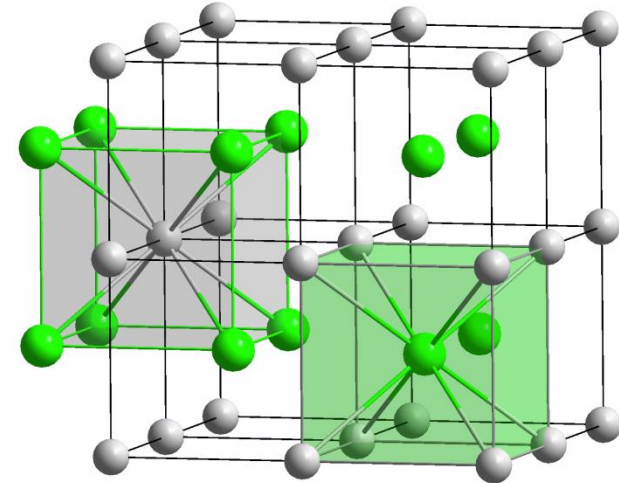
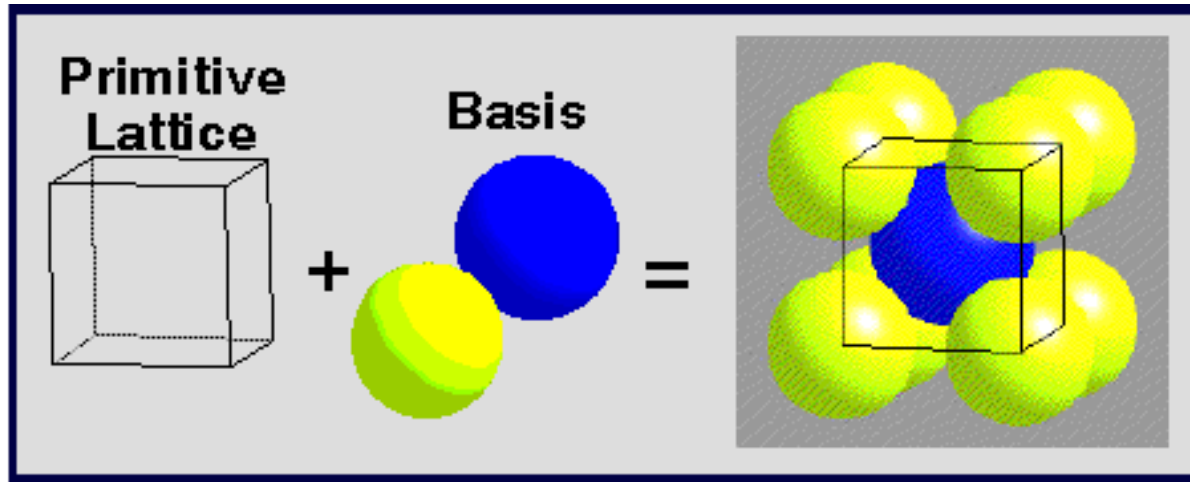


CRYSTALS THAT *CANNOT* BE DESCRIBED IN
TERMS OF INTERSTITIAL FILLING OF A
CLOSE-PACKED STRUCTURE

CsCl STRUCTURE

Not close packed - simple cubic with a two-point basis



Space Group = $Pm\bar{3}m$

Lattice = Primitive cubic (**not BCC!**)

Basis = Cl (0,0,0), Cs ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)

Coordination = 8, 8

Cation Coord. \rightarrow Cubic

Anion Coord. \rightarrow Cubic

Connectivity \rightarrow face sharing cubes

1 CsCl per unit cell

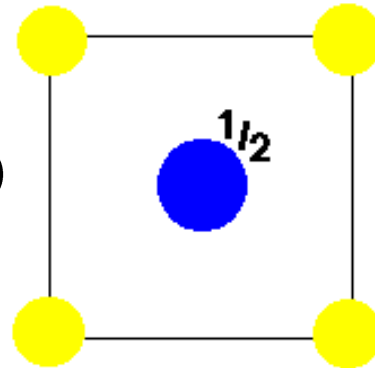


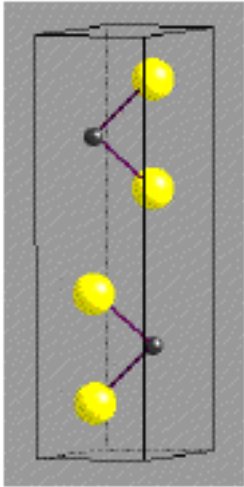
Table 7.11 Some compounds with the CsCl structure

	$a(\text{\AA})$		$a(\text{\AA})$
CsCl	4.123	CuZn	2.945
CsBr	4.286	CuPd	2.988
CsI	4.5667	AuMg	3.259
CsCN	4.25	AuZn	3.19
NH ₄ Cl	3.8756	AgZn	3.156
NH ₄ Br	4.0594	LiAg	3.168
TlCl	3.8340	AlNi	2.881
TlBr	3.97	LiHg	3.287
TlI	4.198	MgSr	3.900

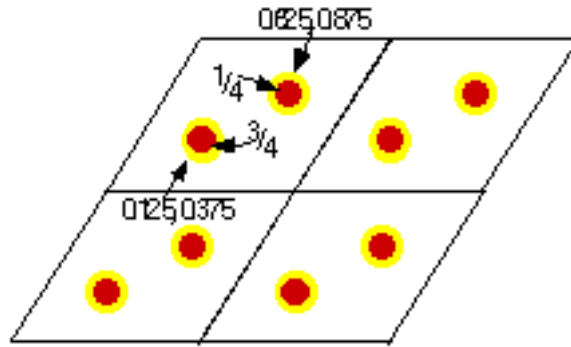
Adoption by chlorides, bromides and iodides of larger cations

MoS₂ STRUCTURE

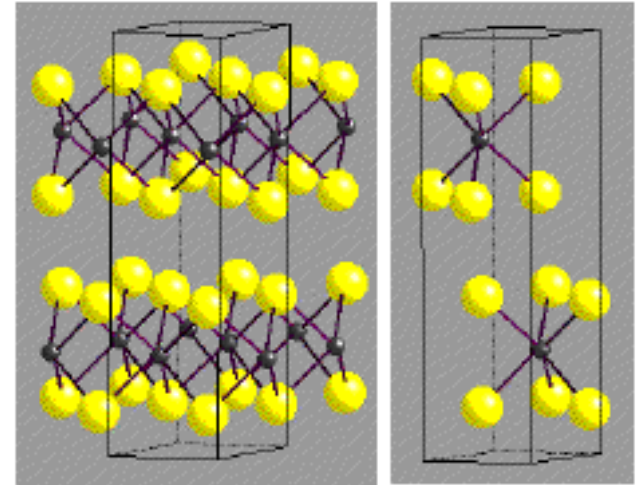
Non-close packed 2D HCP layers of S stacked in AABBAABB... fashion



Unit Cell



Plan View



Clinographic Views

Space Group = P6₃/mmc

Lattice = Primitive hexagonal

Basis = Mo (2/3, 1/3, 3/4) & (1/3, 2/3, 1/4)

S (2/3, 1/3, 1/8), (2/3, 1/3, 3/8),

(1/3, 2/3, 5/8), (1/3, 2/3, 7/8)

Coordination = 6, 3

Cation Coord. → Trigonal prism

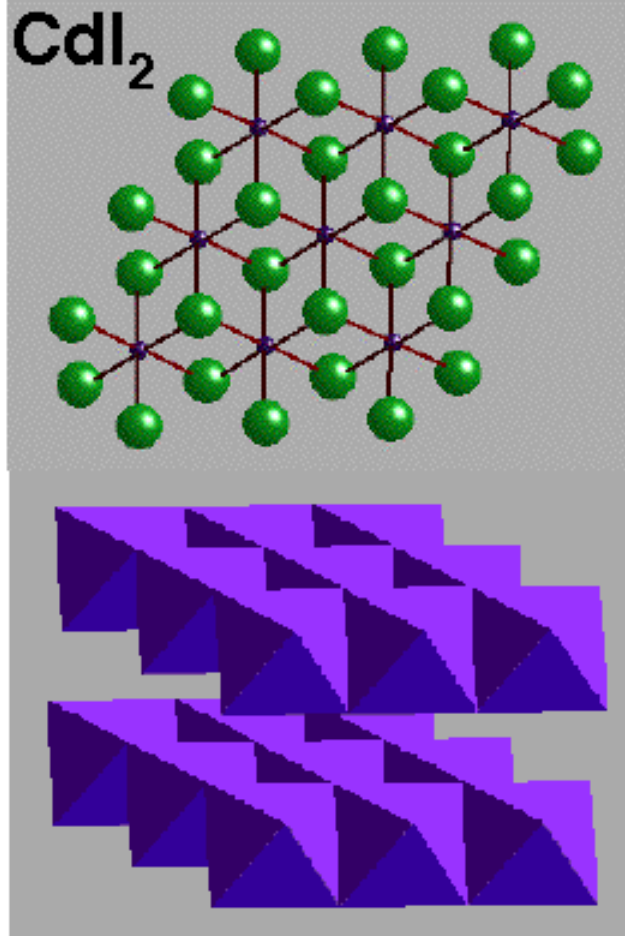
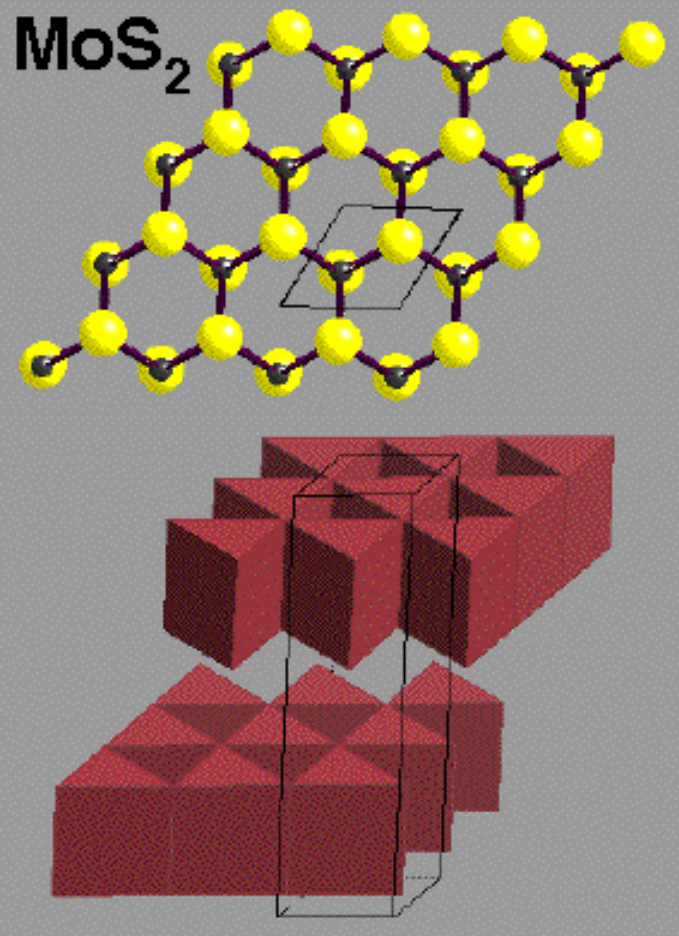
Anion Coord. → Trigonal pyramid

Connectivity → sheets of trigonal prisms

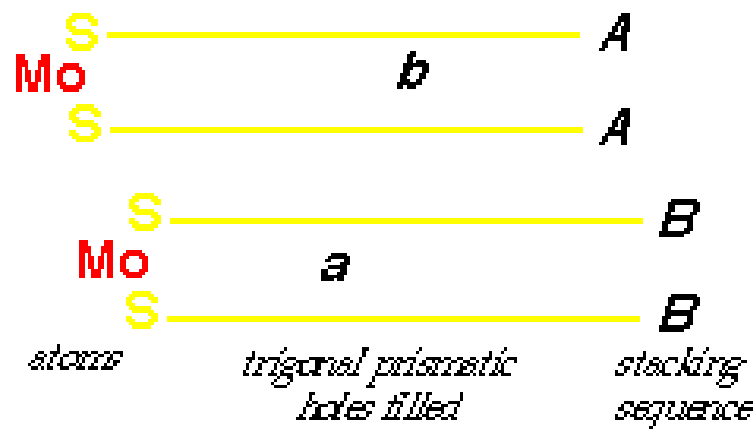
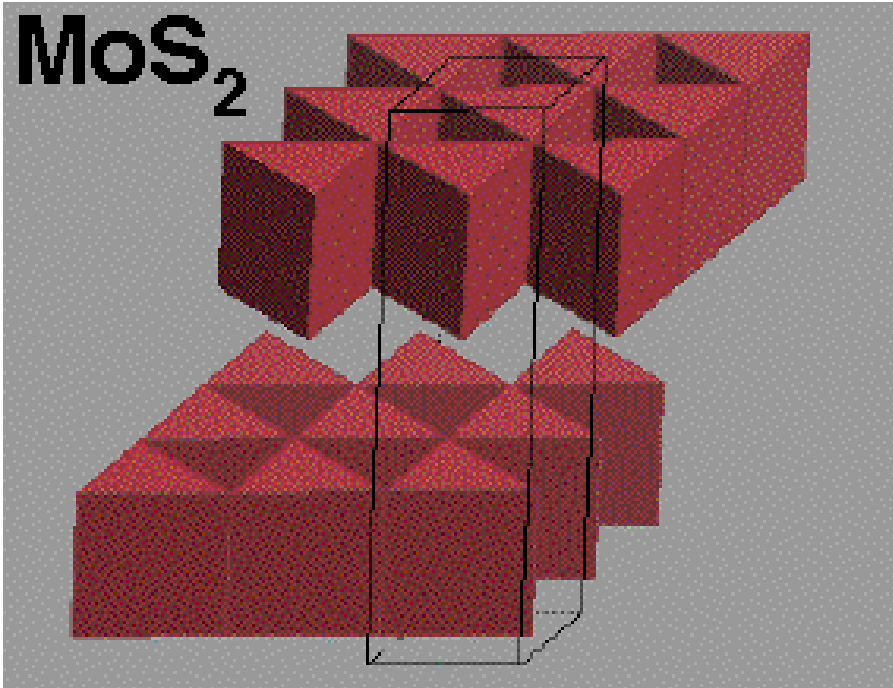
2 MoS₂ per unit cell

- layered structure

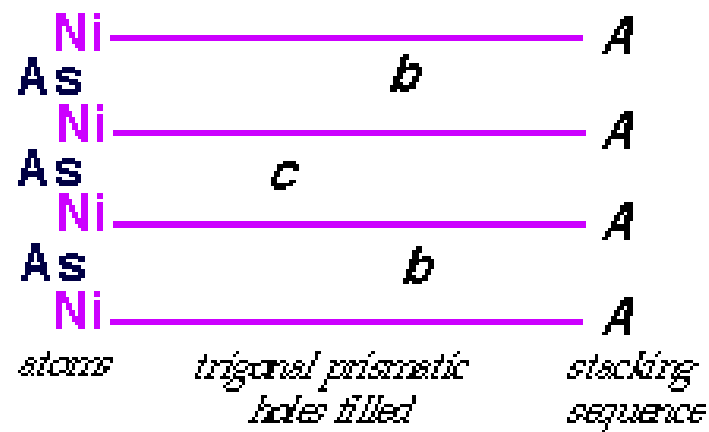
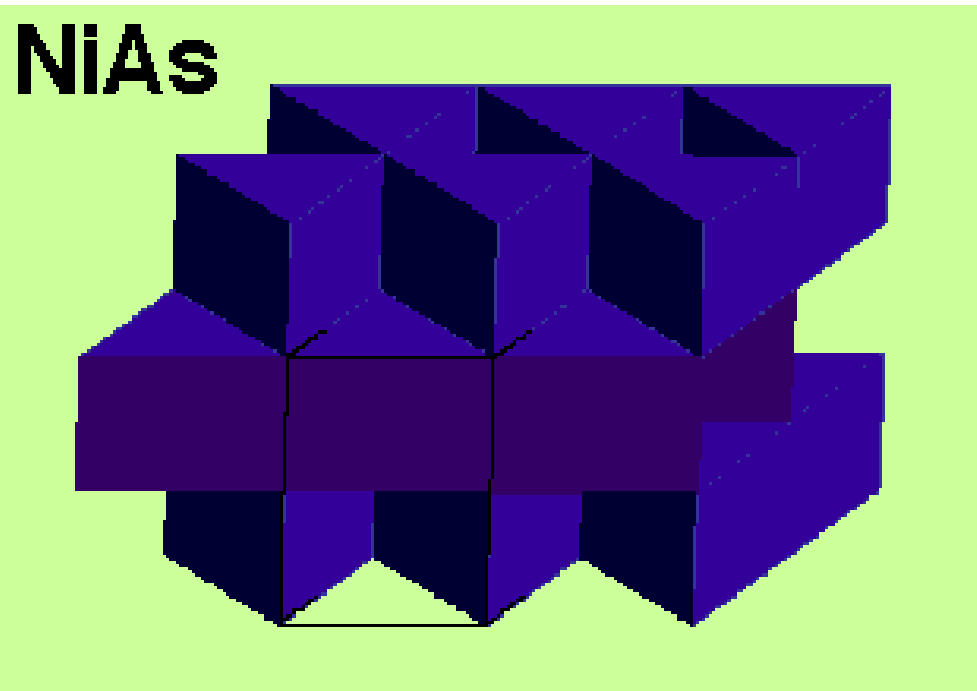




- both MoS₂ and CdI₂ are **LAYERED** structures
- MoS₂ layers are edge-linked MoS₆ **trigonal prisms**
- CdI₂ layers are edge-linked CdI₆ **octahedra**



MoS₆ **trigonal prisms**



AsNi₆ **trigonal prisms**

COVALENT NETWORK STRUCTURES

Concept of **CONNECTEDNESS (P)** of a network connecting structural units (atoms or groups)

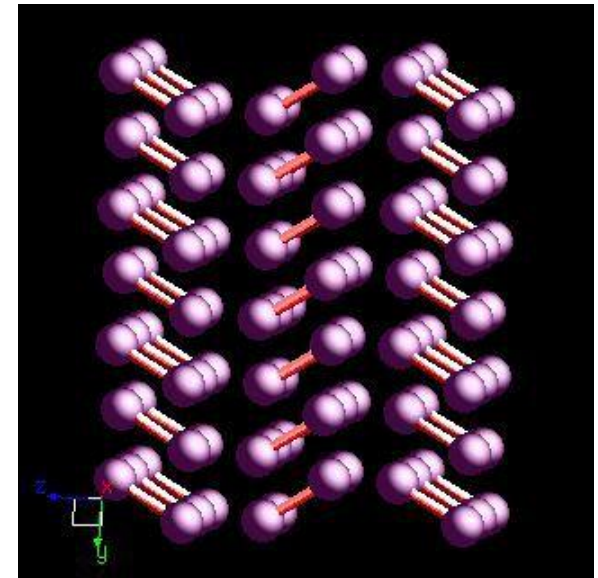
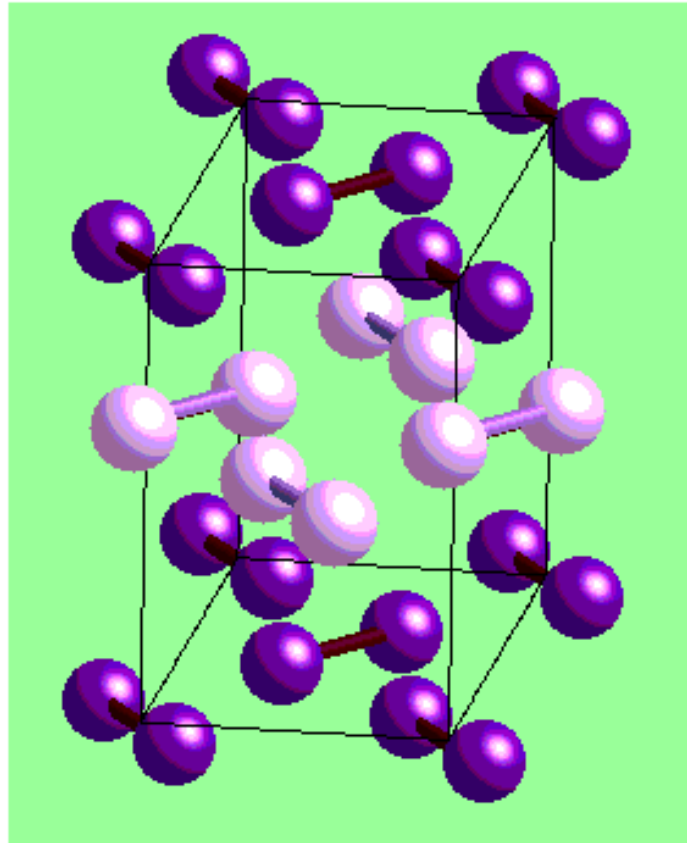
e.g. Structures of Non-Metallic Elements

The "**8-N Rule**"

connectedness = 8 – # valence electrons

$$P = 8 - N$$

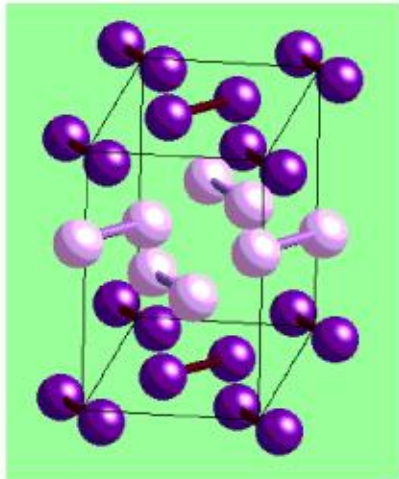
$P = 1$
e.g. I_2 dimers



Space group: **Cmca**
orthorhombic

STRUCTURES OF THE ELEMENTS

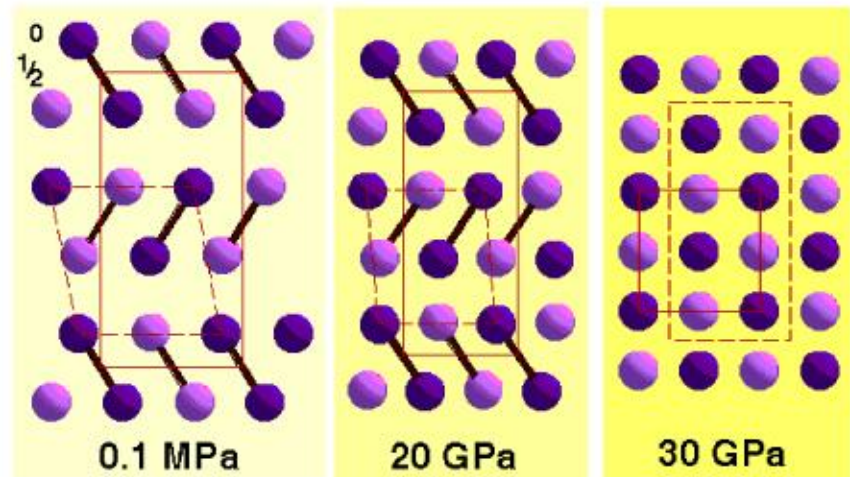
$P = 1$
e.g. I₂ DIMERS



Iodine 8 - N = 1



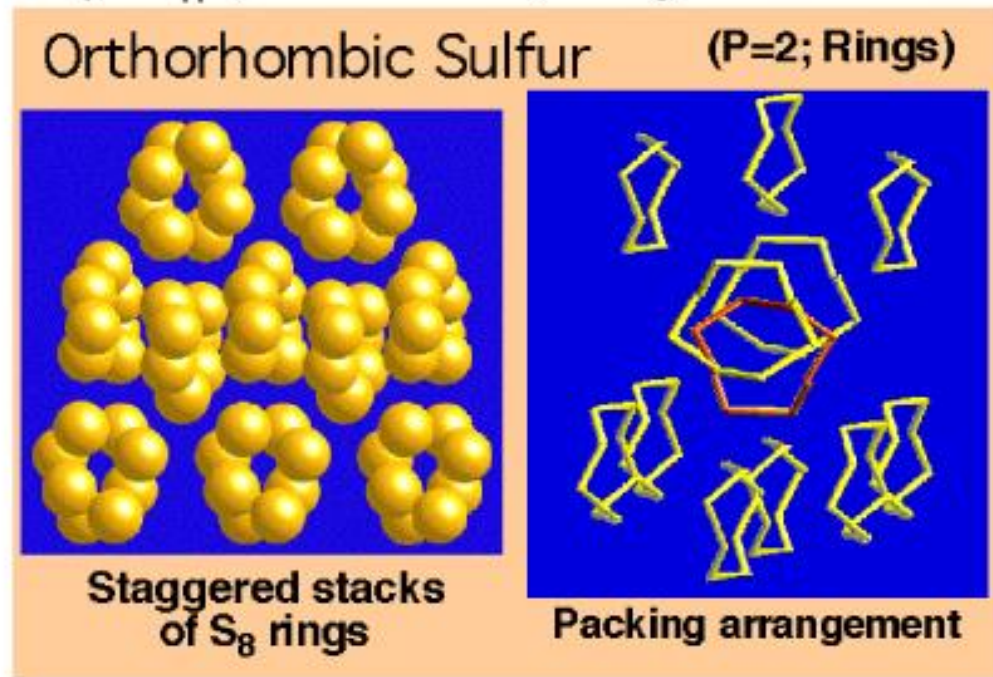
Iodine dimers convert to a metal under pressure



FCC metal

$P = 2$
e.g. S_8 RINGS

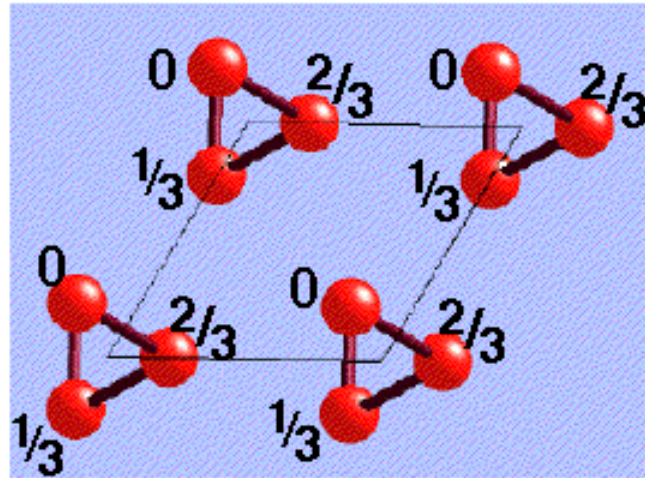
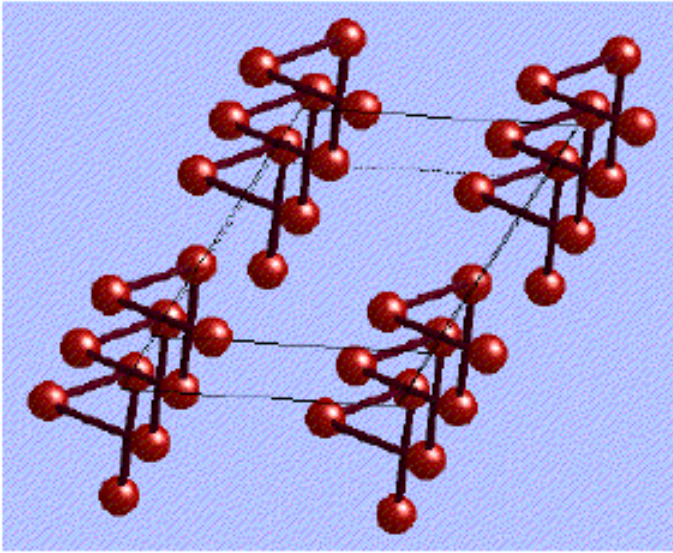
Many S_n ($n = 5 - 20$) rings are known



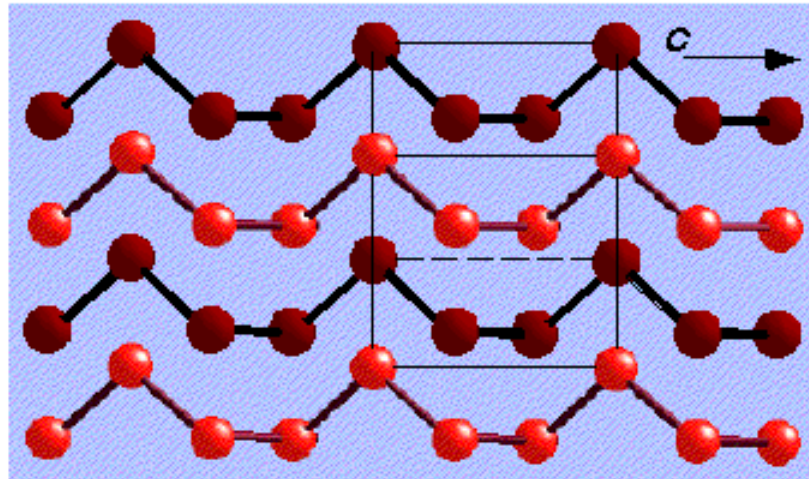
- the packing approximates a **distorted close-packing** arrangement
- apparently **11-coordinate** (3 *left* + 5 *in-plane* + 3 *right*)

$$P = 2$$

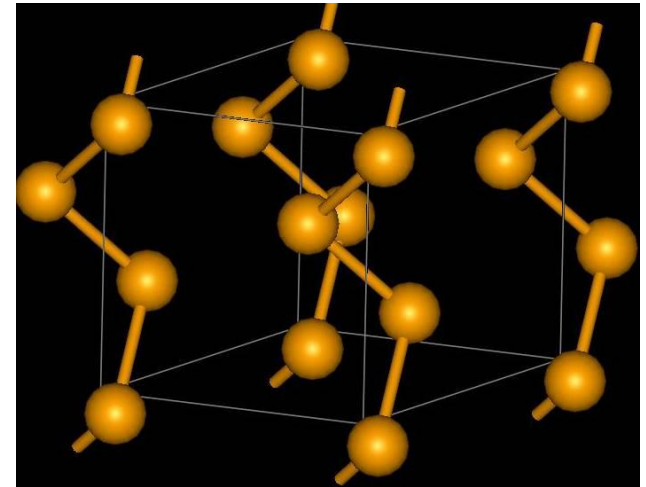
e.g. gray selenium **HELICAL CHAINS**



Chains form a 3-fold Helix down c



Chains along c (shading indicates depth)



- this allotrope of Se is an excellent photoconductor

ALLOTROPY

A *polymorph* is a distinct crystalline form of a substance (e.g., *zinc blende* & *wurtzite*). Polymorphs of elements are known as *allotropes*.

Group 16 elements (chalcogenides)

Yellow sulfur – S_8 rings
Monoclinic sulfur - chains
Plastic sulfur – infinite chains

Carbon

diamond
graphite
fullerenes

Tin

Grey tin (alpha)
White tin (beta)
Rhombic tin (gamma)

Group 15 elements (P, As, Sb)

White phosphorous – P_4 tetrahedra
Red phosphorous - polymeric
Black phosphorous - layered
Scarlet phosphorous
Violet phosphorous

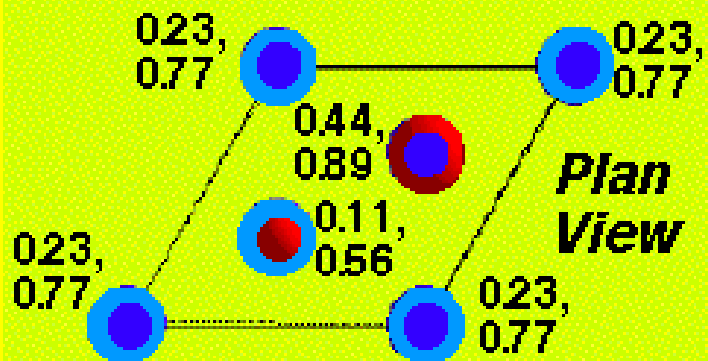
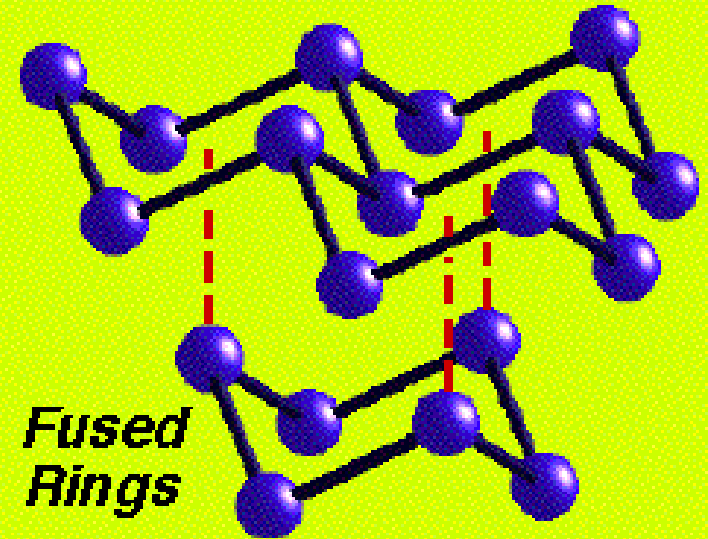
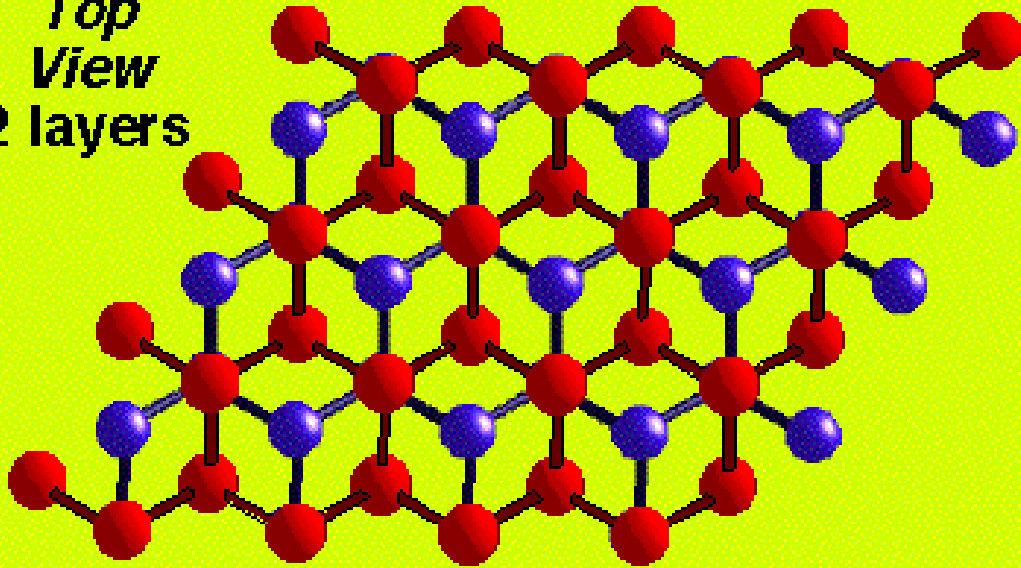


$$P = 3$$

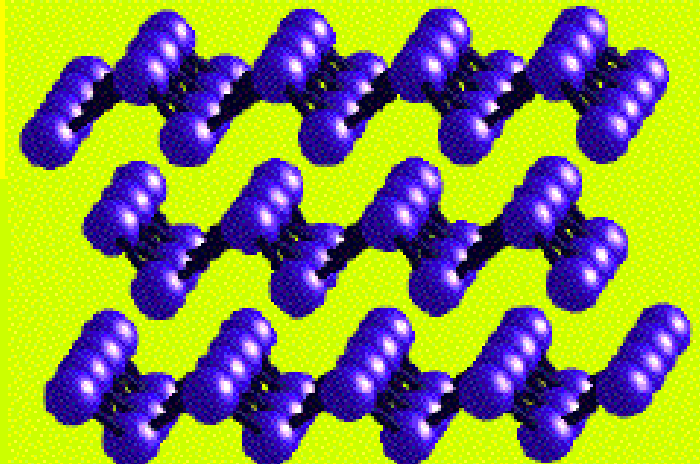
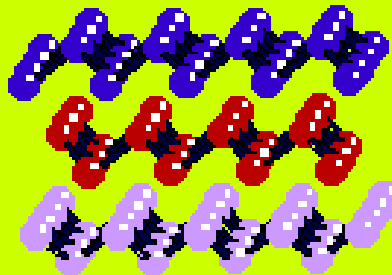
e.g. gray As, Bi *LAYERS*

Interlinked 6-membered rings

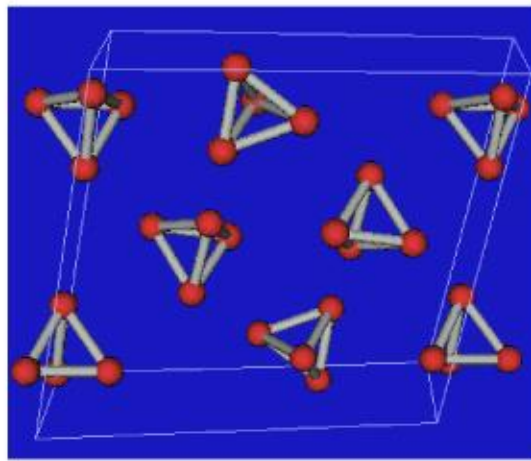
Top View
2 layers



Side View



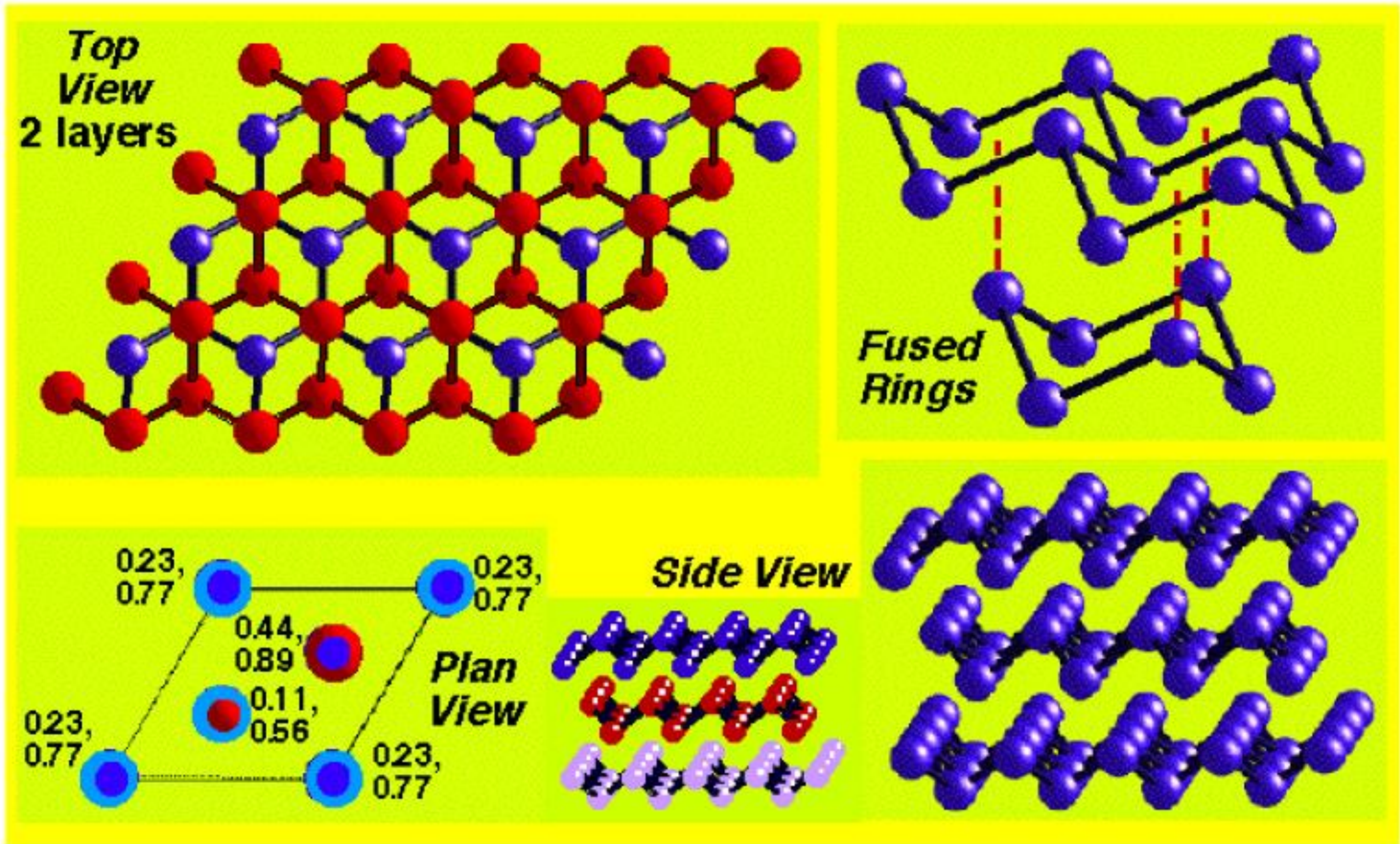
P, white



$$8 - N = 3$$



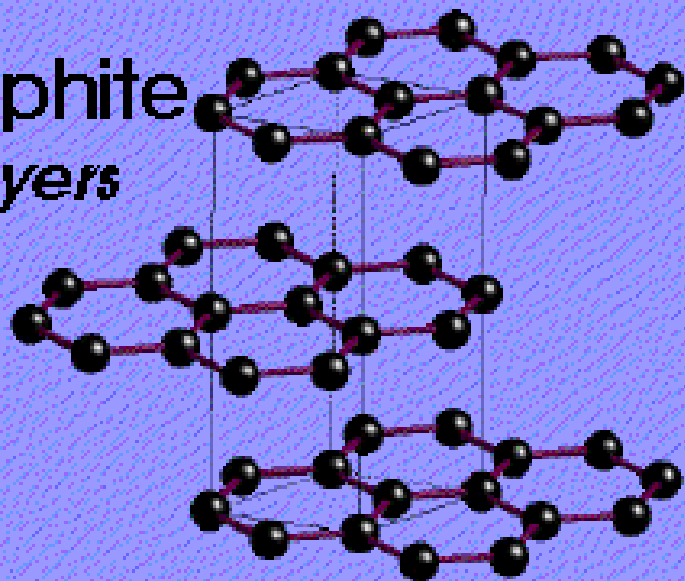
As, gray



$$P = 3$$

e.g. sp^2 carbon *LAYERS* and *CAGES*

Graphite
Layers



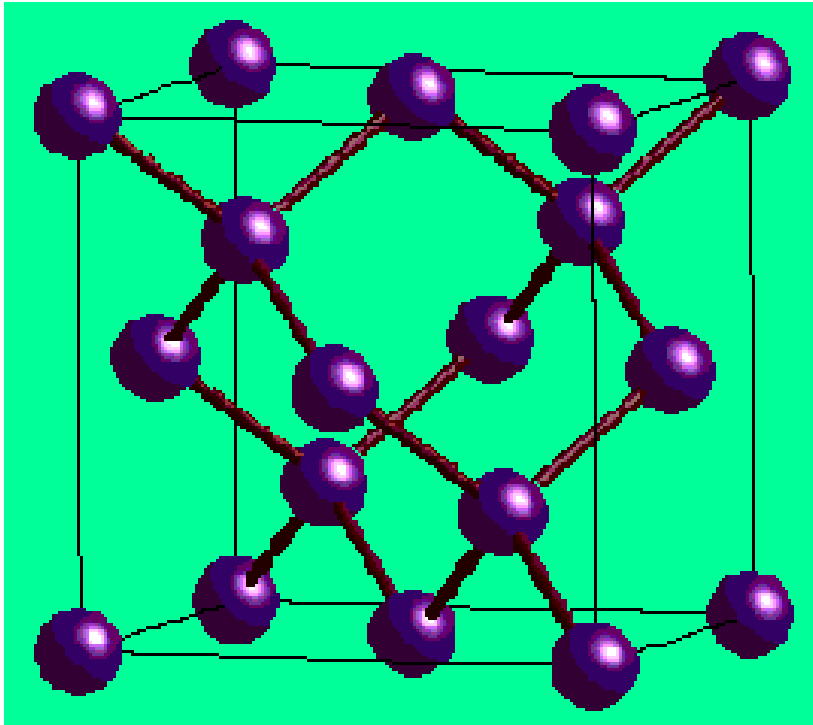
C_{60}

Cages

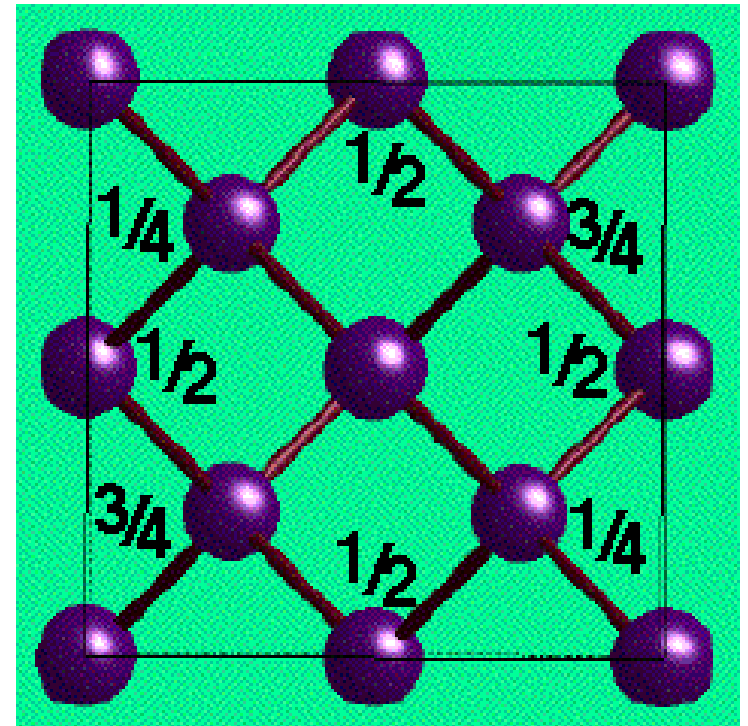


$$P = 4$$

e.g. sp^3 carbon *DIAMOND FRAMEWORK*

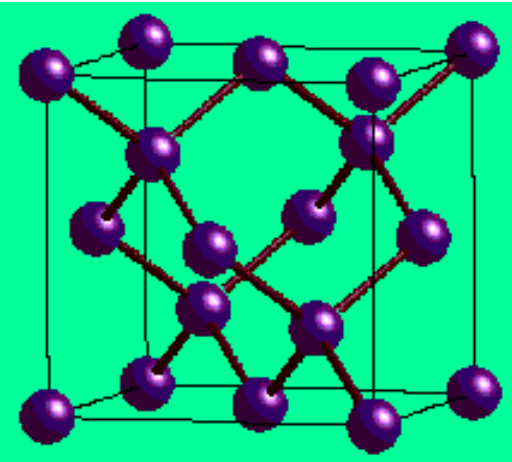


Unit
Cell



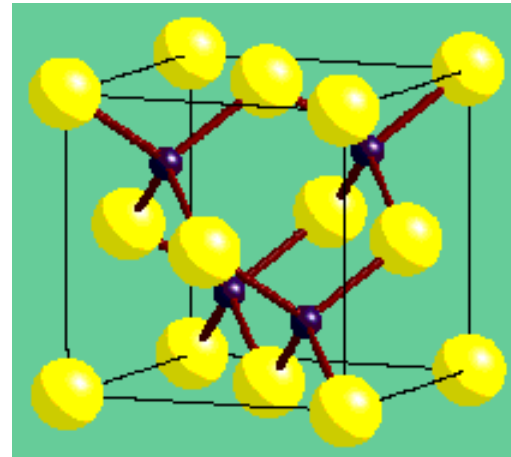
P = 4 Networks

Structures with the *Diamond FRAMEWORK*



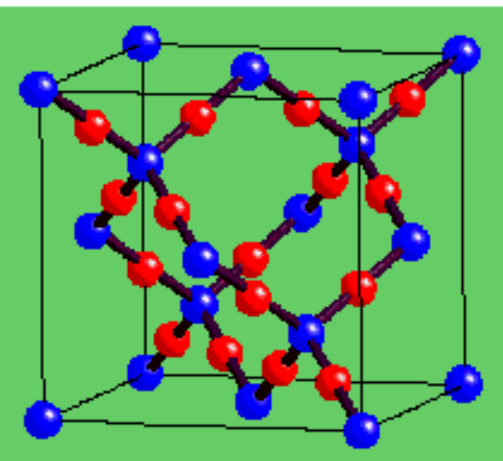
Diamond

The diamond network with a single atom type



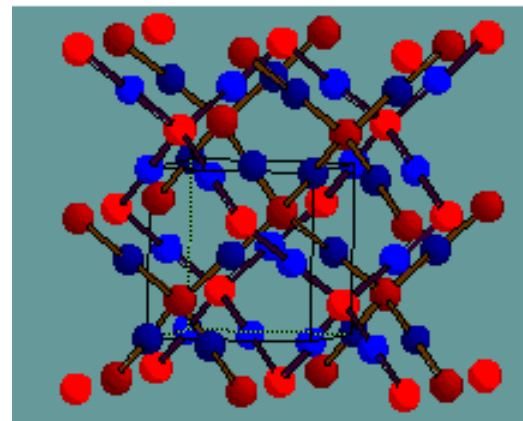
Zinc Blende ZnS

The diamond network with alternate Zn & S atoms



Cristobalite

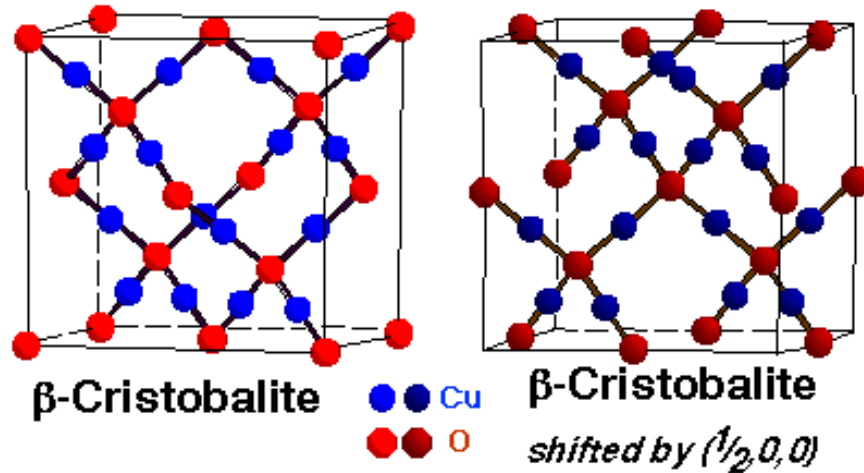
SiO₂
A diamond network of Si atoms with O inserted within each network linkage



Cuprite Cu₂O

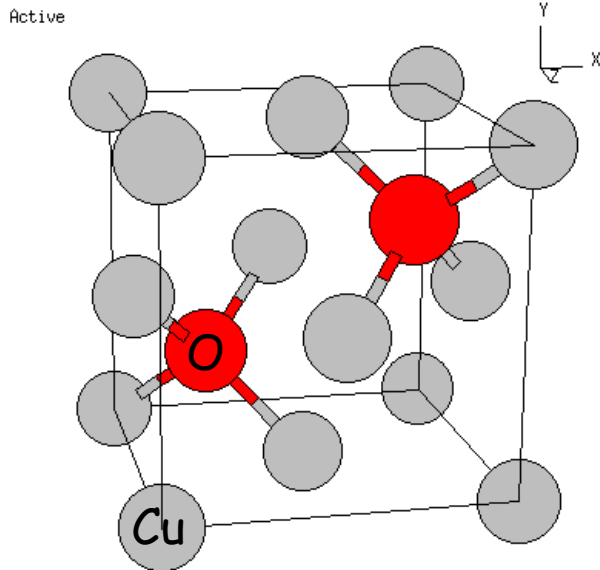
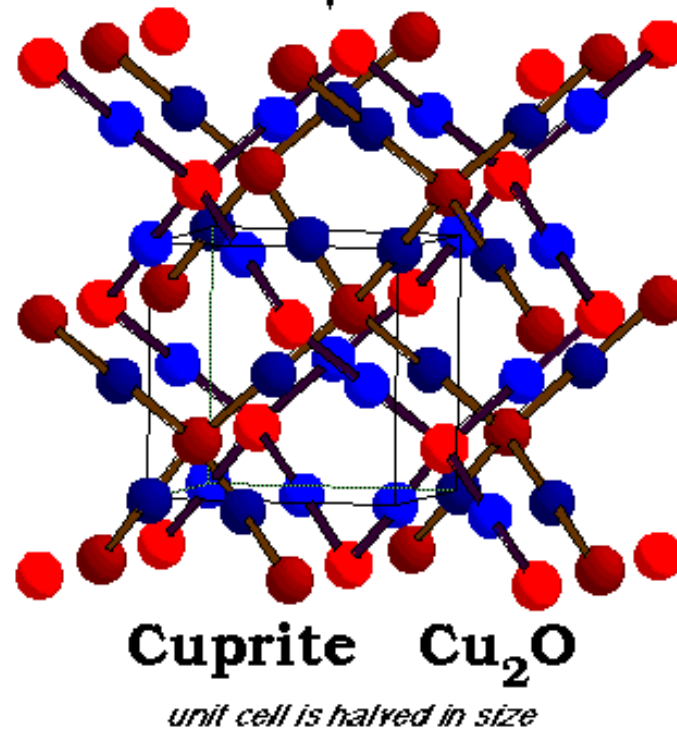
2 interleaved Cristobalite-type networks, with no direct links between them

Cristobalite: a high-temperature polymorph of quartz



interpenetration

cuprite: a cubic semiconductor
 $CN_{Cu} : 2$ $CN_O : 4$



SILICATE MINERALS

Networks of corner-sharing tetrahedral SiO_4^{4-} Units

Chemical formula hints at network structure:

- terminal oxygens count as 1
- bridging oxygens count as 1/2

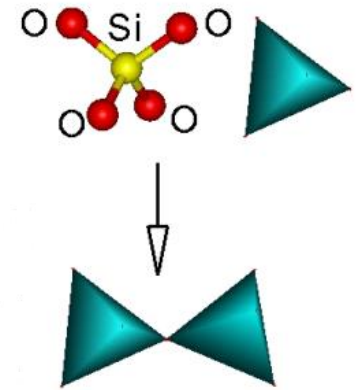


Table 7.15 Relation between chemical formula and silicate anion structure.

Si:O ratio‡	Number of oxygens per Si		Type of silicate anion	Examples
	bridging	non-bridging		
1:4	0	4	isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	dimer $\text{Si}_2\text{O}_7^{6-}$	$\text{Ca}_3\text{Si}_2\text{O}_7$ rankinite, $\text{Sc}_2\text{Si}_2\text{O}_7$ thortveite
1:3	2	2	chains $(\text{SiO}_3)_n^{2n-}$	Na_2SiO_3 , MgSiO_3 pyroxene
			rings, eg $\text{Si}_3\text{O}_9^{6-}$	CaSiO_3^* , $\text{BaTiSi}_3\text{O}_9$ benitoite
			$\text{Si}_6\text{O}_{18}^{12-}$	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ beryl
1:2.5	3	1	infinite sheets $(\text{Si}_2\text{O}_5)_n^{2n-}$	$\text{Na}_2\text{Si}_2\text{O}_5$
1:2	4	0	3D framework	SiO_2^\dagger

* CaSiO_3 is dimorphic. One polymorph has $\text{Si}_3\text{O}_9^{6-}$ rings. The other polymorph has infinite $(\text{SiO}_3)_n^{2n-}$ chains.

† The three main polymorphs of silica, quartz, tridymite and cristobalite each have a different kind of 3D framework structure.

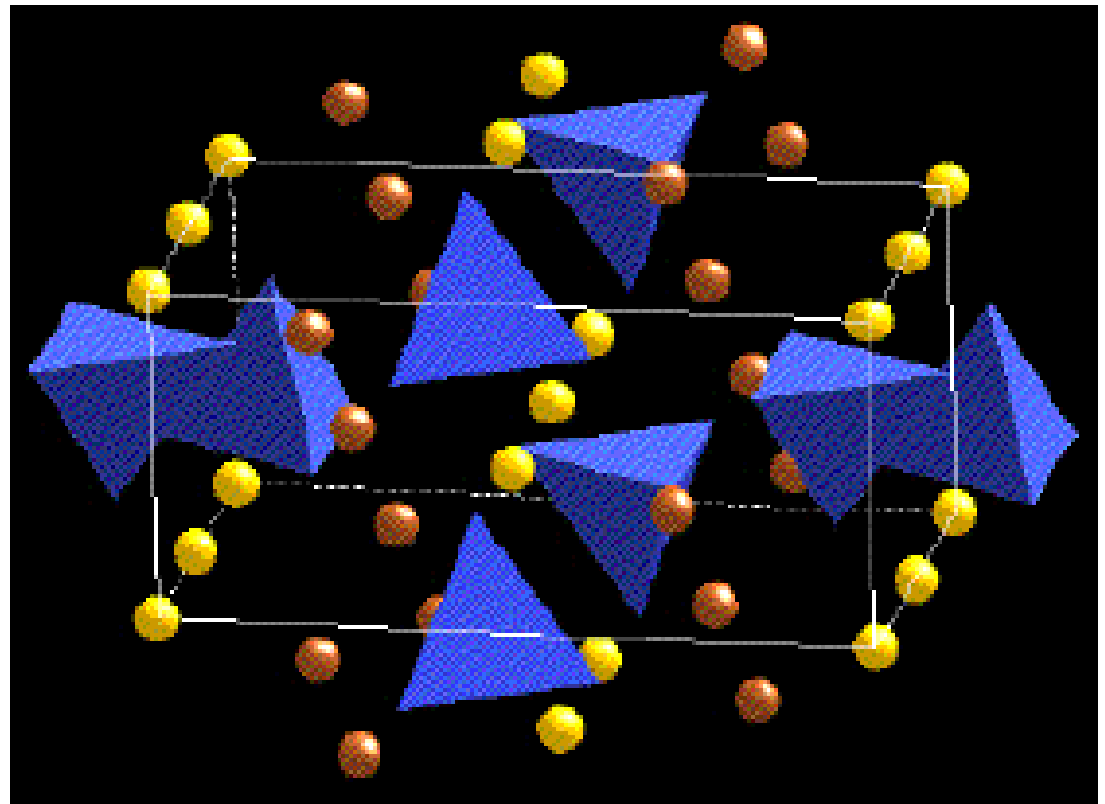
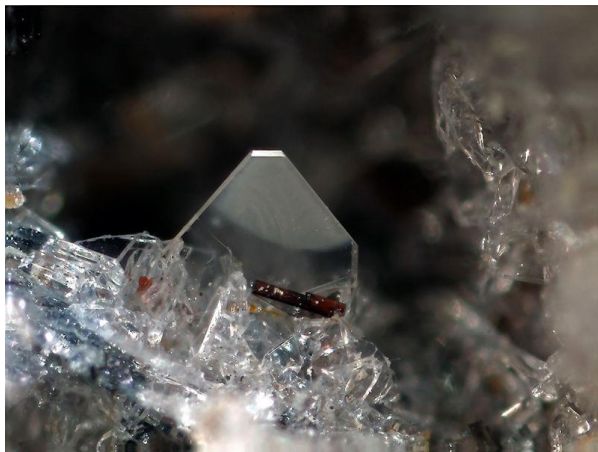
‡ In some structures, as in sphene, CaTiSiO_5 and Ca_3SiO_5 , the Si:O ratio is less than 1:4; these contain SiO_4^{4-} tetrahedra together with extra oxygens entirely unconnected to any silicon.

Si:O = 1:4

P = 0, *Orthosilicate*, SiO_4^{4-}

e.g. Mg_2SiO_4 *Forsterite*

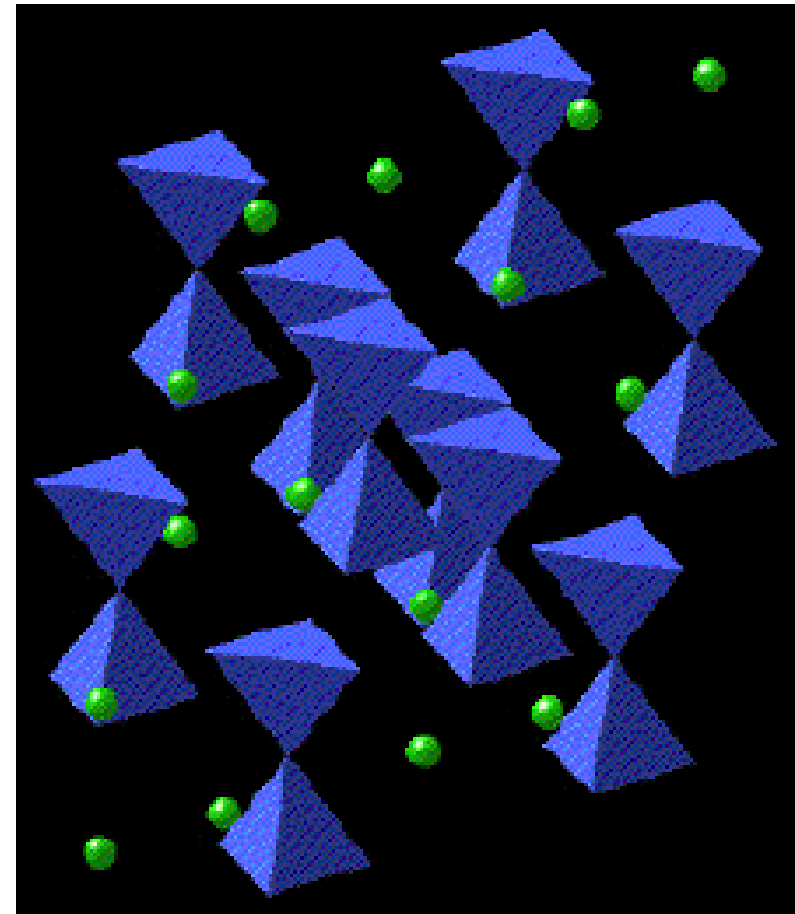
Most abundant mineral in upper mantle



isolated tetrahedra

Si:O = 1:3.5
P = 1, *Pyrosilicate*, $\text{Si}_2\text{O}_7^{6-}$

e.g. $\text{Sc}_2\text{Si}_2\text{O}_7$ Thortveite

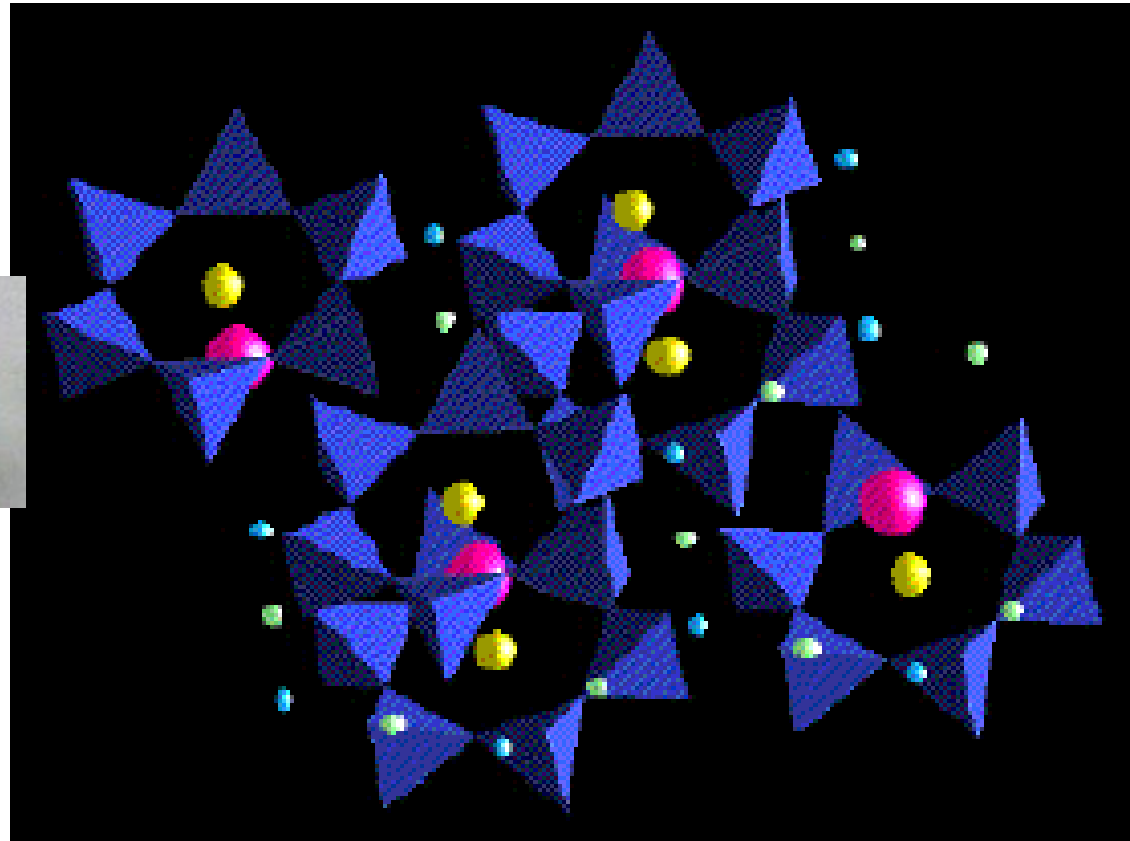


dimers

Si:O = 1:3

P = 2 Rings, $\text{Si}_6\text{O}_{18}^{12-}$

e.g. $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ *Beryl* (the minerals *emerald* [Cr^{2+}], *aquamarine* [Fe^{2+}])

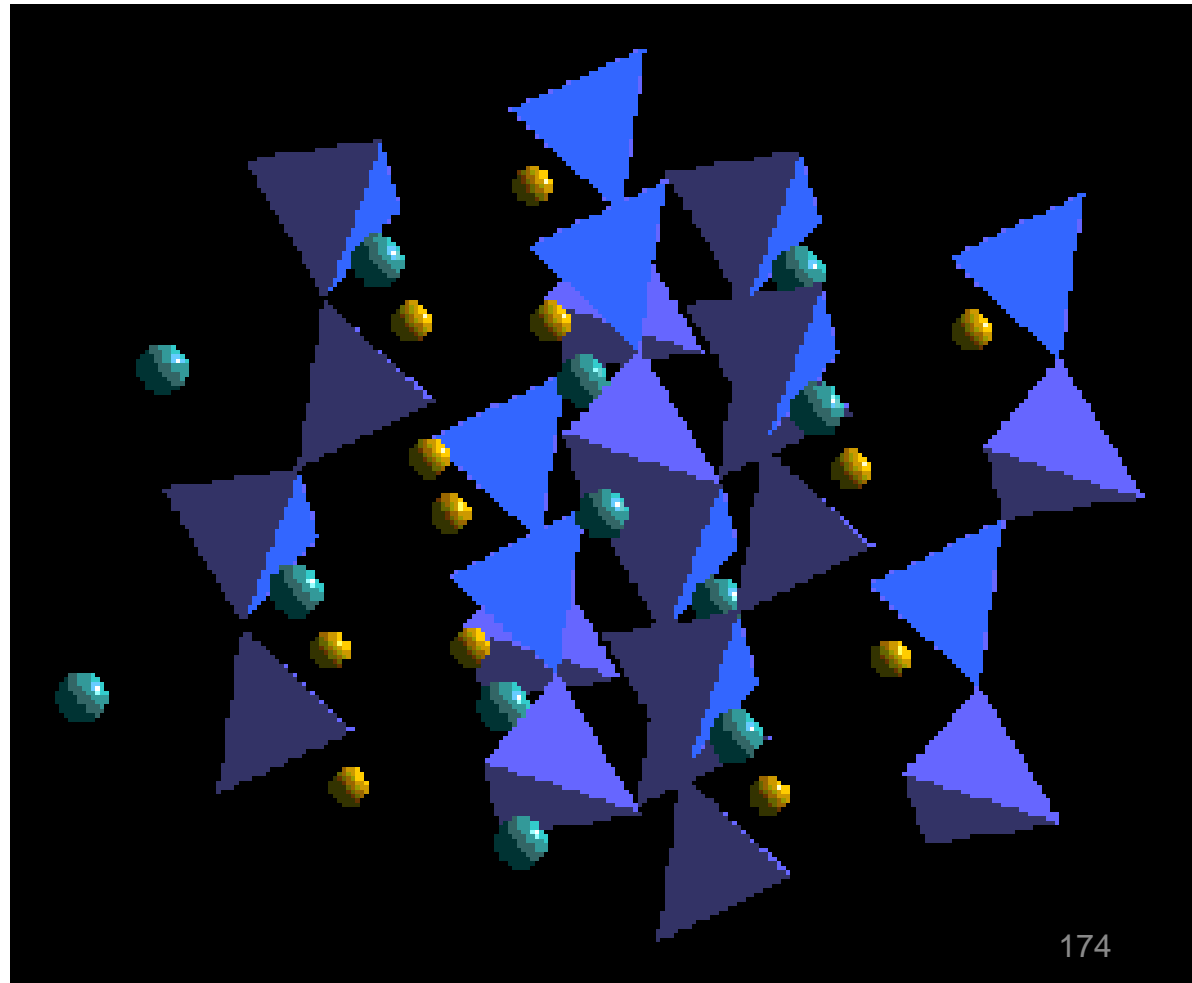
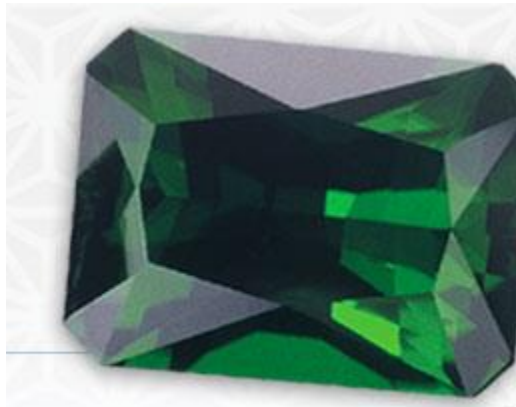


Hexagonal rings - a cyclosilicate

Si:O = 1:3

P = 2 Chains, Pyroxene, $[(\text{SiO}_3)^{2n-}]_n$

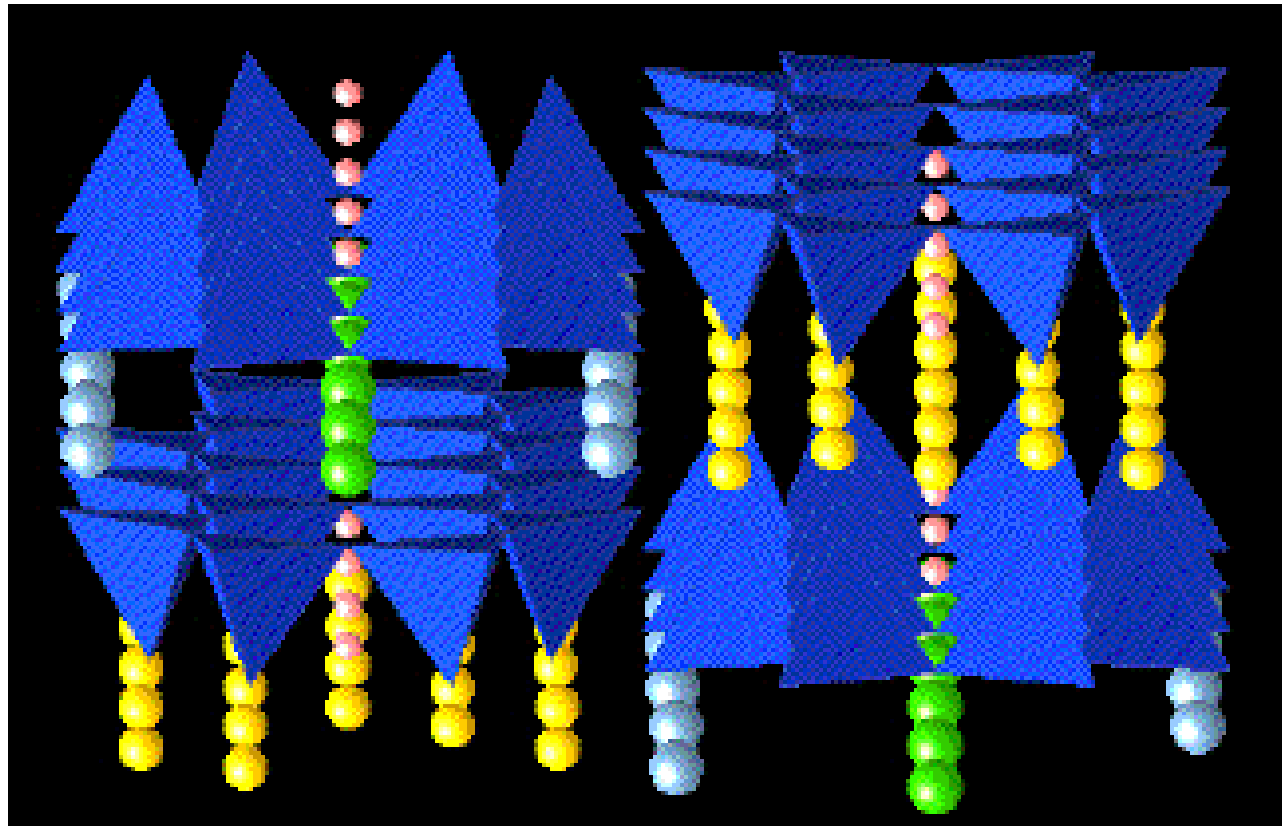
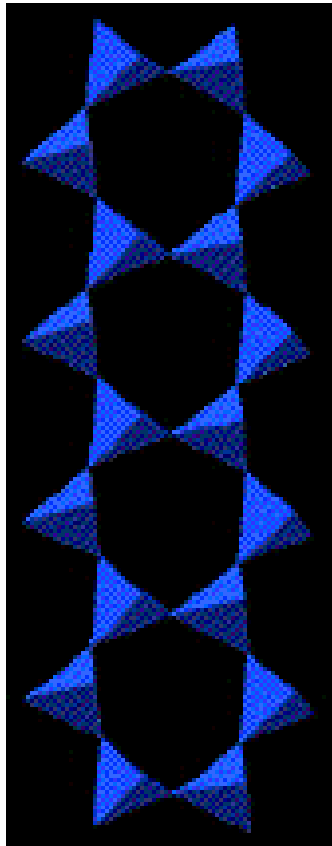
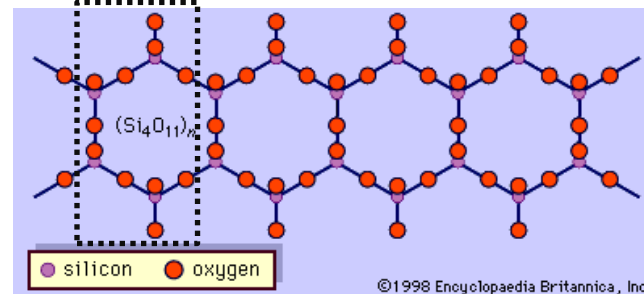
e.g. $\text{CaMgSi}_2\text{O}_6$ Diopside





$P = 2 \text{ \& } 3$, Chain of Rings, *Amphibole*, $[(\text{Si}_4\text{O}_{11})^{6n-}]_n$

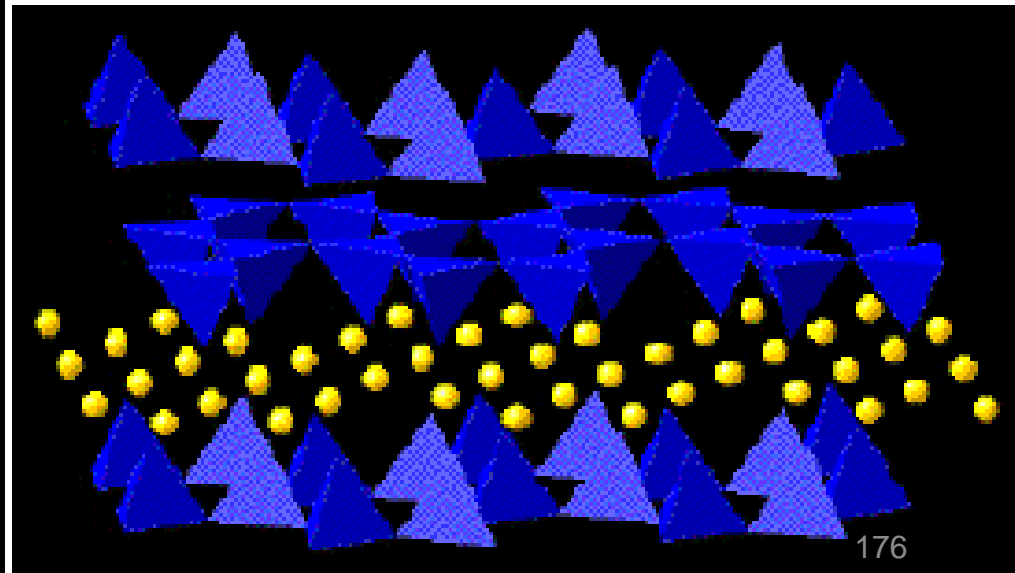
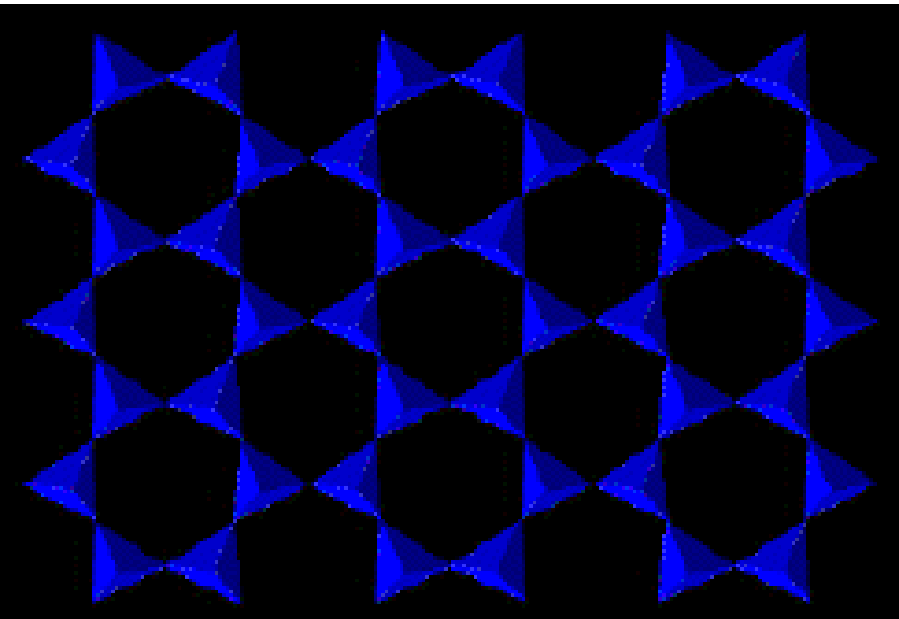
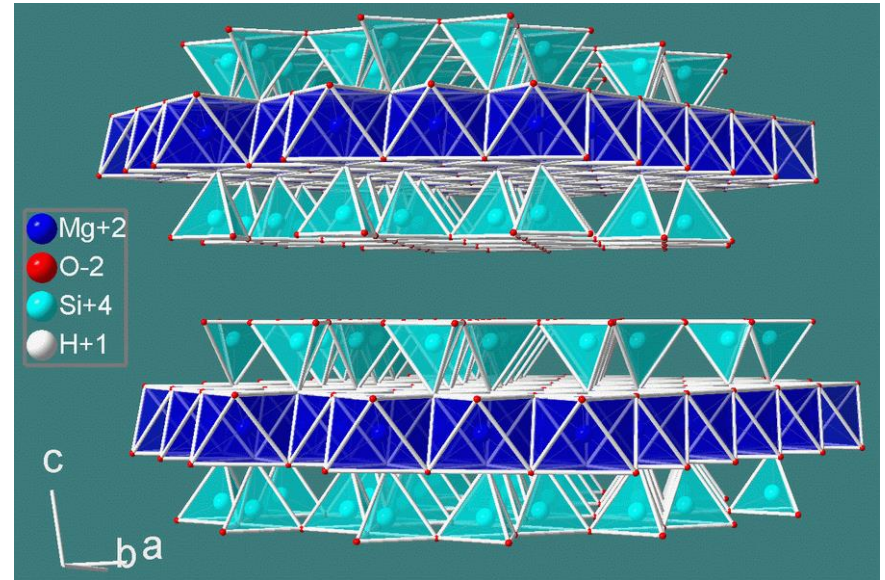
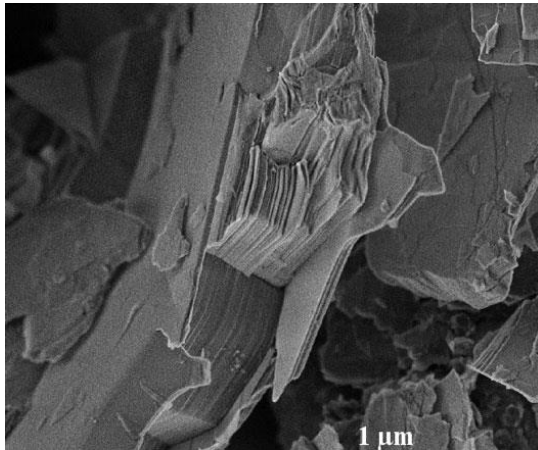
e.g. $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Tremolite



$\text{Si}:\text{O} = 1:2.5$

$P = 3$, Layers, $[(\text{Si}_2\text{O}_5)^{2n-}]_n$

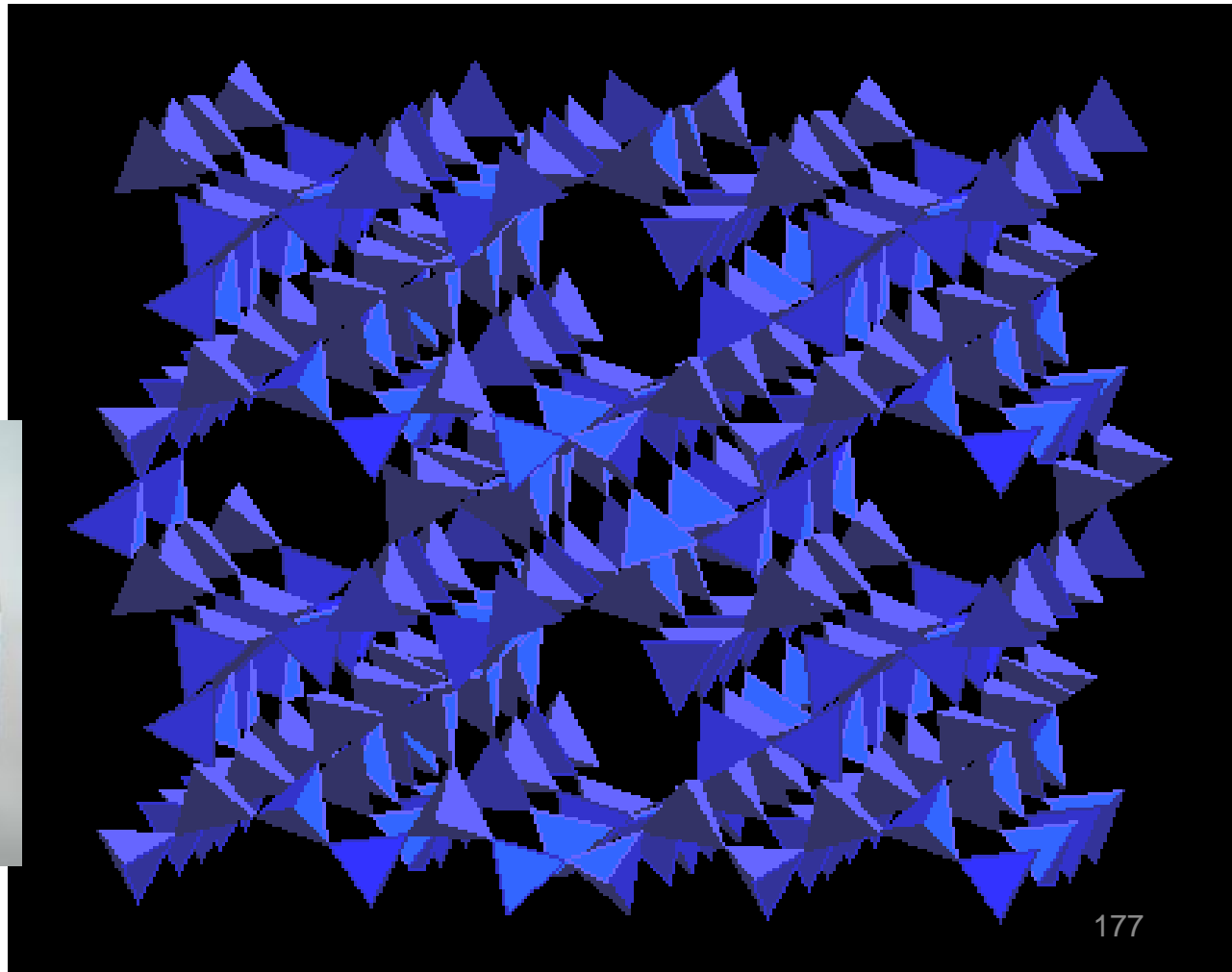
e.g. $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ *Talc*



Si:O = 1:2
P = 4, Tectosilicate, SiO₂

e.g. Mⁿ⁺_{x/n}[(AlO₂)_x(SiO₂)_y].mH₂O Zeolite ZSM-5

Full 3D framework



Reading:
West Ch. 3

SOME REASONS WHY CRYSTALS ADOPT THE STRUCTURES THEY DO

- Atom size
- Type of bonding
- Electron configuration

THE IONIC MODEL OF SOLIDS

The ionic theory of solids (1920s, due to Goldschmidt) considers ions as charged, incompressible, and non-polarizable spheres

Purely ionic bonding is an idealized form of bonding never attained in practice. There is always some covalent character.

Ionic theory is a useful **starting point** for describing solids that in reality have some amount of covalent bonding.



Victor Goldschmidt

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
→ ions have no clearly defined radius and can readily change size (elasticity) and shape (polarizability)

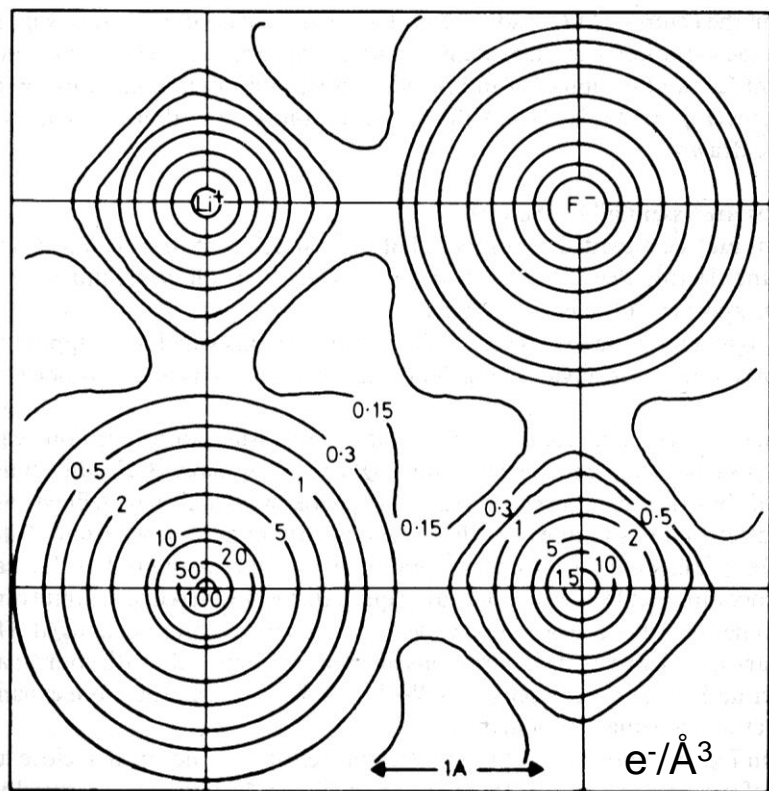
Pauling's Rules:

Goldschmidt's structural principles for ionic crystals were summarized by Linus Pauling in a set of 5 Rules.

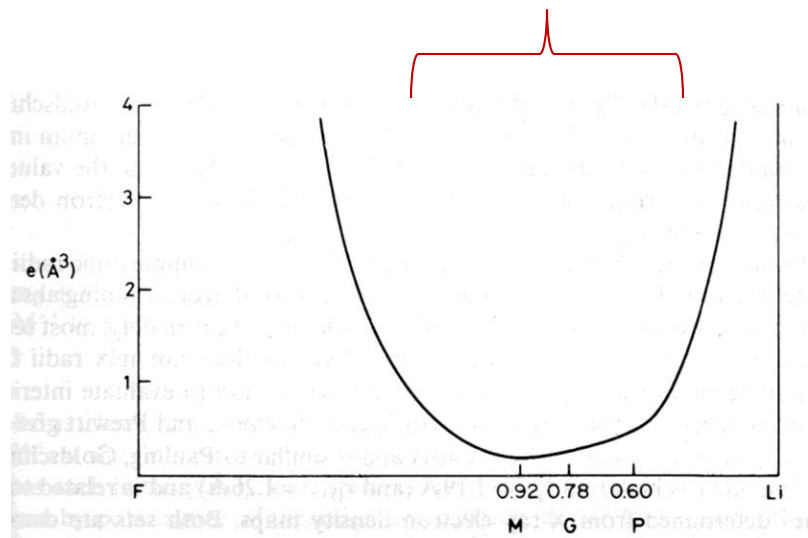
IONIC RADII ARE AMBIGUOUS

Non-polar covalent atomic radii are easily measured, but ionic radii are not.

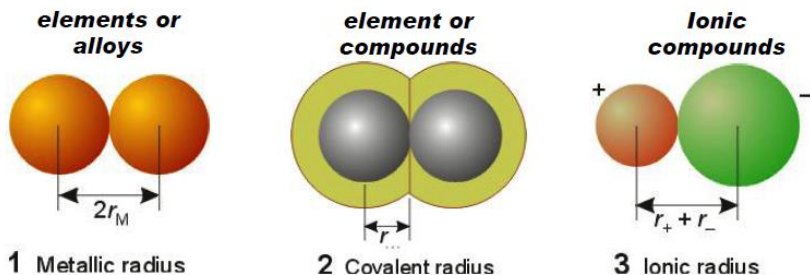
Electron density contour map of LiF (100) from XRD



Broad minimum in density!
Where does Li⁺ end & F⁻ begin?

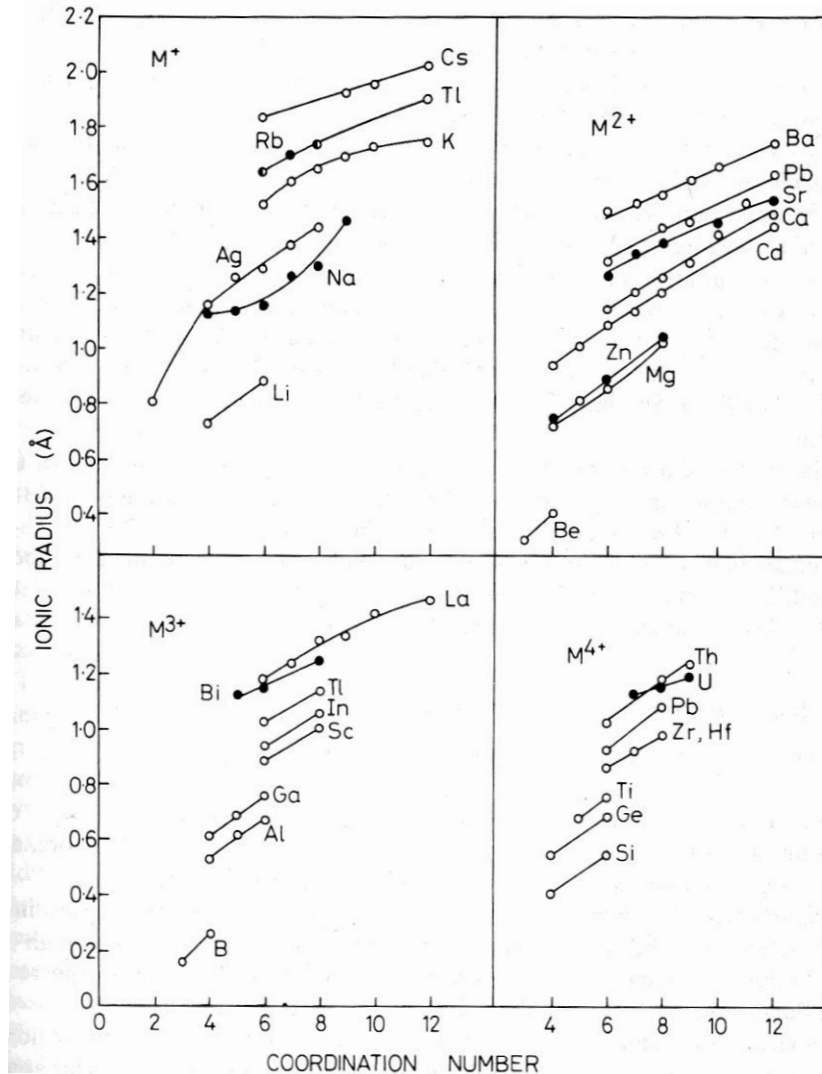


Electron density along Li-F internuclear axis



IONIC RADII ARE VARIABLE

Ions can expand or contract within certain limits (elasticity). Their size varies with coordination number.



Values according to the set of radii by Shannon and Prewitt (1969), referenced to $r_{F^-} = 1.19 \text{ \AA}$ and $r_{O^{2-}} = 1.26 \text{ \AA}$

Shannon-Prewitt radii are:

- additive
- self-consistent

RADII TRENDS

TABLE 2.12 Atomic Radii ($pm = 10^{-12} m$)^a

																		r_{ion} r_{cov} r_{met}				
1 H — —																	2 He (178) — —					
3 Li 76 — 152	4 Be 45 106 115													5 B — 88 98	6 C(d) 16 77 92	7 N 13 70 —	8 O 140 66 —	9 F 133 64 —	10 Ne (158) — —			
11 Na 102 — 186	12 Mg 72 140 160	$Si^{4+} < Al^{3+} < Mg^{2+} < Na^{+}$												13 Al 54 126 143	14 Si 40 118 132	15 P 38 110 —	16 S 184 104 —	17 Cl 181 99 —	18 Ar (188) — —			
19 K 138 — 230	20 Ca 100 — 198	21 Sc 75 — 165	22 Ti 86 — 147	23 V 79 — 131	24 Cr 73 — 125	25 Mn 83 — 136	26 Fe 55 — 124	27 Co 65 — 125	28 Ni 69 — 124	29 Cu 77 135 128	30 Zn 131 131 133	31 Ga 62 126 141	32 Ge 53 123 137	33 As 58 118 —	34 Se 198 114 —	35 Br 196 111 —	36 Kr (205) — —					
37 Rb 152 — 247	38 Sr 118 — 215	39 Y 90 — 183	40 Zr 72 — 162	41 Nb 72 — 143	42 Mo 69 — 136	43 Tc 65 — 137	44 Ru 68 — 135	45 Rh 67 — 134	46 Pd 86 — 138	47 Ag 115 152 145	48 Cd 95 148 149	49 In 80 144 166	50 Sn 69 140 162	51 Sb 76 136 169	52 Te 221 132 —	53 I 220 128 —	54 Xe (225) — —					
55 Cs 167 — 266	56 Ba 135 — 217	57 La 103 — 188	72 Hf 71 — 159	73 Ta 72 — 143	74 W 60 — 137	75 Re 63 — 138	76 Os 63 — 136	77 Ir 68 — 136	78 Pt 80 — 139	79 Au 137 — 144	80 Hg 119 148 150	81 Tl 89 147 173	82 Pb 119 146 175	83 Bi 103 145 170	84 Po 97 — 168	85 At — — —	86 Rd — — —					
87 Fr — — 280	88 Ra — — 247	89 Ac 112 — 188																				
			58 Ce 101 — 184	59 Pr 99 — 183	60 Nd 98 — 183	61 Pm 97 — 182	62 Sm 96 — 183	63 Eu 95 — 198	64 Gd 94 — 181	65 Tb 92 — 180	66 Dy 107 — 179	67 Ho — — 179	68 Er 89 — 178	69 Tm 88 — 177	70 Yb 99 — 194	71 Lu 86 — 175						
			90 Th 94 — 180	91 Pa 104 — 163	92 U 103 — 156	93 Np 101 — 156	94 Pu 100 — 164	95 Am 98 — 173	96 Cm 97 — 175	97 Bk 96 — 171	98 Cf 95 — 170	99 Es — — —	100 Fm — — —	101 Md — — —	102 No — — —	103 Lr — — —						

$Li^{+} < Na^{+}$
 $< K^{+} < Rb^{+}$

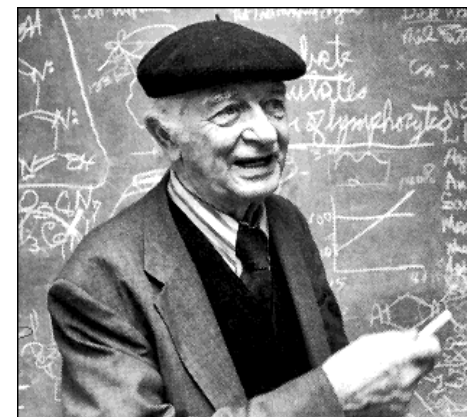
Ionic radii (r_{ion}) given for octahedral coordination

IONIC RADII TRENDS

- 1. Ionic radii increase on going 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 its CN the bigger the ions seems to be !!)**
- 4. The ionic radius of a given atom decreases with increasing charge ($r(\text{Fe}^{2+}) > r(\text{Fe}^{3+})$)**
- 5. Cations are usually the smaller ions in a cation/anion combination (exceptions: $r(\text{Cs}^+) > r(\text{F}^-)$...!!!)**
- 6. Frequently used for rationalization of structures:
“radius ratio” $r(\text{cation})/r(\text{anion}) (< 1)$**

PAULING'S FIVE RULES for IONIC CRYSTALS

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



Linus Pauling

[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, $\text{Al}_2\text{SiO}_4\text{-F}_2$, 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

SIZE MATTERS, VALENCY NOT SO MUCH

Molecules and Molecular Materials

- Absolute coordination numbers are controlled by valency (VSEPR)

Non-Molecular Materials

- Valency has only an indirect bearing on coordination number

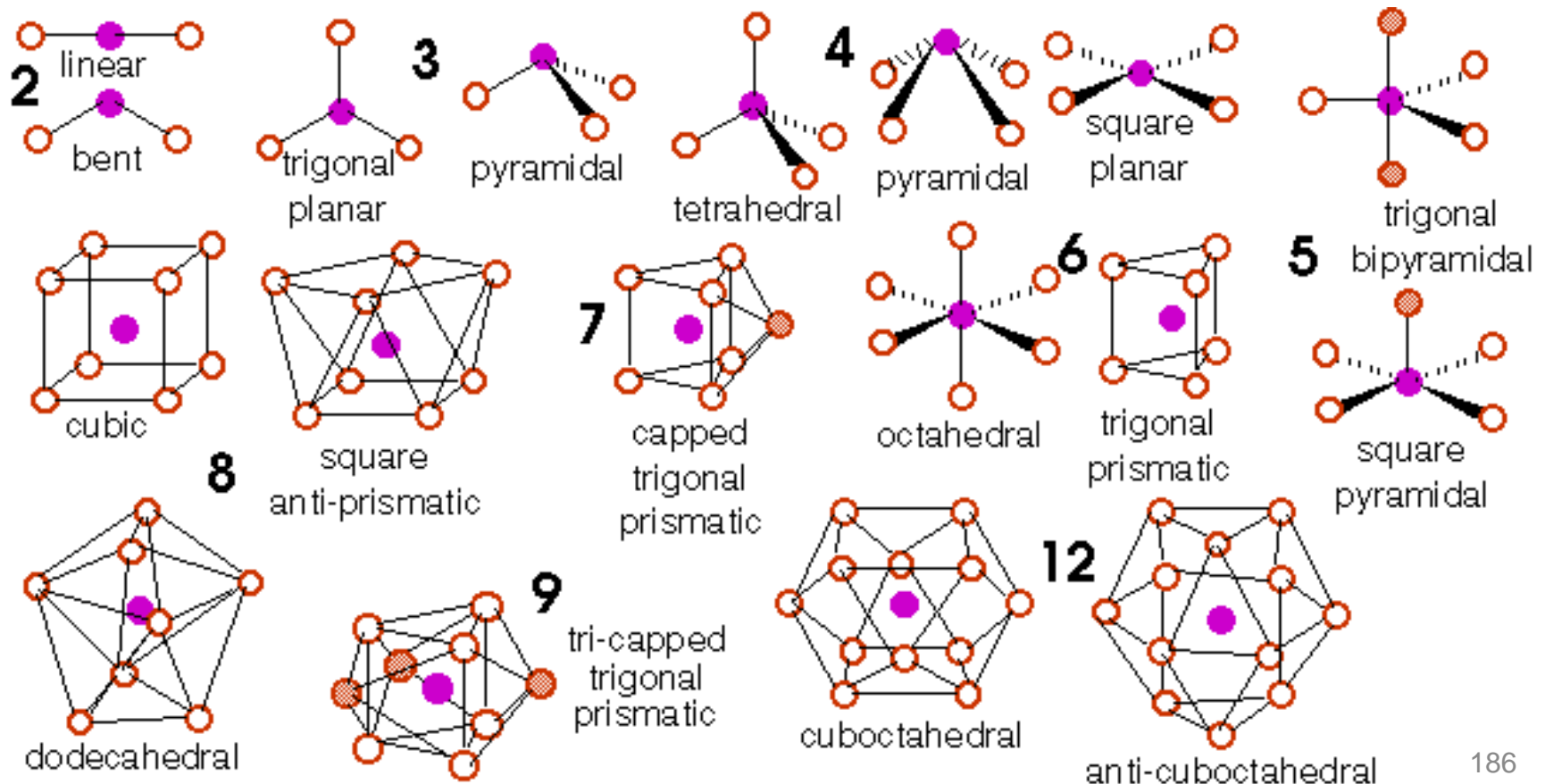
e.g., $\text{Na}^{\text{I}}\text{Cl}$, $\text{Mg}^{\text{II}}\text{O}$, $\text{Sc}^{\text{III}}\text{N}$, $\text{Ti}^{\text{IV}}\text{C}$ are all rock salt (6:6) despite the change in valency and trend from predominantly ionic to covalent bonding

- Ionic Size *does* influence coordination number

PAULING RULE #1: *Coordination Polyhedra*

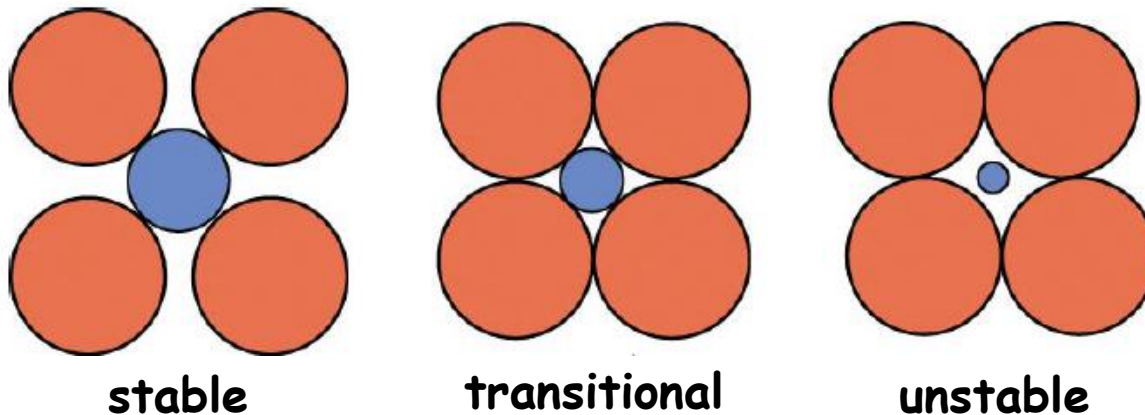
"A coordination polyhedron of anions is formed around every cation (and vice-versa) - it will only be stable if the cation is *in contact* with each of its neighbors."

- Ionic crystals may thus be considered as sets of linked polyhedra
- The cation-anion distance is determined by the radius sum
- The coordination number of the cation is determined by the radius ratio



PAULING RULE #1

In order to maximize the net electrostatic attraction between ions in a structure, 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**


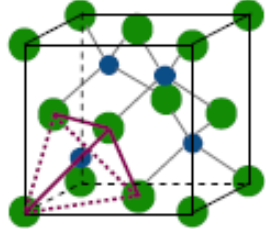

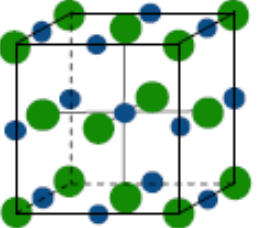


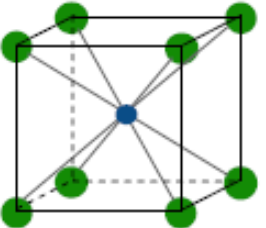
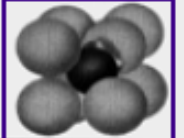
Radius Ratio Rules

The Radius Ratio Rules are correct **ONLY 1/2** of the time!

RADIUS RATIO RULES

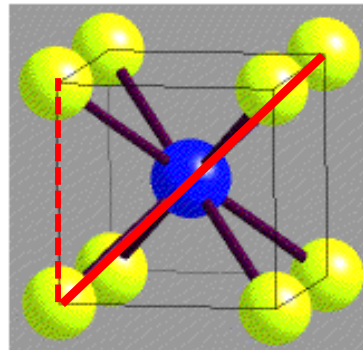
Coordination number increases with r^+/r^-

How many anions (bigger) can be arranged around a cation (smaller)?

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord #				
< 0.155	2	linear			ZnS (zincblende)
$0.155 - 0.225$	3	triangular			NaCl (sodium chloride)
$0.225 - 0.414$	4	T_D			
$0.414 - 0.732$	6	O_H			CsCl (cesium chloride)
$0.732 - 1.000$	8	cubic			

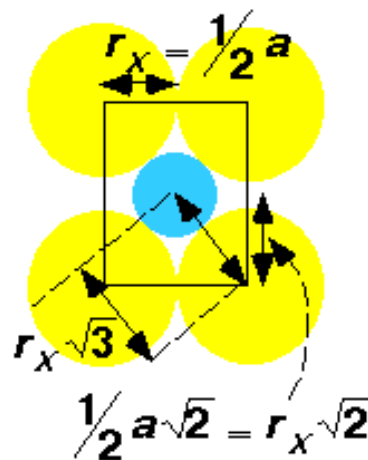
Limiting Radius Ratios

CsCl 8:8



unit cell

cell side a

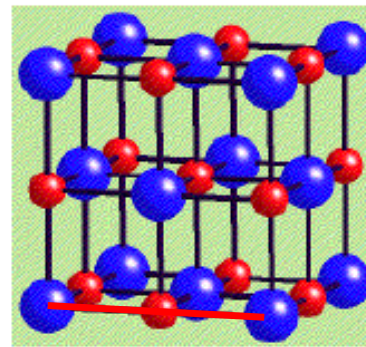


$$r_M + r_X = r_X \sqrt{3}$$

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

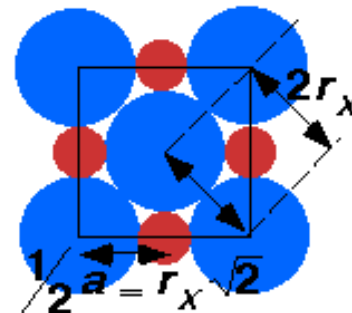
$$= 0.732$$

NaCl 6:6



unit cell

face diagonal $a\sqrt{2}$

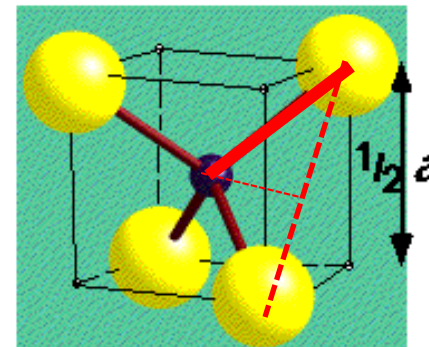


$$r_M + r_X = r_X \sqrt{2}$$

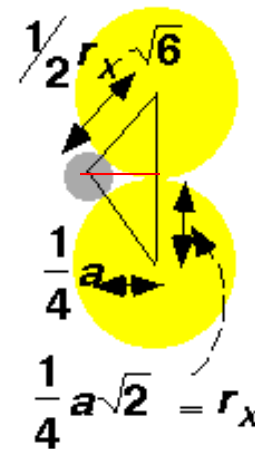
$$r_M / r_X = \sqrt{2} - 1$$

$$= 0.414$$

ZnS 4:4



1/8th unit cell



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

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

$$= 0.225$$

**Red lines =
ions in
contact**

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

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**

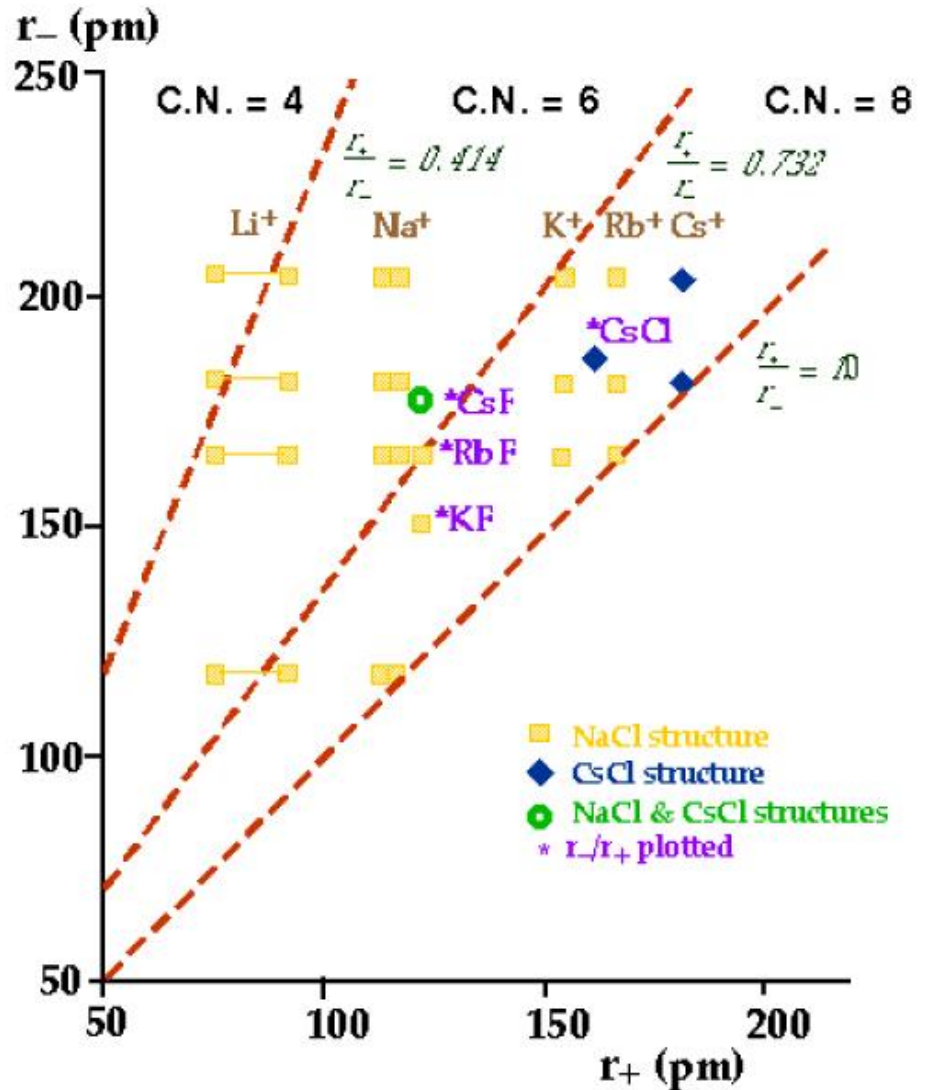
Better results with MX_2 structures!

SiO_2 : 0.32 : CN = 4

TiO_2 : 0.59 : CN = 6

CeO_2 : 0.88 : CN = 8

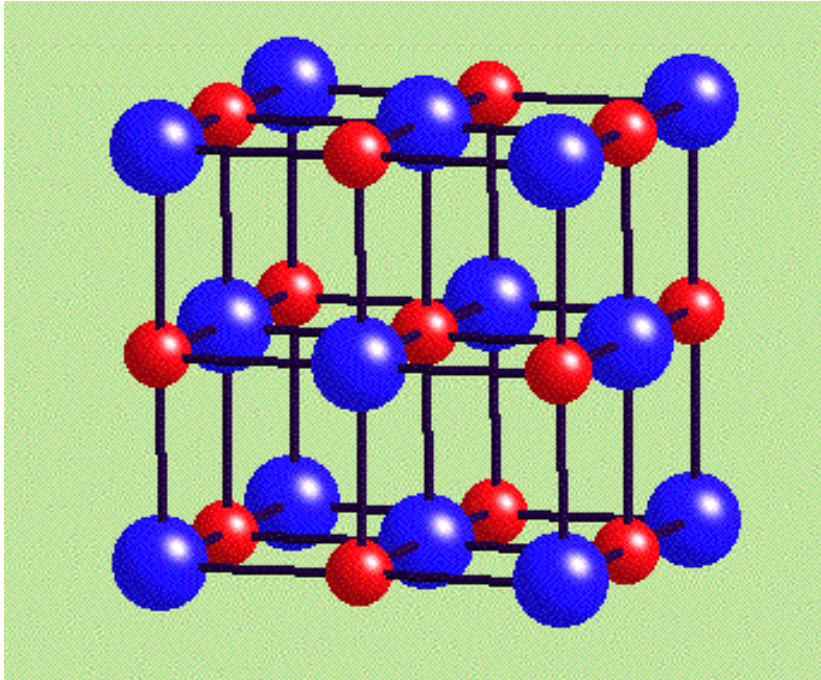
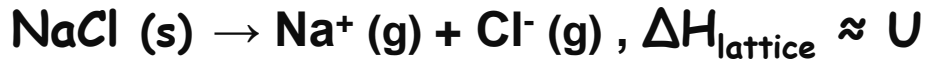
Test with alkali halides



LATTICE ENERGY

Ionic structures are held together by electrostatic forces and, therefore, are arranged so that cations are surrounded by anions, and vice versa

Lattice Energy (U) = energy required to sublime the crystal and convert it into a collection of gaseous ions.



$$U_{\text{NaCl}} = 778 \text{ kJ/mol}$$

Electrostatic potential energy (attraction & repulsion):

$$V = -\frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r}$$

Short-range Pauli repulsion:

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

B: Born constant

n: Born exponent (n = 5-12)

REPULSIVE TERM

The value of the Born-Landé exponent is dependent upon the electronic configuration of the closed shell ions.



Born

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

e.g. Na⁺Cl⁻ = [Ne][Ar]

$$\rightarrow n = (7+9)/2 = 8$$

The more compressible the ion, the larger its Born exponent

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:

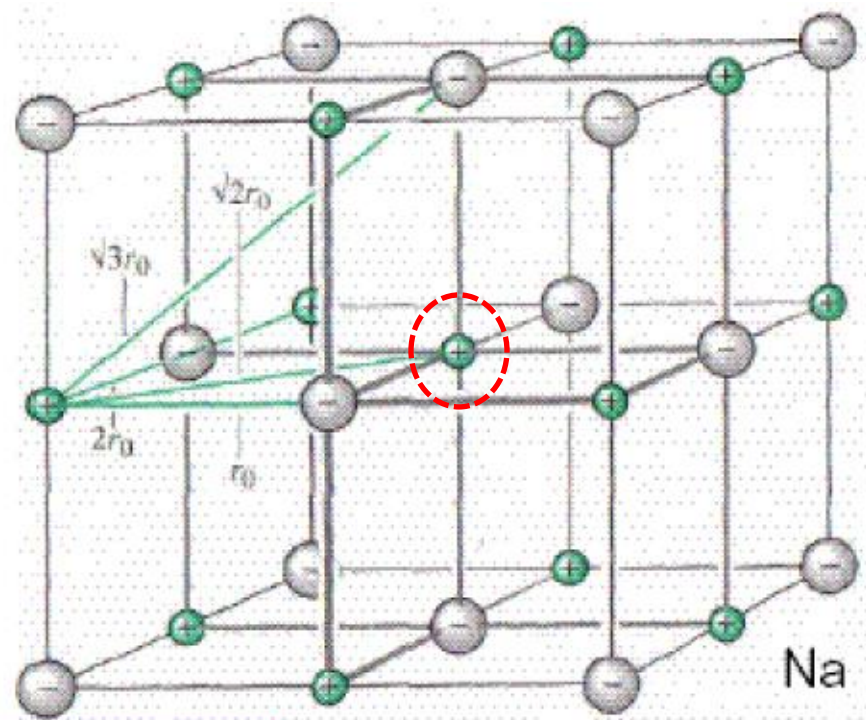
12 Na⁺ at distance $\sqrt{2}r$.

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

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:

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

Net attractive electrostatic energy:

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

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

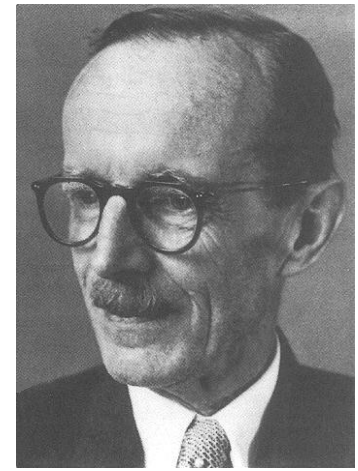
A: Madelung constant

MADELUNG CONSTANT

$$V = -\frac{Z_+ Z_- e^2}{4\pi\epsilon_0 r} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \right)$$

Madelung Constant (A):

The numerical value of the series summation



Madelung

- Depends only on the geometrical arrangements of ions (the crystal structure), not the lattice constant

Crystal structure	Madelung constant	Coordination
Rock salt	1.748	6 : 6
CsCl	1.763	8 : 8
Sphalerite	1.638	4 : 4
Fluorite	2.520	8 : 4
Rutile	2.408	6 : 3

BORN-LANDE EQUATION FOR U

U is the sum of Coulombic attraction and Pauli repulsion:

$$U = -\frac{Z_+ Z_- e^2 NA}{4\pi\epsilon_0 r} + \frac{BN}{r^n}$$

$$\frac{dU}{dr} = \frac{Z_+ Z_- e^2 NA}{4\pi\epsilon_0 r_e^2} - \frac{nBN}{r_e^{n+1}} = 0$$

$$B = \frac{Z_+ Z_- e^2 Ar_e^{n-1}}{4\pi\epsilon_0 n}$$

$$U = -\frac{Z_+ Z_- e^2 NA}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

This is the Born-Landé equation (1918)

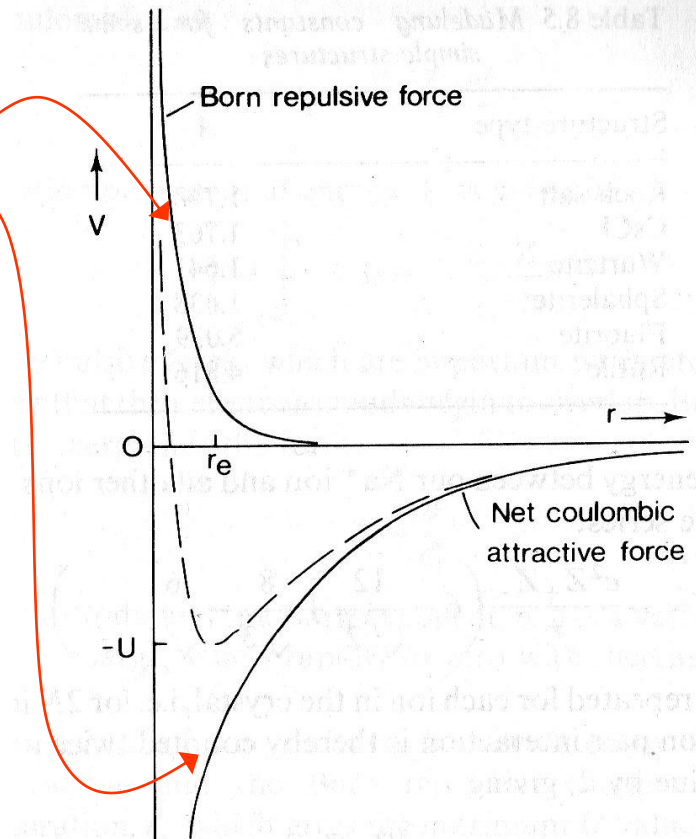


Fig. 8.5 Lattice energy (dashed line) of ionic crystals as a function of internuclear separation


SOME LATTICE ENERGIES

- for a given crystal structure, U depends most strongly on the charge on the ions
- the internuclear separation r_e has a smaller effect

Table 8.6 *Some lattice energies (kJ mol^{-1}).* (Data from Ladd and Lee, 1963)

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

increasing
lattice constant



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

KAPUSTINSKII'S EQUATION

Kapustinskii noted in 1956 that the Madelung constant, the internuclear distance and the empirical formula of simple ionic compounds are interrelated. He derived a formula that can be used to estimate the lattice energy of any hypothetical compound without knowing its structure (i.e., w/o the Madelung constant).

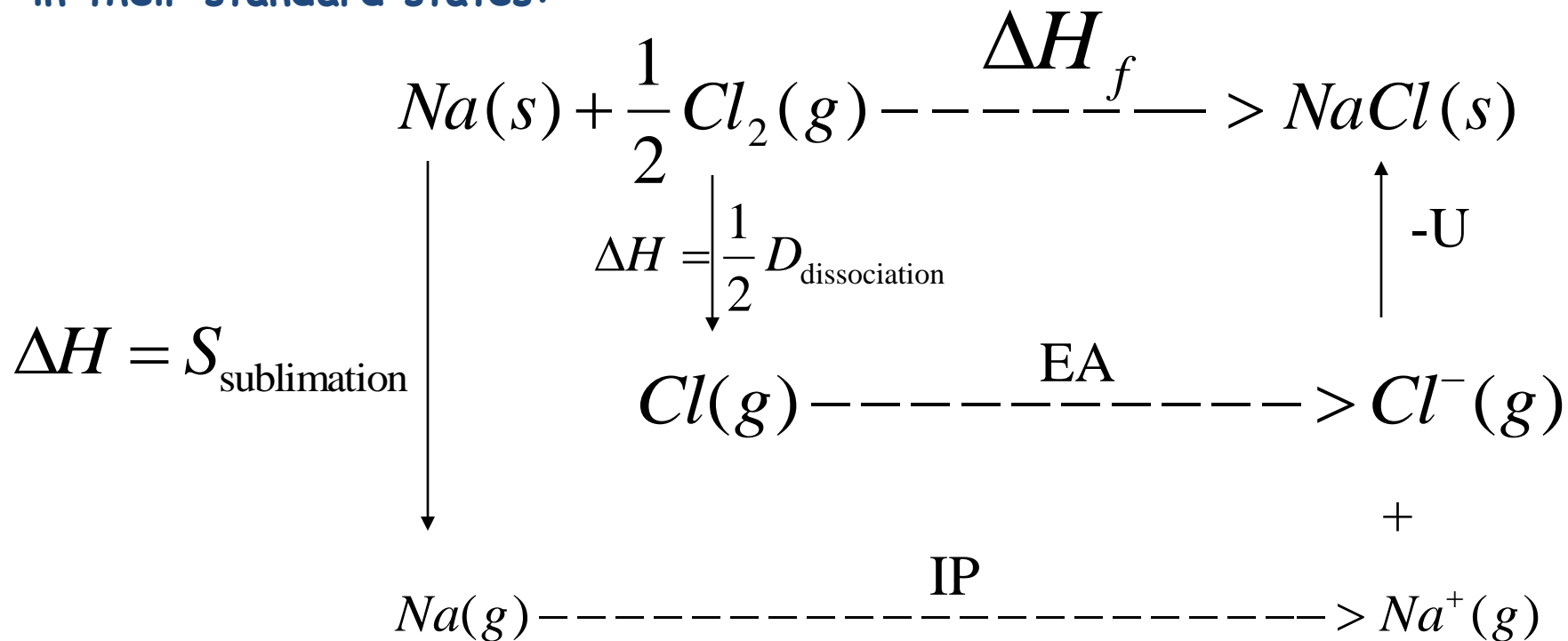
$$U = \frac{(120,200)nZ_+Z_-}{r_+ + r_-} \left(1 - \frac{34.5}{r_+ + r_-} \right) \text{kJ/mol}$$

- n is the # of ions per formula unit
- radii are in picometers

BORN-HABER CYCLES

Lattice energies are calculated from Born-Haber cycles rather than measured directly

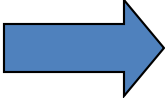
Let's use a B-H cycle to form crystalline NaCl from Na (s) and Cl₂ (g) in their standard states:



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

For NaCl:

S	109 kJ/mol
IP	493.7 kJ/mol
$\frac{1}{2}D$	121 kJ/mol
EA	-356 kJ/mol
ΔH_f	-410.9 kJ/mol

 $U = 778.6 \text{ kJ/mol}$

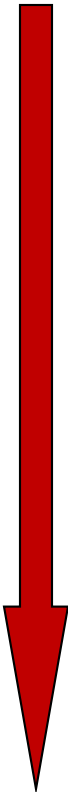
Born-Lande: 764.4 kJ/mol

The Born-Landé equation is a poor approximation to the lattice energy for compounds with significant non-ionic character

	$U_{\text{Born-Landé}}$ (calculation)	$U_{\text{Born-Haber}}$ (experiment)	ΔU	
Rock Salt	AgF	920	953	33
	AgCl	832	903	71
	AgBr	815	895	80
	AgI	777	882	105

CN 4 structure →

Increasingly covalent



The Born-Landé equation is also a poor approximation to the lattice energy for transition metal compounds with crystal field stabilization energy (CFSE):

e.g. MF_2 compounds (high spin rutile)

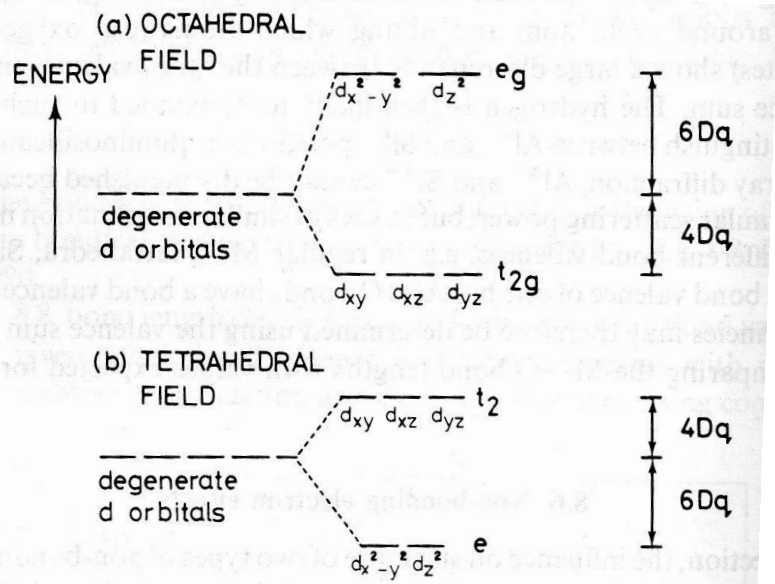
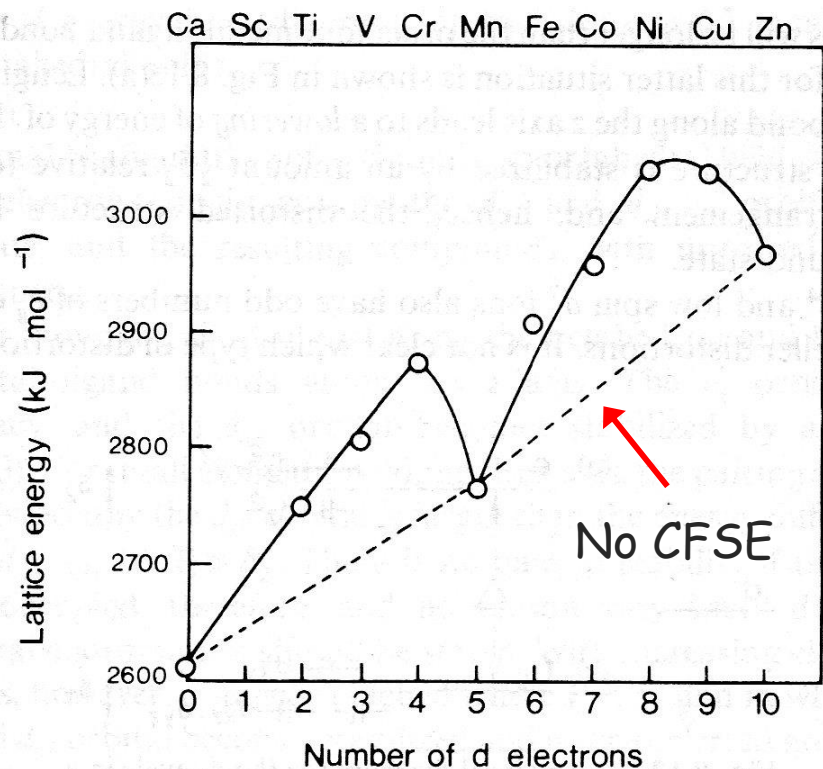


Fig. 8.9 Splitting of d energy levels in (a) an octahedral and (b) a tetrahedral field



Stabilities of unknown compounds

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

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

This method was used by Bartlett to predict that XePtF_6 could be made from Xe & PtF_6 gases.

PAULING RULE #2: *Electrostatic Valence*

Principle (“charge balance”)

“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.”

- A stable 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-anion bonds is:

$$e.b.s. = \frac{m}{n}$$

- For each anion, the sum of the electrostatic bond strengths of the surrounding cations must balance the formal charge on the anion:

$$\sum_{\text{cations}} \frac{m}{n} = x$$

e.g. Fluorite, CaF_2 : Ca^{2+} (8-coordinate) e.b.s. = $2/8$, and $\sum_{\text{#cations}} \frac{1}{4} = x = 1$

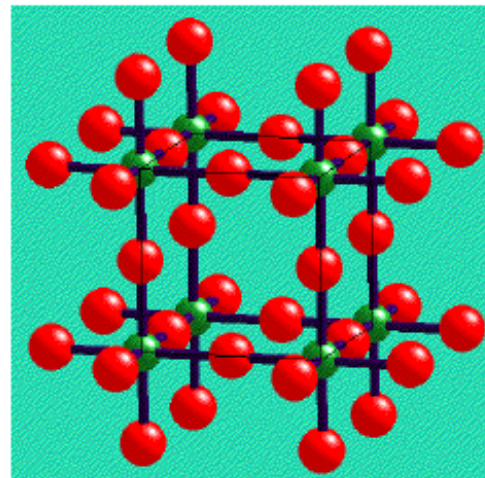
so, # = 4 (F^- is 4-coordinate)

Pauling's 2nd Rule helps with structure prediction/rationalization:

$$\text{ReO}_3: \text{e.b.s. Re}^{6+} = 6/n$$

$$\sum_{\text{cations}} (6/n) = 2$$

$$n = 6, \text{ cations} = 2$$



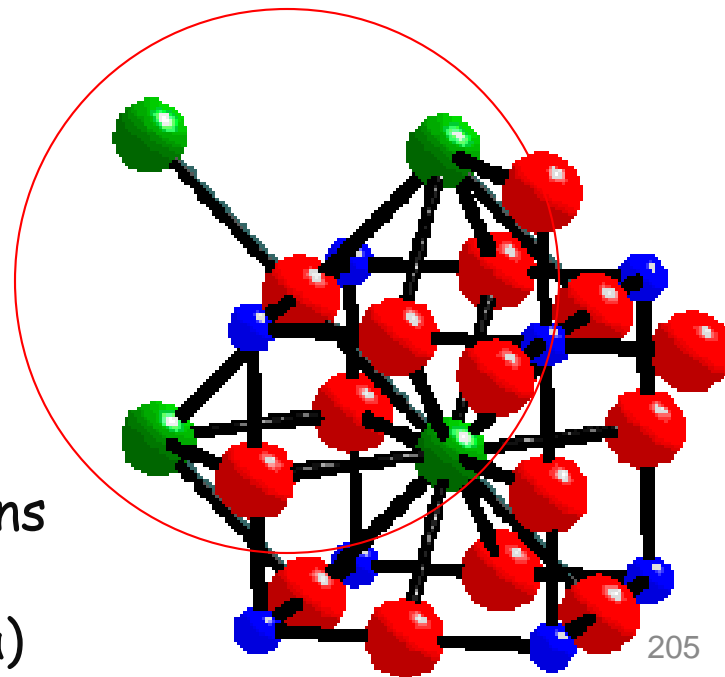
→ Re^{6+} is 6-coordinate & O^{2-} is 2-coordinate

$$\text{CaTiO}_3: \text{e.b.s. Ca}^{2+} = 2/12 = 1/6$$

$$\text{e.b.s. Ti}^{4+} = 4/6 = 2/3$$

$$\sum_{\text{Ca}^{2+}} (1/6) + \sum_{\text{Ti}^{4+}} (2/3) = 2$$

→ O^{2-} is coordinated to 2 Ti^{4+} & 4 Ca^{2+} ions
(each oxygen is common to 2 TiO_6
octahedra and 4 CaO_{12} cuboctahedra)



PAULING RULE #3: *Polyhedral Linking*

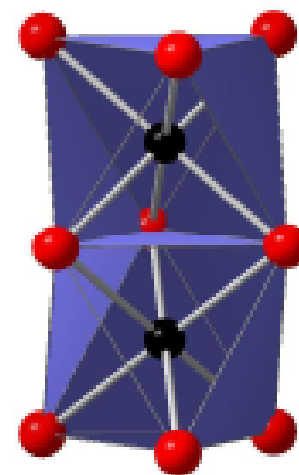
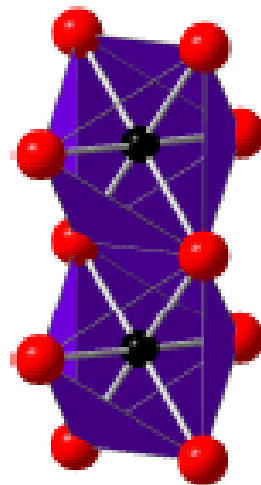
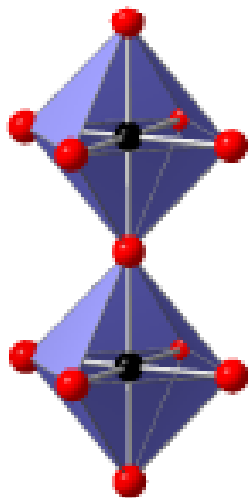
“The stability of structures with different types of polyhedral linking is **vertex-sharing > edge-sharing > face-sharing.**”

- 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

When polyhedra share a common edge or face it brings the cations closer together, thereby increasing electrostatic repulsions.

Cation-Cation Distance

	<i>Corner</i>	<i>Edge</i>	<i>Face</i>
Tetrahedra	2 M-X	1.16 M-X	0.67 M-X
Octahedra	2 M-X	1.41 M-X	1.16 M-X

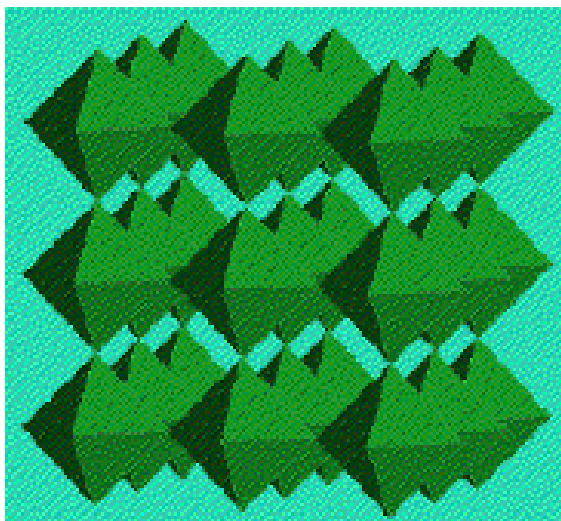


Obeied by compounds of **high polarity**, e.g. oxides/halides

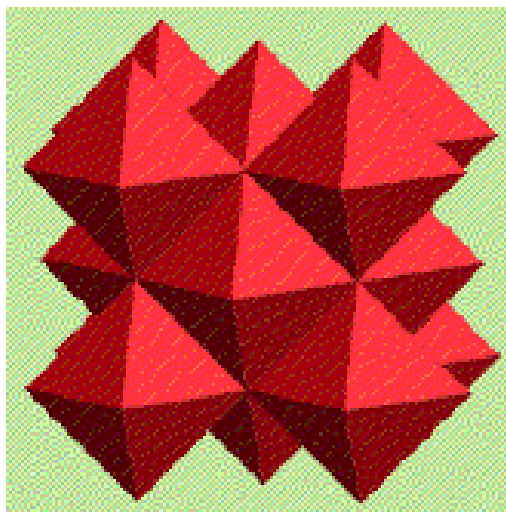
Not obeyed by compounds of lower polarity

e.g. SiO_2 = **vertex**-linked Tetrahedra, but SiS_2 = **edge**-linked Tetrahedra

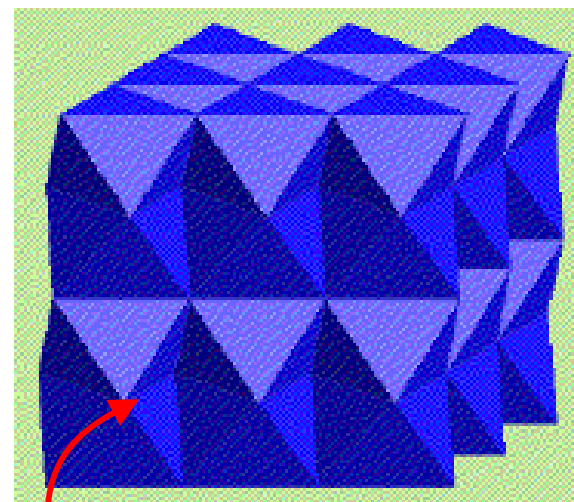
Flouted by some compounds



*Vertex-Sharing
Only*



Edge-Sharing



*Face-Sharing
in Columns*

promotes
Ni-Ni bonding

PAULING RULE #4: *Cation Evasion*

“In a crystal containing different cations, those of large valence and small coordination number tend **NOT** to share polyhedron elements with each other.”

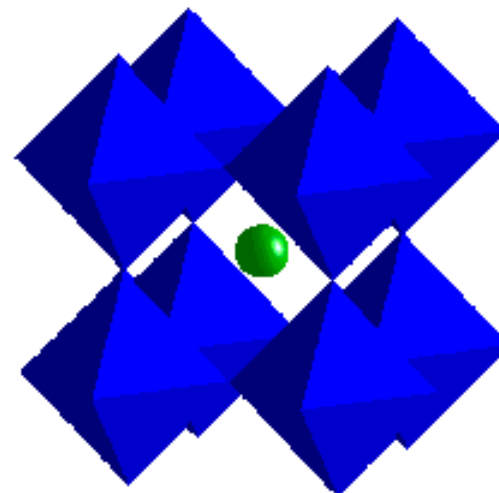
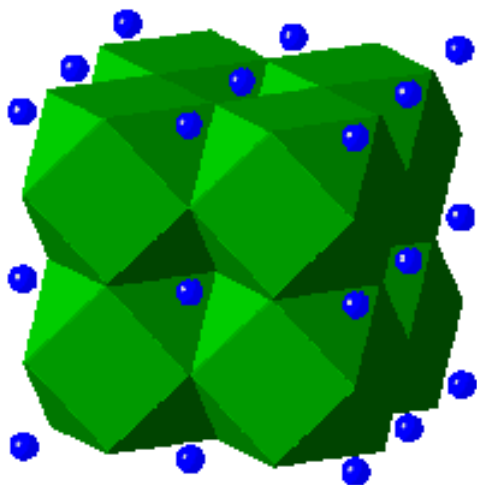
In other words, highly charged cations will tend to be as far apart as possible to minimize electrostatic repulsion.

Partly just a corollary to Rule #3.

e.g., CaTiO_3

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

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



PAULING RULE #5: *Parsimony*

“The number of essentially different kinds of constituents in a crystal tend to be small.”

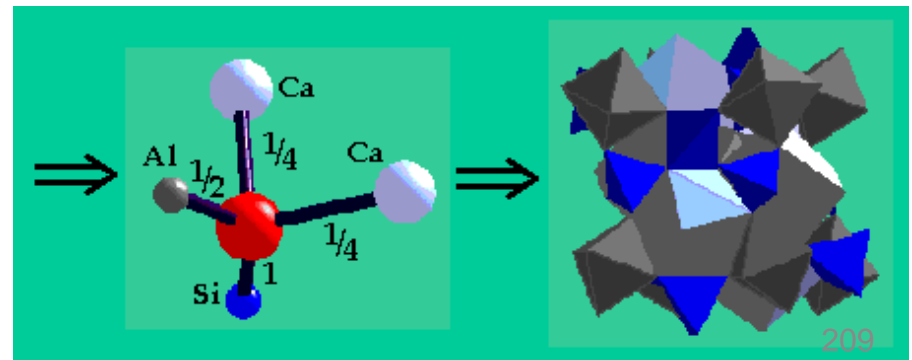
i.e. as far as possible, **similar environments** for chemically similar atoms

e.g., Treating the mineral Garnet $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ as an ionic crystal...

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

O^{2-} formal charge of 2 is satisfied by a number of alternative combination of bonds

- Pauling Rule 5: Each O^{2-} most likely in the same environment
- Only one possible arrangement:



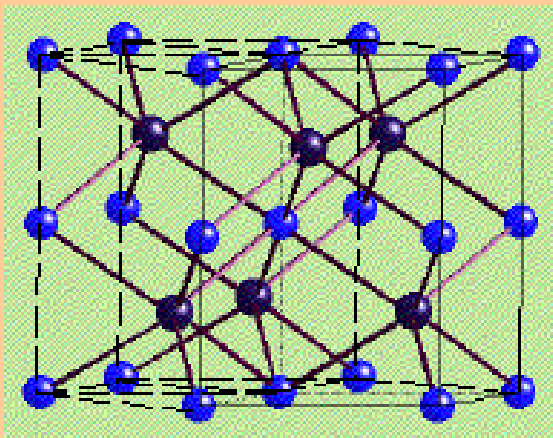
SUMMARY OF PAULING'S RULES

1. Around every cation, a coordination polyhedron of anions forms, in which the cation-anion distance is determined by the radius sum and the coordination number is determined by the radius ratio.
2. The Electrostatic Valence Rule: An ionic structure will be stable to the extent that the sum of the strengths of the electrostatic bonds to an anion equals the charge on that anion.
3. The sharing of edges, and particularly faces by two anion polyhedra decreases the stability of a crystal.
4. An extension of the third rule: In a crystal which contains different cations, those with high charge and low coordination numbers tend not to share elements of their coordination polyhedra.
5. The Rule of Parsimony: The number of essentially different kinds of constituents in a crystal tends to be small.

WHEN PAULING'S RULES ARE BROKEN

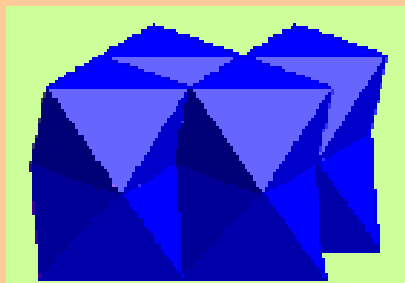
Pauling's Rules are disobeyed by compounds that are not well described by the ionic model. Often special structural influences on the bonding are responsible.

Non-ionic bonding



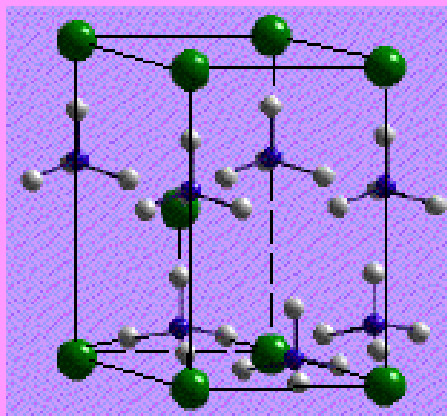
NiAs

*Metal-Metal
Bonding*



→ face sharing

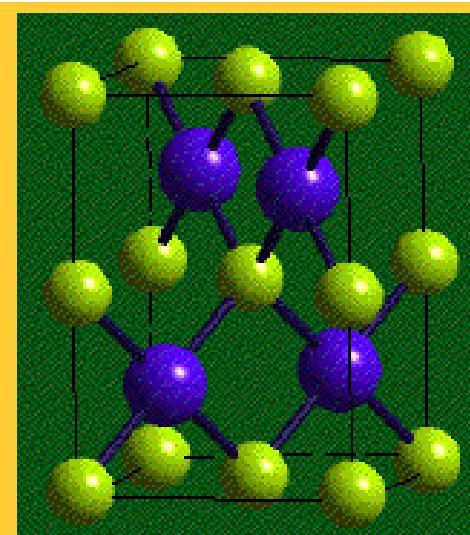
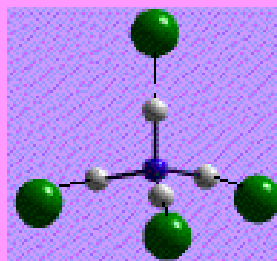
d Electron effects



NH₄F

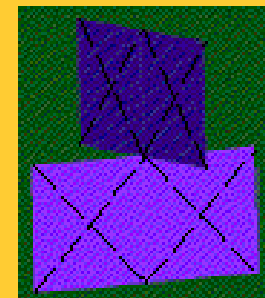
H-Bonding

→ wurtzite



PtS

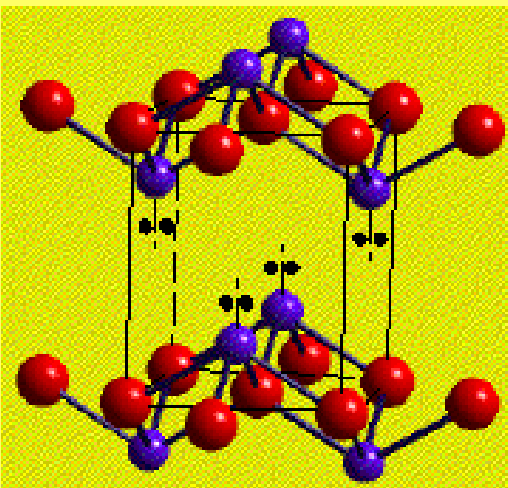
*Planar
Bonding*



Jahn-Teller distortions

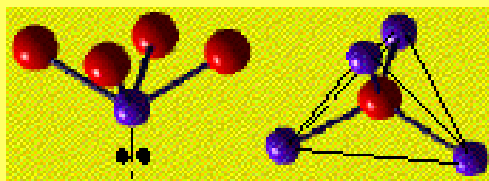
WHEN PAULING'S RULES ARE BROKEN

The inert pair effect

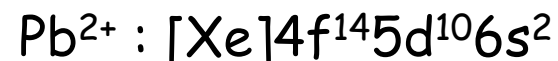


PbO

Lone Pairs



- Divalent Group IV ions have stereochemically active lone pairs

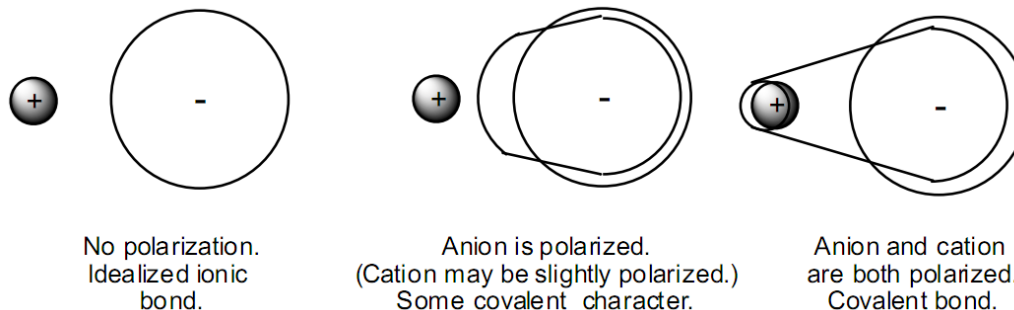


- Most common with heavy p-block elements
Tl, Sn, Pb, Sb, Bi

Distorted coordination polyhedra
(tetragonally-distorted CsCl structure)

FAJANS' ("fayans") RULES FOR COVALENCY

Covalent bonding, partial or complete, occurs when the outer charge density on an anion is *polarized* by and toward a neighboring cation



Fajans' Rules (1923) are used to predict the polarization of a chemical bond, depending on the charge of the cation and the relative sizes of cation and anion.

Ionic	Covalent
Low positive charge	High positive charge
Large cation	Small cation
Small anion	Large anion

Polarization (covalency) will be increased by:

1. **High charge and small size of the cation**

Ionic potential $Z_+/r_+ = \text{polarizing power}$

2. **High charge and large size of the anion**

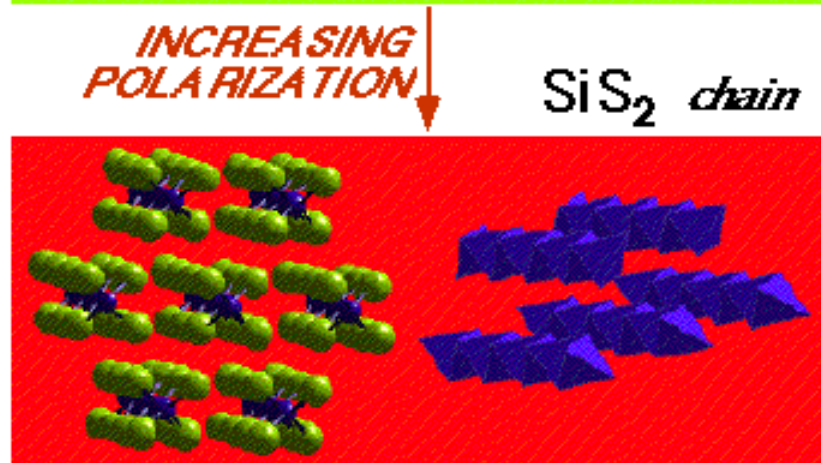
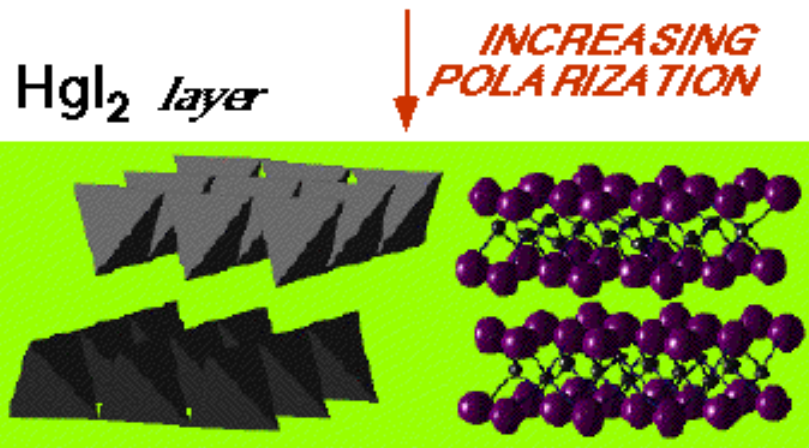
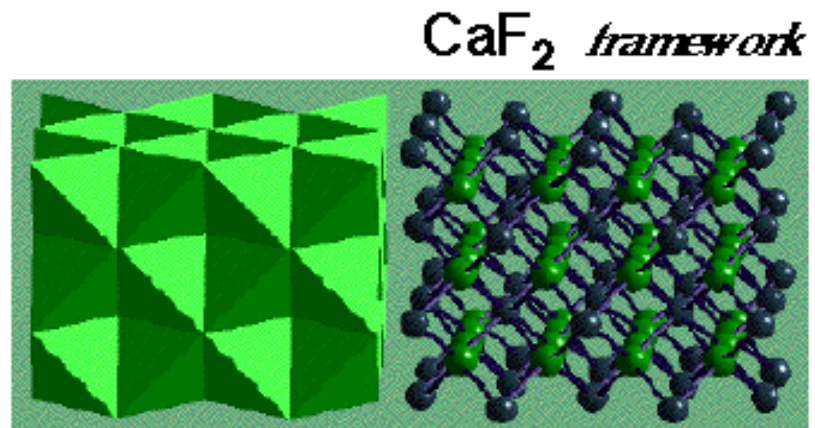
The polarizability of an anion is related to the deformability of its electron cloud (i.e. its "*softness*")

Indirect evidence that the structure is **NOT** ionic

Increasing Polarization (less ionicity) in bonding



low-dimensionality layers/chains



More covalent

MOOSER-PEARSON PLOTS

Structure maps based on average atomic size and electronegativity differences.

Electronegativity: A measure of the net attractive force felt by a foreign electron in the vicinity of an atom.

- larger \bar{n} , larger orbitals
→ less directionality
(more ionic)
e.g., Si, Ge, Sn, Pb
covalent → metallic
- almost perfect division of compounds into 4 structures
(critical ionicities)
- suggests increased ionicity of wurtzite over zinc blende

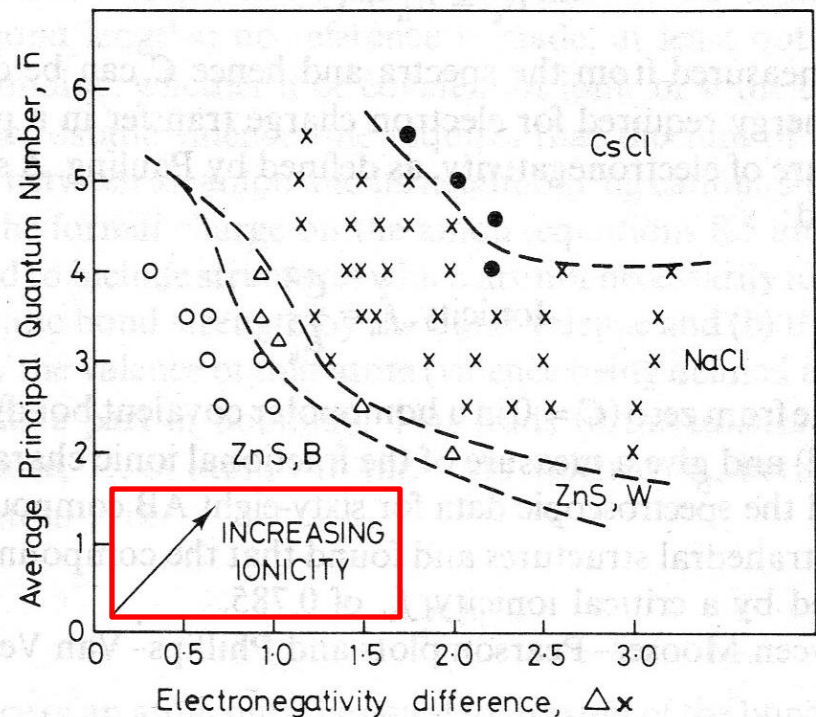
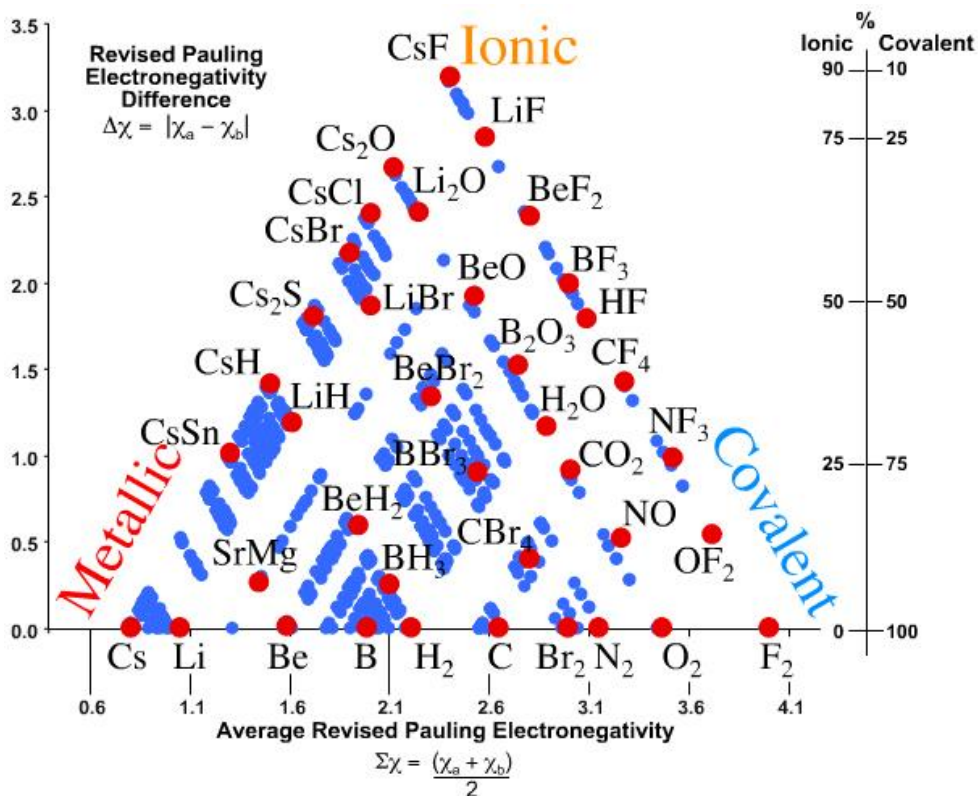


Fig. 8.7 Mooser-Pearson plot for AB compounds containing A group cations. (From Mooser and Pearson, 1959.) Arrow indicates direction of increasing bond ionicity

TRIANGLES OF BONDING

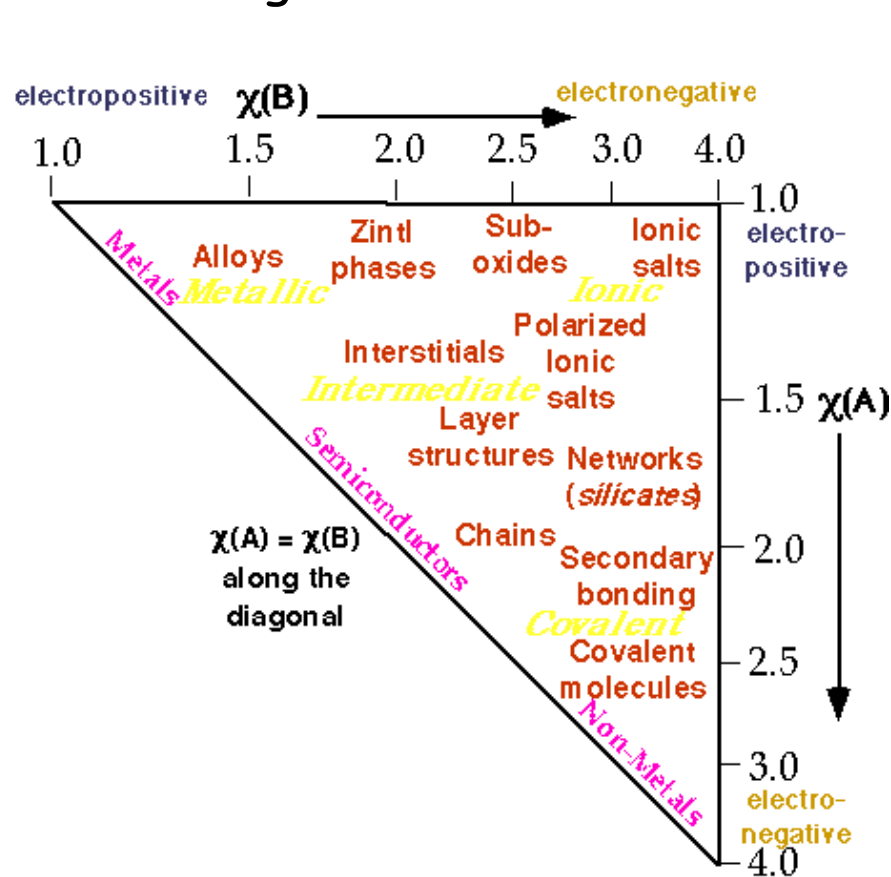
Jensen's Triangle (1995)

for binary A_xB_y compounds



Ketelaar's Triangle (1947)

AB compounds, according to the electronegativities of A and B



ZINTL PHASES

Intermetallic compounds of an alkali or alkaline earth and a p-block element.

