

Materials 218/UCSB: Class VI & VII, Part I: Pauling's rules for ionic crystals, and the concept of Bond Valence

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- Pauling's rules:

First rule *Radius ratio etc.* A coordination polyhedron is formed around each cation. The distance between the cation and the anion is the sum of the ionic radii ($r_+ + r_-$). The number (coordination number CN) of anions around the cation is determined by the radius ratio r_+/r_- .

Illustration: The cell parameters of the alkali halides AX (A = Li, Na, K, Rb, Cs; X = F, Cl, Br, I) are derived from sums of the ionic radii (r_+ and r_-) while the nature of the structure type (NaCl or CsCl) depends on the radius ratio r_+/r_- .

How are radii determined experimentally? They were originally compiled from tables of interatomic spacings ($r_+ + r_-$), obtained from experimental cell parameters. For the AX species:

	Li	Na	K	Rb	Cs
F	2.01	2.31	2.66	2.82	3.00
Cl	2.57	2.81	3.14	3.27	3.56*
Br	2.75	2.98	3.29	3.43	3.71*
I	3.00	3.23	3.53	3.66	3.95*

* These compounds have the CsCl structure, the rest have the NaCl structure.

If one of the radii could be fixed, the rest can be determined. Landé in 1920 said that I^- is so large and Li^+ so small (from the number of electrons) that $r_{Li^+} + r_{I^-}$ is effectively equal to r_{I^-} . This allows all other radii to be determined.

The modern approach is based on an extensive analysis of crystallographic data: See R. D. Shannon and C. T. Prewitt, *Acta. Crystallogr. B* **25** (1969) 925; R. D. Shannon, *Acta. Crystallogr. A* **32** (1976) 751; F. Scordari in C. Giacovazzo (eds.) *Fundamentals of Crystallography* IUCr-Oxford, New York, 1992 pp 420-421.

In structures with many atoms, the larger, less-charged cations are the most willing to change their coordinations – in a structure with Na^+ , Ca^{2+} , and Si^{4+} , the sodium atoms would be most willing to change their coordinations from what is dictated by r_+/r_- , the calcium next and the silicon least of all.

Second rule *The valence sum rule.* The valence of an anion in a stable ionic structure tends to compensate the strengths of the electrostatic bonds which reach it from the cations situated at the centers of polyhedra of which the anion is a vertex, and *vice versa*.

If V_- is the valence of the anion, V_+ the valence of the cation and Z the coordination number of the cation, then the *electrostatic bond strength* s is determined by:

$$s = V_+/Z \quad \text{and} \quad -V_- = \sum s$$

The summation is over all the cations to which the anion is bonded.

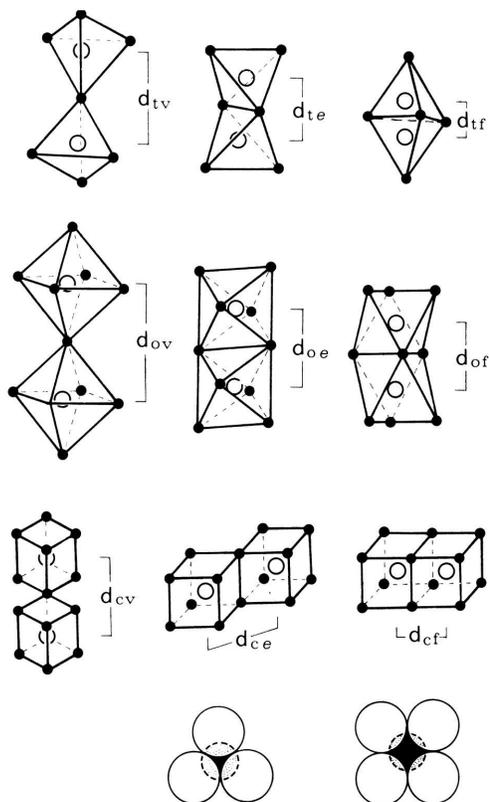
In the NaCl structure, $V_- = -1$, $V_+ = +1$ and $Z = 6$ (each Na^+ sits in the center of an octahedron of Cl^-). Then $s = 1/6$ and $-V_- = 6 \times 1/6$.

In the rutile structure of TiO_2 , $V_- = -2$ and $V_+ = +4$. Ti^{4+} are octahedral so $Z = 6$. This means that $s = 4/6 = 2/3$. From $\sum s = -(-2)$, we find that each O^{2-} is bonded to three Ti^{4+} .

The electrostatic valence rule is a precursor to the concept of bond valence.

If the electrostatic valence rule does not work, it is often an indicator of something wrong with the structure determination, or that something has been overlooked (for example, what one thinks is O^{2-} is actually OH^-).

Third rule *Linking of polyhedra*. Polyhedra formed by anions can share corners, edges or faces. The sharing of edges and faces has a high energy cost, and this cost increases as the charge on the central cation increases.



Vertex (corner), edge and face sharing of polyhedra (after Scordari). Note that in the smaller polyhedra (particularly in tetrahedra) edge or face sharing bring the cation centers uncomfortably close to one another. The sketches at the bottom at the bottom show how cation (black) charges are screened through the faces of octahedra (left) and cubes (right).

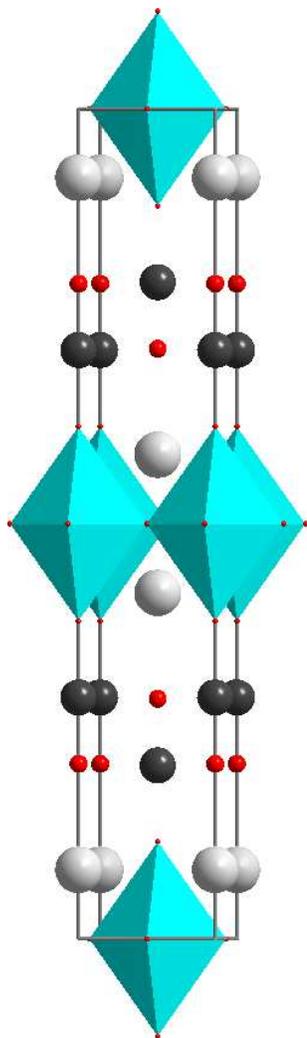
Illustration: In most (if not all silicates) SiO_4 tetrahedra link up by sharing of corners, but never of edges and faces. In the rock salt structure, one finds edge-shared octahedra, and in the perovskite structure, octahedra are corner-shared. In the CsCl structure, cubes share faces.

Fourth *High valence, low coordination number rule*. In a crystal containing various cations, polyhedra formed around cations with high charge (valence) and low coordination number tend not to share features.

Illustration: The planar carbonate in crystals never shares its oxygen with another carbonate ion. Likewise, sulfate ions like to remain isolated. Phosphate ions sometimes share corners.

Fifth rule *The rule of parsimony.* The number of essentially different constituents in a crystal structure tends to remain small. In other words, structures tend to be as simple as possible.

Illustration: The oxide superconductor, $Tl_2Ba_2CuO_6$ has, for a compound with four distinct ions and 10 atoms in the unit cell, is as simple as a structure with so many atoms could *possibly* be.



The red atoms are O (including at the corners of the octahedra), Cu atoms sit at the centers of the octahedra, Ba are grey, and Tl are black. The space group is the body-centered tetragonal $I4/mmm$ (No. 139).

- Bond Valence, and Bond Valence Sums:

I. D. Brown and R. D. Shannon [*Acta. Crystallogr. A* **29** (1973) 266] suggested that the strength of the bond s (used by Pauling in his electrostatic valence rule) between a cation and its neighboring oxide ion correlates very well with the distance of separation R , according to:

$$s = s_0 (R/R_0)^{-N}$$

where R_0 and N are empirical, *ie.* determined by wading through hundreds of crystal structures, and fitting. s_0 is the ideal electrostatic valence. All three values have been tabulated for hundreds of ions, and “calculators” of the bond valence can be found through a suitable web search.

Here are some values from the Brown-Shannon paper:

Cation	s_0	R_0 (Å)	N
H ⁺	0.5	1.184	2.2
Li ⁺	0.25	1.954	3.9
Be ²⁺	0.5	1.639	4.3
B ³⁺	1.0	1.375	3.9
Na ⁺	0.166	2.449	5.6
Mg ²⁺	0.333	2.098	5.0

For example, we can calculate for oxides with octahedral Mg, the bond valence per Mg-O bond would be:

$$s = 0.333 (R/2.098)^{-5.0}$$

When $R = 2.098$ Å, $s = 0.333$. The bond valence sum of Mg²⁺ is then $6 \times 0.333 = 2$ as one would expect.

If the Mg²⁺ are 4-coordinate (as they are in the spinel structure), then we can calculate what R should be, since $s = 2/4 = 0.5$:

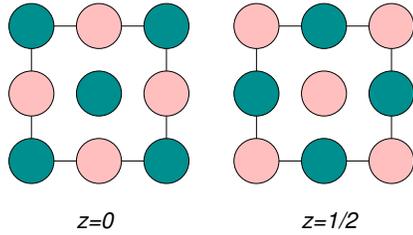
$$0.5 = 0.333 (R/2.098)^{-5.0} \quad \text{which solves to } R = 1.934 \text{ Å}$$

The value can be compared with experiment, which is $R = 1.91$ Å.

- AB crystal structures (NaCl, CsCl, ZnS (wurtzite), ZnS (zinc blende) NiAs)

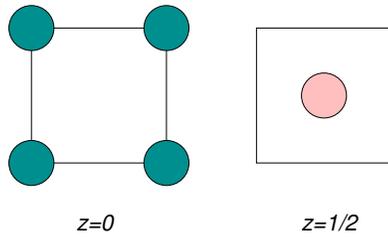
NaCl: SG = $Fm\bar{3}m$ (No. 225) $a = 5.63 \text{ \AA}$

Atom	x	y	z
Na	0	0	0
Cl	1/2	1/2	1/2



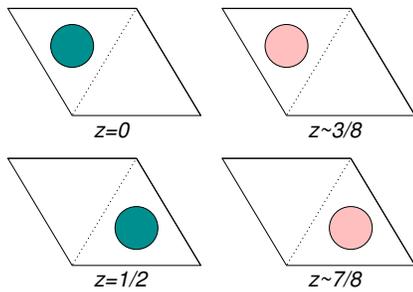
CsCl: SG = $Im\bar{3}m$ (No. 229) $a = 4.11 \text{ \AA}$

Atom	x	y	z
Cs	1/2	1/2	1/2
Cl	0	0	0



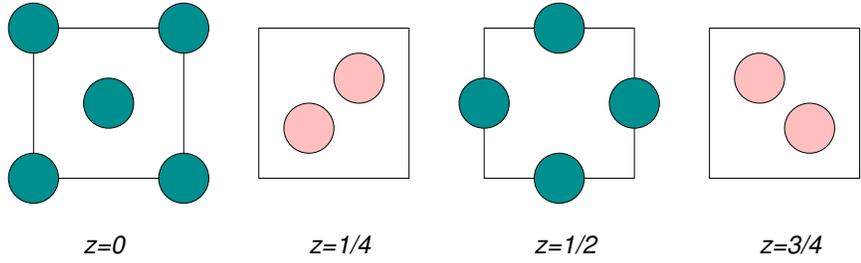
ZnS (wurtzite): SG = $P6_3mc$ (No. 186) $a = \text{\AA} = 6.23 \text{ \AA}$

Atom	x	y	z
Zn	2/3	1/3	0
S	2/3	1/3	$\sim 3/8$



ZnS (zinc blende): SG = $F\bar{4}3m$ (No. 216) $a = 5.41 \text{ \AA}$

Atom	x	y	z
Zn	0	0	0
S	1/4	1/4	1/4



NiAs: SG = $P6_3/mmc$ (No. 194) $a = 3.60 \text{ \AA}$ $c = 5.01$

Atom	x	y	z
Ni	0	0	0
As	2/3	1/3	1/4

