

Crystal chemistry and its relations with mineral symmetry

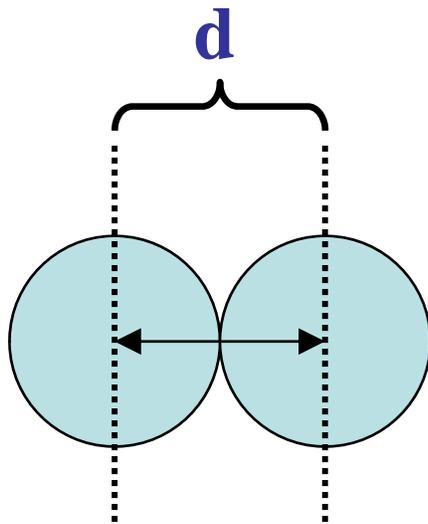
Symmetric arrangements of ions
and bonds in minerals; building
crystalline solids

Atoms and ions vary in size, but the dimensions are difficult to quantify and measure.

The radius is defined by the maximum radial charge density of the outermost electron shells of an atom.

Is also dependent on type and number of nearest neighbours, bond type, and charge.

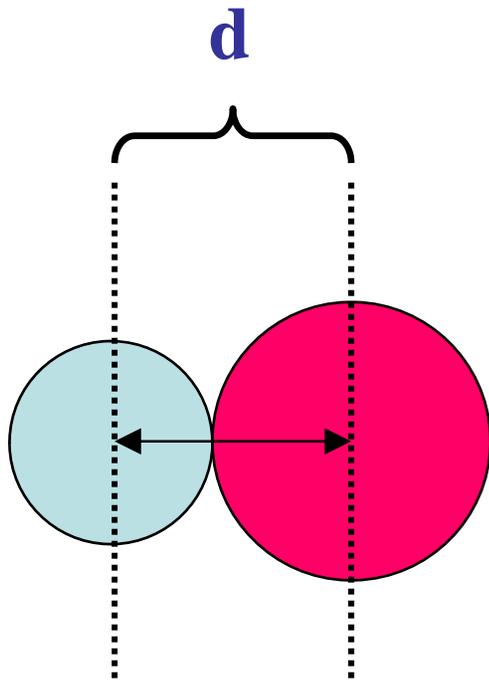
Ionic Radii in metals



$$d = 2r$$

Because of the nature of the metallic bond, the radius of each individual atom is assumed to be one-half of the bond-length (d).

Ionic Radii in ionic and covalent substances



When two oppositely charged ions are bonded together the bond-length (d) is the sum of two different radii (r^+ and r^-)

$$d = r^+ + r^-$$

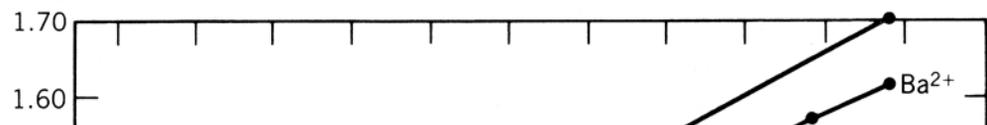
Bond Length and Coordination Numbers

It is a logical assumption that bond length will vary as a function of ionic radii.

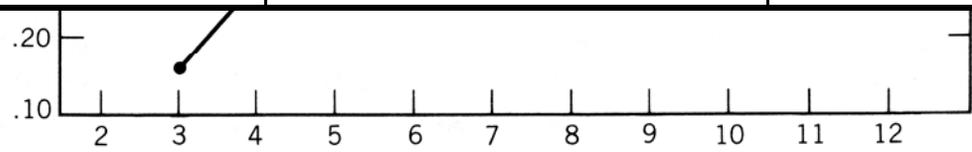
Ionic radii, and subsequently bond length, will vary as a function of the *coordination number* [CN]).

Coordination Number is defined as the number of atoms that surround a particular atom or ion in a structure.

NOTE that the ionic radii increases (along with effective bond length) as the coordination number increases.



Ionic form	Coordination #	Ionic radius
O ²⁻	none	1.4
Si ⁴⁺	4	0.26
Al ³⁺	4 to 6	0.39 to 0.54
Fe ³⁺	4 to 6	0.49 to 0.65
Mg ²⁺	6	0.72
Fe ²⁺	6	0.78
Ca ²⁺	6 to 8	1.00 to 1.12
Na ¹⁺	6 to 8	1.02 to 1.18
K ¹⁺	8 to 12	1.51 to 1.64



Coordination number (C.N.)

Coordination of Ions: Building crystalline solids

When considering atoms, linked by electrostatic bonds, they are best regarded as being a simple spherical geometry.

The coordinated ions cluster about a central point defining a center at the apices of a polyhedron.

The coordination number is correlated to the stoichiometry of a mineral, for the total number of ions of all kinds in any stable ionic crystal structure must ensure electrical neutrality.

Coordination polyhedra and Paulings Rules

Pauling Rules are five guidelines for the generation of crystal structures from the combination of ionic and covalent bonds

The radius ratio is the geometrical relationship between R_A (the radius of the anion) and R_C (the radius of the cation)

The coordination number and radius ratio are used to define the major structural units of coordination polyhedra:

triangle, tetrahedral, trigonal bipyramid, octahedron,
square antiprism, cube, dodecahedron

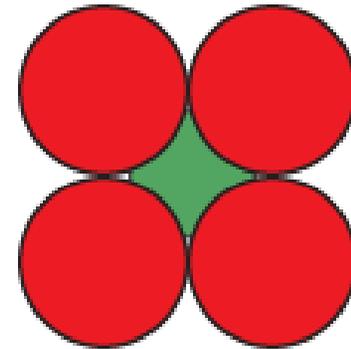
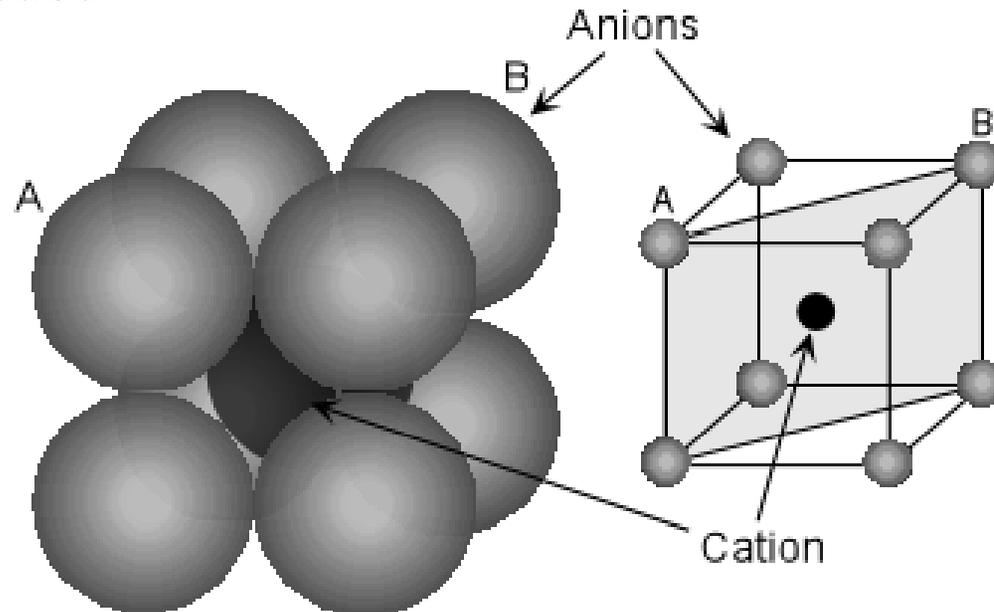
Pauling's Rules

- 1) Around every cation is a coordination polyhedra of atoms with cation-anion distances determined by radius sums & the CN determined by the RR
- 2) Electronic structure is stable as long as the strength of electrostatic bonds that reach an anion is equal to its charge
- 3) The most stable structure of two or more bonded polyhedra is via an anion. Sharing of edges and especially faces leads to decreased stability.
- 4) In structures with different charged cations, those with the highest charge and lowest CN tend not to share elements of coordination polyhedra
- 5) The Principle of Parsimony: the number of essentially different constituents tends to be as small as possible

Decreasing the (theoretical) radius ratio

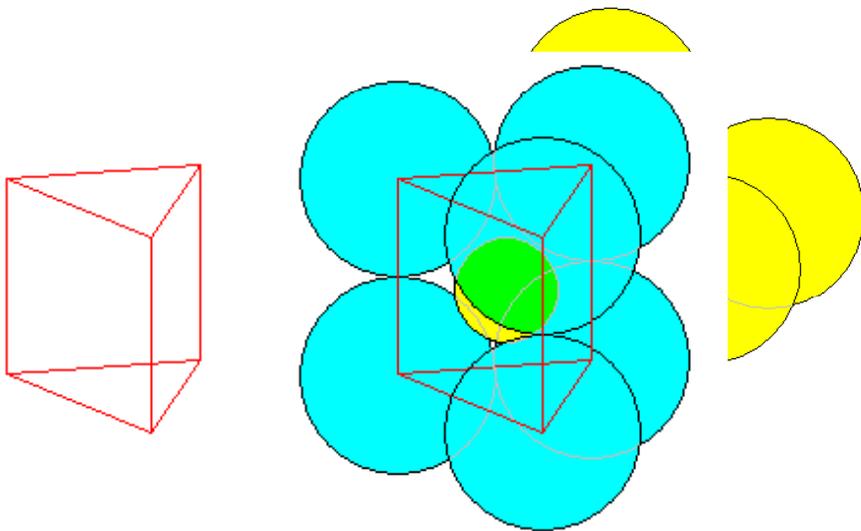
As the radius ratio decreases, the cations get smaller relative to the anion. i.e. fewer anions can be accommodated around a single cation ($r > 0.732$).

With a C.N. of 8, cubic coordination also results, with each of the 8 anions found at the 8 corners of a cube.



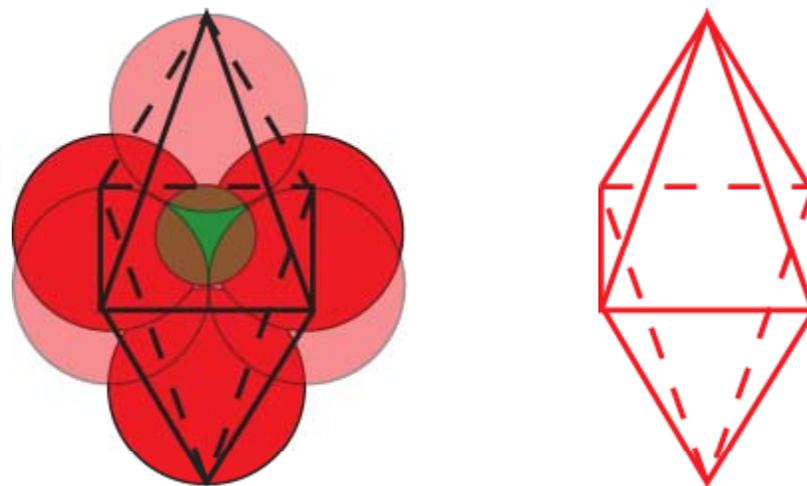
For radius ratios < 0.732

The next C.N. down is 7.



A pentagonal dipyramid

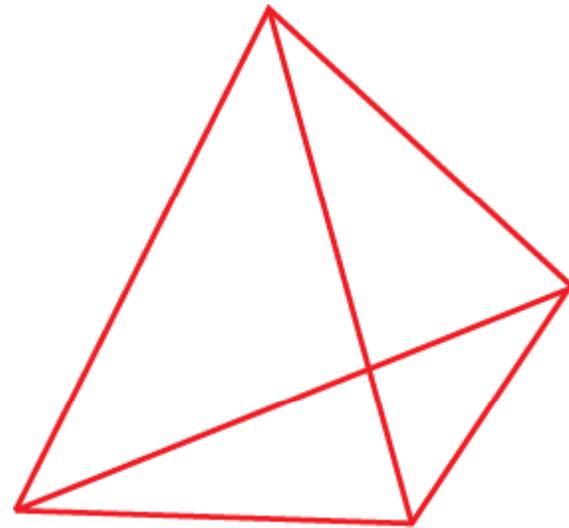
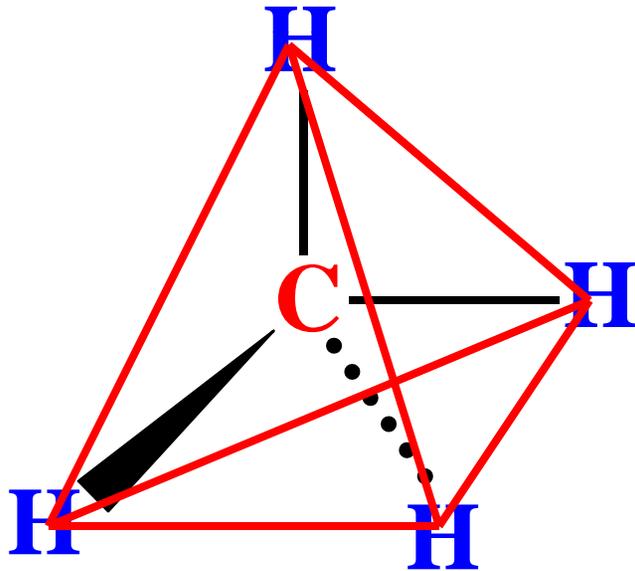
The one after that is 6,
which has **TWO** forms.



This 6-fold coordination is
called **octahedral**
coordination

For radius ratios < 0.414

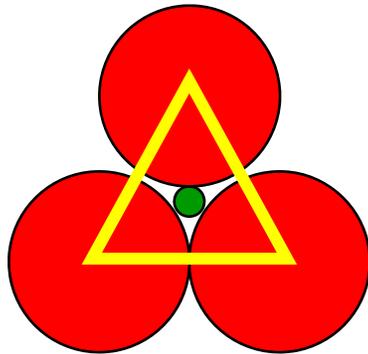
At these ratios 4-fold coordination becomes more stable, and the polyhedrons takes on the form of a regular tetrahedron.



Triangular and Linear Coordination

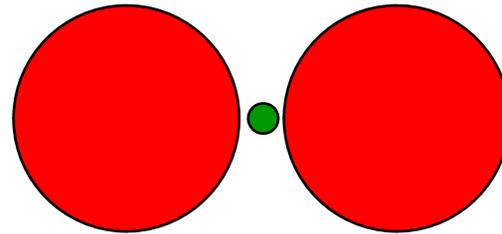
These coordination arrangements are most common in the anion groups or very rare minerals.

3-coordination (rr of 0.225 to 0.155).



Common groups include CO_3 , NO_3 , and BO_3 .

2-coordination (rr < 0.155).



Common minerals include UO_3 , CoO_3 , and $(\text{NO}_2)^{-2}$.

REVIEW

Coordination Number (CN) = the number of atoms that surround a particular atom or ion in a structure.

- decreases with the increase in length of ionic radii
- associated with a particular RR range

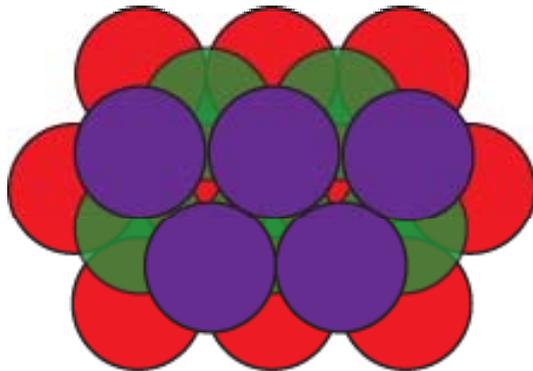
Radius Ratio (RR) = RA/RC

Models of the arrangement of atoms are based on Pauling's 5 Rules which define the relationship between CN, RR, and the shape of the unit cell formed by the anions

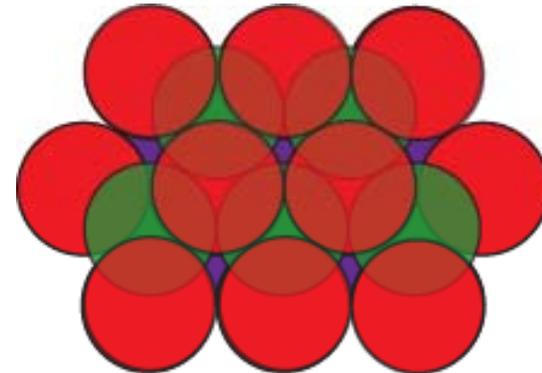
Packing

Simple packing systems are best visualised using identical spheres.

Cubic Close Packing (CCP)



Hexagonal Close Packing (HCP)



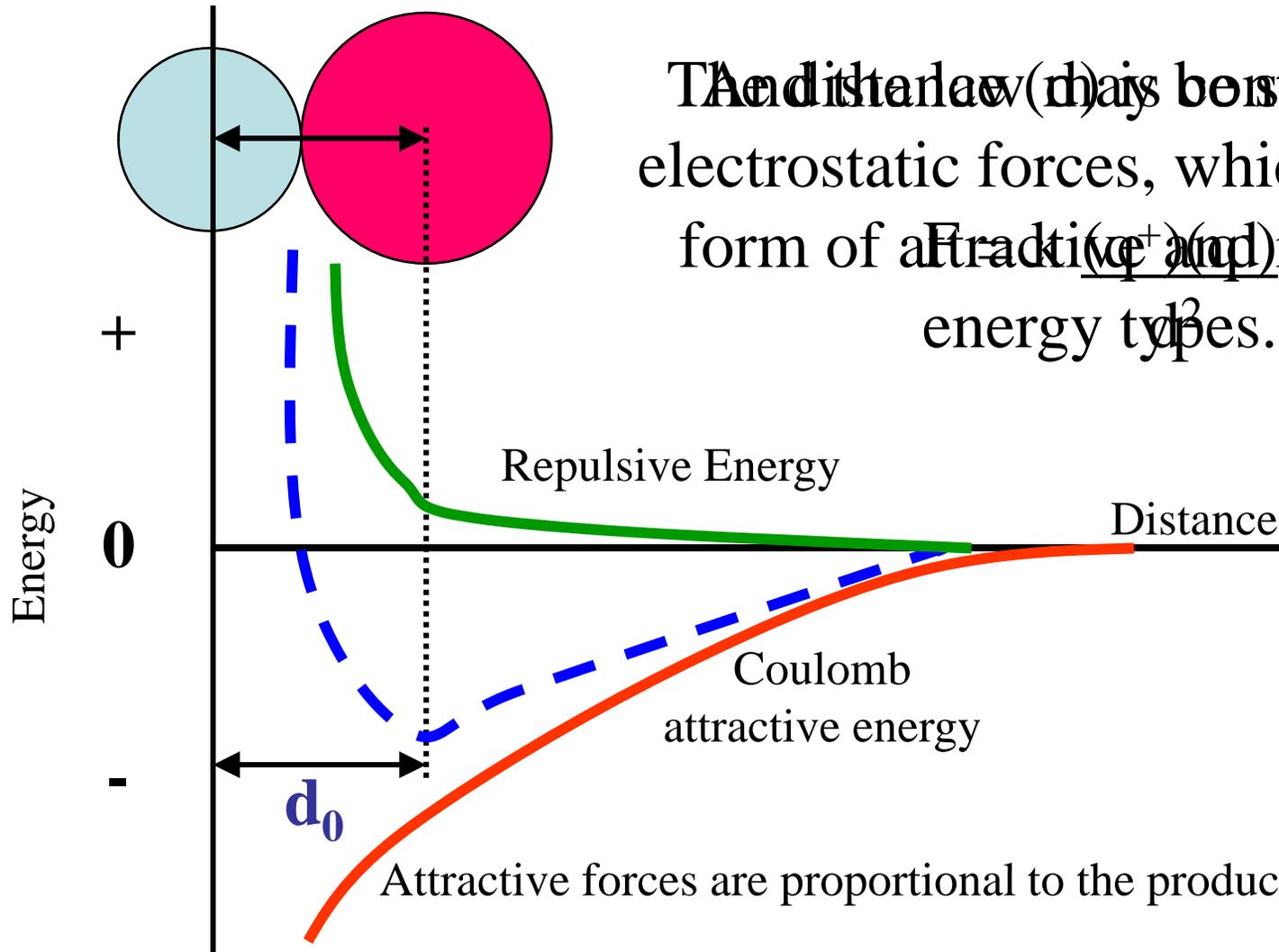
Stacking sequence - ABC

Stacking sequence - ABA

Both arrangements have C.N. = 12.

12

Coulomb's Law (1787 – French Physicist)



Attractive forces are proportional to the product of their charges.

Attractive forces are inversely proportional to the square of d .