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A Short Intro to Pauling's Rules

Pauling's rules are a set of five heuristics to predict the coordination of cations in a crystal structure. These rules are for idealized spherical ions with perfectly ionic bonding between cations and anions. The coordination number (CN) of a cation is the number of oxygens it is bonded with. The five rules are:

1. Radius ratio: describes the minimum radius required for a cation in a given coordination.
2. Electrostatic valence: the electrostatic bond strength of each of the bonds between cation and coordinated anions.
3. Polyhedron corner, edge, and face sharing: the most stable structures minimize the contact between polyhedra.
4. Multiple-cation structures: cations with high valence and small coordination number tend to be structurally separated by other cations with lower valence and higher coordination.
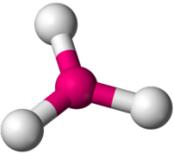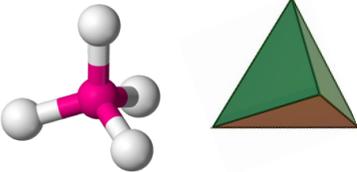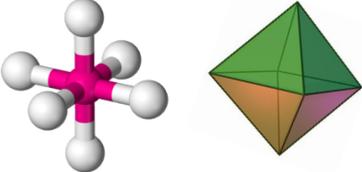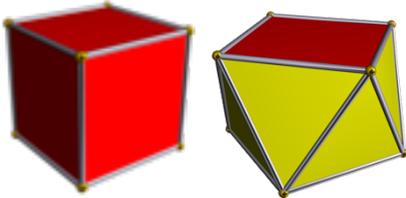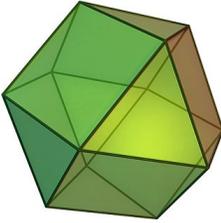5. Parsimony: the simpler the structure, the better.

In more detail:

Radius Ratio

$$rr = \frac{R_c}{R_a}$$

Where rr = radius ratio; R_c = radius of cation (Å); R_a = radius of anion (Å).
Depending on the radius ratio, Pauling's rules predict different CN:

CN	Polyhedron	Radius Ratio
3	triangle	$0.155 \leq rr < 0.225$
4	tetrahedron	$0.225 \leq rr < 0.414$
6	octahedron	$0.414 \leq rr < 0.645$

8	cube or anticube (in the anticube, the bottom face is rotated 45º from the upper face; it still has 8 corners but it now has 10 sides instead of 6)	$0.645 \leq rr \leq 0.732$
12	cuboctahedron 	$0.732 < rr \leq 1$

## Electrostatic Valence

$$s = \frac{z}{v}$$

Where $s = evb = $ electrostatic valence of the bond; $z = $ charge of cation; $v = $ CN (i.e. number of oxygens the cation is bonded with.

For example: SiO_4: $s = \frac{+4}{4} = +1$

MgO_6: $s = \frac{+2}{6} = +\frac{1}{3}$

A higher *evb* is a "stronger" bond.

## Sharing of polyhedron corners, edges, and faces:

Sharing more of a polyhedron brings the positively-charged cations closer together, which is less stable. For example, two silica tetrahedra:
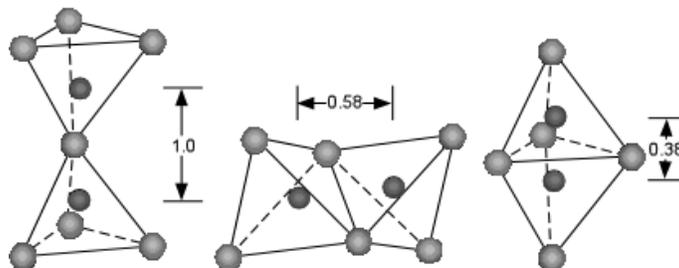
The farther apart the Si^{4+} cations, the more stable the configuration. This is especially true of low-CN, high-charge cations.
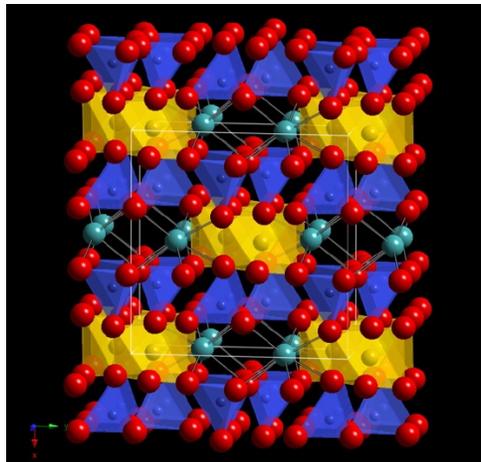
Different Cations

Cations with high valence (charge) and low CN tend not to share bridging oxygens if possible. For example, in zircon structure, Zr^{4+} and Si^{4+} have the same charge, but Si^{4+} is in a smaller coordination. The more stable structure is therefore to have the Si tetrahedra (blue) not share any elements, while the Zr anticubes (green) share edges with each other and share edges and corners with the Si tetrahedra.
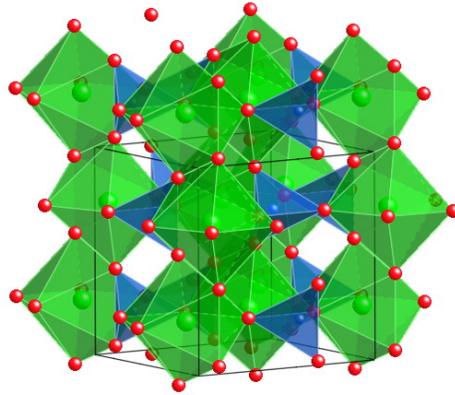
Zircon Structure

Parsimony

Cations of the same species tend to have the same CN throughout the crystal structure. For example, in diopside ($CaMgSi_2O_6$), Si is always in tetrahedral coordination (blue), Mg is always in the M1 octahedral site (yellow), and Ca is always in the larger M2 octahedral site (teal ball-and-stick)

Diopside structure