Lattice Energy

Pauling Rules

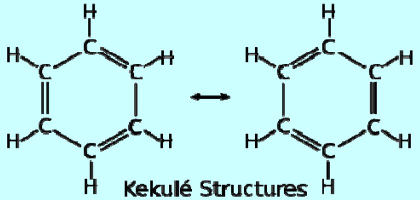
Bonding Models for Covalent and Ionic Compounds

G. N. Lewis 1923
Electron pair sharing
Orbital overlap
Chemical bond
Number of bonds = atomic valence

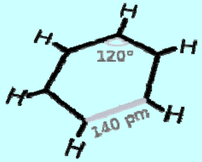
Born, Lande, Magelung, Meyer 1918
Electrostatic attraction (Coulomb) + Repulsion

C_6H_6

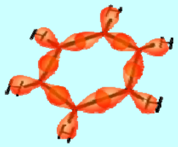
Benzene
Molecular formula



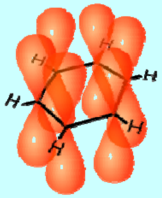
Kekulé Structures
(Isomers)



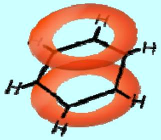
Planar Hexagon
Bond Length 140 pm



Sigma Bonds
sp^2 Hybridized orbitals

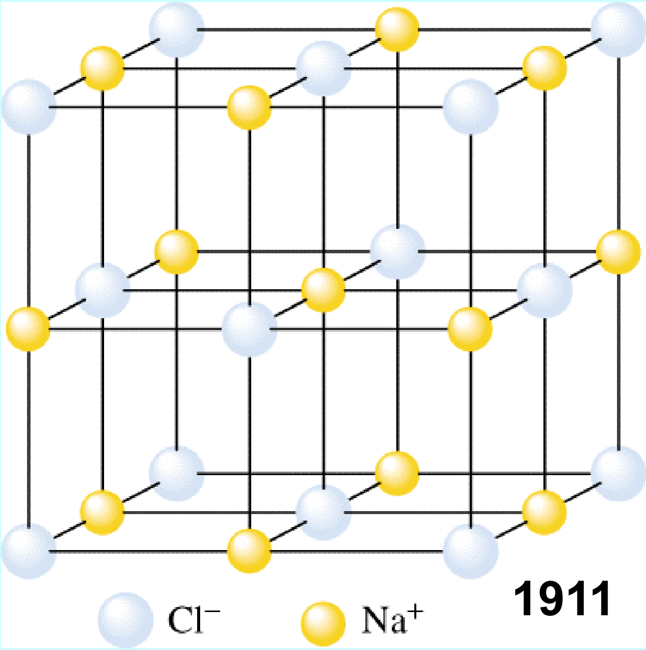


6 p_z orbitals



delocalized pi system

Benzene ring
Simplified depiction



1911

Organic (molecular, covalent) vs. Inorganic (nonmolecular, ionic) bonding

Lattice Enthalpy, *L*

The **lattice enthalpy** change, L, is the standard molar enthalpy ΔH_L^0 change for the process:

$$M^+_{(gas)} + X^-_{(gas)} \rightarrow MX_{(solid)} \qquad (L)$$

The formation of a solid from ions in the gas phase is always **exothermic**

Lattice enthalpies are usually **negative**

L is the most important energy factor in determining the stability of an ionic compound

The most stable crystal structure of a given compound is the one with the highest (**most negative**) lattice enthalpy *L*

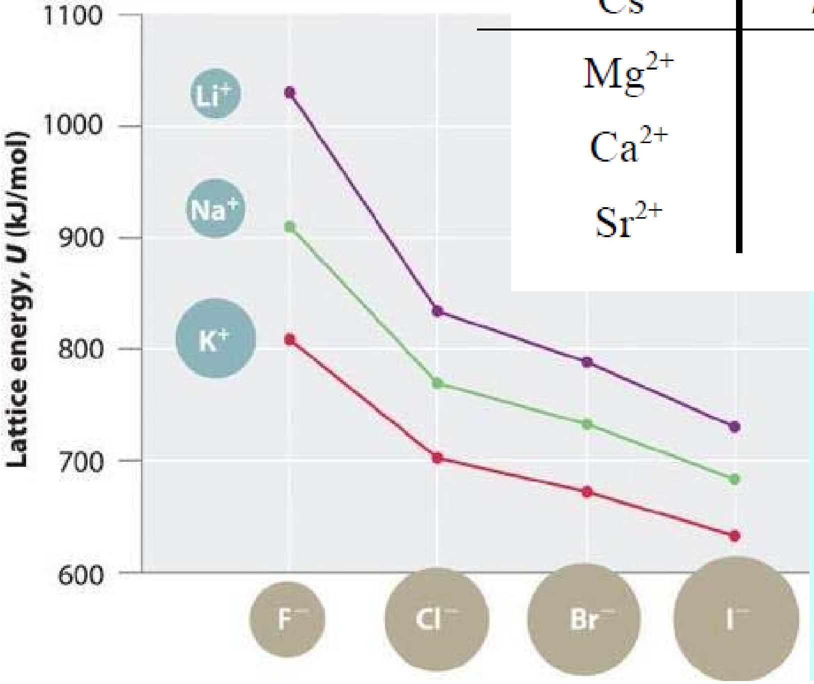
(entropy considerations neglected)

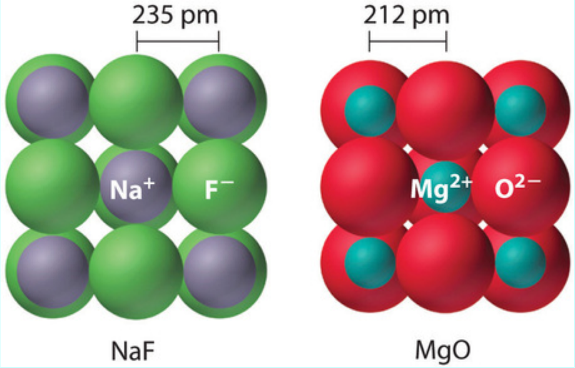
Lattice Enthalpy, L, kJ/mol

$$E_{coul} = \frac{1}{4\pi\varepsilon_0}\frac{Z_A Z_B e^2}{d}$$

All compounds adopt the NaCl structure, except CsCl, CsBr, CsI

	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1049.0	862.0	818.6	762.7	2830
Na^+	927.7	786.8	751.8	703	2650
K^+	825.9	716.8	688.6	646.9	2250
Rb^+	788.9	687.9	612	625	2170
Cs^+	758.5	668.2	635	602	2090
Mg^{2+}		2522			3795
Ca^{2+}		2253			3414
Sr^{2+}		2127			3217

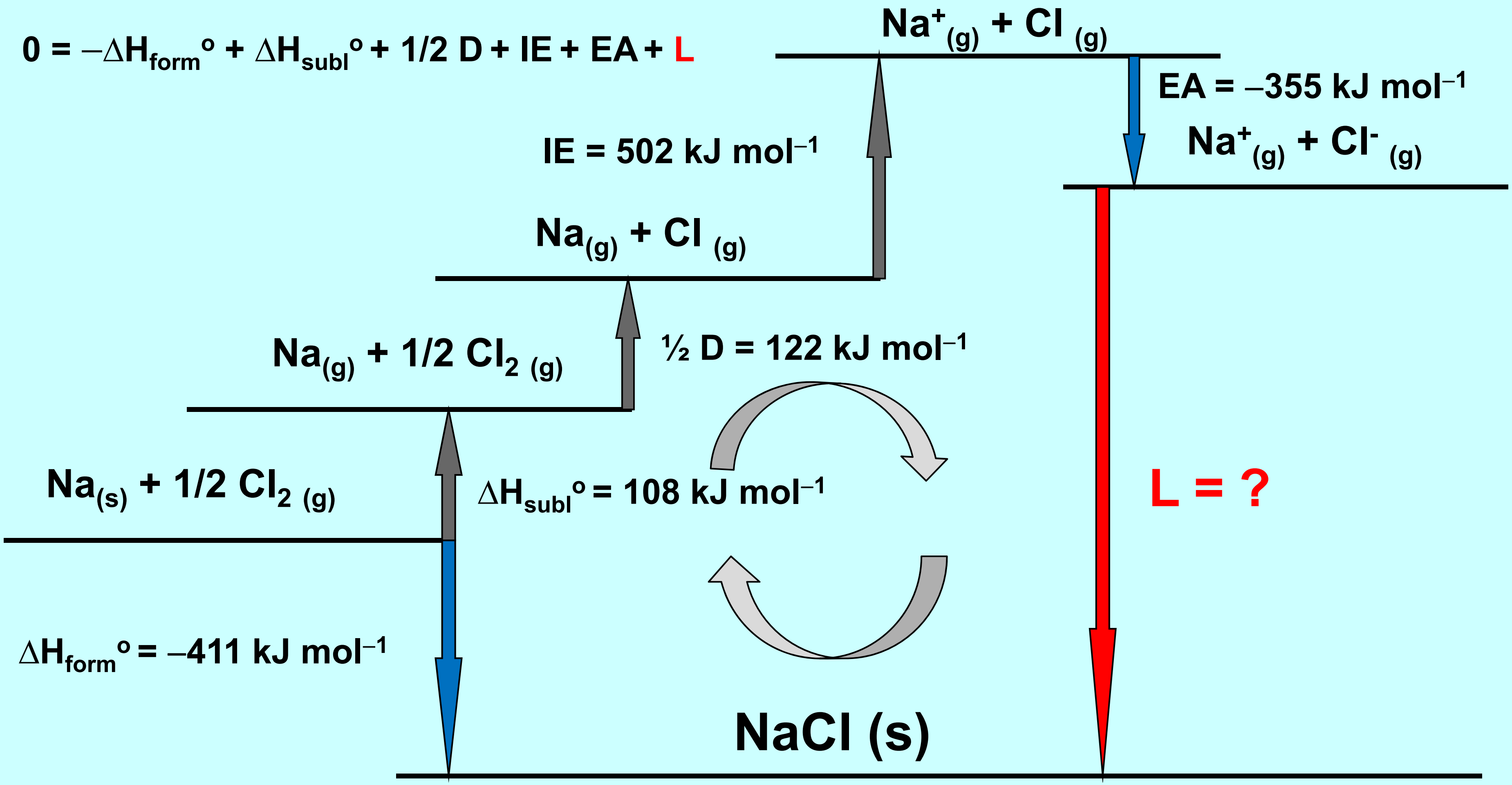




ScN **7547**

Born-Haber Cycle

$0 = -\Delta H_{form}^{o} + \Delta H_{subl}^{o} + 1/2\ D + IE + EA + L$



$Na^{+}_{(g)} + Cl_{(g)}$

$EA = -355\ kJ\ mol^{-1}$

$Na^{+}_{(g)} + Cl^{-}_{(g)}$

$IE = 502\ kJ\ mol^{-1}$

$Na_{(g)} + Cl_{(g)}$

$\tfrac{1}{2}\ D = 122\ kJ\ mol^{-1}$

$Na_{(g)} + 1/2\ Cl_{2\ (g)}$

$Na_{(s)} + 1/2\ Cl_{2\ (g)}$

$\Delta H_{subl}^{o} = 108\ kJ\ mol^{-1}$

$L = ?$

$\Delta H_{form}^{o} = -411\ kJ\ mol^{-1}$

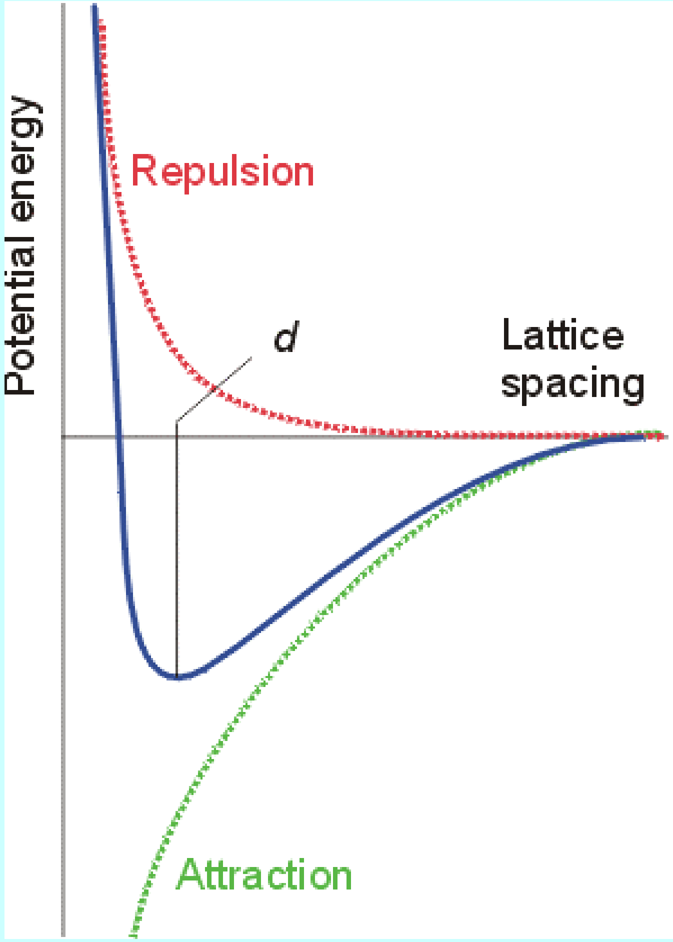
NaCl (s)

$0 = 411 + 108 + 122 + 502 + (-355) + L$

$L = -788\ kJ\ mol^{-1}$

All enthalpies: kJ mol^{-1} for normal conditions → standard enthalpies

Lattice Enthalpy, L



$$L = E_{Coul} + E_{rep}$$

One ion pair

$$E_{coul} = \frac{1}{4\pi\varepsilon_0}\frac{Z_A Z_B e^2}{d}$$

(calculated exactly)

$$E_{rep} = \frac{B}{d^n}$$

(modelled empirically)
n **= Born exponent**
(experimental measurement of compressibility or Pauling)
B **= a constant**

Coulombic Contribution to L

Coulombic contributions to lattice enthalpies, E_{Coul}

$$E_{Coul} = -N_A A \left(\frac{z_+ z_- e^2}{4\pi\varepsilon_0 d} \right)$$

Coulomb potential of an ion pair

E_{Coul} : Coulomb potential (electrostatic potential)
A : Madelung constant (depends on structure type)
N_A: Avogadro constant
z : charge number
e : elementary charge (1.6022×10^{-19} C)
ε_o: dielectric constant (vacuum permittivity, 8.854×10^{-12} F m^{-1})
d : shortest distance between cation and anion

Lattice Enthalpy, L

1 mol of ions

$E_{\mathrm{Coul}} = N_A A \, (e^2 / 4 \pi e_0) \, (z_A z_B / d)$

A = Madelung constant - a single ion interacts with all other ions

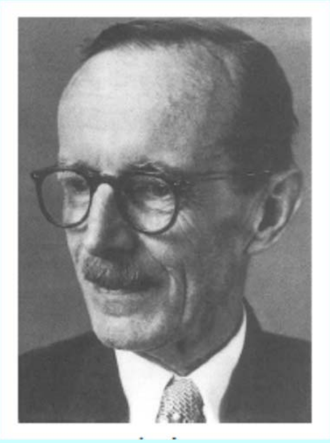
$E_{\mathrm{rep}} = N_A B / d^n$

$$L = N_A A \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d} + N_A \frac{B}{d^n}$$

$$\mathbf{L = E_{Coul} + E_{rep}}$$

Find minimum $dL/d(d) = 0$

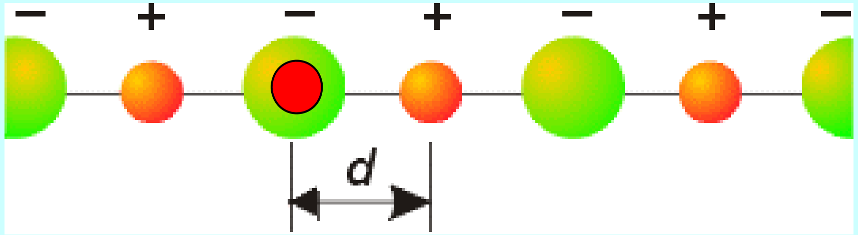
Madelung Constant, A



Erwin Madelung
(1881 – 1972)

Count all interactions in the crystal lattice of one ion with all others

The simplest example : 1D lattice

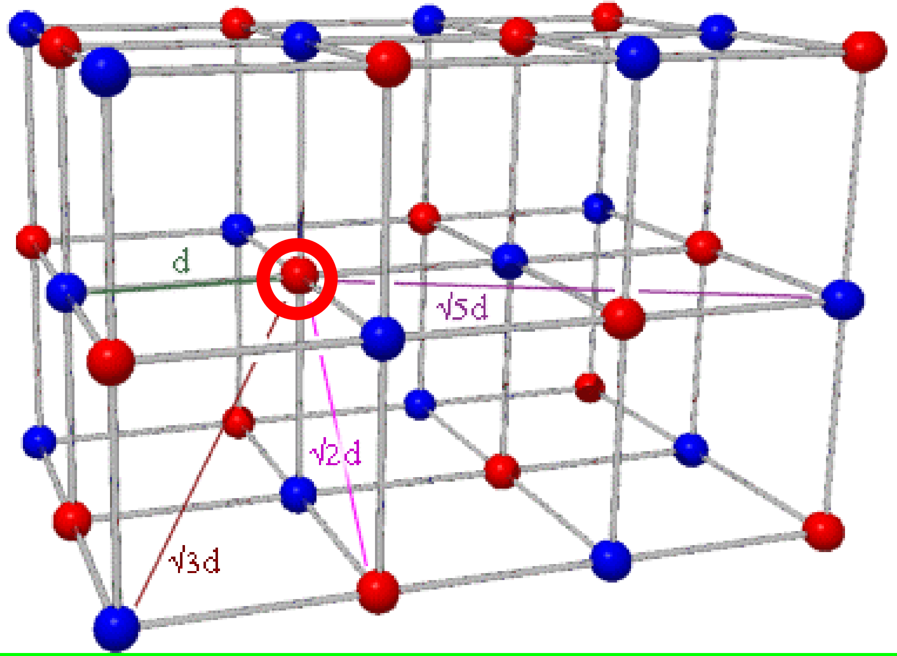


$$E_{coul} = \frac{e^2}{4\pi\varepsilon_0}\frac{Z_A Z_B}{d}\left[+2\frac{1}{1}-2\frac{1}{2}+2\frac{1}{3}-2\frac{1}{4}+\ldots.\right] = \frac{e^2}{4\pi\varepsilon_0}\frac{Z_A Z_B}{d}2\ln 2$$

Madelung constant A = 1.3862944……
for an infinite linear chain of ions
= sum of convergent series

Madelung Constant for NaCl

Neighbors	Distance
6 Cl	d
12 Na	√2 d
8 Cl	√3 d
6 Na	√4 d
24 Cl	√5 d



3D ionic solids: Coulomb attraction and repulsion

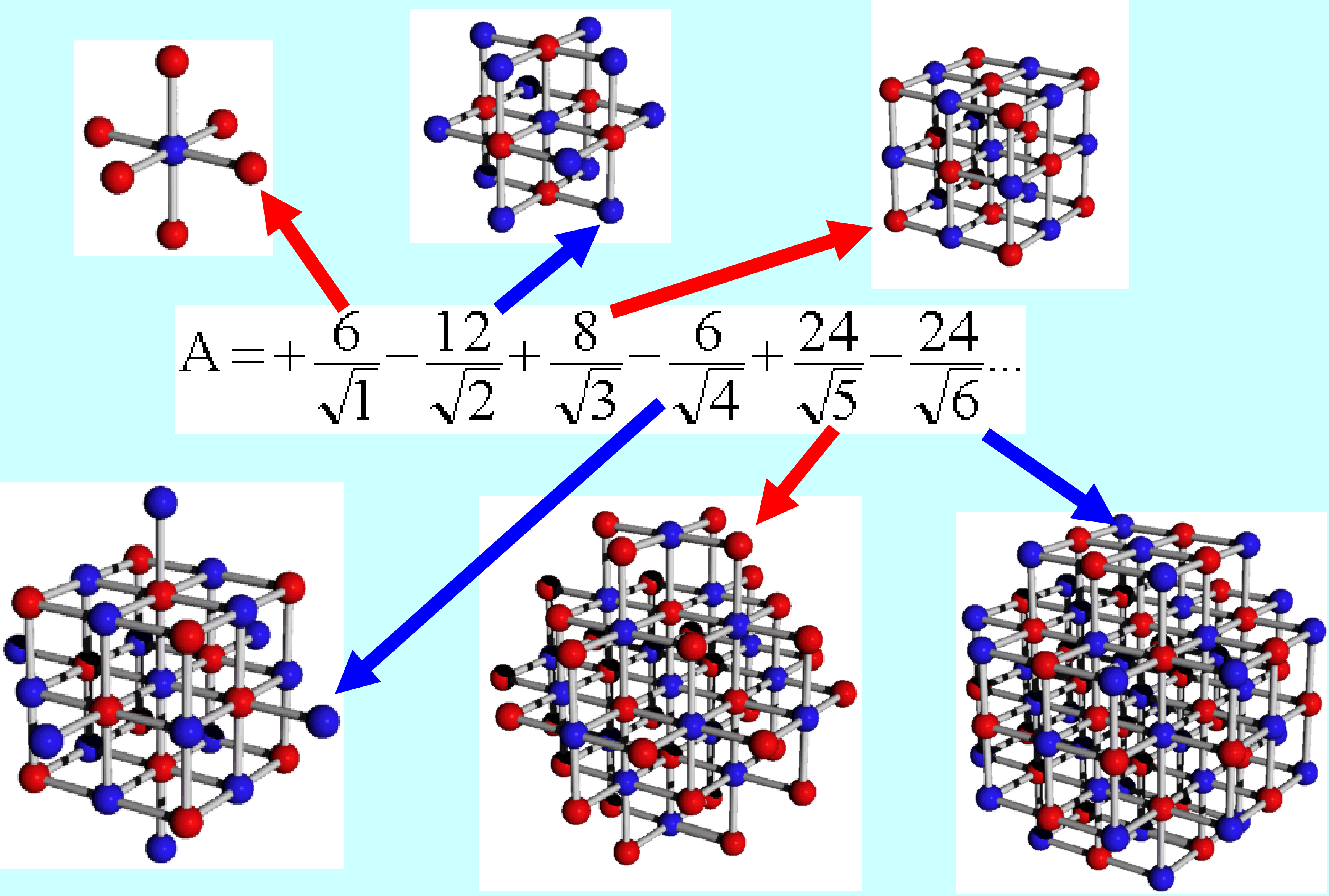
A single ion interacts with all other ions

$$E_{coul} = \frac{e^2}{4\pi\varepsilon_0}\frac{Z_A Z_B}{d}\left[+6\frac{1}{1} - 12\frac{1}{\sqrt{2}} + 8\frac{1}{\sqrt{3}} - 6\frac{1}{\sqrt{4}} + 24\frac{1}{\sqrt{5}} + \ldots.\right] = \frac{e^2}{4\pi\varepsilon_0}\frac{Z_A Z_B}{d}M$$

Sum of convergent series

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} \ldots. = 1.74756$$

Madelung Constant for NaCl



$$A = +\frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \ldots$$

Madelung Constants for Some Structural Types

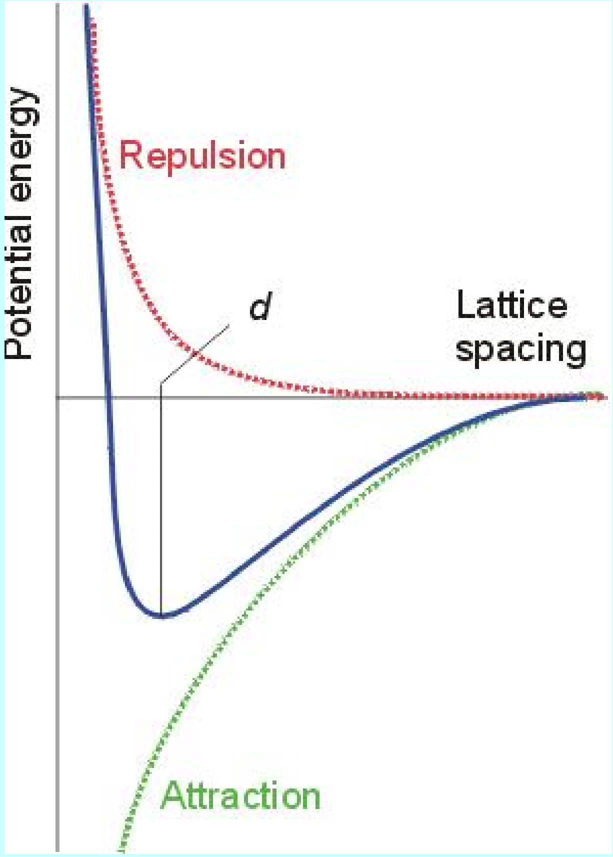
Structure	A	A/ν	Coordination
CsCl	1.762675	0.882	(8,8)
NaCl	1.747565	0.874	(6,6)
CaF_2	2.51939	0.840	(8,4)
ZnS Wurtzite	1.64132	0.821	(4,4)
ZnS Sphalerite	1.63805	0.819	(4,4)
$CdCl_2$	2.244	0.75	(6,3)
CdI_2	2.191	0.73	(6,3)
TiO_2 Rutile	2.408	0.803	(6,3)
Al_2O_3 Corundum	4.172	0.834	(6,4)
Linear Lattice	1.3862944		(2,2)
Ion Pair	?		(1,1)

ν = the number of ions in a formula unit

Max Born
1882 – 1970

Born Repulsion, E_{rep}

Repulsion arising from overlap of electron clouds



Because the electron density of atoms decreases exponentially towards zero at large distances from the nucleus the Born repulsion shows the same behavior

approximation:

$$\boxed{E_{rep} = \frac{B}{d^n}}$$

B and ***n*** are constants for a given atom type

n can be derived from compressibility measurements or Pauling values

(e.g., for NaCl, n = 8)

The Born-Landé Equation (1918)

Total Lattice Enthalpy from Coulomb interaction and Born repulsion

$$\Delta \mathrm{H}_L^0 = \min\left(E_{Coul} + E_{rep}\right)$$

set first derivative of the sum to zero

$$\boxed{\Delta \mathrm{H}_L^0 = -A \frac{z_+ z_- e^2}{4\pi\varepsilon_0 d} N_A (1 - \frac{1}{n})}$$

Lattice Enthalpy Calculation

Born–Lande

$$L = N_A A \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{1}{n}\right)$$

For compounds of mixed ion types, use the average value (e.g., for NaCl, n = 8).

Pauling's approximate values of ***n***

El. config.	***n***	Example
He-He	5	LiH, Be^{2+}
Ne-Ne	7	NaF, MgO, Al^{3+}
Ar-Ar	9	KCl, CaS, CuCl, Zn^{2+}, Ga^{3+}
Kr-Kr	10	RbBr, AgBr, Cd^{2+}, In^{3+}
Xe-Xe	12	CsI, Au^{+}, Tl^{3+}, Ba^{2+}, Hg^{2+}

Born–Mayer

$$L = N_A A \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)$$

$d^* = 0.345$ Å

The Kapustinskii Equation

Kapustinskii found that if the Madelung constant for a given structure is divided by the number of ions in one formula unit (ν) the resulting values are almost constant:

Structure	Madelung constant (A)	A/ν	Coordination
CsCl	1.763	0.882	8:8
NaCl	1.748	0.874	6:6
CaF_2	2.519	0.840	8:4
α-Al_2O_3	4.172	0.834	6:4

A general lattice energy equation that can be applied to any crystal regardless of the crystal structure

$$L = K \times \nu \times \frac{Z_A Z_B}{r_+ + r_-} \times \left(1 - \frac{G}{r_+ + r_-}\right)$$

K, G = constants

The Kapustinskii Equation

The most important advantage of the Kapustinskii equation

- **it is possible to apply the equation for lattice calculations of crystals with polyatomic ions (e.g., KNO_3, $(NH_4)_2SO_4$ ...)**
- **a set of „thermochemical radii“ was derived for further calculations of lattice enthalpies**

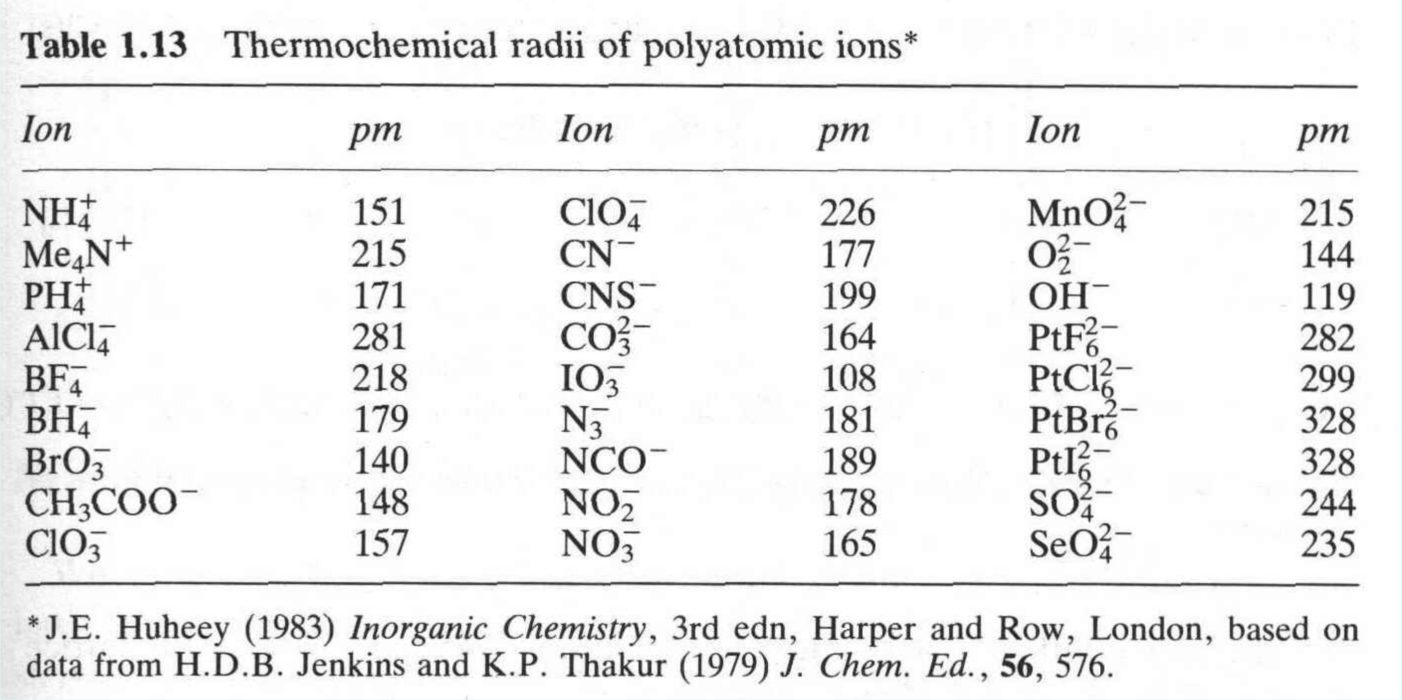


Table 1.13 Thermochemical radii of polyatomic ions*

Ion	*pm*	*Ion*	*pm*	*Ion*	*pm*
NH_4^+	151	ClO_4^-	226	MnO_4^{2-}	215
Me_4N^+	215	CN^-	177	O_2^{2-}	144
PH_4^+	171	CNS^-	199	OH^-	119
$AlCl_4^-$	281	CO_3^{2-}	164	PtF_6^{2-}	282
BF_4^-	218	IO_3^-	108	$PtCl_6^{2-}$	299
BH_4^-	179	N_3^-	181	$PtBr_6^{2-}$	328
BrO_3^-	140	NCO^-	189	PtI_6^{2-}	328
CH_3COO^-	148	NO_2^-	178	SO_4^{2-}	244
ClO_3^-	157	NO_3^-	165	SeO_4^{2-}	235

*J.E. Huheey (1983) *Inorganic Chemistry*, 3rd edn, Harper and Row, London, based on data from H.D.B. Jenkins and K.P. Thakur (1979) *J. Chem. Ed.*, **56**, 576.

Experimental and Calculated Lattice Enthalpies

NaCl

Born–Lande calculation L = – 765 kJ mol^{-1}

Only ionic contribution considered

Experimental Born–Haber cycle L = – 788 kJ mol^{-1}

Lattice Enthalpy consists of ionic and covalent contributions

Applications of Lattice Enthalpy calculations

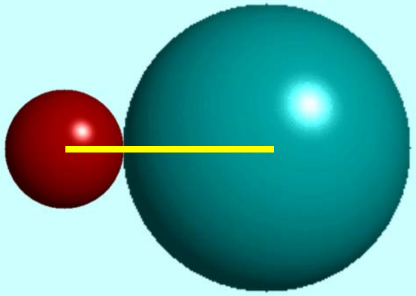
- thermal stabilities of ionic solids
- stabilities of oxidation states of cations
- solubility of salts in water
- calculations of electron affinity data
- lattice enthalpies and stabilities of „non existent“ compounds

Pauling's Rules

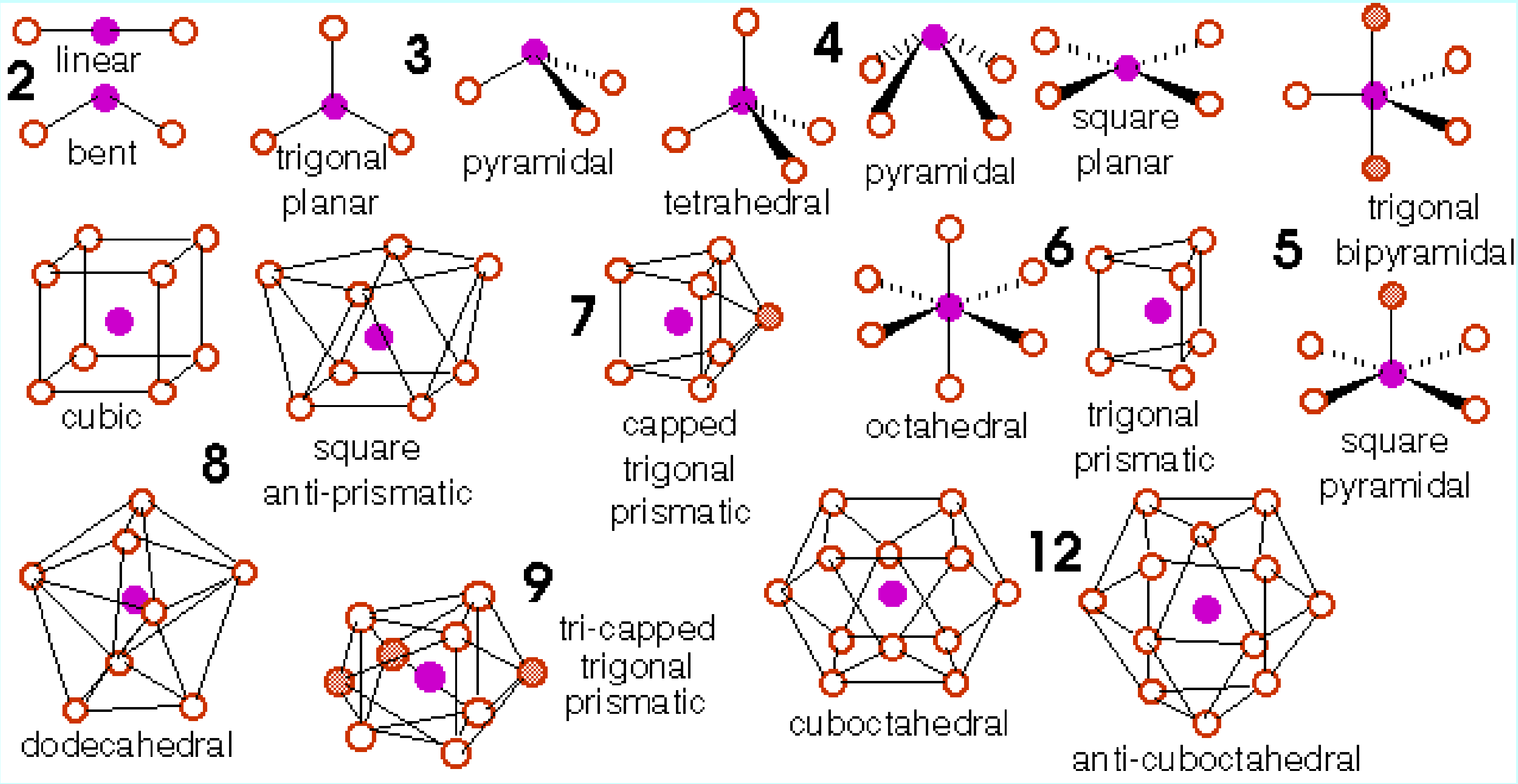
Five principles which could be used to determine the structures of complex ionic/covalent crystals

Pauling's Rule no. 1 Coordination Polyhedra

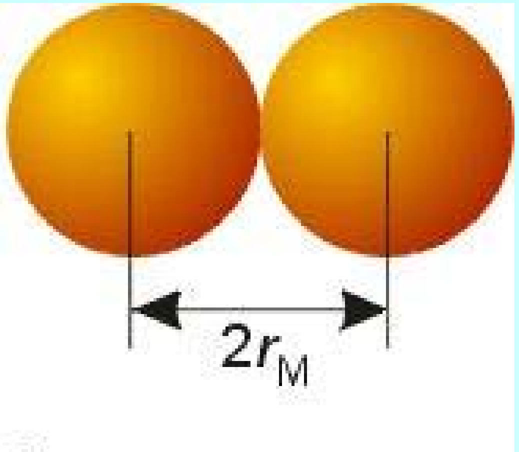
- **A coordinated polyhedron of anions is formed about each cation**
- **Cation-Anion distance is determined by sums of ionic radii**
- **Cation coordination environment is determined by radius ratio**



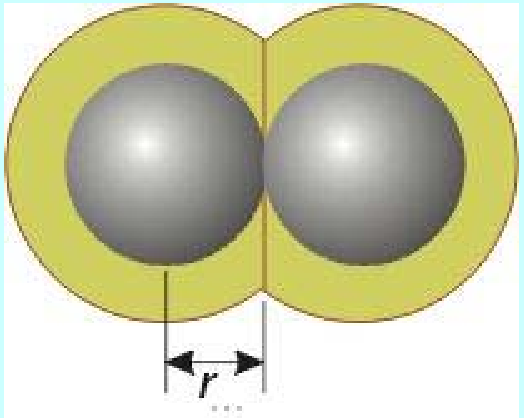
Coordination Polyhedra



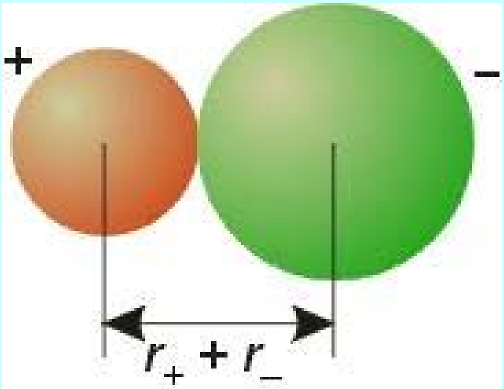
Different Types of Radii



1 Metallic radius



2 Covalent radius



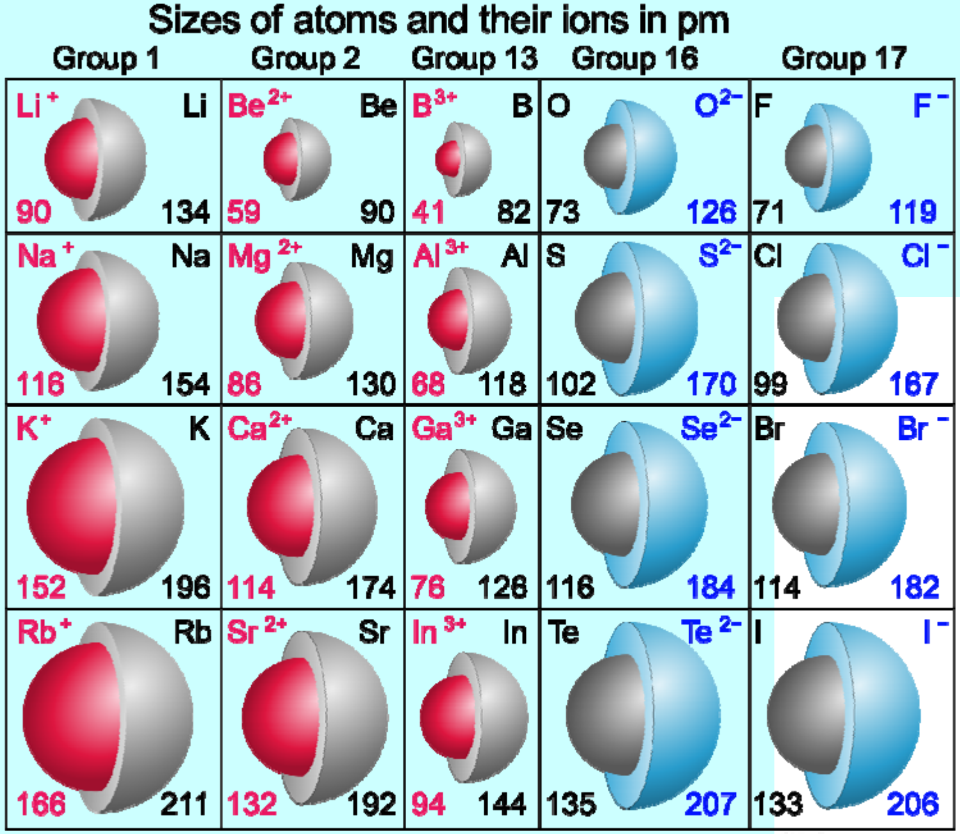
3 Ionic radius

The radius of one ion was fixed to a reasonable value

(r(O^{2-}) = 140 pm) (Linus Pauling)

That value is then used to compile a set of self consistent values for all other ions

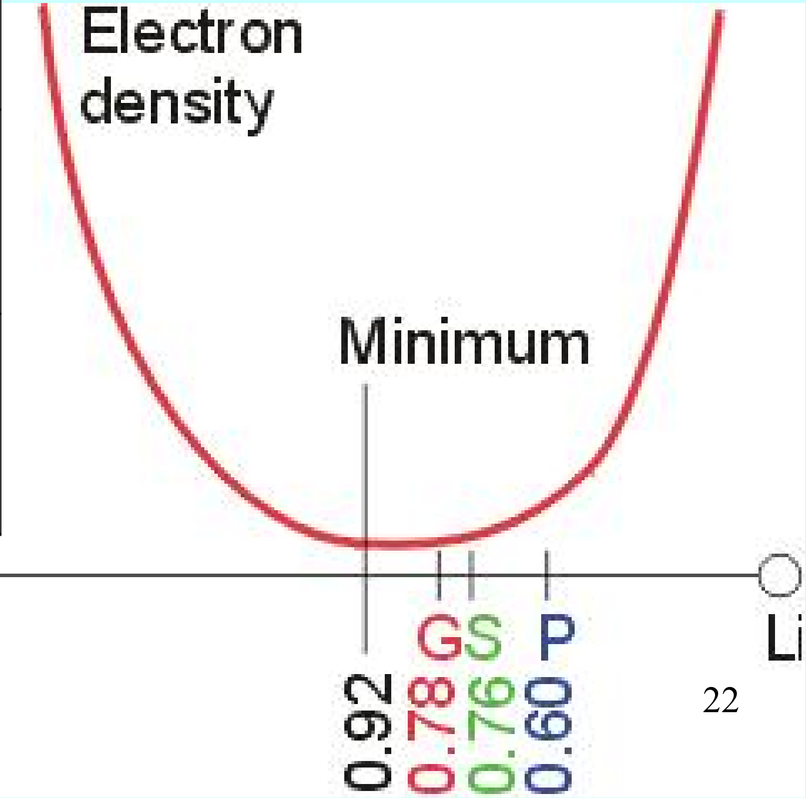
Variation of the Electron Density along the Li – F Axis in LiF



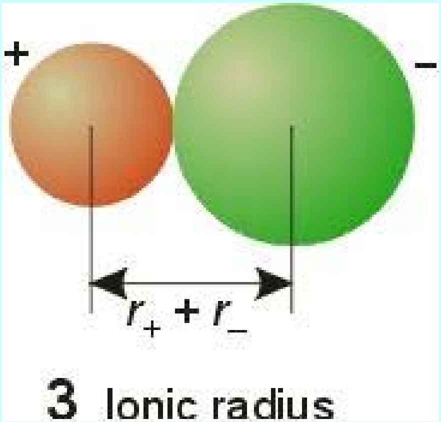
Sizes of atoms and their ions in pm

Group 1	Group 2	Group 13	Group 16	Group 17
Li^+ 90 Li 134	Be^{2+} 59 Be 90	B^{3+} 41 B 82	O 73 O^{2-} 126	F 71 F^- 119
Na^+ 116 Na 154	Mg^{2+} 86 Mg 130	Al^{3+} 68 Al 118	S 102 S^{2-} 170	Cl 99 Cl^- 167
K^+ 152 K 196	Ca^{2+} 114 Ca 174	Ga^{3+} 76 Ga 126	Se 116 Se^{2-} 184	Br 114 Br^- 182
Rb^+ 166 Rb 211	Sr^{2+} 132 Sr 192	In^{3+} 94 In 144	Te 135 Te^{2-} 207	I 133 I^- 206

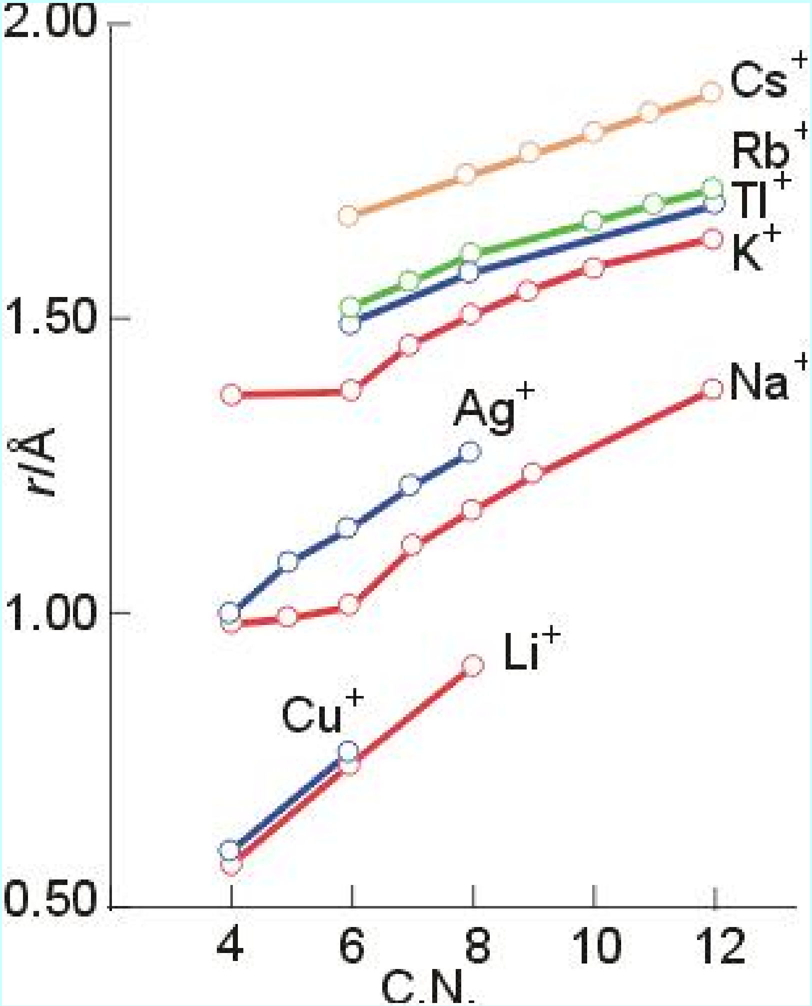
P – Pauling radius
G – Goldschmidt radius
S – Shannon radius



Variation of Ionic Radii with Coordination Number

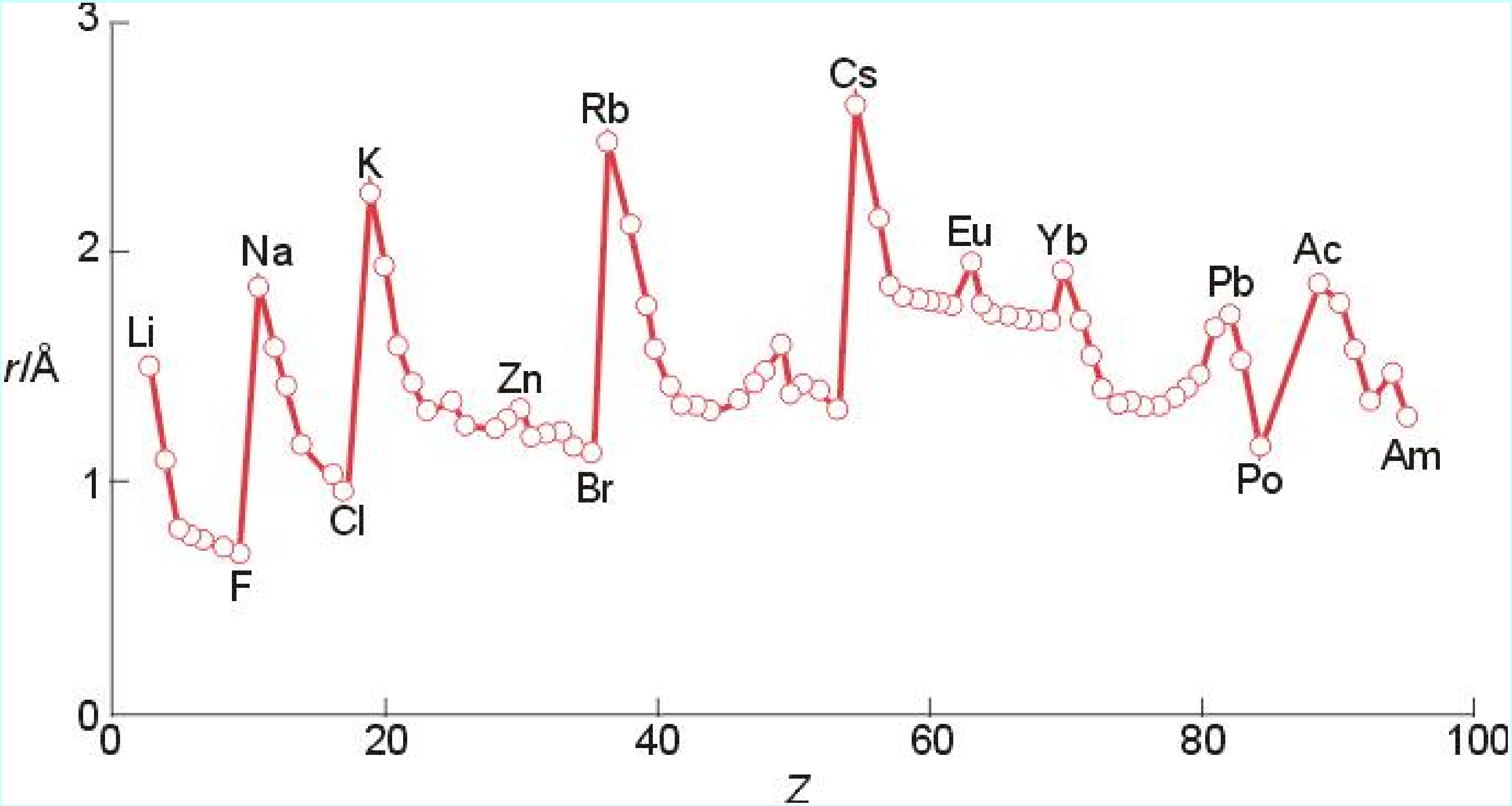


3 Ionic radius



As the coordination number (CN) increases, the Ionic Radius increases

Variation of Atomic Radii through the Periodic Table



Ionic Radii

R.D. Shannon and C.T. Prewitt, Acta Cryst. B25, 925-945 (1969)
R.D. Shannon, Acta Cryst. A32, 751-767 (1976)

As the coordination number (CN) increases, the Ionic Radius increases

Sr^{2+}

CN	Radius, Å
6	1.32
8	1.40
9	1.45
10	1.50
12	1.58

As the oxidation state increases, cations get smaller (6-fold coordination, in Å)

Mn^{2+}	0.810
Mn^{3+}	0.785
Mn^{4+}	0.670
Ti^{2+}	1.000
Ti^{3+}	0.810
Ti^{4+}	0.745

Ionic Radii

The radius increases down a group in the periodic table

The exception - 4d/5d series in the transition metals - the lanthanide contraction

(6-fold coordination, in Å)

Al^{3+}	0.675
Ga^{3+}	0.760
In^{3+}	0.940
Tl^{3+}	1.025
Ti^{4+}	0.745
Zr^{4+}	0.86
Hf^{4+}	0.85

Right to left across the periodic table the radius decreases

(6 coordinate radii, in Å)

La^{3+}	1.172
Nd^{3+}	1.123
Gd^{3+}	1.078
Lu^{3+}	1.001

General Trends for Ionic Radii

1. Ionic radii increase down a group

(Lanthanide contraction restricts the increase of heavy ions)

2. Radii of equal charge ions decrease across a period

3. Ionic radii increase with increasing coordination number

the higher the CN the bigger the ion

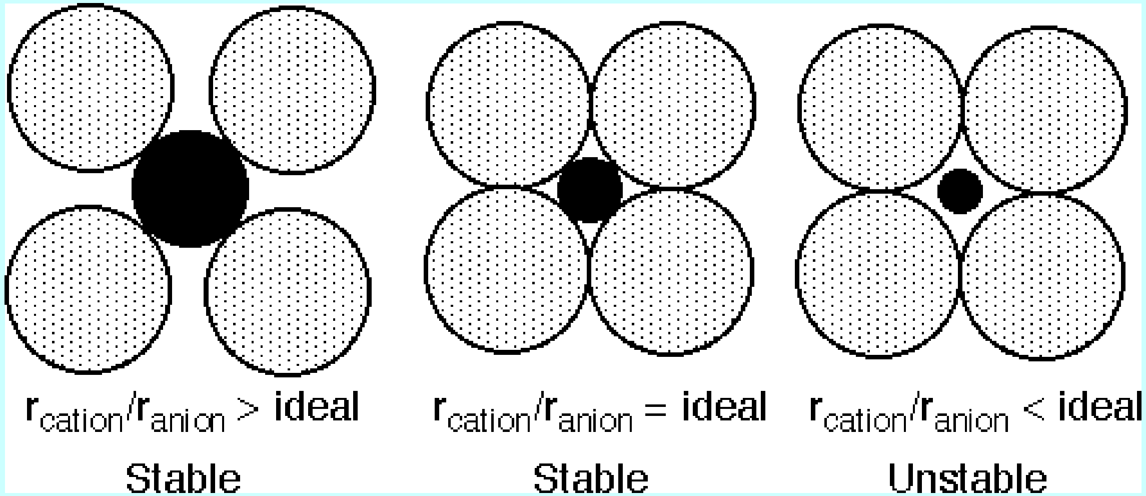
4. The ionic radius of a given atom decreases with increasing charge ($r(Fe^{2+}) > r(Fe^{3+})$)

5. Cations are usually the smaller ions in a cation/anion combination (exceptions: $r(Cs^{+}) > r(F^{-})$)

6. Frequently used for rationalization of structures:

„radius ratio“ r(cation)/r(anion) (< 1)

Cation/Anion Radius Ratio

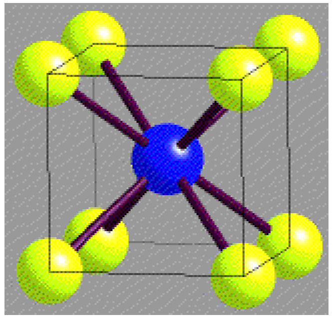


CN	r/R
12 – hcp/ccp	1.00 (substitution)
8 – cubic	0.732 – 1.00
6 – octahedral	0.414 – 0.732
4 – tetrahedral	0.225 – 0.414

Optimal radius ratio for given CN
ions are in touch

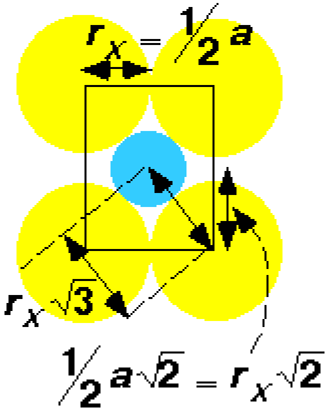
Limiting Radius Ratios

CsCl 8:8



unit cell

cell side a

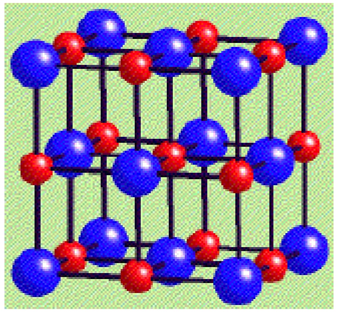


$r_M + r_X = r_X\sqrt{3}$

$r_M / r_X = \sqrt{3} - 1$

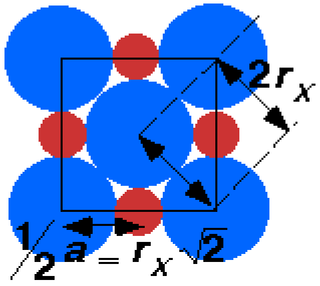
$= 0.732$

NaCl 6:6



unit cell

face diagonal $a\sqrt{2}$

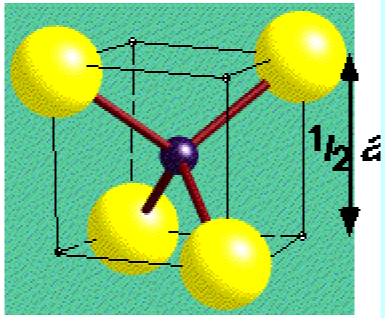


$r_M + r_X = r_X\sqrt{2}$

$r_M / r_X = \sqrt{2} - 1$

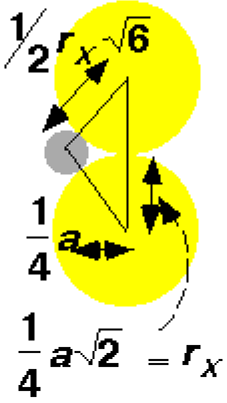
$= 0.414$

ZnS 4:4



$^1/_8$th unit cell

body diagonal $a\sqrt{3}$



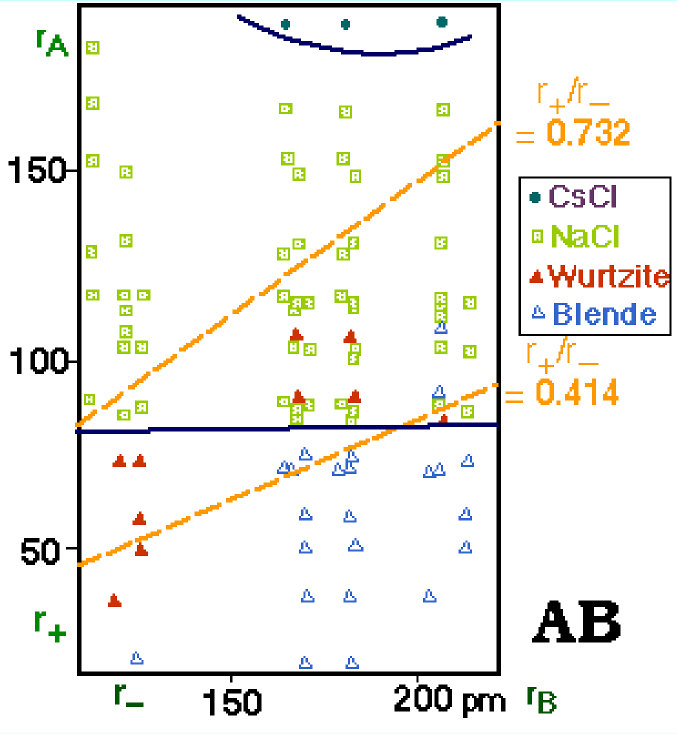
$r_M + r_X = \frac{1}{2}r_X\sqrt{6}$

$r_M / r_X = \frac{1}{2}\sqrt{6} - 1$

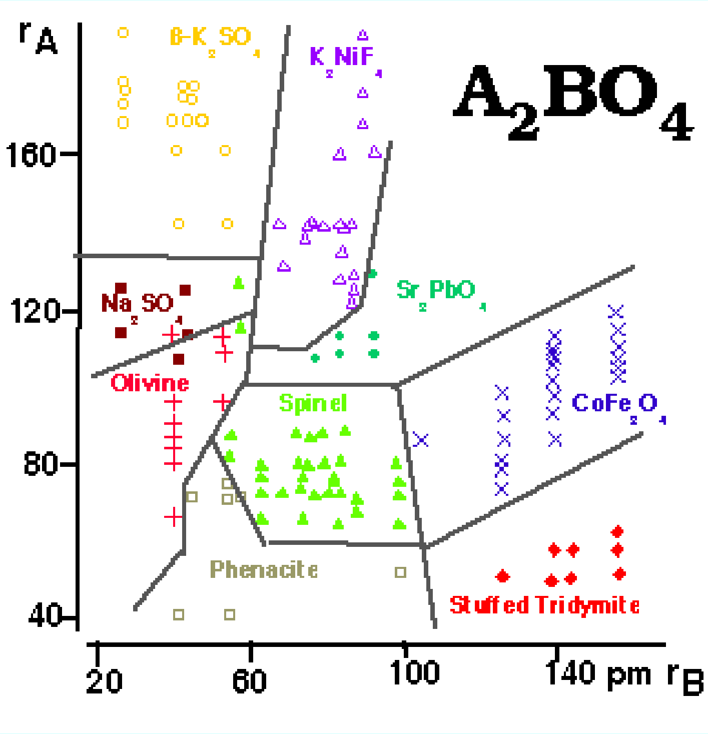
$= 0.225$

Structure Map

Dependence of the structure type on parameters, such as ionic radii, ionicity, electronegativity etc.



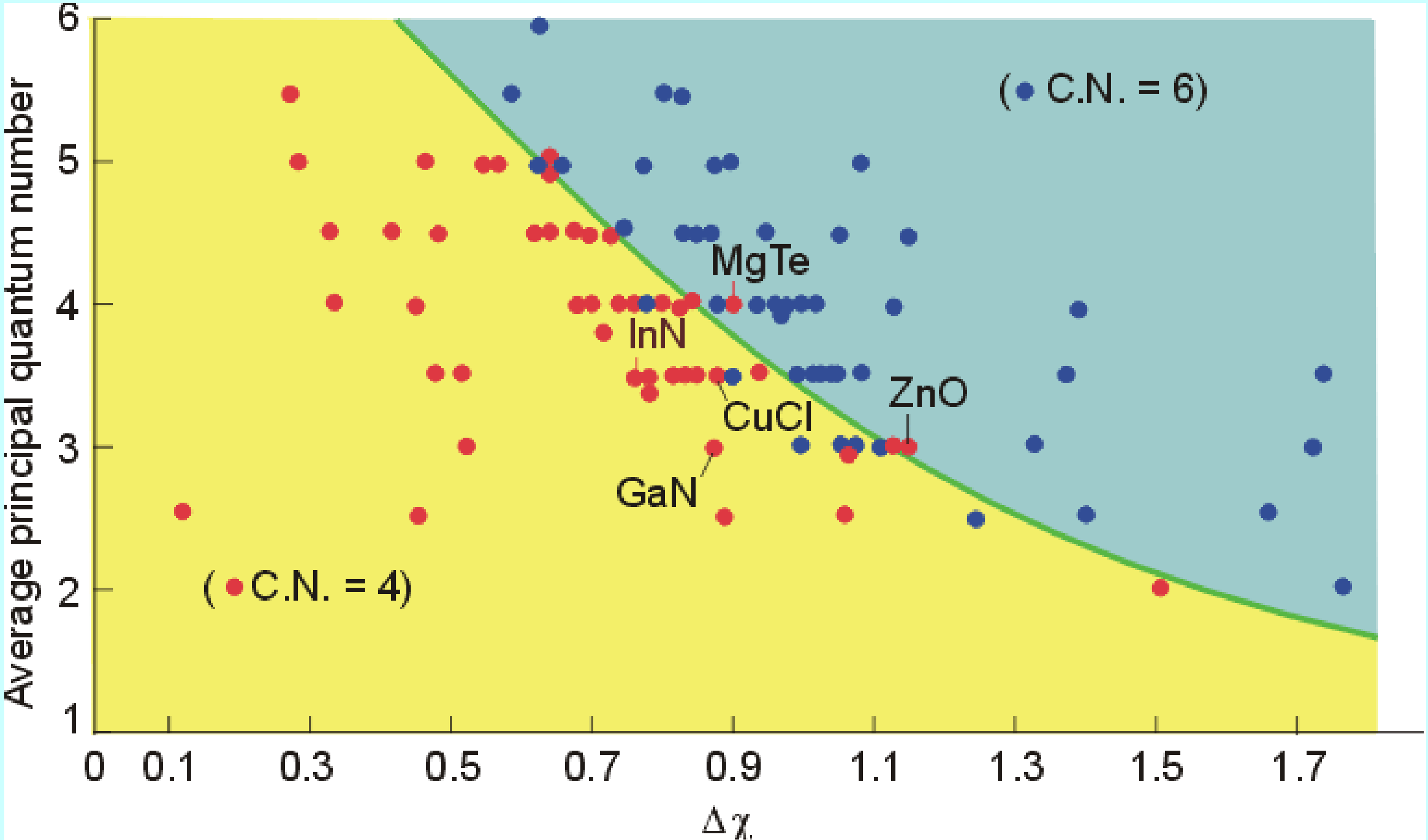
Structural map as function of radius ratios for AB compounds



Structural map as function of radius ratios for A_2BO_4 compounds

Structure Map

Dependence of the structure type (coordination number) on the electronegativity difference and the average principal quantum number (size and polarizability)
AB compounds



the electronegativity difference

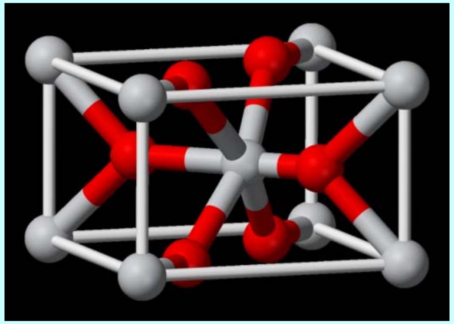
Pauling's Rules

Pauling's Rule no. 2 Bond Strength

The strength of an electrostatic bond $\mathbf{s_{ij} = valence / CN}$
The bond valence sum (BVS) of each ion equals its oxidation state V_i

The valence of an ion (V_i, equal to the oxidation state of the ion) is equal to a sum of the valences of its bonds (s_{ij}): $V_i = \Sigma s_{ij}$

In a stable ionic structure the charge on an ion is balanced by the sum of electrostatic bond strengths (s_{ij}) to the ions in its coordination polyhedron



TiO_2 (Rutile) Ti - oxidation state of +4, coordinated to 6 oxygens
$V_{Ti} = +4 = 6 (s_{ij})$ $s_{ij} = +2/3$

The bond valence of oxygen, coordinated by 3 Ti atoms
$Vo = 3 (s_{ij}) = 3 (-2/3) = -2$

Each bond has a valence of s_{ij} with respect to the cation and $-s_{ij}$ with respect to the anion

Bond Strength

Brown, Shannon, Donnay, Allmann:
Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}

$$s_{ij} = \exp\frac{R_{ij} - d_{ij}}{b}$$

R_{ij} = standard single bond length - determined empirically from (many) structures where bond distances and ideal valences are accurately known

Tables of R_{ij} values for given bonding pairs (i.e., Nb-O, Cr-N, Mg-F, etc.) have been calculated, just as tables of ionic radii are available

A constant *b* = 0.37

$R = d$ $s = e^0 = 1$
$R < d$ $s = e^{-1} < 1$ a bond longer than R is weaker than 1
$R > d$ $s = e^1 > 1$ a bond shorter than R is stronger than 1

Bond Valence Sum (BVS)

Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

Use of the bond valence sum (BVS) concept:

A) To check experimentally determined structures for correctness, or bonding instabilities
B) To predict new structures
C) To locate light atoms such as hydrogen or Li ion, which are hard to find experimentally
D) To determine ordering of ions which are hard to differentiate experimentally, such as Al^{3+} and Si^{4+}, or O^{2-} and F^{-}
E) To check/confirm oxidation states of atoms (Co^{2+} /Co^{3+} , Fe^{2+} / Fe^{3+})

Bond Valence Sum (BVS)

$$s_{ij} = \exp\frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

$FeTiO_3$ (mineral Ilmenite) possesses the **corundum** structure – an hcp array of oxides with cations filling 2/3 of octahedral holes.

Decide which oxidation states (valences) are present:

Fe(II) Ti(IV) or Fe(III) Ti(III)

Bond Distances (d_{exp}, Å)	Tabulated R_{ij} values	Constants
Fe–O = 3×2.07 and 3×2.20	R_0(Fe–O) = 1.795 Å	b = 0.30
Ti–O = 3×1.88 and 3×2.09	R_0(Ti–O) = 1.815 Å	b = 0.37

Oxygen valence and coordination number?
Each oxygen is bound to Fe and Ti with both bond distances

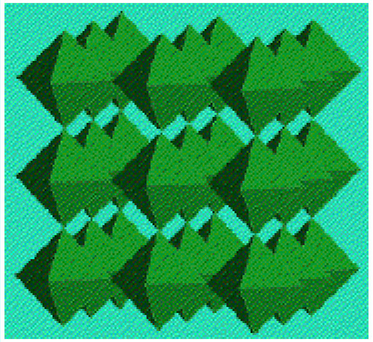
Pauling’s Rules

Pauling’s Rule no. 3   Polyhedral Linking

The presence of shared edges, and particularly shared faces decreases the stability of a structure
This is particularly true for cations with large valences and small coordination number

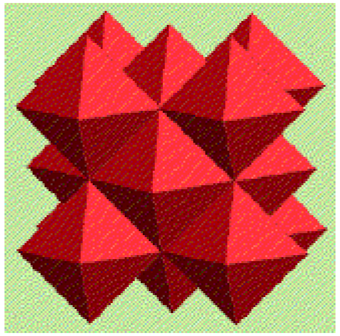
Avoid shared polyhedral edges and/or faces

ReO_3



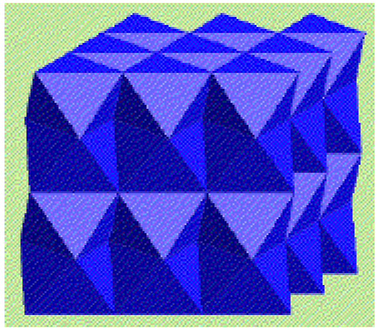
Vertex-Sharing Only

NaCl



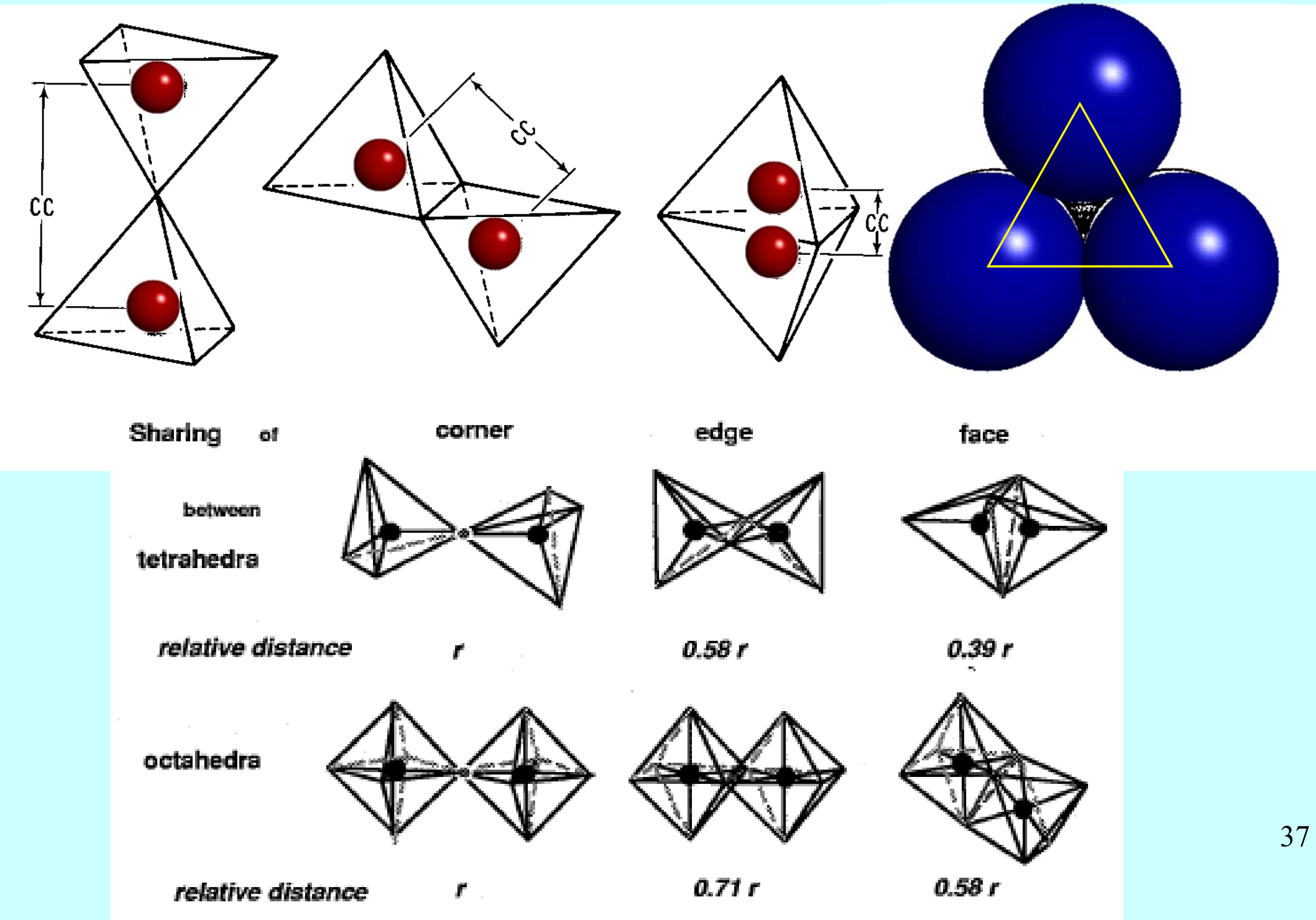
Edge-Sharing

NiAs



Face-Sharing in Columns

Polyhedral Linking



Polyhedral Linking

The Coulombic interactions in stable structures

- Maximize the cation-anion interactions (attractive)
- Minimize the anion-anion and cation-cation interactions (repulsive)

- Increase the coordination number
- Decrease the cation-anion distance
- If ions too close - electron-electron repulsions

The cation-cation distance decreases and the Coulomb repulsion increases as

- **the degree of sharing increases (corner < edge < face)**
- **CN decreases (cubic < octahedral < tetrahedral)**
- **cation oxidation state increases (a stronger Coulomb repulsion)**

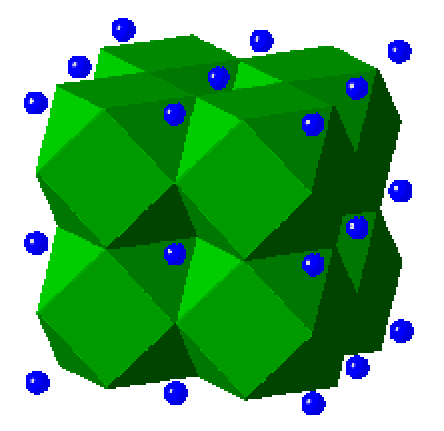
Pauling's Rules

Pauling's Rule no. 4 Cation Evasion

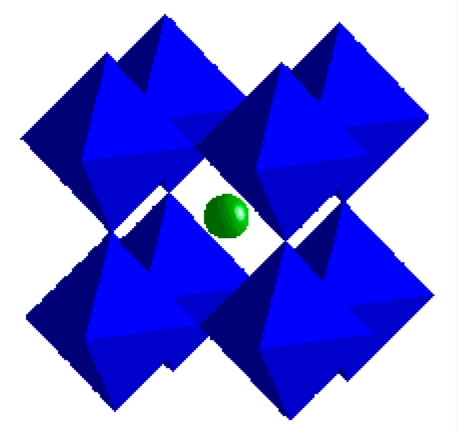
In a crystal containing different cations those with large valence and small coord. number tend not to share polyhedral elements (anions)

Perovskite, $CaTiO_3$

Ca^{II} 12-coordinate **CaO_{12}** cuboctahedra
share **FACES**



Ti^{IV} 6-coordinate **TiO_6** octahedra
share only **VERTICES**



Pauling's Rules

Pauling's Rule no. 5 Environmental Homogeneity

The rule of parsimony

The number of chemically different coordination environments for a given ion tends to be small

Once the optimal chemical environment for an ion is found, if possible, all ions of that type should have the same environment

Strukturbericht Symbols

A partly systematic method for specifying the structure of a crystal
A - monatomic (elements), **B** - diatomic with equal numbers of atoms of each type (AB), **C** - a 2-1 abundance ratio (AB_2), **D**0 - 3-1, etc.

Structure type	Struktur bericht	Space group (S.G. No.)	Lattice
Cu	**A1**	Fm-3m (225)	fcc
W, Fe	**A2**	Im-3m (229)	bcc
Mg	**A3**	$P6_3$/mmc (194)	hcp
C - diamond	**A4**	Fd-3m (227)	diamond
NaCl	**B1**	Fm-3m (225)	
CsCl	**B2**	Pm-3m (221)	
ZnS	**B3**	F43m (216)	Zincblende
ZnS	**B4**	$P6_3$/mc (186)	Wurtzite
CaF_2	**C1**	Fm-3m (225)	Fluorite

Pearson Symbols

Indicate the crystal symmetry and the number of atoms in the unit cell
e.g., NaCl - a face-centered (**F**) cubic (**c**) structure with 8 atoms in the unit cell = cF8
monoclinic (**m**), hexagonal (**h**), orthorhombic (**o**), asymmetric (**a**), primitive (**P**)
the Pearson symbol does not necessarily specify a unique structure (see cF8)

Structure type	**Pearson Symbol**	**Struktur bericht**	**Space group (S.G. No.)**
Cu	**cF4**	**A1**	Fm-3m (225)
W, Fe	**cI2**	**A2**	Im-3m (229)
Mg	**hP2**	**A3**	$P6_3/mmc$ (194)
C - diamond	**cF8**	**A4**	Fd-3m (227)
NaCl	**cF8**	**B1**	Fm-3m (225)
CsCl	**cP2**	**B2**	Pm-3m (221)
ZnS (zb)	**cF8**	**B3**	F43m (216)
ZnS (w)	**hP4**	**B4**	$P6_3/mc$ (186)
CaF_2	**cF12**	**C1**	Fm-3m (225)

Space Group Symbols (230)

primitive (**P**), face-centered (**F**), body-centered (**I**), base-centered (**A**, **B**, **C**), rhombohedral (**R**)

S. G. Class	**Centering**	**Symbol syntax (examples)**
Triclinic	P	P1, P-1
Monoclinic	P, C, B	Paxis, Pplane, Paxis/plane (**P2_1, Cm**, **P2_1/c)**
Orthorhombic	P, F, I, C, A	Paxisaxisaxis, Pplaneplaneplane (**Pmmm, Cmc2_1)**
Tetragonal	P, I	P**4**, P4axisaxisaxis, P4planeplaneplane (**I4/m, P4mm**)
Trigonal	P, R	P**3**axis, P3plane (**R-3m)**
Hexagonal	P	P**6**, P6axisplane (**P6_3/mmc)**
Cubic	P, F, I	Paxis**3**plane, Pplane3plane (**Pm-3m, Fm-3m)**