

**A return to Paulings Rules and
structures related to elemental
chemistry**

The coordination polyhedra are rarely perfect – Why?

Electrostatic forces dictate that ions tend to group/arrange themselves so that ions of like-type are as far apart as possible, yet be consistent with the coordination and stoichiometry dictated by the ion of opposite charge.

Hence, coordination polyhedra are commonly linked through corners and edges, but generally not through faces.

Paulings Rules

Remembering the basics in packing and electrostatic forces a set of broad generalisations can be made.

They were first discussed by Linus Pauling (in 1929).

Rule 1: A coordination polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the coordination number of the cation by the radius ratio.

Essentially – the larger the ionic radii the greater the cation-anion distance, while the lower the radius ratio, the lower the coordination number.

Rule 2: The electrostatic valency principle.

The rule states that the total strength of the valency bonds that reach an anion from all the neighbouring cations is equal to the charge of the anion. N

Essentially, we are looking for a definition of **bond strength**.

In this case it is defined as an ion's valence charge divided by its coordination number. (e.v. = z/n).

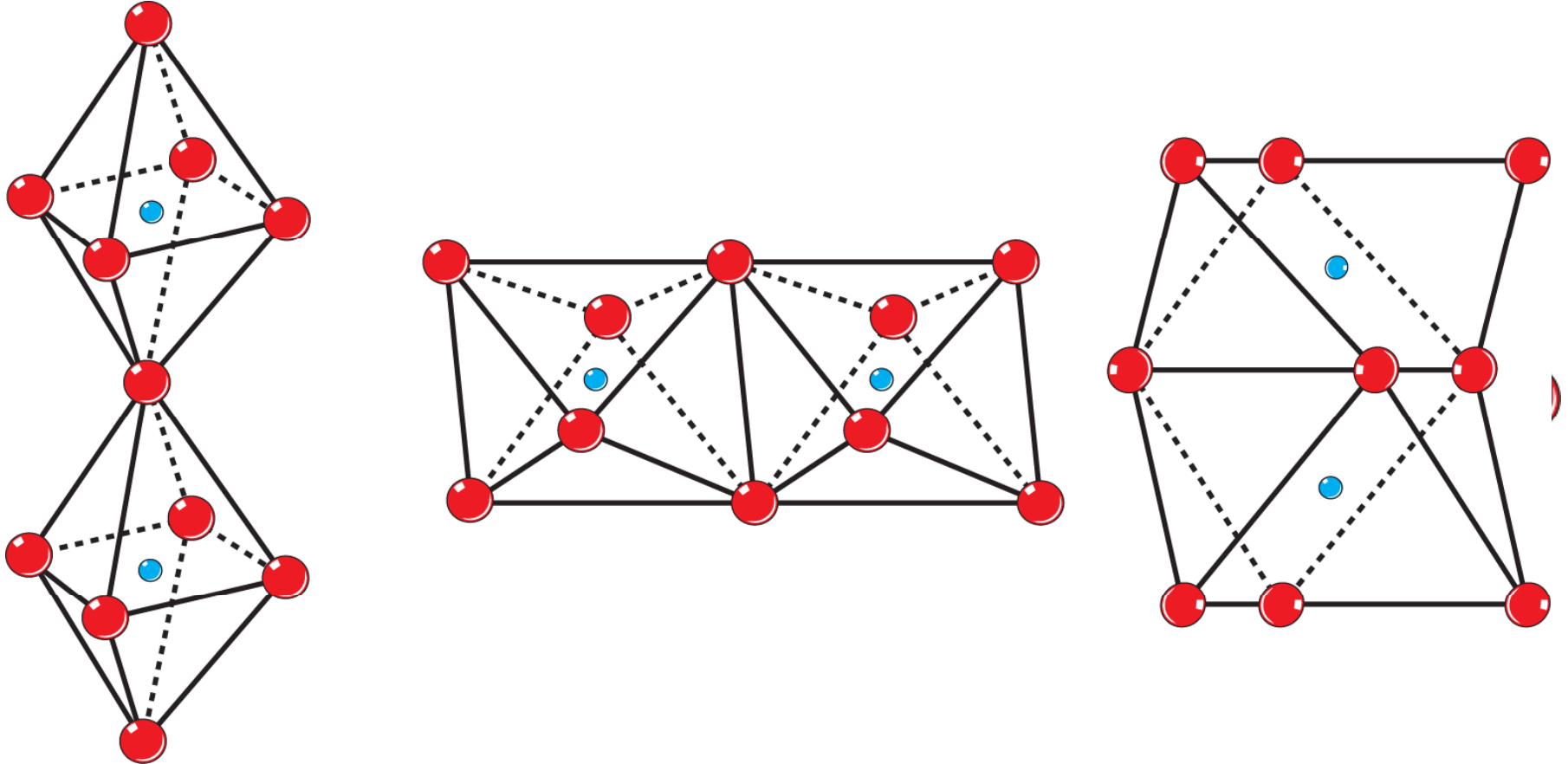
The number is called the electrostatic valency (e.v.).

In simple minerals of two elements, all bonds are of equal strength – **isodesmic**.

When small highly charged cations coordinate with larger and less strongly charged anions (carbonates and nitrates) the e.v. of the sub-group bonds is $>$ one-half the total charge on the anion. This means that the anionic unit is internally more strongly bond than the cation is to the anion in the mineral structure. Such compounds are said to be **anisodesmic**.

Rule 3: Points < edges < faces.

The existence of edges, and particularly faces, common to two anion polyhedra in a coordinated structure decreases its stability.



The effect is increased for large cations with high valency and small coordination number, and when the RR approaches the lower limit for the polyhedron.

Rule 4: cation-cation repulsion minimisation

In crystals containing different cations, those of high valency (small C.N.) tend not to share polyhedral elements with each other.

When they do, shared edges contract to put more negative charge between the cations. This causes the cations to be displaced from their polyhedral centres, away from the shared edges of faces, minimising the repulsive forces.

Rules 1 to 4 are all conceived so that cation-anion attractions are maximised, while cation-cation and anion-anion attractions are minimised.

Rule 5: The principle of parsimony

Minerals are, essentially, simple chemical compounds with compositional variation limited to a small range of different elements.

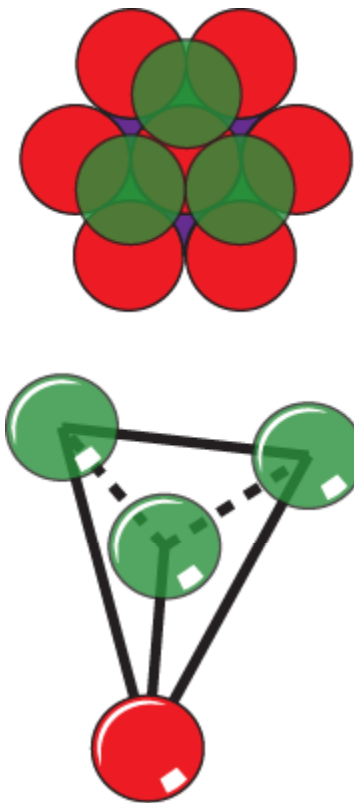
This is because there are only a few types of contrasting cation and anion sites.

Thus, in structures with complex compositions, a number of different ions may occupy the same structural position (or site).

These ions are considered as a single “constituent”.

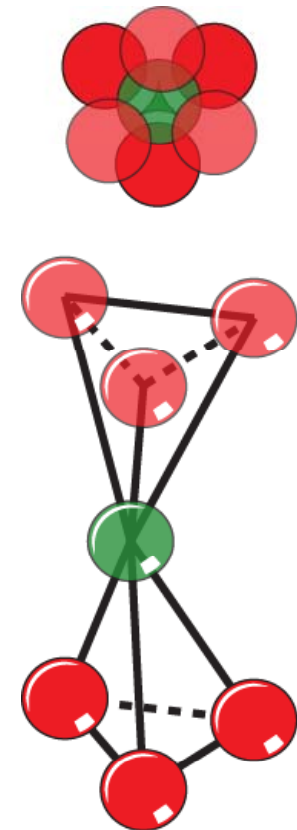
Common structure types and packing

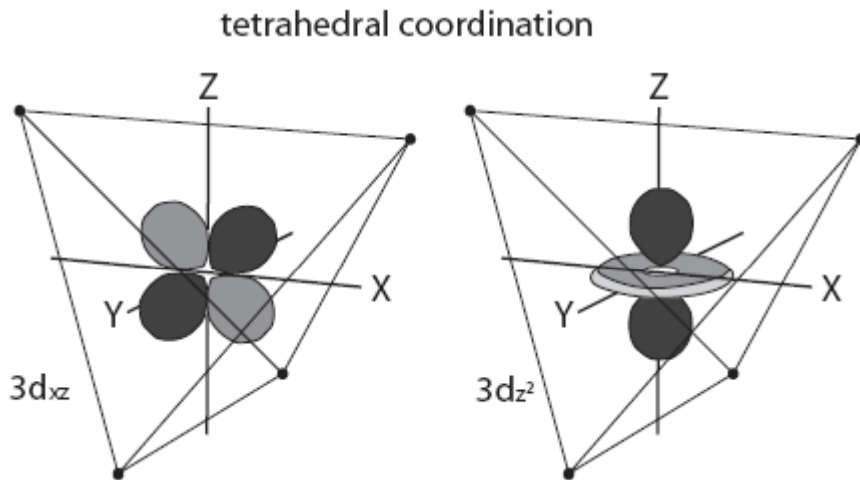
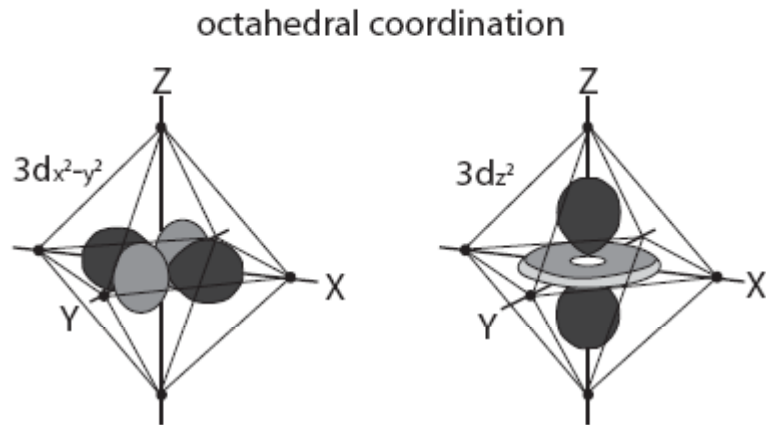
When the radius ratio equalled 1 and the C.N. equalled 12, two close-packing arrangements were identified.



Careful examination of the of packing arrangements shows that there are two types of interstitial site – tetrahedral and octahedral.

However, as we will see when we examine basic structures, not all sites need necessarily be fully occupied by cations.



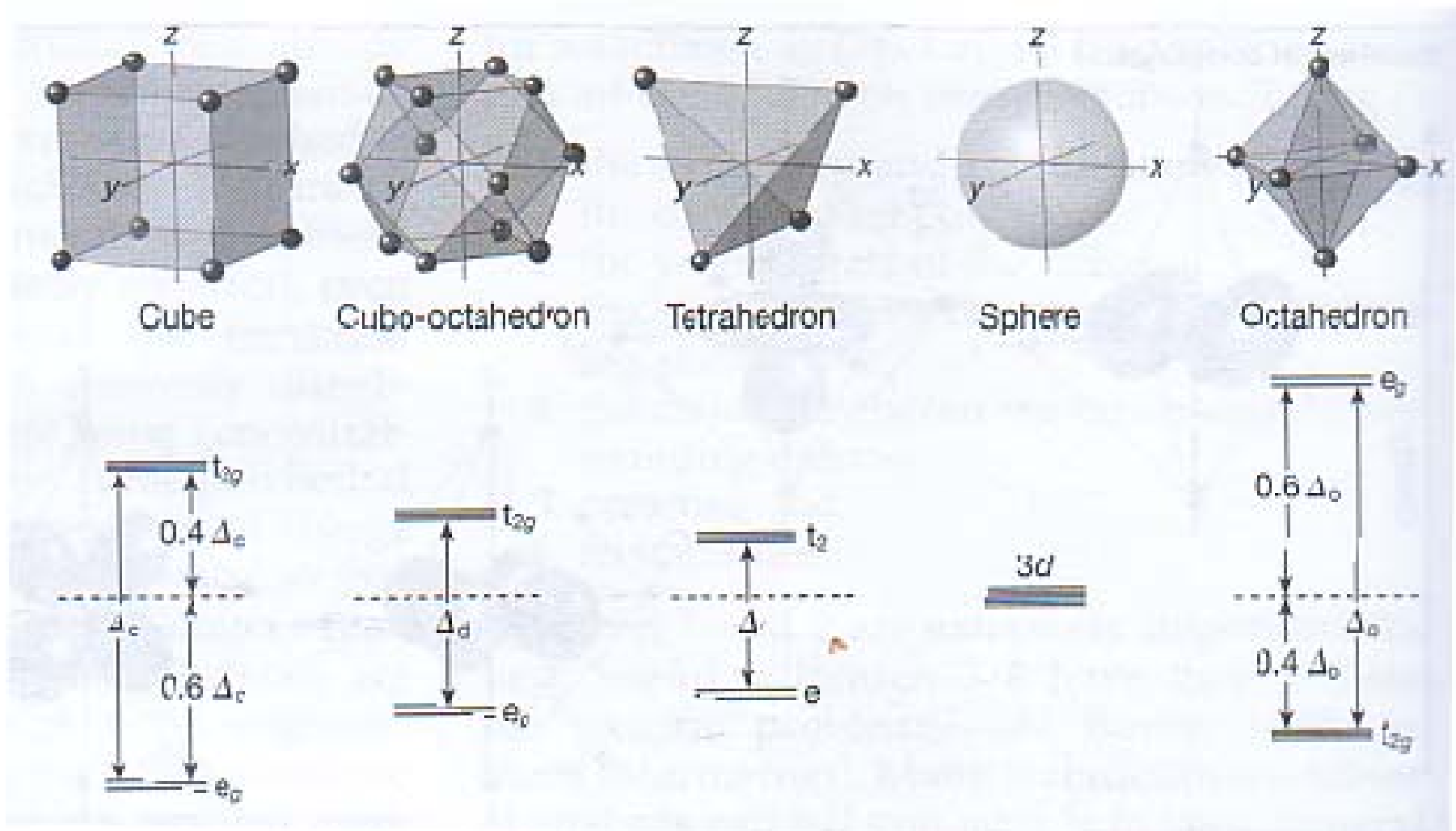


- If charge is unevenly distributed such that e^- closest to O in the polyhedra corners are repelled most strongly
- In the octahedral case, repulsion raises the energy of the orbitals usually oriented along the axes to create [3d_{xy}](#), [3d_{xz}](#), and [3d_{yz}](#) with orbitals between the axes
- In the tetrahedral case, the opposite happens with each 3d_{xz}, 3d_{xy}, and 3d_{yz} (with orbital between the axes) reverting to a lower energy state because of the proximity of O

This is the concept of *crystal field splitting*

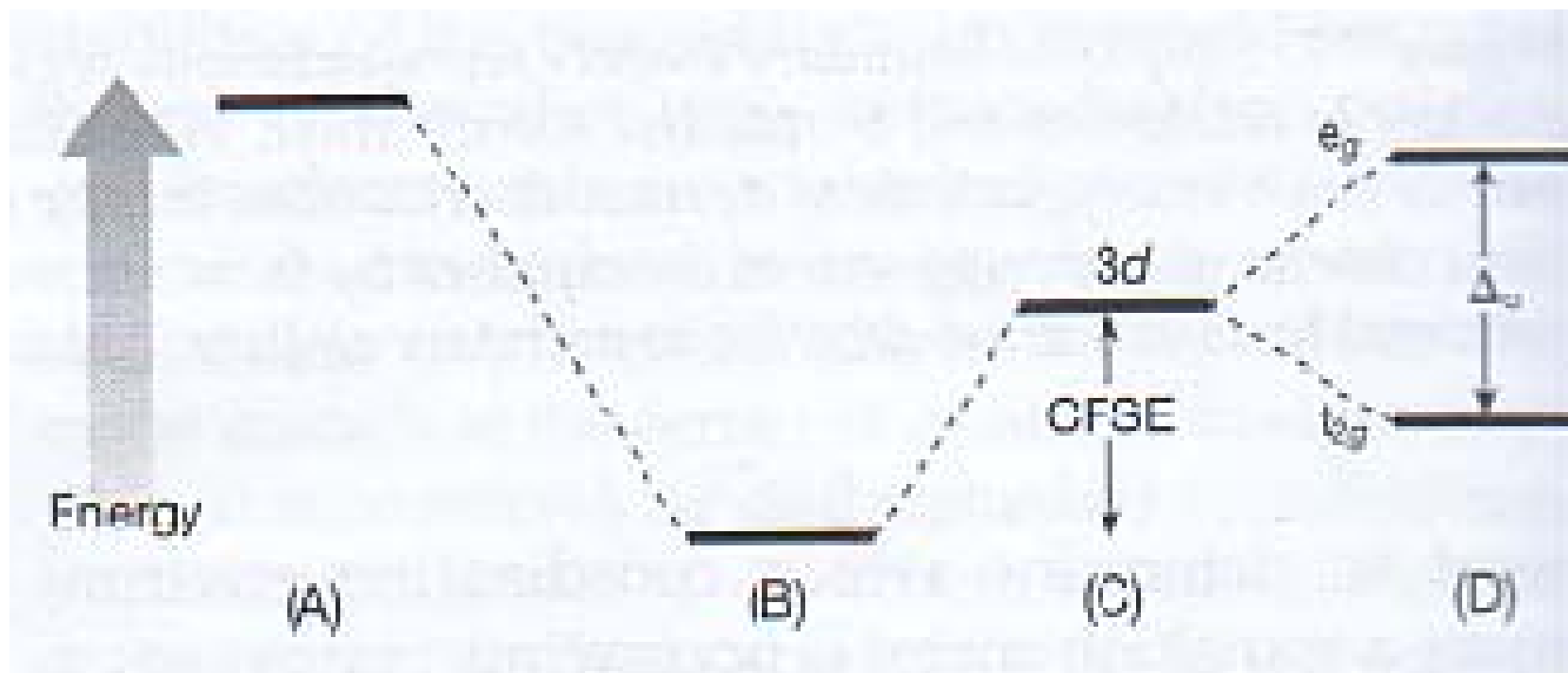
Crystal Field Stabilization Energy: The relative contribution of energy from e- in various orbital shells – this value describes the total change in energy between the imperfectly symmetrical state and the coordinated state

Crystal Field Splitting: The difference in energy between the lowest and highest orbitals – this value most strongly depends on the symmetry and coordination number of the polyhedra and the valance state of the cations



Crystal field splitting of 3d orbitals (Δ): These values will be characteristic for each type of coordination polyhedra

e_g orbitals are those that represent $d_{x^2-y^2}$ and d_{z^2} while t_{2g} lie between the axes



The Δ value represents the amount of energy that will be needed to move an e^- from the low energy orbital to any higher energy orbital

For the transition metals, light absorption spectra can actually be used to determine the coordination environment that is occupied

CFSE is essentially a value representing the sum of all e^- in all orbitals

- the total destabilizing effects should be zero if all orbitals are full

- high CFSE values indicate that a cation would (energetically) prefer a certain polyhedral arrangement over another

Goldschmidt's Rules of Substitution

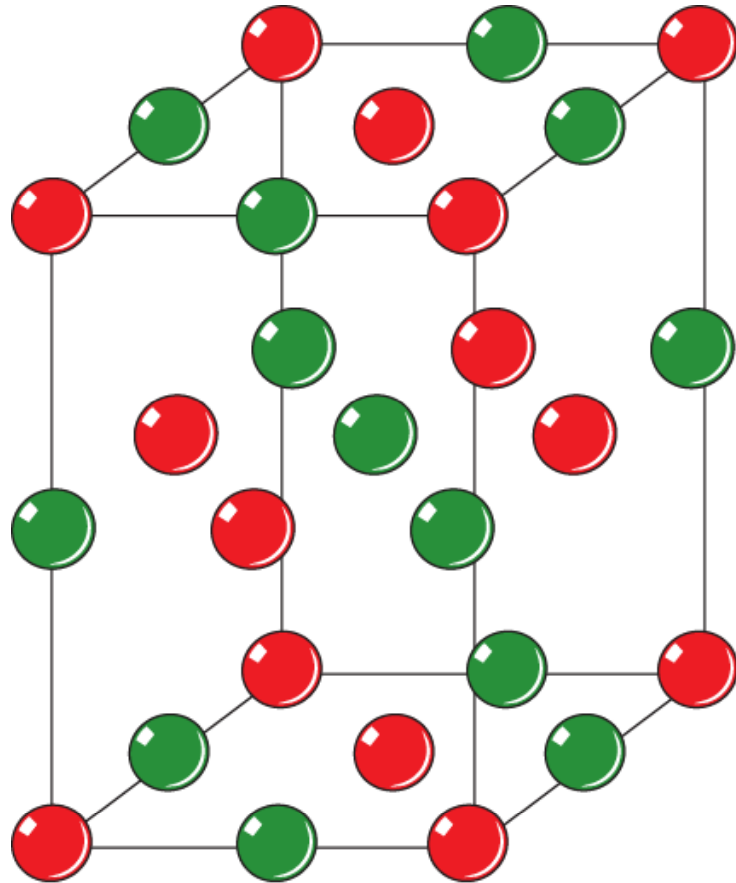
Rule 1: The ions of one element can extensively replace those of another in ionic crystals if their radii differ by less than about 15% and they have the same charge

Rule 2: Ions whose charges differ by one unit will substitute readily for each other provided electrical neutrality is maintained. Ions with charges that differ by great than one do not substitute

Rule 3: When two different ions can occupy a particular position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with the anions

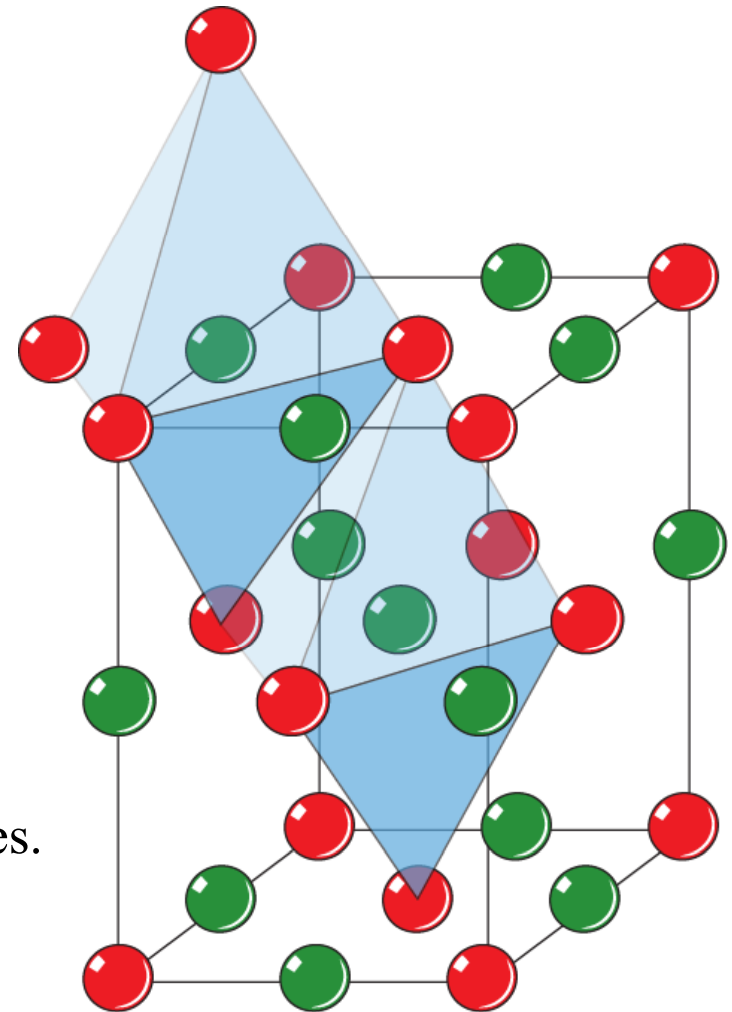
Rule 4: Even when size and charge are similar, the ions with the lower electronegativity will form stronger bonds and this be preferentially concentrated when growing crystals from a melt.

Simple Cubic Packing (SCP) – NaCl Structure

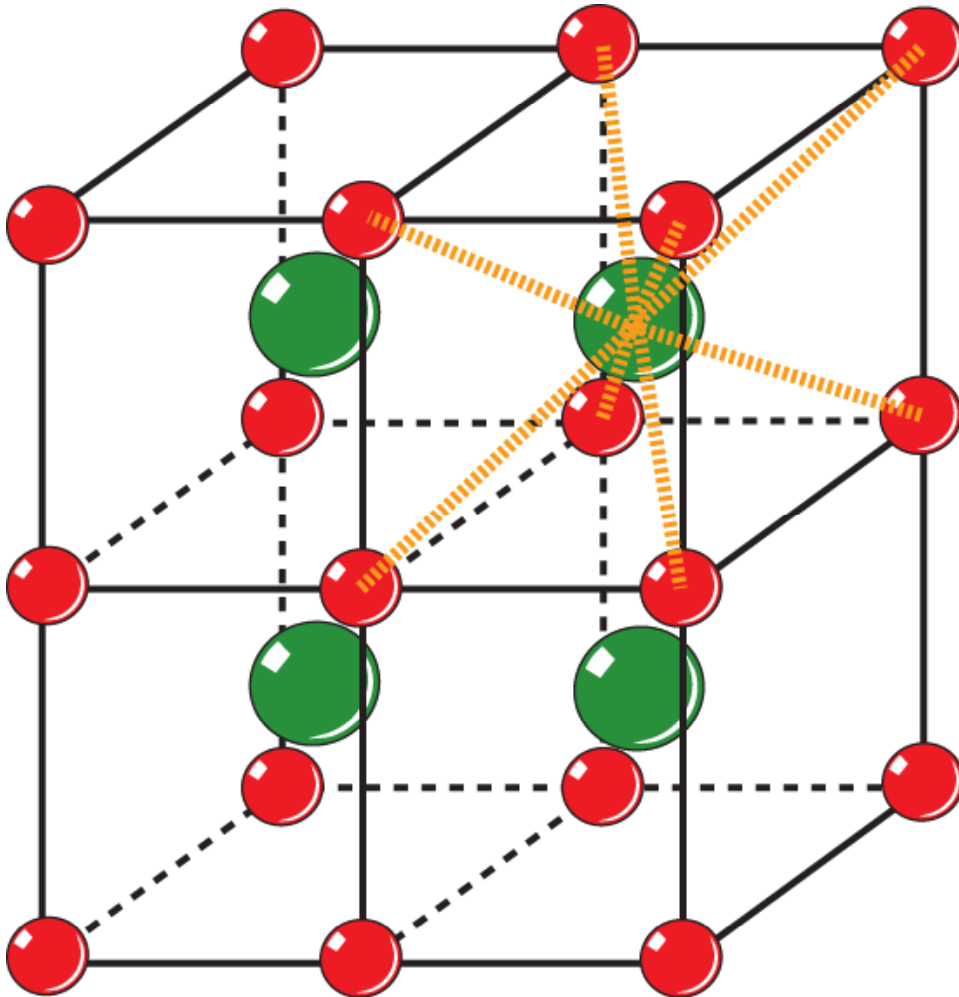


CCP structure with cations filling octahedral sites.
All tetrahedral sites are empty.

Structure contains edge sharing octahedra.



CsCl Structure – Body Centered Cubic

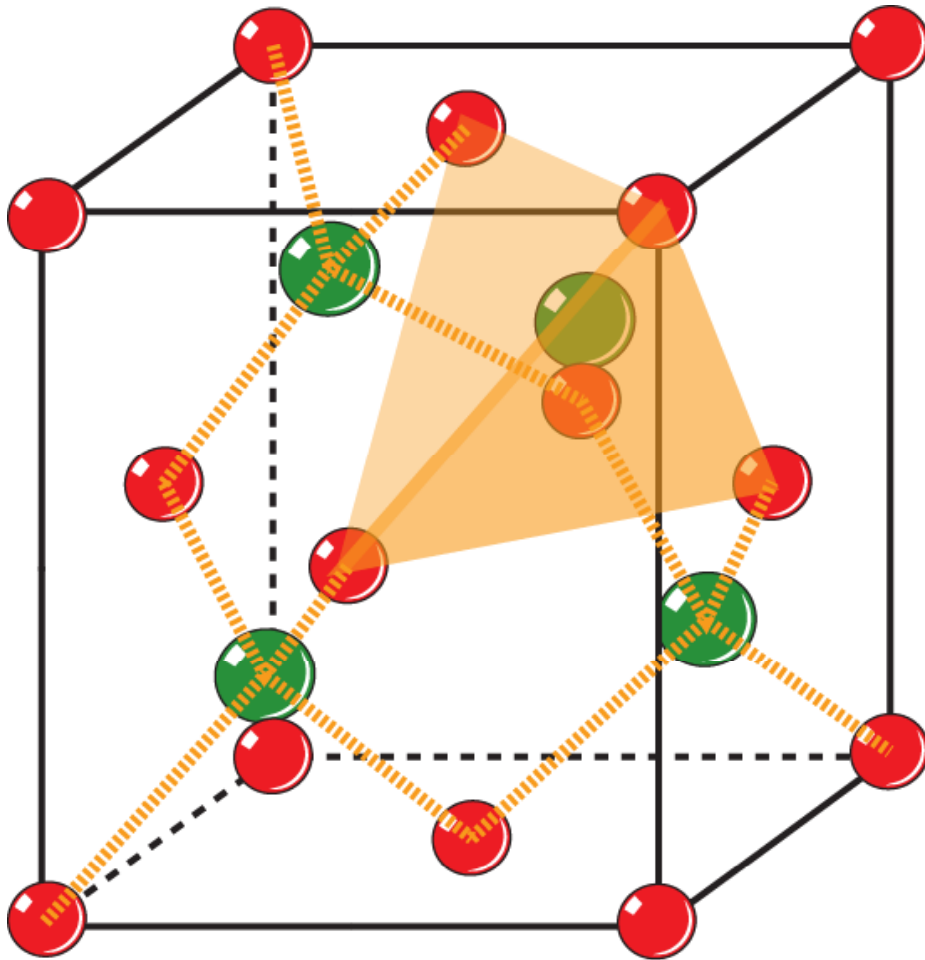


The larger ionic radius of Cs decreases the r.r. and C.N.

The anions have a SCP arrangement with cations filling the large interstitial sites.

Overall structure is centred cubes that share faces.
(Unattractive for highly charged cations)

ZnS (sphalerite) Structure – Tetrahedral coordination analogous with diamond.

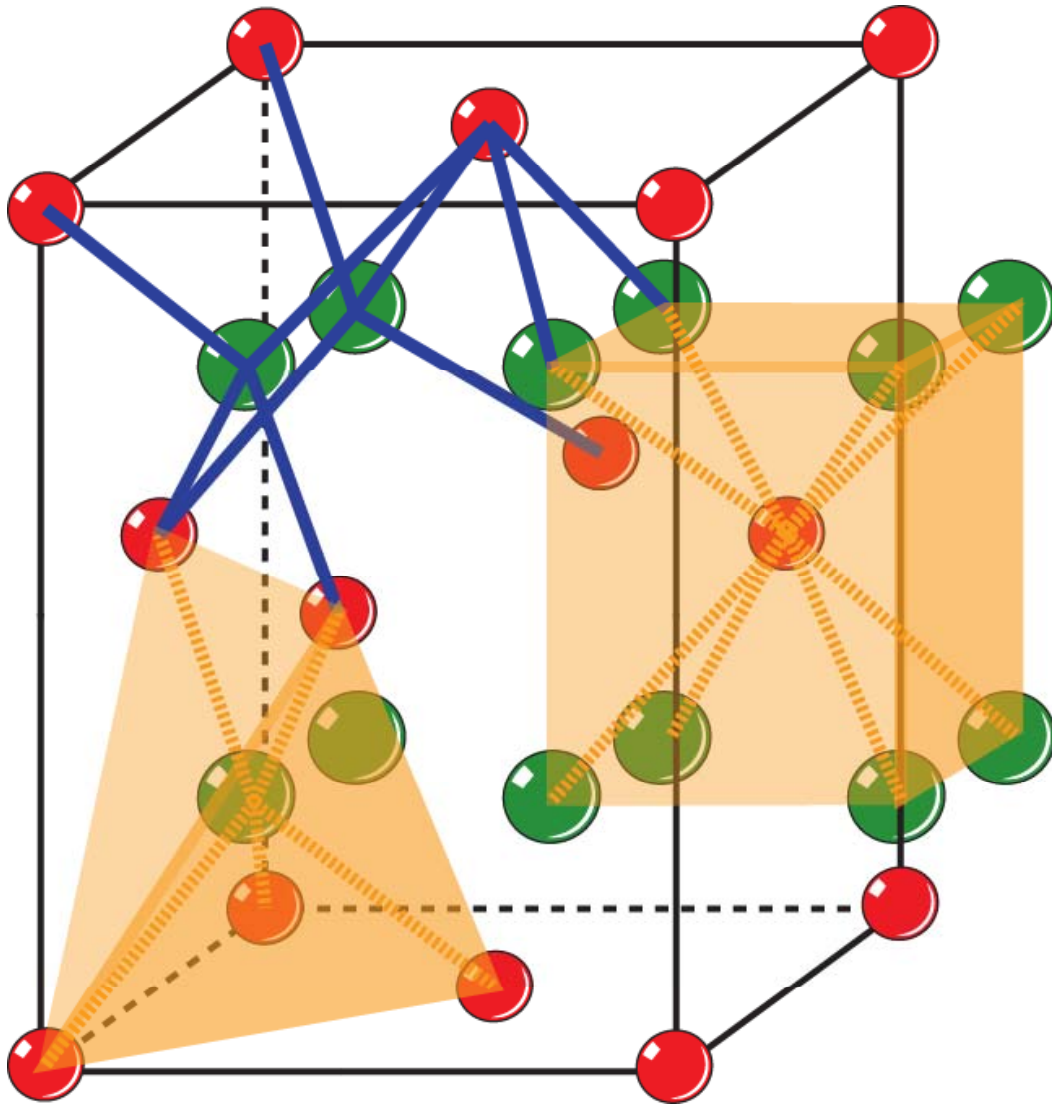


The S²⁻ anions create a face centred cube structure.

The interstitial tetrahedrally coordinated sites are filled by Zn²⁺.

It is a derivative of the diamond structure – 50% of the carbon atoms replaced by S, the rest by Zn.

CaF₂ Structure



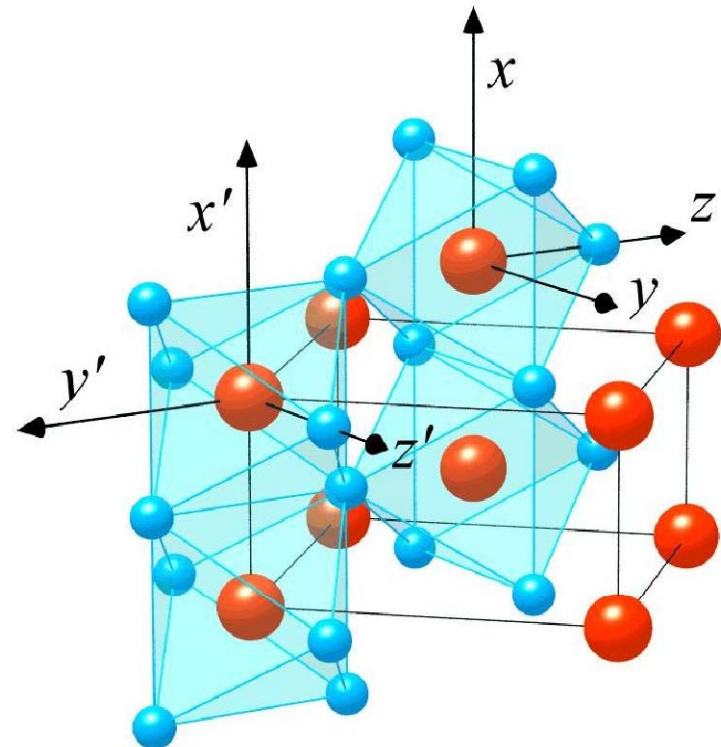
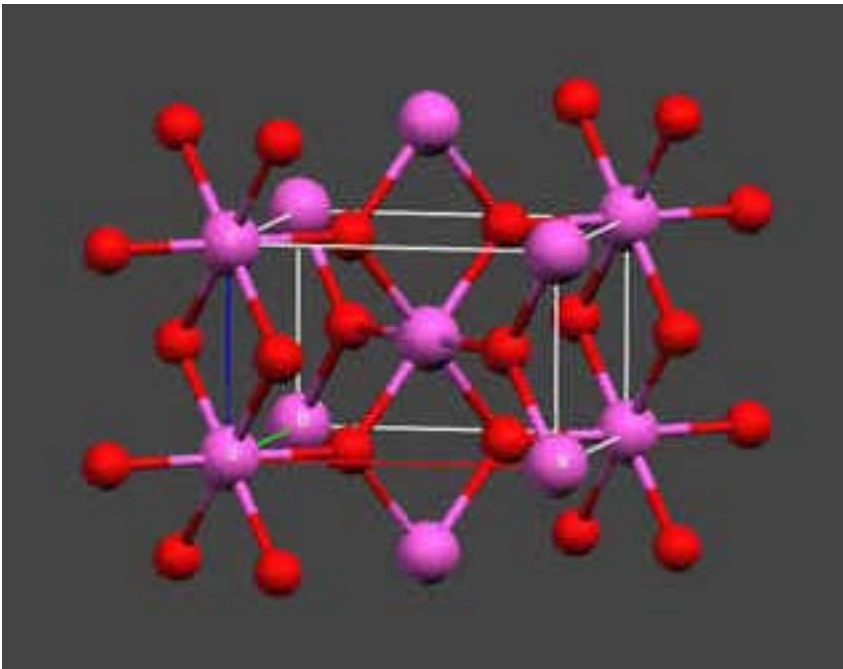
Ca²⁺ cations are arranged at the corners and face centres of a cubic unit cell (FCC).

F¹⁻ anions have a SCP arrangement with Ca²⁺ occupying the void of alternating cubic interstices.

Each Ca is coordinated by 8 F.
Each F is coordinated by 4 Ca.

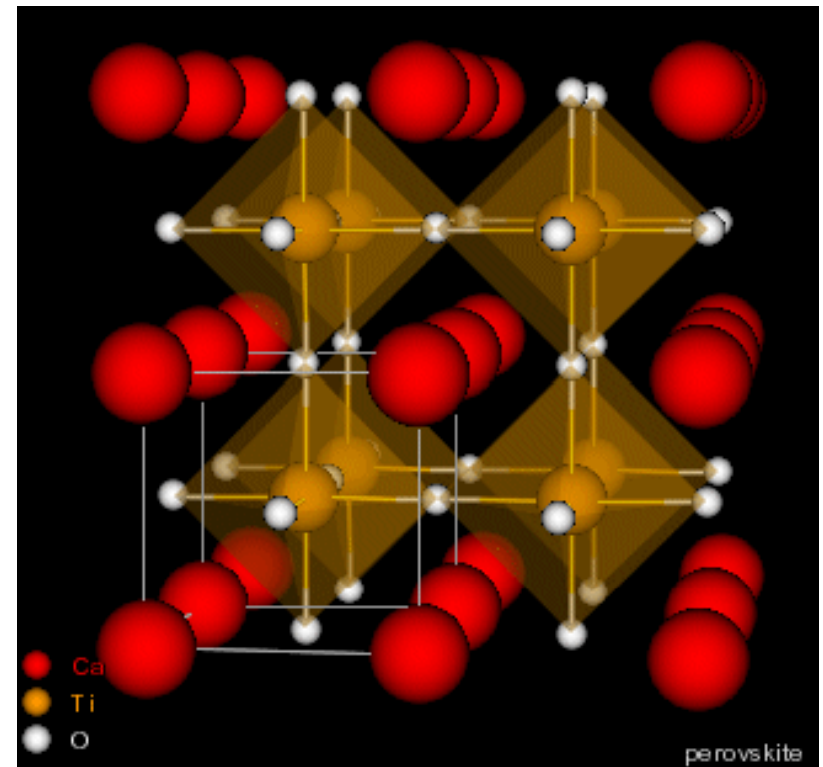
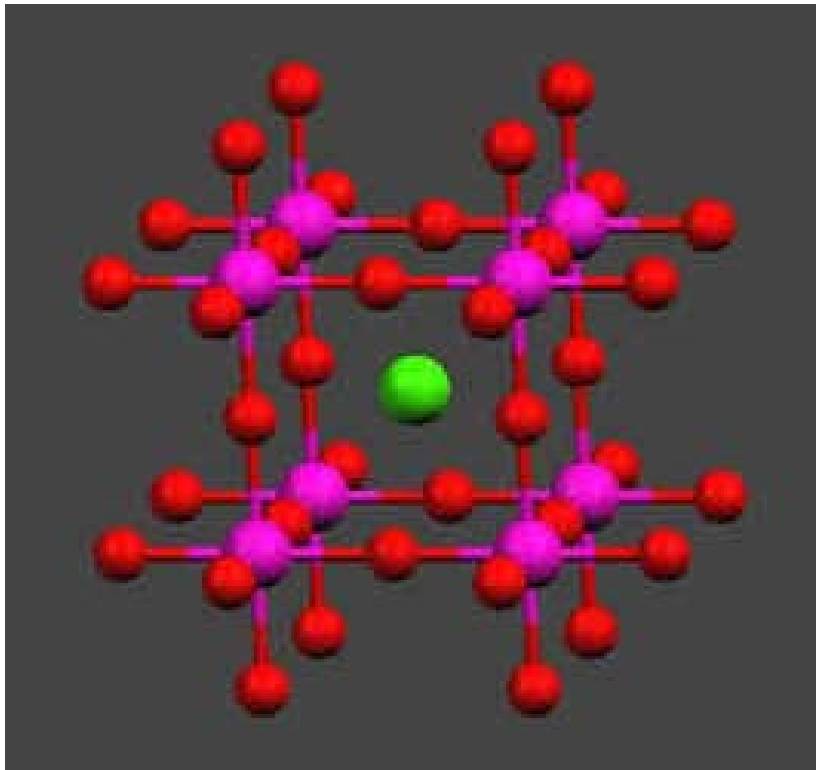
3 Additional Structures

- Rutile (TiO_2)
 - Based on HCP with Ti occupying half the octahedral interstitial sites.
 - The anions are coordinated by 3 cations.



3 Additional Structures

- Perovskite (ABO_3)
 - Based on CCP of oxygen with 25% replaced by a large cation (A) with 10-fold coordination.
 - B cation in apical sharing octahedron.



3 Additional Structures

- Spinel (AB_2O_4)
 - Based on CCP of oxygen with $\frac{1}{8}$ of tetrahedral interstices (A) and $\frac{1}{2}$ of the octahedral interstices occupied.
 - The smaller T-site – smaller cations (Fe^{2+} , Mg^{2+} , Mn^{2+})
 - The larger O-site – larger cations (Al^{3+} , Cr^{3+} , Fe^{3+})

