

## Lecture 4: Visualizing Crystal Structures; Pauling's Rules

When the bonding in a crystal is principally ionic, the crystal structure is fairly simple because the ions may be regarded as rigid spheres. The geometry of these rigid spheres is governed by Pauling's rules.

### Pauling's Rules for Ionic Structures

#### Rule 1: Interatomic distances and coordination

*The distance between a cation and anion is the sum of their radii. The coordination of an ion is determined by the radius ratio rule.*

In detail—

An ion in a crystal structure tends to gather as many oppositely charged ions around itself as its size permits. The number of surrounding ions is called the coordination number (CN) of the central ion. Large ions have high coordination numbers because of their large surface areas and small anions have low coordination numbers.

Since ions tend to surround themselves with as many oppositely charged ions as possible, predicting coordination numbers requires using only the relative size of ions. The relative size of ions is expressed as a radius ratio.

$$\text{Radius ratio} = R_C / R_A$$

$R_C$  is the radius of the cation.  $R_A$  is the radius of the anion.

As shown in the chart below, ranges of radius ratios correspond to certain coordination numbers. Overlap and uncertainty arise because treating ions as rigid spheres with constant radii is not a perfectly valid assumption. Ions are not spherical and their radii change slightly with different coordination numbers.

The geometry of ions about a central ion is visualized as a coordination polyhedron. In mineralogy, these polyhedra are usually constructed from the arrangement of anions; cations sit at the center of the polyhedra, or may be absent altogether. Coordination polyhedra are constrained by coordination numbers, but only uniquely determined by radius ratios and the type of bonding in a mineral.

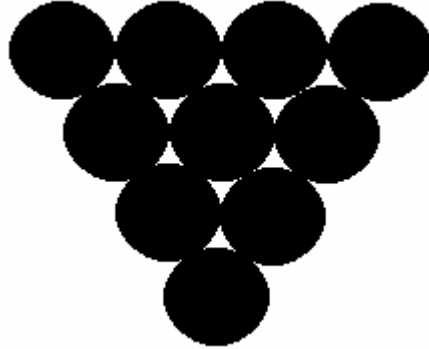
| Radius Ratio | Coordination Number | Ionic Polyhedra | Covalent Polyhedra  |
|--------------|---------------------|-----------------|---------------------|
| 0 - ∞        | 2                   | Line            |                     |
| 0.155 - ∞    | 3                   | Triangle        |                     |
| 0.225 - ∞    | 4                   | Tetrahedron     |                     |
| 0.414 - ∞    | 4                   |                 | Square              |
| 0.414 - ∞    | 5                   |                 | Tetrahedral Pyramid |
| 0.414 - ∞    | 6                   | Octahedron      |                     |
| 0.529 - ∞    | 6                   |                 | Trigonal Prism      |
| 0.625 - ∞    | 8                   |                 | Square Antiprism    |
| 0.732 - ∞    | 8                   | Cube            |                     |
| 1.00 - ∞     | 12                  |                 | Cuboctahedron       |
| 1.00 - ∞     | 12                  |                 | Disheptahedron      |

#### Aside on Hexagonal Closest Packing and Cubic Closest Packing

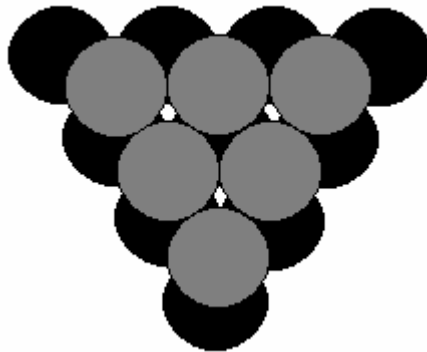
In native metals, the atoms are the same size, the coordination number is 12, and the coordination polyhedra are either cuboctahedrons or disheptahedrons. These coordination polyhedra are not easy to

visualize. Playing with layers of identical closest-packed spheres gives a more intuitive feel for their shapes.

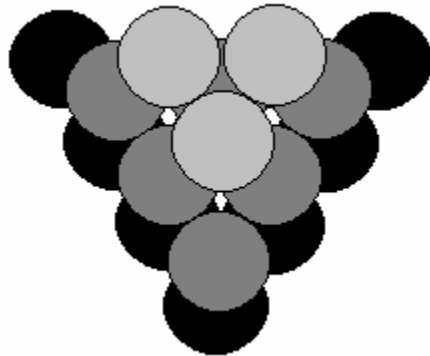
One layer of closest-packed spheres has hexagonal symmetry and triangular depressions.



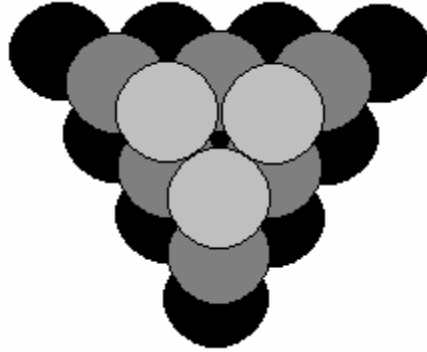
Putting another layer on top covers half of the triangular depressions with the bottoms of spheres. The remaining depressions are overlain by other triangular depressions.



There are two choices about where to put the third layer. It can be stacked so that it superimposes the first layer to form the sequence ABABAB, making an arrangement called hexagonal closest packing (HCP). The coordination polyhedra for HCP are disheptahedra.



Alternatively, the third layer can be stacked so that it does not superimpose the first layer. This arrangement forms the sequence ABCABC and is called cubic closest packing (CCP). The coordination polyhedra for CCP are cuboctahedra.



**Rule 2: Electrostatic valency principle**

*In a stable crystal structure, the total strength of the bonds from coordinating ions that reaches the central ion is equal to the charge of the central ion.*

The strength of an ion's bond may be expressed as the ratio of its charge (z) to its coordination (CN):

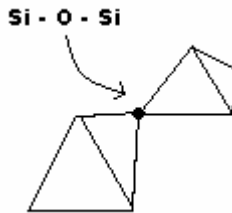
$$\text{Bond strength} = z / \text{CN}$$

In other words, ions with high charges that are bonded to few neighboring ions have the high bond strengths. Pauling's second rule says that summing the bond strengths of all the ions coordinated around a central ion equals the charge of the central ion. It expresses local charge balance in a crystal.

Consider rutile (TiO<sub>2</sub>) for example. In rutile, Ti<sup>4+</sup> is in octahedral coordination, so its bond strength is

$$4+ / 6 = 2/3 +$$

\*\* Rule 2 also limits the number of polyhedra that can meet at a point. In silicate minerals, for example, Si is found in tetrahedral coordination and its bond strength is 1+. Since oxygen has a charge of 2-, only two tetrahedra can meet at a single oxygen.



**Rule 3: Sharing polyhedra I**

*The stability of a crystal is decreased when polyhedra share edges. It is decreased even more when they share faces.*

Anion polyhedra that share edges or faces reduce the stability of a crystal because they bring cations closer together. The closer cations experience more electrostatic repulsion.

**Rule 4: Sharing polyhedra II**

*Cations with high valency and low coordination numbers tend to not share their coordinating polyhedra.*

Pauling's fourth rule says that highly charged cations will tend to be as far apart as possible to minimize electrostatic repulsion.

**Rule 5: Parsimony**

*The number of different kinds of constituents in a crystal tends to be small.*

“Constituents” refers to crystallographic sites (ie, coordination polyhedra) and not types of ions. Amphibole, for example, can contain as many as thirteen different anions, but has only five distinct crystallographic sites. The number of crystallographic sites is limited because the types of polyhedra that can be stacked together while maintaining crystal symmetry is limited.