratio rule.³⁰ Nevertheless, there is some decent degree of sorting among these octet structures, although the regions for the 4-coordinate ZnO- and ZnS-types and 6-coordinate NaCl-type structures overlap significantly. As a result, atomic or ionic sizes are just one factor that influence solid-state structures. In general, small atoms or ions prefer low coordination numbers and large atoms or ions prefer high coordination numbers. (See also Slide #40.)

³⁰ J.K. Burdett, G.D. Price, S.L. Price, *Phys. Rev. B* **1981**, B24, 2903-2912.