Principles of Laves

1.Space Principle: Space is used most efficiently
2.Symmetry Principle: Highest possible symmetry is adopted
3.Connection Principle: There will be the most possible "connections" between components
(*i.e. coordination numbers are maximized*)

•*Followed by metals and inert gases - close-packed structures*
•*Deviations: BCC metals*
•*'Ionic' compounds strive to follow the principles.*


The 'Ionic Model' (Goldschmidt')

"Ions are essentially Charged, Incompressible, Non-Polarizable Spheres"

More sophisticated models assume ions are composed of two parts:
a central hard, unperturbable core, where most electron density is concentrated
a soft, polarizable outer sphere, which contains very little electron density

Pauling's Rules

Goldschmidt's structural principles for IONIC crystals were summarized by Pauling in a series of Rules.

Historically Pauling's Rules have been widely used, & are still useful in many situations.

1
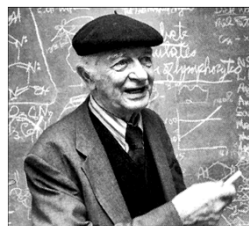
[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 192]

THE PRINCIPLES DETERMINING THE STRUCTURE OF COMPLEX IONIC CRYSTALS

By LINUS PAULING

RECEIVED SEPTEMBER 5, 1928   PUBLISHED APRIL 5, 1929

1.   **The Relative Stability of Alternative Structures of Ionic Crystals.**—
The elucidation of the factors determining the relative stability of alternative crystalline structures of a substance would be of the greatest significance in the development of the theory of the solid state.   Why, for example, do some of the alkali halides crystallize with the sodium chloride structure and some with the cesium chloride structure?   Why does titanium dioxide under different conditions assume the different structures of rutile, brookite and anatase?   Why does aluminum fluosilicate, Al_2SiO_4-F_2, crystallize with the structure of topaz and not with some other structure?   These questions are answered formally by the statement that in each case the structure with the minimum free energy is stable.   This answer, however, is not satisfying; what is desired in our atomistic and quantum theoretical era is the explanation of this minimum free energy in terms of atoms or ions and their properties.

Efforts to provide such a treatment for simple alternative structures, such as the sodium chloride and cesium chloride structures and the fluoride and rutile structures, have been made with the aid of the Born potential expression and modifications of it.   Assuming that all ions repel each

Linus Pauling, *J. Amer. Chem. Soc.* **51**, 1010 (1929)

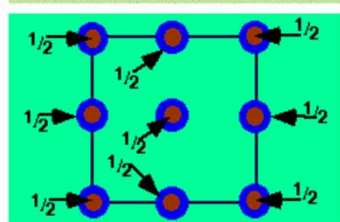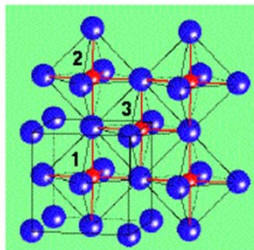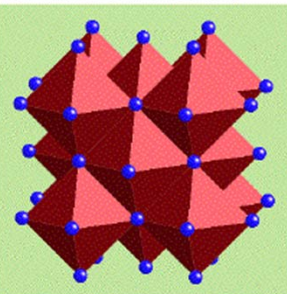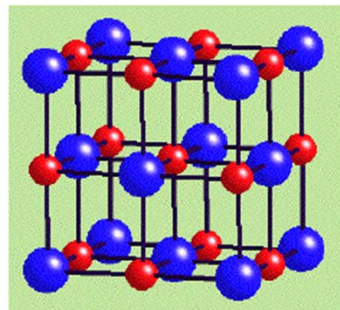## Pauling Rule 1: *Coordination Polyhedra*

"A coordination polyhedron of anions is formed around every cation (and vice-versa) - it will only be stable if the cation is in contact with each of its neighbors.

•**Ionic crystals may thus be considered as sets of linked polyhedra.**
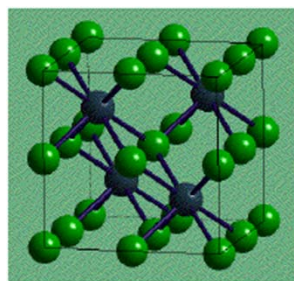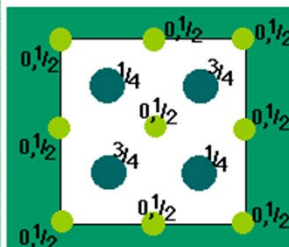•**The cation-anion distance is regarded as the sum of the ionic radii."**
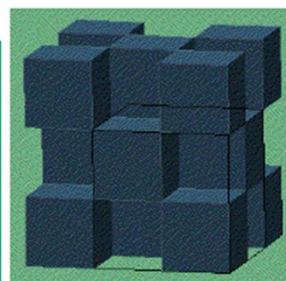

2
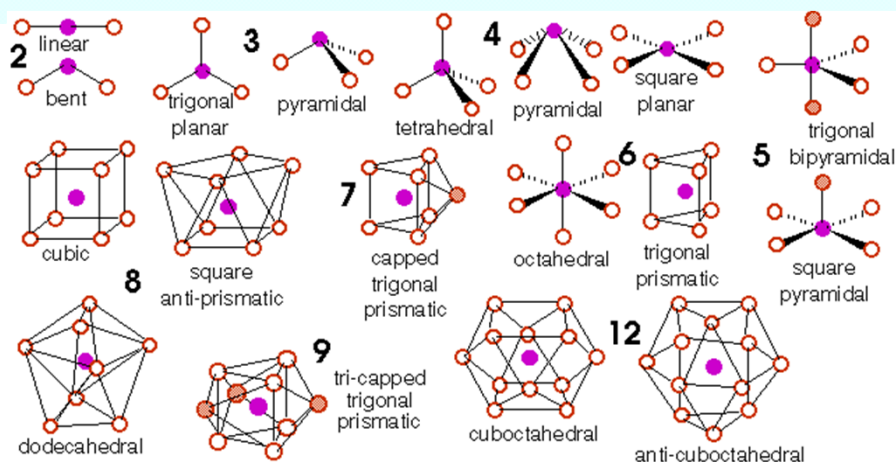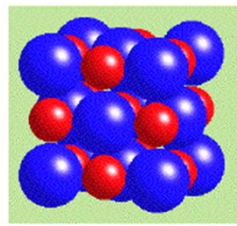
NaCl
Rock Salt
(*Halite*)
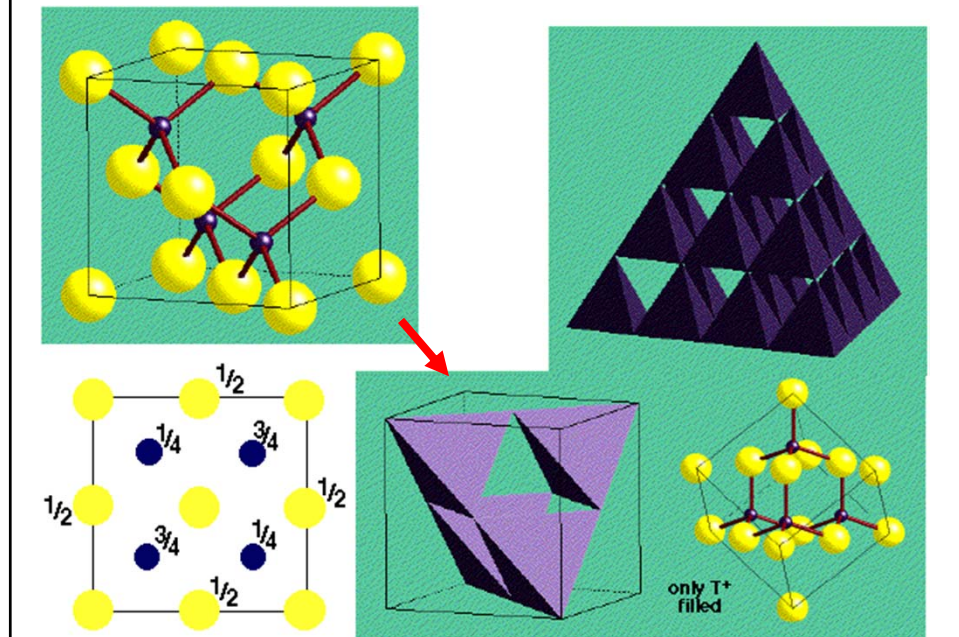
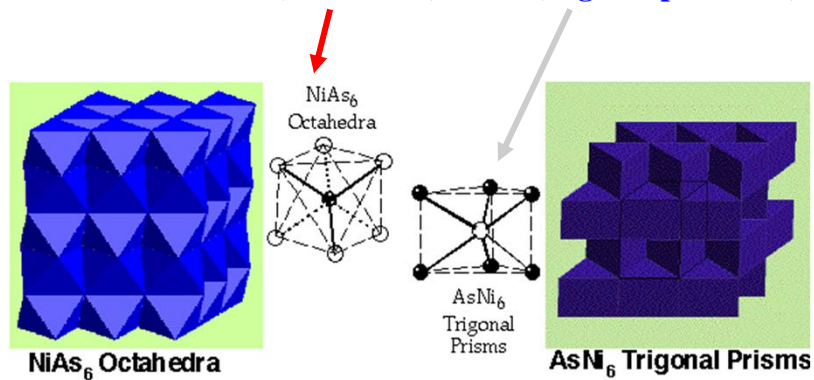**NaCl; ccp, O sites: 100%**

Fluorite B-cell   Plan view   CaF$_8$ Cubes

Zinc Blende: ZnS

only T$^+$ filled

- **HCP As with Ni in all Octahedral holes**
- *Lattice*: **Hexagonal - P**
- *a = b, c*
- *Motif*: **2Ni at (0,0,0) & (0,0,$^1/_2$) 2As at ($^2/_3$,$^1/_3$,$^1/_4$) & ($^1/_3$,$^2/_3$,$^3/_4$)**
- **2NiAs in unit cell**
- *Coordination*: **Ni 6 (octahedral) : As 6 (trigonal prismatic)**

NiAs$_6$ Octahedra

NiAs$_6$ Octahedra

AsNi$_6$ Trigonal Prisms

AsNi$_6$ Trigonal Prisms

Pauling Rule 1: *Coordination Polyhedra*

Molecular Materials
 •Absolute coordination numbers are controlled by valency (VSEPR)

Non-Molecular Materials

 •*Valency* has only an indirect bearing on coordination number
 e.g. $Na^I Cl$, $Mg^{II}O$, $Sc^{III}N$, $Ti^{IV}C$ all have the Rock Salt (6:6) Structure despite change in valency and from predominantly ionic to covalent bonding

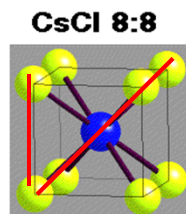 •Ionic Size does influence coordination number

---

The Coordination Number of the Cation will be Maximized subject to the criterion of Maintaining Cation-Anion Contact

Determined by comparison of the ratio of the ionic radii, r_+/r_- with values derived from the **geometric contact criterion**
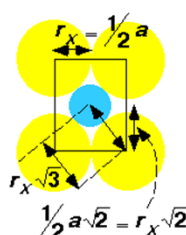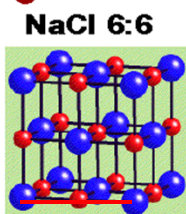
Radius Ratio Rule

Limiting Radius Ratios

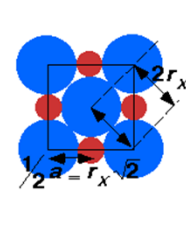| CsCl 8:8	NaCl 6:6	ZnS 4:4
unit cell	unit cell	$1/8^{th}$ unit cell
cell side a	face diagonal $a\sqrt{2}$	body diagonal $a\sqrt{3}$

Radius Ratio Rule

Red line: Contacting

$r_X = \frac{1}{2}a$

$r_X\sqrt{3}$

$\frac{1}{2}a\sqrt{2} = r_X\sqrt{2}$

$\frac{1}{2}a = r_X\sqrt{2}$

$\frac{1}{2}r_X\sqrt{6}$

$\frac{1}{4}a$

$\frac{1}{4}a\sqrt{2} = r_X$

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

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

$= 0.732$

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

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

$= 0.414$

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

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

$= 0.225$

CsCl 8:8

unit cell

cell side a

$r_X = \frac{1}{2}a$

$r_X\sqrt{3}$

$\frac{1}{2}a\sqrt{2} = r_X\sqrt{2}$
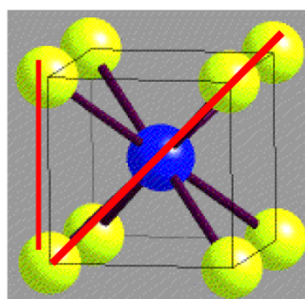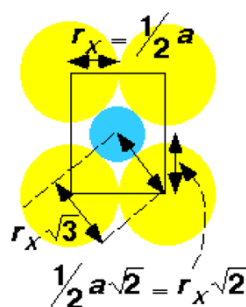
$r_M + r_X = r_X\sqrt{3}$

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

$= 0.732$

NaCl 6:6

unit cell

face diagonal $a\sqrt{2}$

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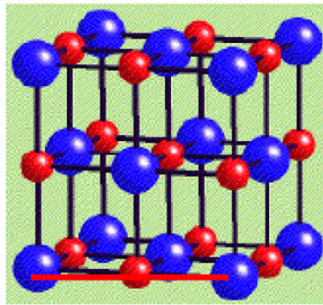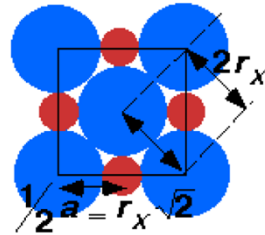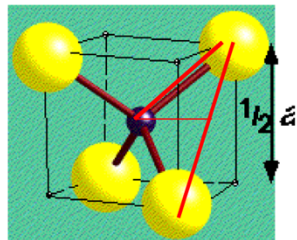
$$r_M / r_X = \sqrt{2} - 1$$

$$= 0.414$$

ZnS 4:4

1/8th unit cell
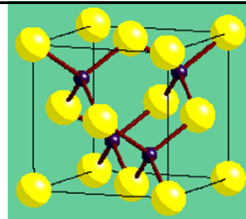
Zinc Blende ZnS

The diamond network with alternate Zn & S atoms

body diagonal $a\sqrt{3}$

$$\tfrac{1}{2} r_X\sqrt{6}$$

$$\tfrac{1}{4} a$$

$$\tfrac{1}{4} a\sqrt{2} = r_X$$
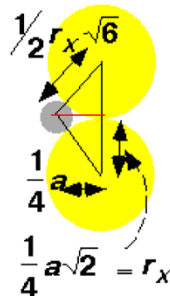
$$r_M + r_X = \frac{1}{2} r_X\sqrt{6}$$

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

$$= 0.225$$

Limiting Radius Ratios - **anions in the coordination polyhedron of cation are in contact with the cation and with each other**

If cations were to shrink further (i.e. r_+/r_- decrease), cation-anion contact would be lost in contravention of Pauling's 1st Rule.

Radius Ratio	Coordination no.	Binary (AB) Structure-type
$r_+/r_- = 1$	12	none known
$1 > r_+/r_- > 0.732$	8	CsCl
$0.732 > r_+/r_- > 0.414$	6	NaCl
$0.414 > r_+/r_- > 0.225$	4	ZnS

What's the Numerical Value of a specific Ionic Radius?

F^- 0.1 mm Li^+
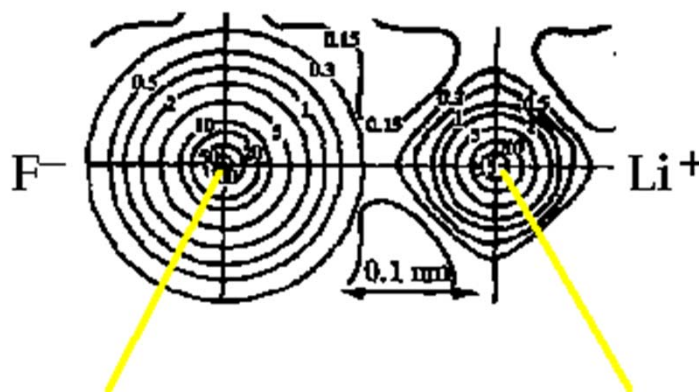
CRC Handbook of Physics and Chemistry

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Limiting Radius Ratios: do they work?

- For Li$^+$ and Na$^+$ salts, ratios calculated from both r_6 and r_4 are indicated
- Radius ratios suggest adoption of **CsCl** structure more than is observed in reality
- **NaCl** structure is **observed more** than is predicted
- **Radius ratios are only correct ca. 50% of the time,**
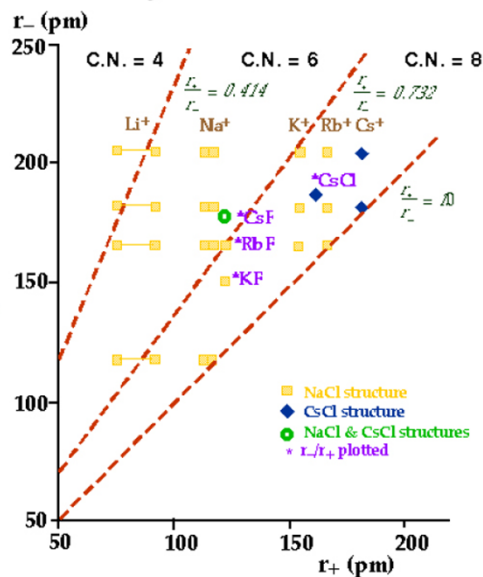
Lattice Energy = net potential energy of the arrangement of charges that form the structure.
= energy required to sublime the crystal and convert it into a collection of gaseous ions.

$$NaCl(s) --> Na^+(g) + Cl^-(g)$$

$$\Delta H = -U$$
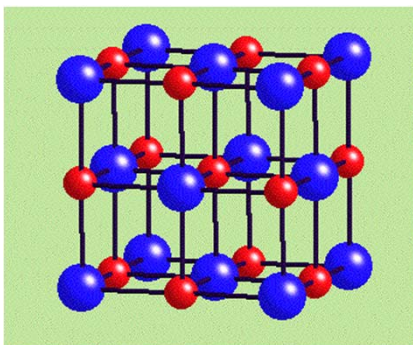

Electrostatic force
(Attraction & repulsion)

$$V = -\frac{Z_+ Z_- e^2}{r}$$

Short range repulsion:

$$V = \frac{B}{r^n}$$

B: Born exponent; n =5-12

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Ion Conf.	n
He	5
Ne	7
Ar, Cu+	9
Kr, Ag+	10
Xe, Au+	12

Example: NaCl structure

Start with one Na^+ cation.

Next neighbors: 6 Cl^- at distance r.

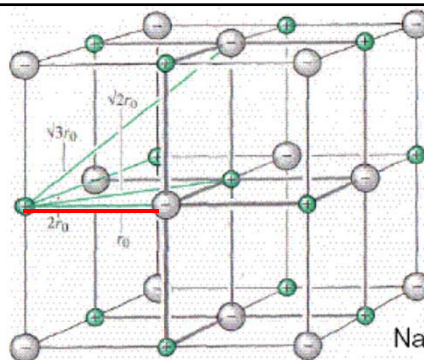$$V_1 = -6\, Z_+Z_-e^2/r$$

Next nearest neighbors:

12 Na^+ at distance $\sqrt{2}r$.

$$V_2 = +12\, Z_+Z_-e^2/(\sqrt{2}r)$$

Next next:

8 Cl^- at distance $\sqrt{3}r$.

$$V_3 = -8\, Z_+Z_-e^2/(\sqrt{3}r)$$

Net attractive electrostatic energy between one Na^+ and the rest:

$$V = V_1 + V_2 + V_3 + \ldots = -Z_+Z_-e^2/r \cdot \{6 - 12/\sqrt{2} + 8/\sqrt{3} - 6/\sqrt{4} + \ldots\}$$

Net attractive electrostatic energy:

repeat summation for each ion, i.e. for $2N$ ions per mole NaCl, then divide by 2!

$$V = -Z_+Z_-e^2/r \cdot N \cdot A$$

A: Madelung constant

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$$V = -\frac{Z_+Z_-e^2}{r}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + ...\right)$$

Madelung Constant

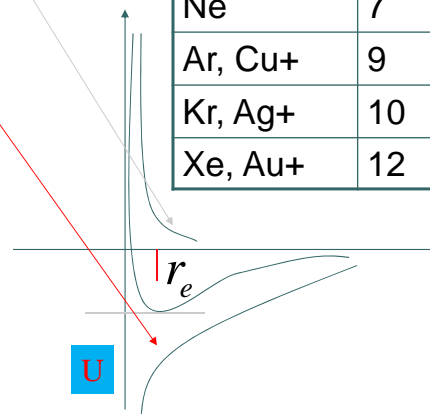| Structure Type	Madelung Constant
CsCl	1.763
NaCl	**1.748**
ZnS (*Wurtzite*)	1.641
ZnS (*Zinc Blende*)	1.638

$$U = -\frac{Z_+Z_-e^2NA}{r} + \frac{BN}{r^n}$$

$$\frac{dU}{dr} = \frac{Z_+Z_-e^2NA}{r^2} - \frac{nBN}{r^{n+1}} = 0$$

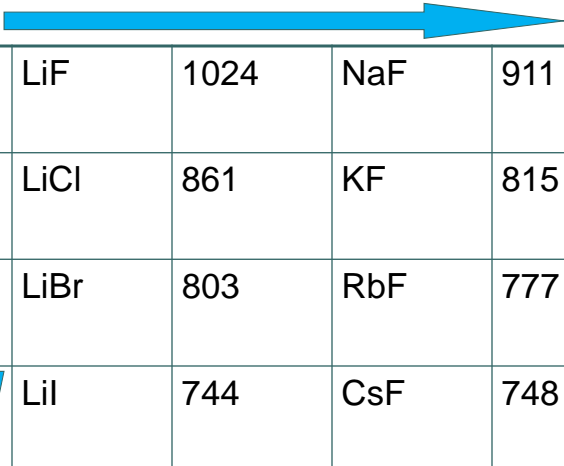$$B = \frac{Z_+Z_-e^2Ar^{n-1}}{n}$$

$$U = -\frac{Z_+Z_-e^2NA}{r_e}\left(1 - \frac{1}{n}\right)$$

N: Avogadro No.

Ion Conf.	n
He	5
Ne	7
Ar, Cu+	9
Kr, Ag+	10
Xe, Au+	12

r_e

U

Some Lattice Energies:

MgO	3938 kJ/mol	LiF	1024	NaF	911
CaO	3566	LiCl	861	KF	815
SrO	3369	LiBr	803	RbF	777
BaO	3202	LiI	744	CsF	748

Melting point: MgO: 2800 °C
CaO: 2572 °C
BaO: 1923 °C

Born-Habor Cycle/Thermochemical Calculation

$$Na(s) + \frac{1}{2}Cl_2(g) \dashrightarrow^{\Delta H_f} NaCl(s)$$

$$\Delta H = \frac{1}{2}D_{dissociation}$$

$$\Delta H = S_{sublimation}$$

U

$$Cl(g) \xrightarrow{EA} Cl^-(g)$$

+

$$Na(g) \xrightarrow{IP} Na^+(g)$$

$$\Delta H_f = S + \frac{1}{2}D_{dissociation} + IP + EA + U$$

12
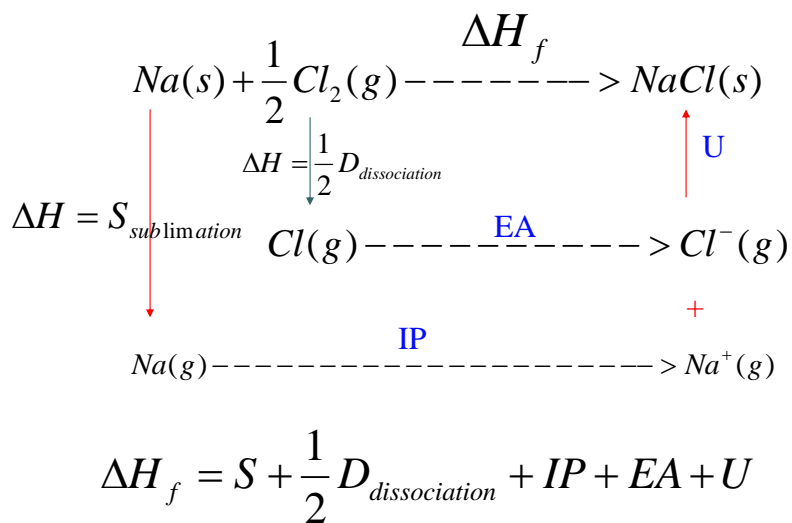
For NaCl:

S	109kJ/mol
IP	493.7kJ/mol
1/2D	121kJ/mol
EA	-356kJ/mol
U	-764.4kJ/mol

➡ ΔH_f =-396.7kJ/mol

Experimentally:

-410.9kJ/mol

	$U_{calc.}$	$U_{Born\text{-}Haber}$	ΔU
AgF	920	953	33
AgCl	832	903	71
AgBr	815	895	80
AgI	777	882	105

Increasing covalency!

Stabilities of unknown compunds

- If calc. $\Delta_f H$ is positive (and 'large') compound cannot be made → prediction!
  - Assume **ArCl** has rock salt structure & $r(Ar^+)$ is between $r(Na^+)$ and $r(K^+)$ then $U(ArCl) \sim -745$ kJ mol^{-1}

S	1/2D	IP	EA	U	$\Delta_f H$ (calc.)
0	121	1524	-356	-745	+544

Pauling Rule 2: *Electrostatic Valence Principle* ("Bond Strength")

"In a stable ionic structure the charge on an ion is balanced by the sum of electrostatic bond strengths to the ions in its coordination polyhedron"

i.e. A stable ionic structure must be arranged to preserve *Local Electroneutrality*

Electrostatic Bond Strength (e.b.s.)

•For a cation M^{m+} surrounded by n anions X^{x-}, the electrostatic bond strength of the cation is defined as:
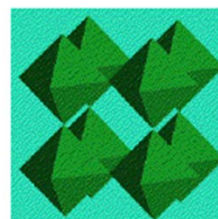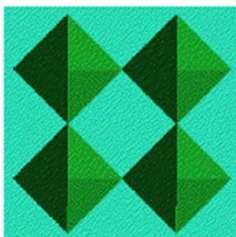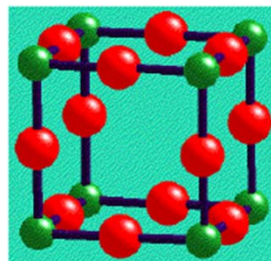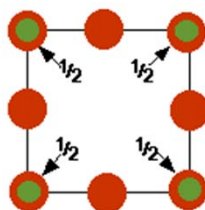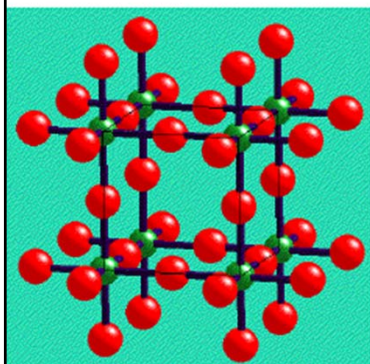
$$e.b.s = \frac{m}{n}$$

•For each anion (cation) the sum of the electrostatic bond strengths of the surrounding cations (anions) must balance the negative (positive) charge on the anion (cation)

$$\sum \frac{m}{n} = x$$

For a binary compound A_xB_y the coordination numbers of A and B are in the ratio y:x

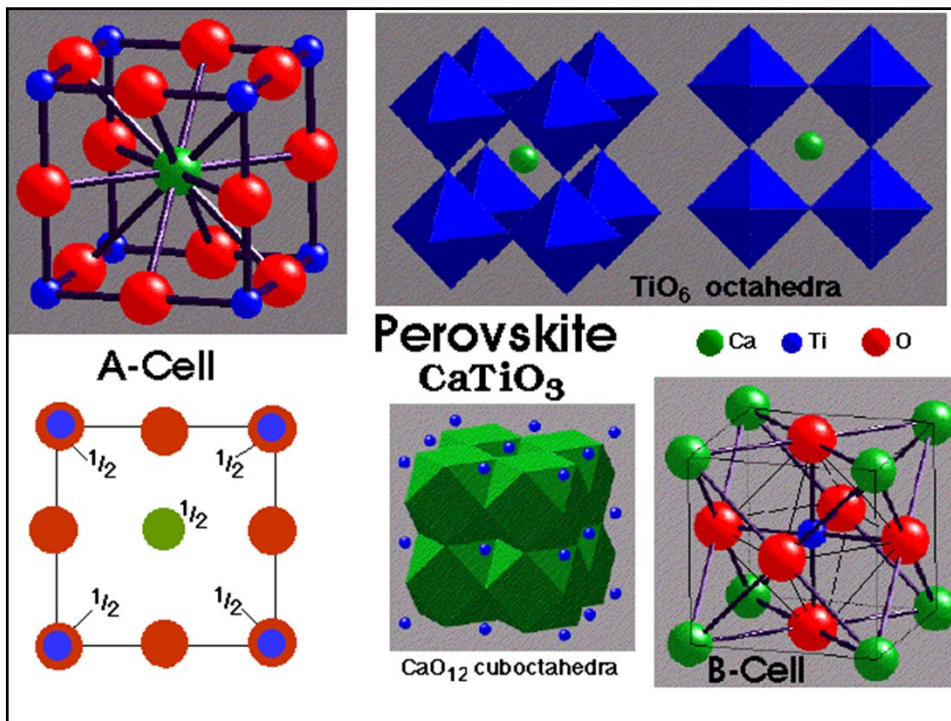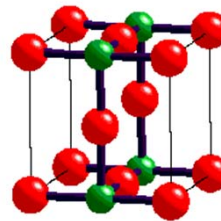Fluorite, CaF_2 Ca^{2+} (8-coordinate), F^- (4-coordinate)

ReO₃
Rhenium Trioxide

•*Lattice*: **Primitive** Cubic
•**1ReO$_3$ per unit cell**
•*Motif*: **Re at (0, 0, 0); 3O at ($^1/_2$, 0, 0), (0, $^1/_2$, 0), (0, 0, $^1/_2$)**
•**Re: 6 (octahedral coordination)**
•**O: 2 (linear coordination)**
•**ReO$_6$ octahedra share only vertices**
•**May be regarded as ccp oxide with $^1/_4$ of ccp sites vacant** (*at center of the cell*)

Examples:
  •**WO$_3$, AlF$_3$, ScF$_3$, FeF$_3$, CoF$_3$,**
  •**Sc(OH)$_3$ (*distorted*)**

A-Cell

TiO$_6$ octahedra

Perovskite CaTiO$_3$

● Ca ● Ti ● O

CaO$_{12}$ cuboctahedra

B-Cell

- *Lattice*: **Primitive Cubic (idealised structure)**
- **1CaTiO$_3$ per unit cell**
- *A-Cell Motif*: **Ti at (0, 0, 0); Ca at ($^1/_2$, $^1/_2$, $^1/_2$); 3O at ($^1/_2$, 0, 0), (0, $^1/_2$, 0), (0, 0, $^1/_2$)**
- **Ca 12-coordinate by O (cuboctahedral)**
- **Ti 6-coordinate by O (octahedral)**
- **O distorted octahedral (4xCa + 2xTi)**
- **TiO$_6$ octahedra share only vertices**
- **CaO$_{12}$ cuboctahedra share faces**
- **Ca fills the vacant ccp site in ReO$_3$, $\Rightarrow$ a CaO$_3$ ccp arrangement with $^1/_4$ of octahedral holes (those defined by 6xO) filled by Ti**
- *Examples*: **NaNbO$_3$, BaTiO$_3$, CaZrO$_3$, YAlO$_3$, KMgF$_3$**
- **Many undergo small distortions: e.g. BaTiO$_3$ is *ferroelectric***

Allow *Structure Prediction/Rationalization*
*e.g. In **Perovskite**, CaTiO$_3$*
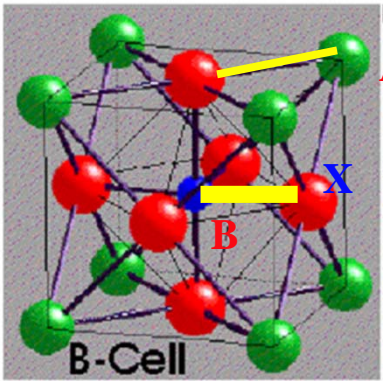
- **Ca^{2+} is 12-**coordinated by O^{2-} $\Longrightarrow$ Ca-O bond has e.b.s. = $^2/_{12}$ = **$^1/_6$**
- **Ti^{4+} is 6-**coordinated by O^{2-} $\Longrightarrow$ Ti-O bond has e.b.s. = $^4/_6$ = $^2/_3$
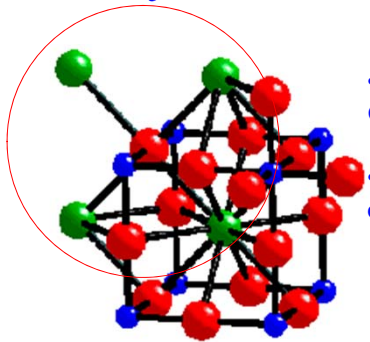
- **O^{2-} has a total valency of 2 $\Longrightarrow$ satisfied by {4 x Ca^{2+}($^1/_6$)} +{2 x Ti^{4+}($^2/_3$)}**

- **Each Oxygen must be common to 4 CaO$_{12}$ cuboctahedra & 2 TiO$_6$ octahedra**

Pauling Rule 2: *Electrostatic Valence Principle* ("Bond Strength")

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Perovskite Structure: ABO₃

Tolerance factor:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

t	Effect	Possible structure
>1	A cation too large to fit in interstices	Hexagonal perovskite
0.9-1.0	ideal	Cubic perovskite
0.71-0.9	A cation too small	Orthorhombic perovskite
<0.71	A cation same size as B cation	Possible close packed lattice

Perovskite: most widely studied oxide structure

Wide range of chemistries possible
- thousands of examples known

Unique properties of perovskites:

- high T_c cuprate superconductors
- Colossal Magneto-Resistance $(La,Sr)MnO_3$
- fast ion conduction (Li^+, O^{2-}), batteries, fuel cells
- mixed electronic/ionic conduction, fuel cells
- oxidation/reduction catalysts
- ferroelectric / piezoelectric ceramics $(BaTiO_3, Pb(ZrTi)O_3)$
- important mineral structure in lower mantle $(MgSiO_3)$
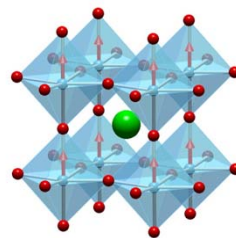- frequency filters for wireless communications : $Ba(Zn_{1/3}Ta_{2/3})O_3$

Ferroelectrics

BaTiO$_3$: Ba^{2+} r=1.56 Å   t=0.992
Ti^{4+} r=0.75 Å
O^{2-} r=1.26 Å

KNbO$_3$ K$^+$ 1.65 Å   t=1.01
Nb^{5+} 0.78 Å

LiNbO$_3$ Li$^+$ 1.06 Å   t=0.81
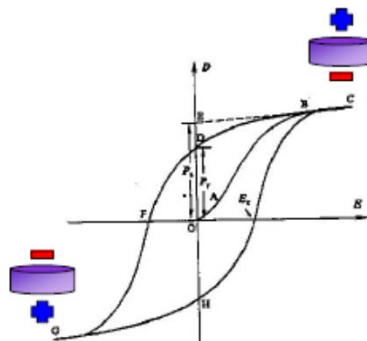Nb^{5+} 0.78 Å

Rhombhedral distortion

What is a Ferroelectric

A ferroelectric material develops a spontaneous polarization (builds up a charge) in response to an external electric field.

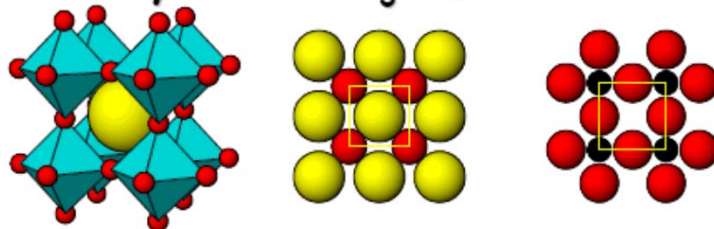·The polarization does not go away when the external field is removed.

·The direction of the polarization is reversible.
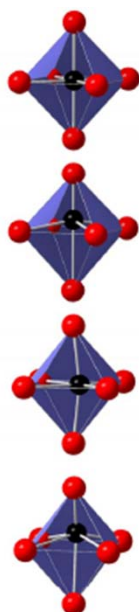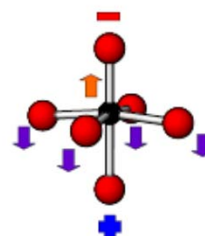
Applications of Ferroelectric Materials
·Multilayer capacitors
·Non-volatile FRAM (Ferroelectric Random Access Memory)

Why is BaTiO₃ Ferroelectric

a shift of Ti⁴⁺ toward one of the corners of the octahedron.

• The direction of the shift can be altered through application of an electric field.

BaTiO₃ Phase Transitions

Cubic (Pm3m)
T > 393 K
Ti-O Distances (Å)
6x2.00

Tetragonal (P4mm)
273 K < T < 393 K
Ti-O Distances (Å)
1.83, 4x2.00, 2.21
Toward a corner

Orthorhombic (Amm2)
183 K < T < 273 K
Ti-O Distances (Å)
2x1.87, 2x2.00, 2x2.17
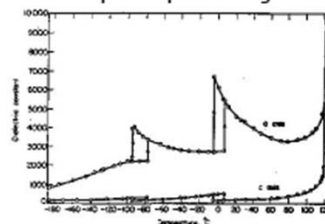*Toward an edge*

Rhombohedral (R3m)
183 K < T < 273 K
Ti-O Distances (Å)
3x1.88, 3x2.13
Toward a face

In the cubic structure BaTiO₃ is paraelectric. That is to say that the orientations of the ionic displacements are not ordered and dynamic.

Below 393 K BaTiO₃ becomes ferroelectric and the displacement of the Ti⁴⁺ ions progressively displace upon cooling.

See Kwei et al. J. Phys. Chem. **97**, 2368 (1993).

Magnetoresistive materials:

LaMnO$_3$: 1.30 Å ; 0.72 Å t=0.91
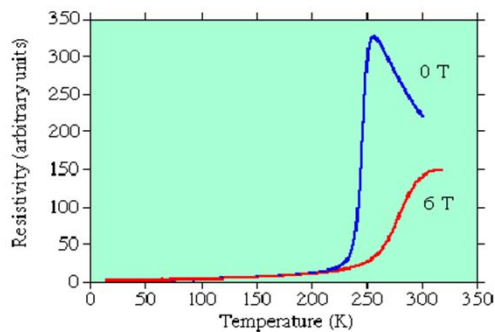
La$_{0.5}$Sr$_{0.5}$MnO$_3$: 1.28 Å, 0.695 Å t=0.92

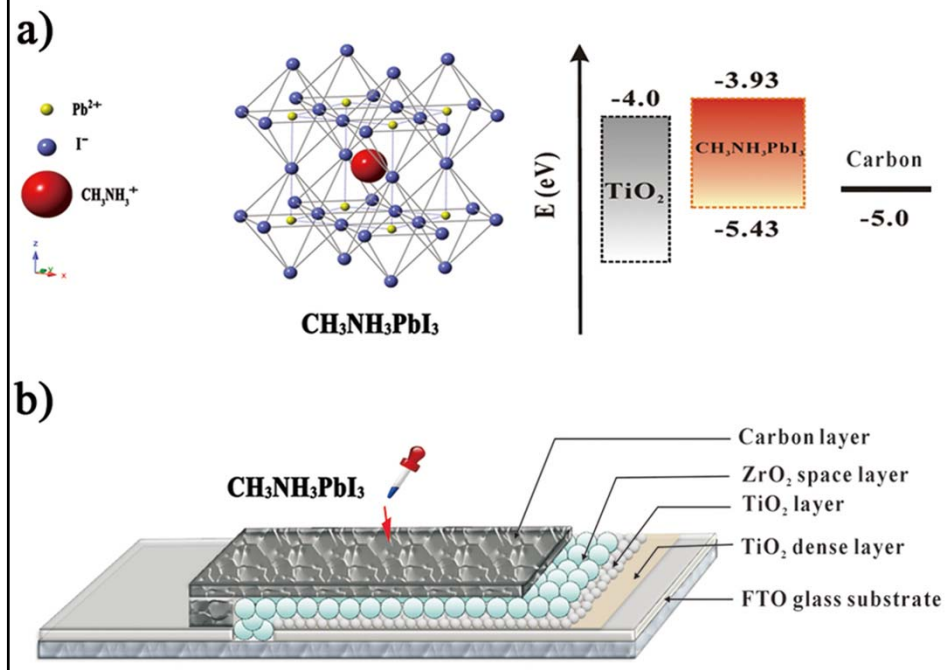Mn^{3+} , d^4:

large Jahn-Teller effect, tetragonal distortion

Colossal Magnetoresistance

Temperature Dependence

As the temperature is increased through the ferromagnetic Curie temperature $T_{c'}$ the electrical resistance rises sharply, and becomes strongly dependent on applied magnetic field.

a)

- Pb^{2+}
- I$^-$
- CH$_3$NH$_3^+$

CH$_3$NH$_3$PbI$_3$

E (eV)

-4.0   TiO$_2$

-3.93   CH$_3$NH$_3$PbI$_3$ Carbon

-5.43   -5.0

b)

CH$_3$NH$_3$PbI$_3$

- Carbon layer
- ZrO$_2$ space layer
- TiO$_2$ layer
- TiO$_2$ dense layer
- FTO glass substrate

Pauling Rule 3: *Polyhedral Linking*

"The stability of structures with different types of polyhedral linking is vertex-sharing > edge-sharing > face-sharing"

➤ **effect is largest for cations with high charge and low coordination number**

➤ **especially large when r$_+$/r$_-$ approaches the lower limit of the polyhedral stability**

Sharing edges/faces brings ions at the center of each polyhedron closer together, hence increasing electrostatic repulsions

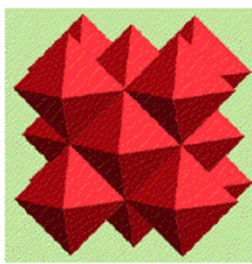*i.e. disposition of ions of similar charge will be such as to minimize the Electrostatic Energy between them*

Linus Pauling, *J. Amer. Chem. Soc.* **51**, 1010 (1929)

When polyhedra share a common edge or face it brings the cations closer together, thereby increasing electrostatic repulsions.
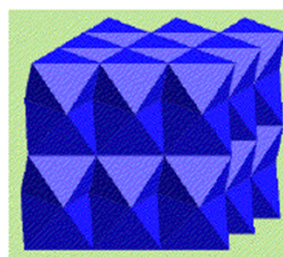
	Corner	Edge	Face
		Cation-Cation Distance	
Tetrahedra	2 M-X	1.16 M-X	0.67 M-X
Octahedra	2 M-X	1.41 M-X	1.16 M-X
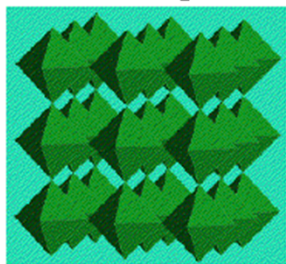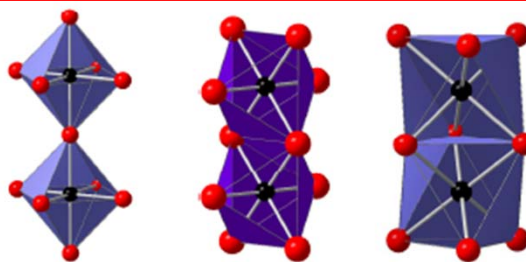
ReO$_3$ — *Vertex-Sharing Only*

NaCl — *Edge-Sharing*

**NiAs** — *Face-Sharing in Columns*

Ni-Ni interaction

Pauling Rule 4: *Cation Evasion in >Binaries*

"In a crystal containing different cations, those of high valency and small coordination number tend NOT to share polyhedron elements with each other"

e.g. In *Perovskite*, $CaTiO_3$

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

Ti^{IV} 6-coordinate TiO_6 octahedra share only **VERTICES**
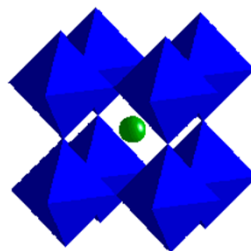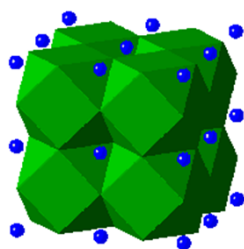
Pauling Rule 5: Environmental Homogeneity

"The number of essentially different kinds of constituent in a crystal tend to be small"
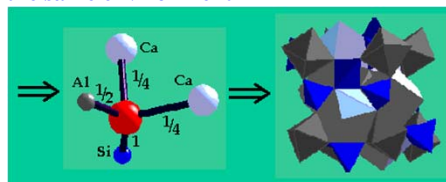
i.e. similar environments for chemically similar atoms

Treating the mineral *Garnet* $Ca_3Al_2Si_3O_{12}$ as an ionic crystal

	Ca^{2+}	Al^{3+}	Si^{4+}
coordination	8	6	4
e.b.s.	$1/4$	$1/2$	1

O^{2-} bond strength of 2 is satisfied by a number of alternative combination of bonds
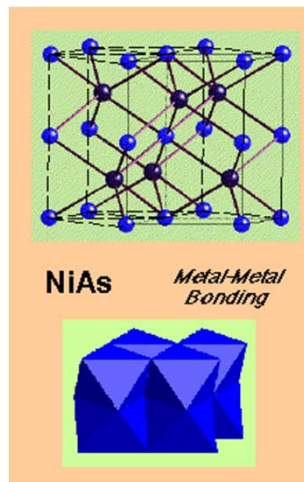• Pauling Rule 5: Each O^{2-} would prefer the same environment
• Only one possible arrangement:

When Pauling's Rules are <u>NOT</u> Obeyed
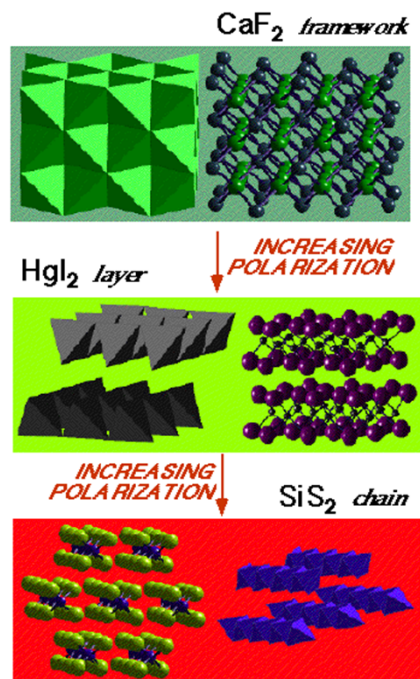## Special structural influences in the bonding

PbO — *Lone Pairs*

NiAs — *Metal-Metal Bonding*
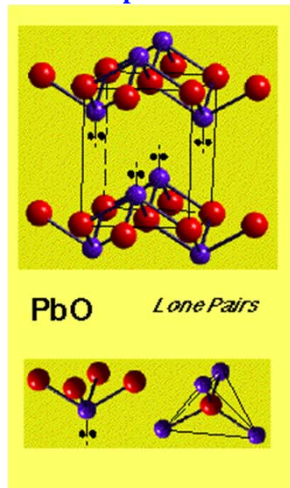
Distorted coordination polyhedra

Face-sharing

Indirect evidence that the structure is NOT ionic

> **Increasing Polarization in bonding**
>
> ⬇
>
> **low-dimensionality - layers/chains**

CaF_2 *framework*

INCREASING POLARIZATION

HgI_2 *layer*

INCREASING POLARIZATION

SiS_2 *chain*

Fajan's Rules (*Polarization*)

Polarization will be increased by:

1. High charge and small size of the cation
Ionic potential Z_+/r_+ (= *polarizing power*)

2. High charge and large size of the anion
The polarizability of an anion is related to the deformability of its electron cloud (*i.e.* its "*softness*")


Mooser-Pearson Plots
Combining Bond Directionality, Size and Electronegativity in a <u>Structure Map</u>

- x-axis is **Electronegativity Difference**, $\Delta\chi$ (partially related to bond ionicity)
- y-axis is the **average principal quantum number** $\bar{n}$
    - c_i = no. of atoms of i per formula unit
    - $\bar{n}$ is related to *bond directionality*
- larger $\bar{n}$ **larger orbitals**, **less directionality**

$$\bar{n} = \frac{\Sigma c_i n_i}{\Sigma c_i}$$

Mooser-Pearson Plot for **AB**
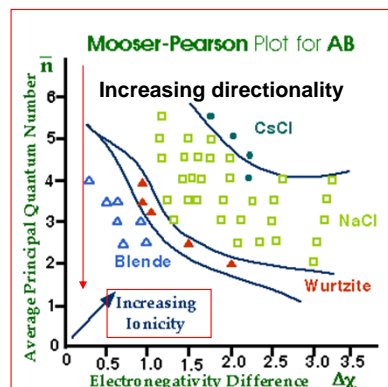
Oxide Structures & Networks
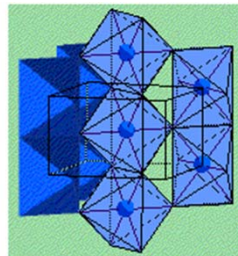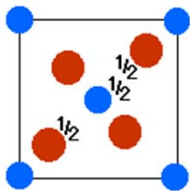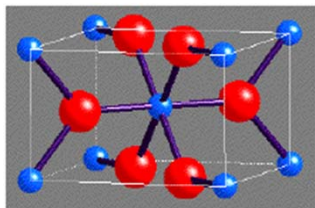
- *Unit Cell*: **Primitive Tetragonal ($a = b \neq c$)**
- **2TiO$_2$ per unit cell**
- *Motif*: **2Ti at (0, 0, 0); ($^1/_2$, $^1/_2$, $^1/_2$) & 4O at ±(0.3, 0.3, 0); ±(0.8, 0.2, $^1/_2$)**
- **Ti: 6 (octahedral coordination)**
- **O: 3 (trigonal planar coordination)**
- **TiO$_6$ octahedra share edges in chains along c**
- **Edge-sharing Chains are linked by vertices**
- *Examples*:
    - **oxides: MO$_2$ (*e.g.* Ti, Nb, Cr, Mo, Ge, Pb, Sn)**
    - **fluorides: MF$_2$ (*e.g.* Mn, Fe, Co, Ni, Cu, Zn, Pd)**

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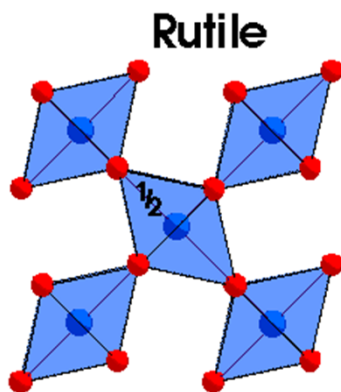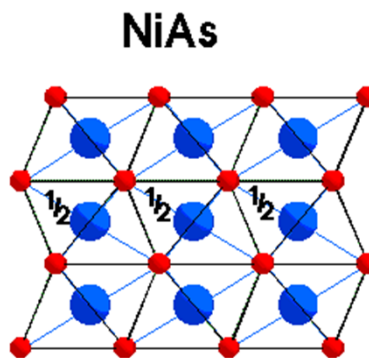
i.e. **Rutile is distorted hcp O with Ti in $^1/_2$ Octahedral holes.**
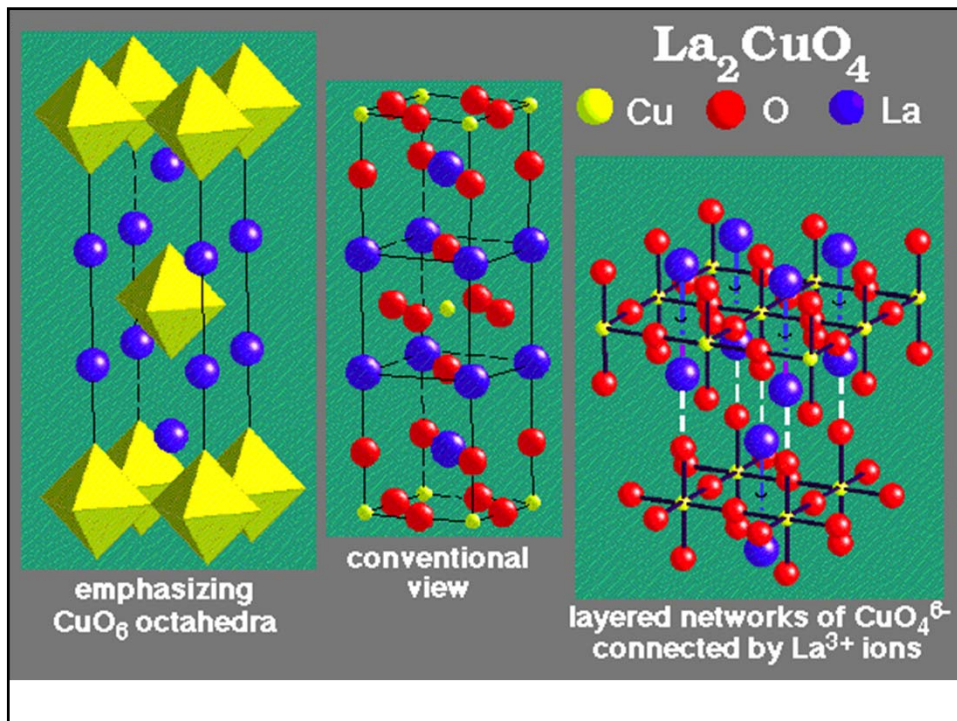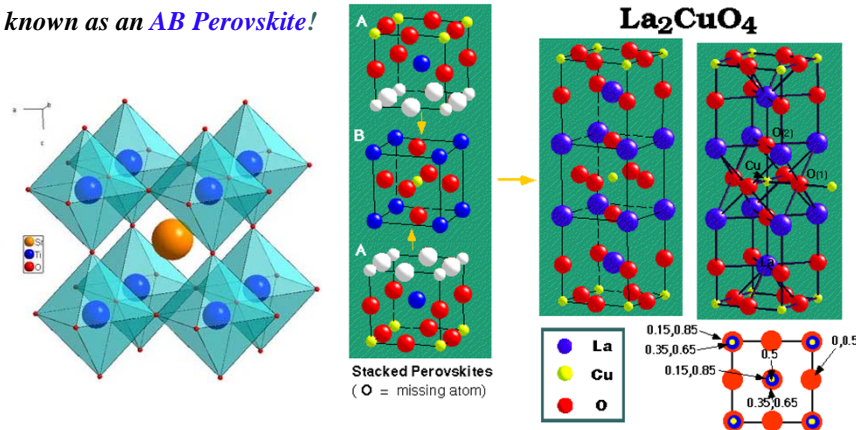
Anatase: ccp version

La$_2$CuO$_4$ {*K$_2$NiF$_4$ structure*}

Doped La$_2$CuO$_4$ was the first (1986) High-T$_c$ Superconducting Oxide (T$_c$ ~ 40 K)

Bednorz & Müller were awarded a Nobel Prize
La$_2$CuO$_4$ may be viewed as if constructed from an ABAB... arrangement of Perovskite cells
*- known as an AB Perovskite!*

Stacked Perovskites
(O = missing atom)

La$_2$CuO$_4$

emphasizing
CuO$_6$ octahedra

conventional
view

layered networks of CuO$_4$$^{6-}$
connected by La^{3+} ions

We may view the structure as based on:

    1. Sheets of elongated CuO_6 octahedra, sharing only vertices
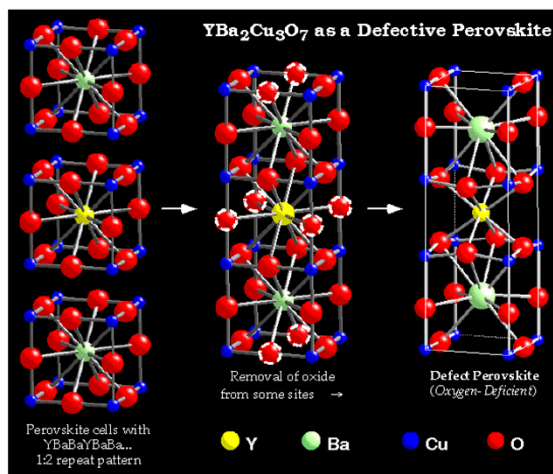   **2. Layered networks of $CuO_4{}^{6-}$, connected only by La^{3+} ions**

      Comparison of La_2CuO_4 with the related Nd_2CuO_4

La_2CuO_4 Nd_2CuO_4

Rock Salt

Fluorite
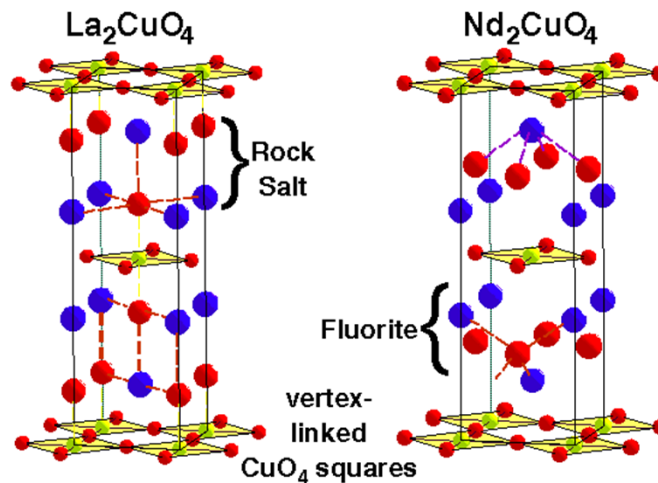
vertex-linked CuO_4 squares

- **Common structural motif of vertex-linked CuO_4 squares.**
- **This motif occurs in all the high temperature superconducting copper oxides.**
- **The structures differ in the structure of the 'filling' in the 'sandwich' of copper oxide layers - known as Intergrowth Structures.**

- **$YBa_2Cu_3O_7$ can be viewed as an Oxygen-Deficient Perovskite.**

$YBa_2Cu_3O_7$ as a Defective Perovskite

Perovskite cells with YBaBaYBaBa... 1:2 repeat pattern

Removal of oxide from some sites →

Defect Perovskite (Oxygen-Deficient)
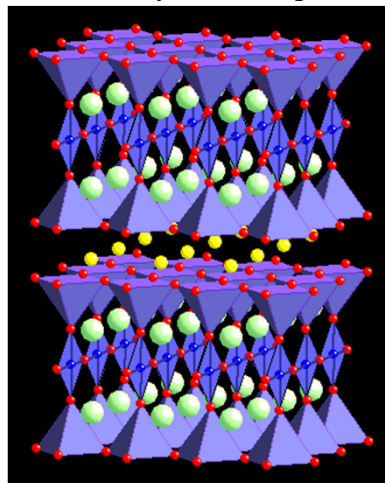
○ Y   ● Ba   ● Cu   ● O

•Two types of Cu site

Layers of CuO_5 square pyramids (elongation $\Rightarrow$ essentially *vertex-linked CuO_4 squares* again)

Chains of vertex-linked CuO_4 squares

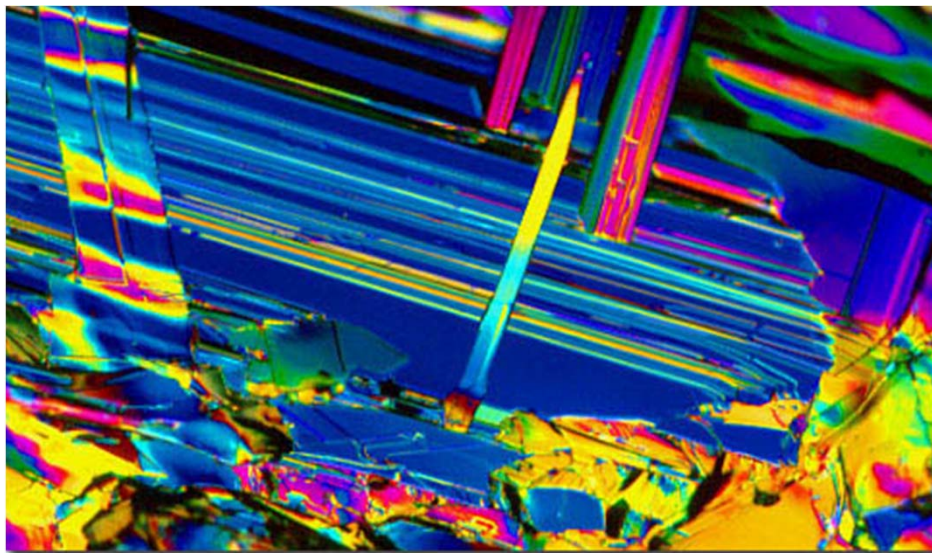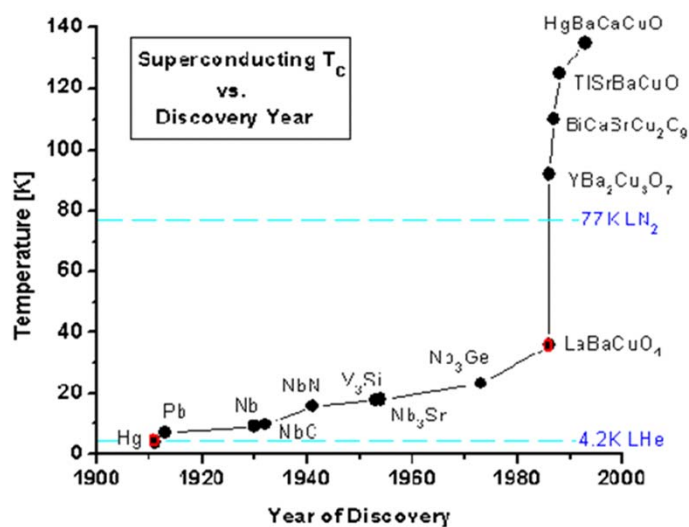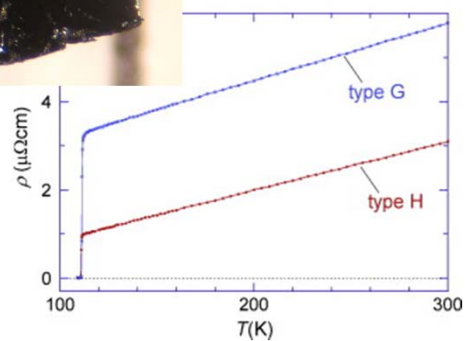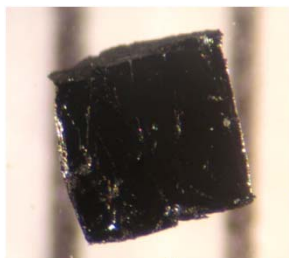These are indicated in a Polyhedral Representation

CuO2
BaO
CuO
BaO
CuO2
Y
CuO2

$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$
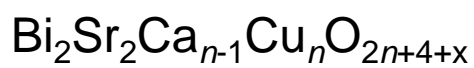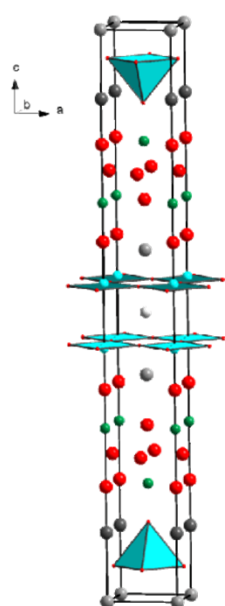
Infinite-layer-structure oxide: SrCuO2