Lecture 1

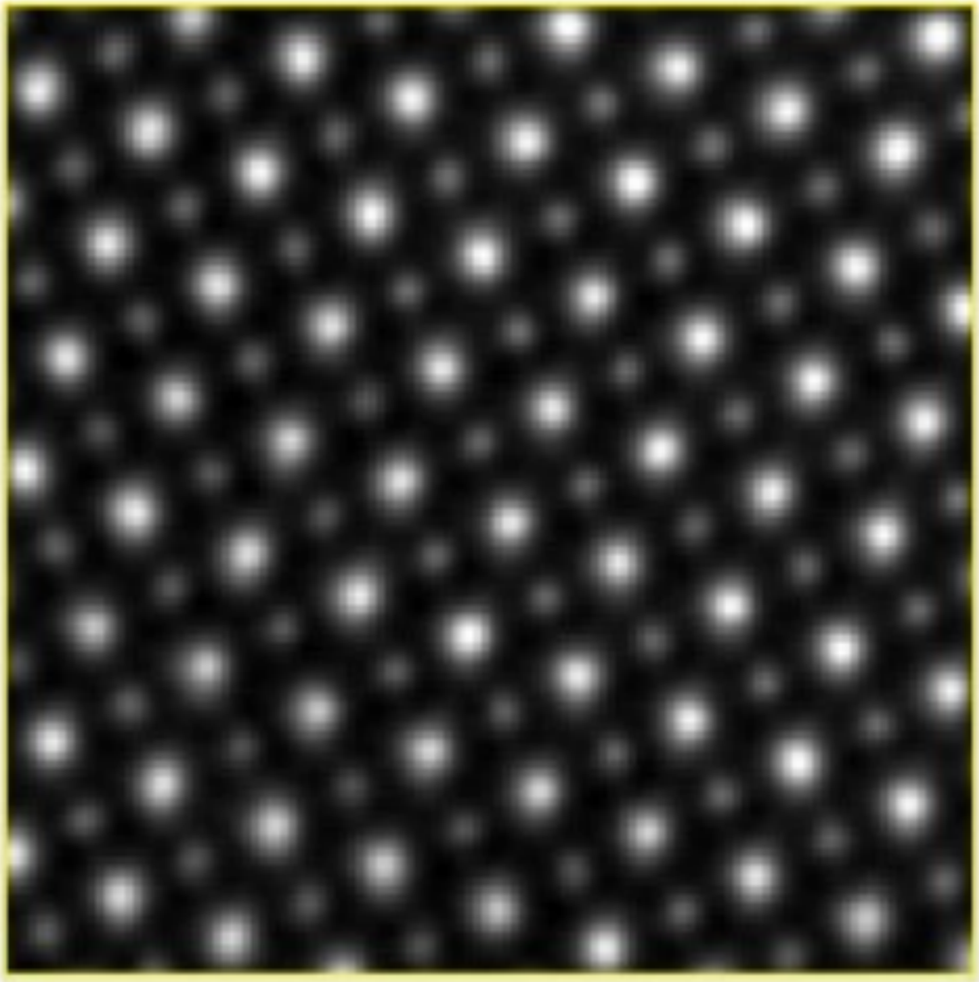
Chemical bonding, ionic size, and how elements bond to form crystalline structures

- 1. Interatomic bonds (classification)
- 2. The influence of the type of bond, ionic size, valence and bond strength on the material properties
- 3. The size of the radius of the most used atoms and the trend of the radiuses over the periodic table
- 4. Pauling rules
- 5. Structures

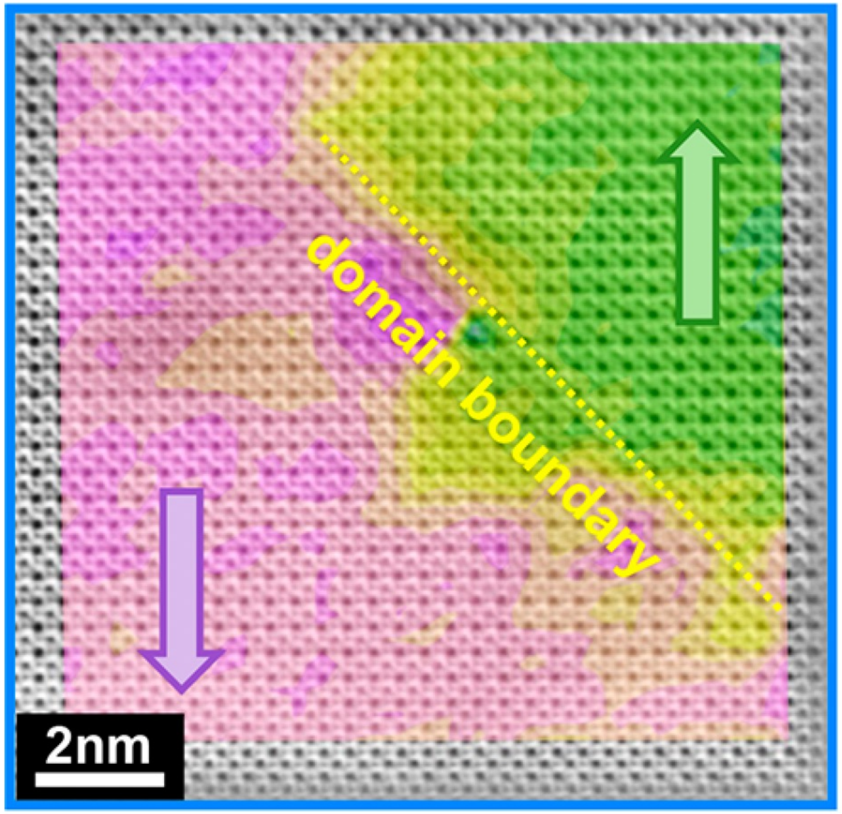
Application Vesta:

http://jp-minerals.org/vesta/en/download.html

BaTiO$_3$, HR TEM picture



Polarization, extracted from atom positions



Ionic and covalent bonding

- Solids form because their energy is lower than the energy of separated elements that form the solid. This will be discussed in detail later.

- An ionic compound AB forms between an active metallic element A and an active nonmetal B. This means that A “easily” looses an electron while B “easily” accepts an electron. “Easily” means without ”too much” energy input.

- A covalent bonding occurs when energies of bonding electrons of A and B are comparable (i.e., ionic bonding is unfavorable)

  It may occur also in single element compounds such as Si or C

- To semiquantify these statements, Pauling introduced concept of

  relative **electronegativity – to quantify the degree of ionicity**

Electronegativity

- Electronegativity describes tendency of an atom to attract bonding electrons

- It is defined relative to that for a selected atom, e.g., H (2.2) or F (4)
- Electronegativity of a given atom depends on molecular environment of the element, but the trends for elements in periodic table remain approximately the same
- H-H (436 kJ/mol); F-F (159 kJ/mol); H-F (570 kJ/mol)

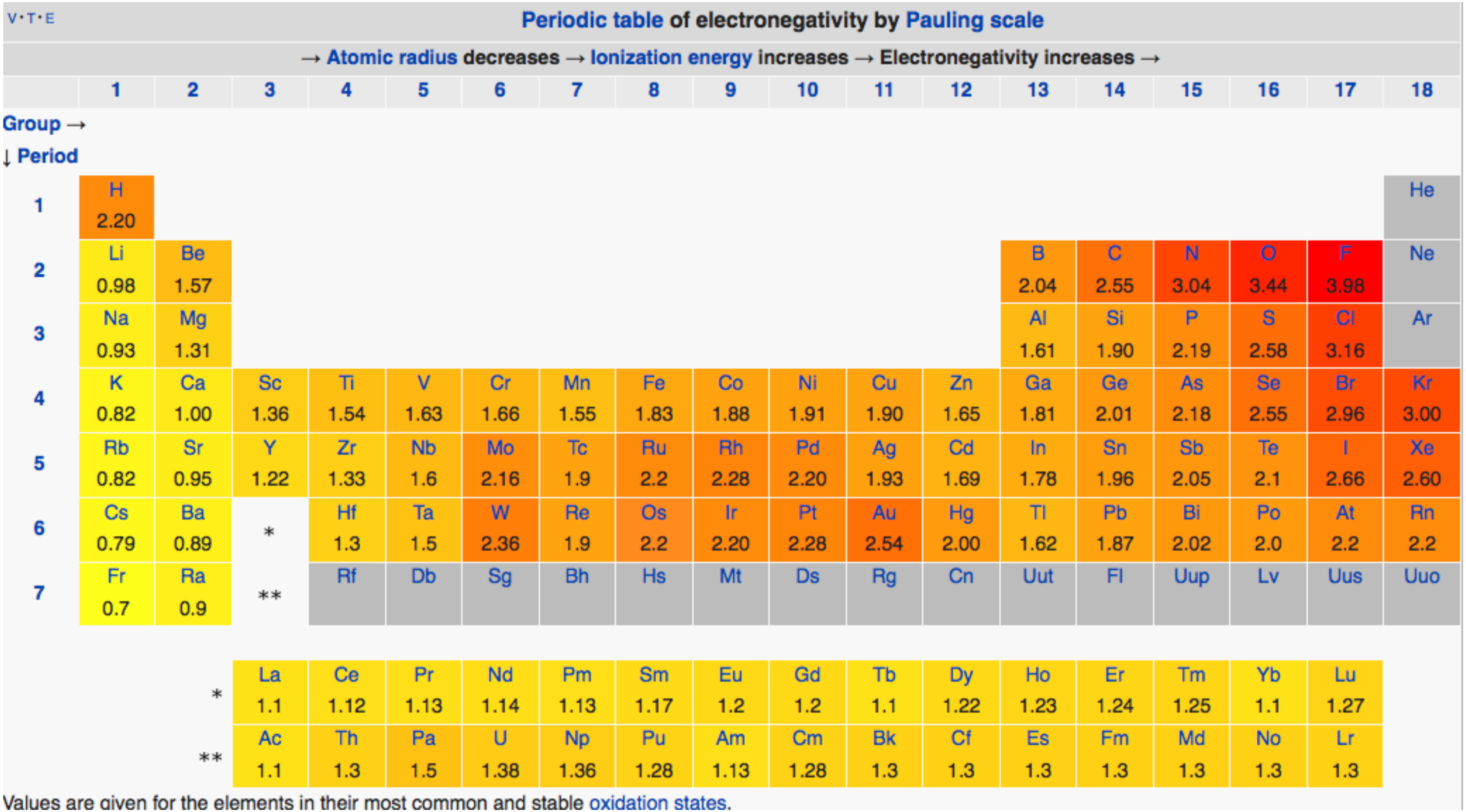
Difference in electronegativity for elements A and B:

$$\Delta = \chi_A - \chi_B = \sqrt{E_d(AB) - \frac{E_d(AA) + E_d(BB)}{2}} \times (eV)^{-1/2}$$

E_d energy of dissociation

Electronegativity table

https://commons.wikimedia.org/wiki/File:Periodic_table_Pauling_electronegatvity.jpg
https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry/Review_of_Chemical_Bonding



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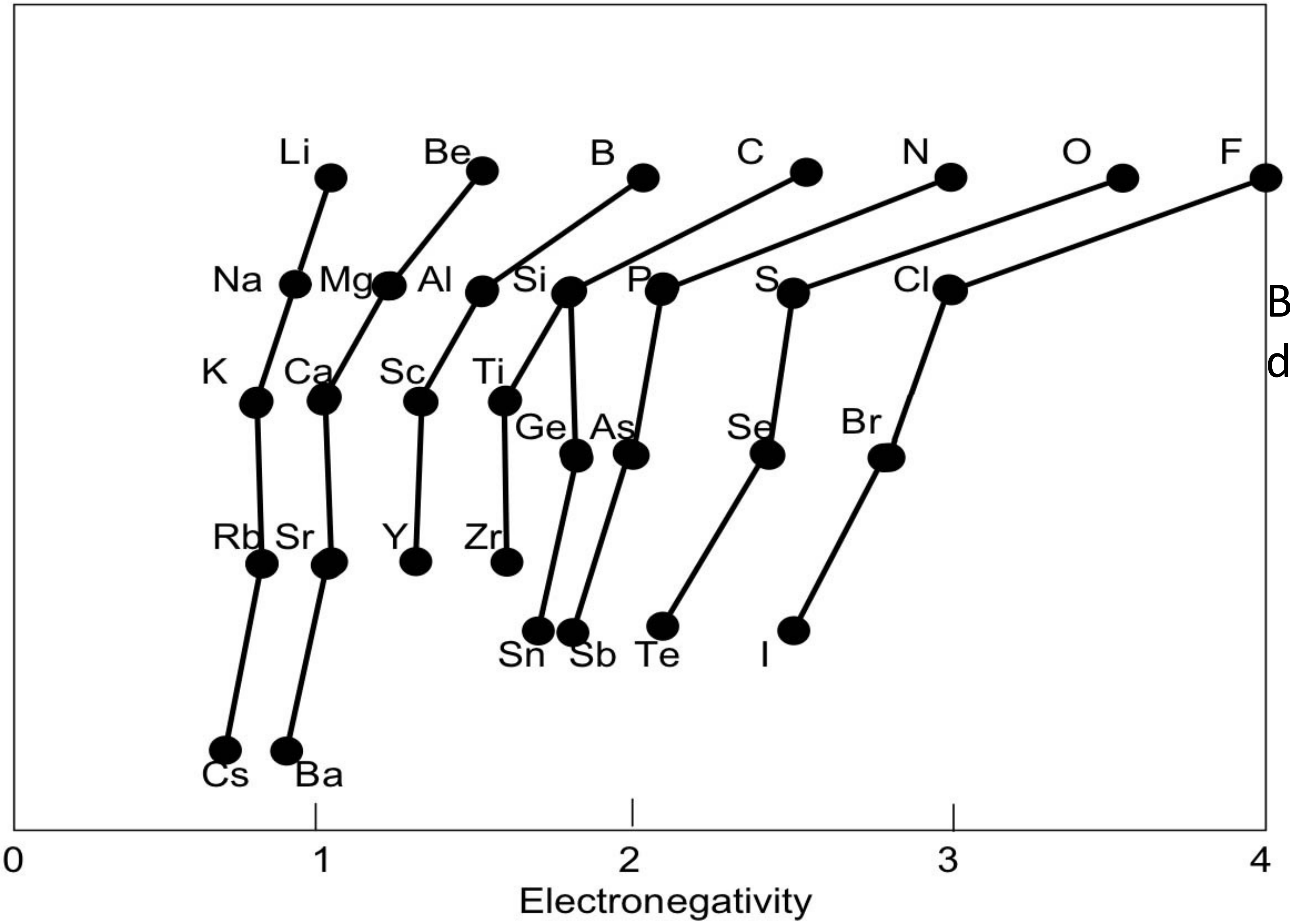
Periodic table of electronegativity by Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
		*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
		**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

Values are given for the elements in their most common and stable oxidation states.

Electronegativity trend



Rough guide:

$$\Delta > 1.7$$

Bond predominantly ionic

$$\Delta < 1.7$$

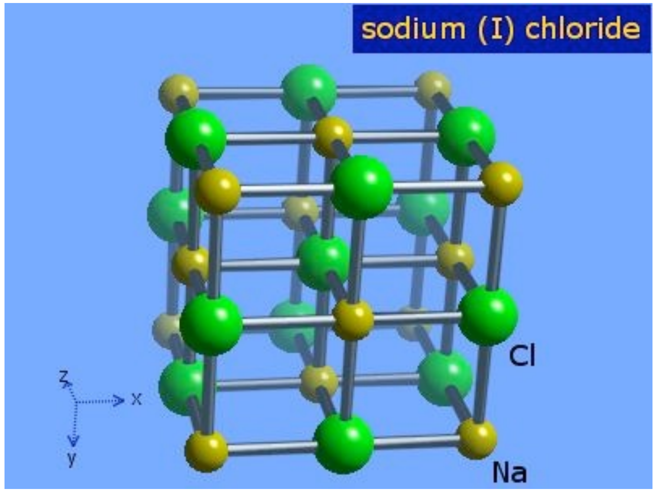
Bond predominantly covalent

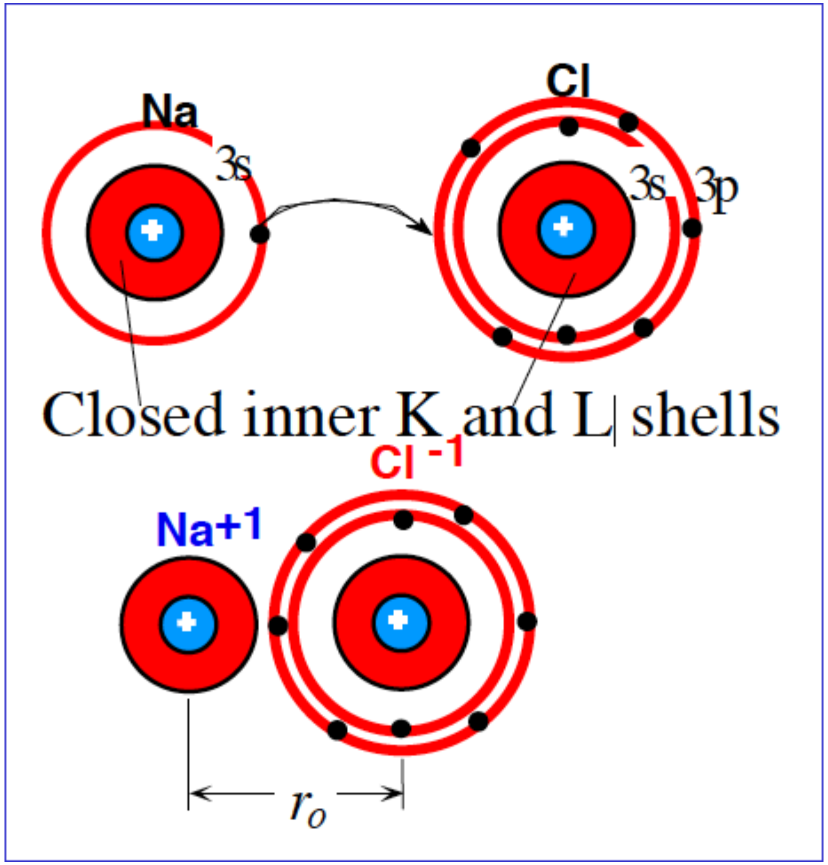
See “mixed bonding” for an explanation

Ionic bonding

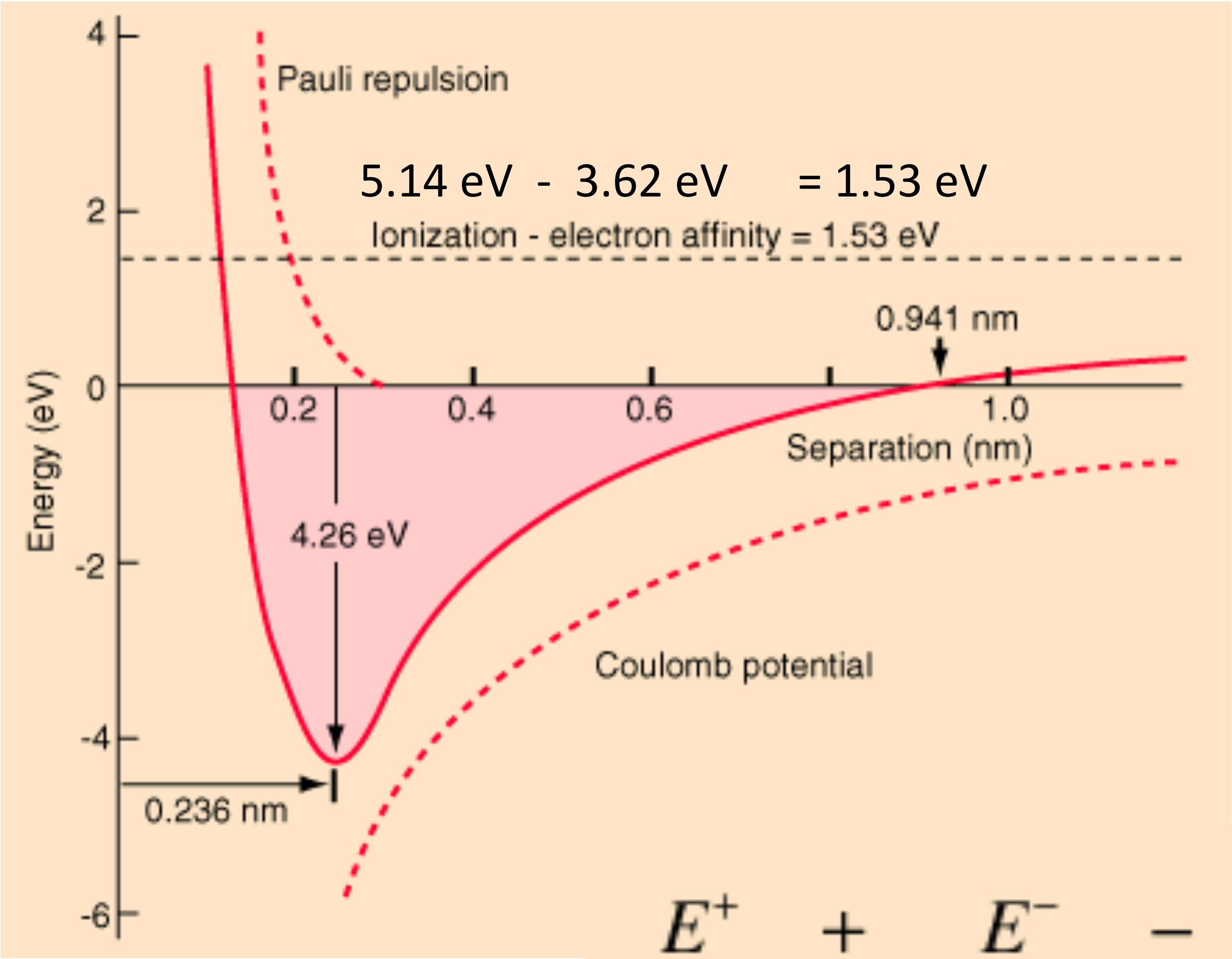
- Electrostatic bonding between positively charged ions (cations) and negatively charged ions (anions).

- Materials with ionic bonding tend to :
  - exhibit high melting and boiling point
  - be poor electrical and thermal conductors
  - be hard and brittle

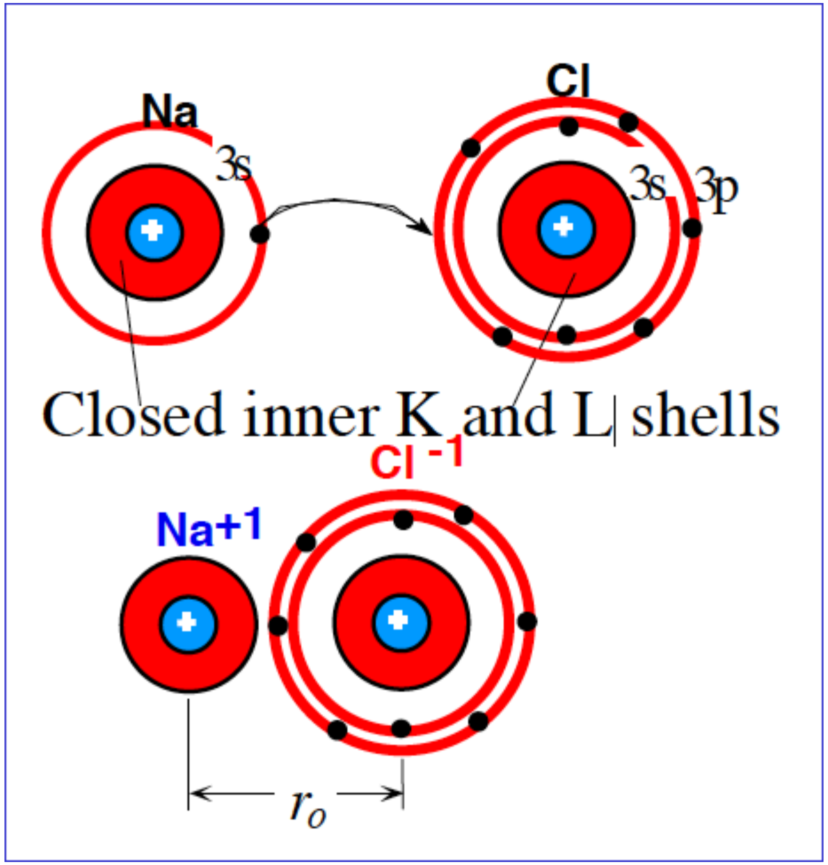




Ionic bonding



5.14 eV - 3.62 eV = 1.53 eV

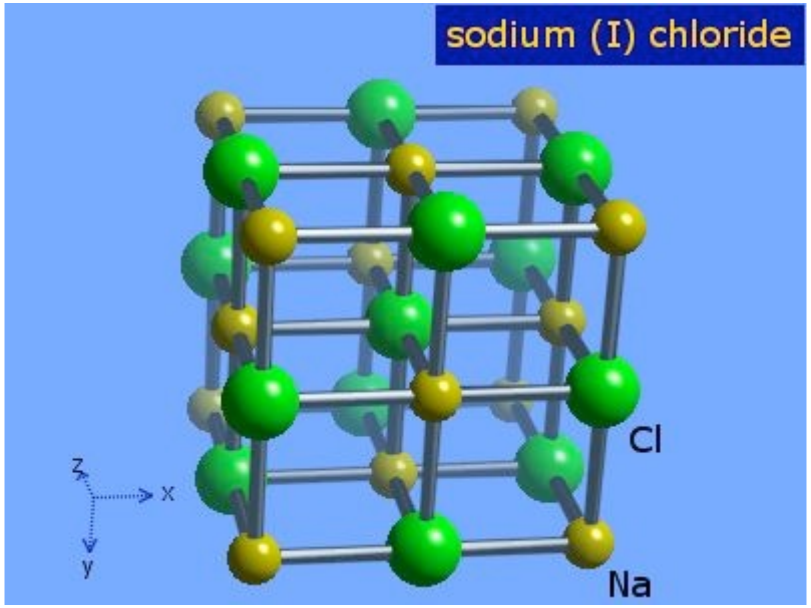


$$\underbrace{E^{+}}_{\text{Ionization energy}} + \underbrace{E^{-}}_{\text{Electron affinity}} - \underbrace{\frac{Ke^{2}}{r}}_{\text{Coulomb attraction of ions}} + \underbrace{C\frac{e^{-ar}}{r}}_{\text{Pauli repulsion energy}} = E_{dissociation}$$

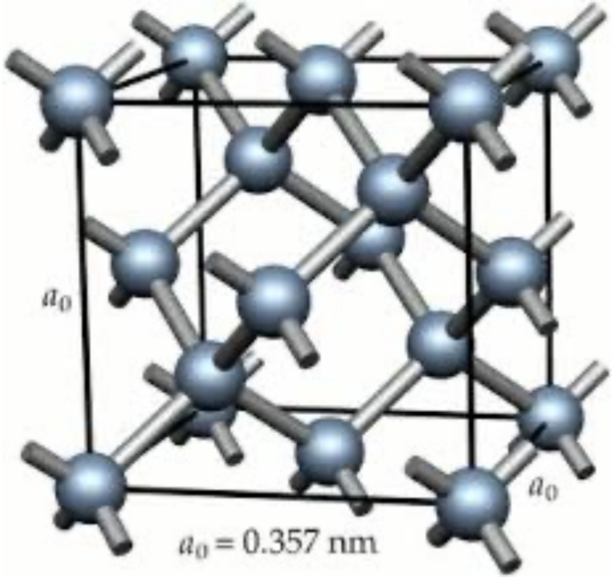
Ionic bond

- Ionic bond is omnidirectional (symmetrical nature of the Coulomb force: $1/r^2$)
- The simplest example: NaCL

Ionic NaCl



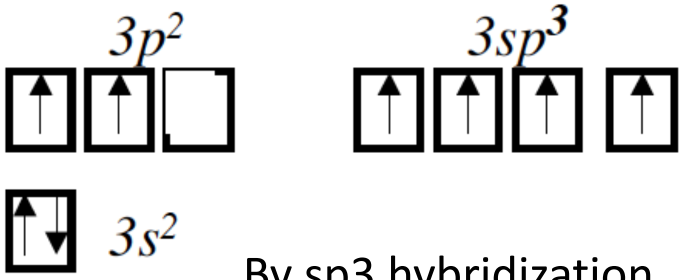
Diamond (covalent)



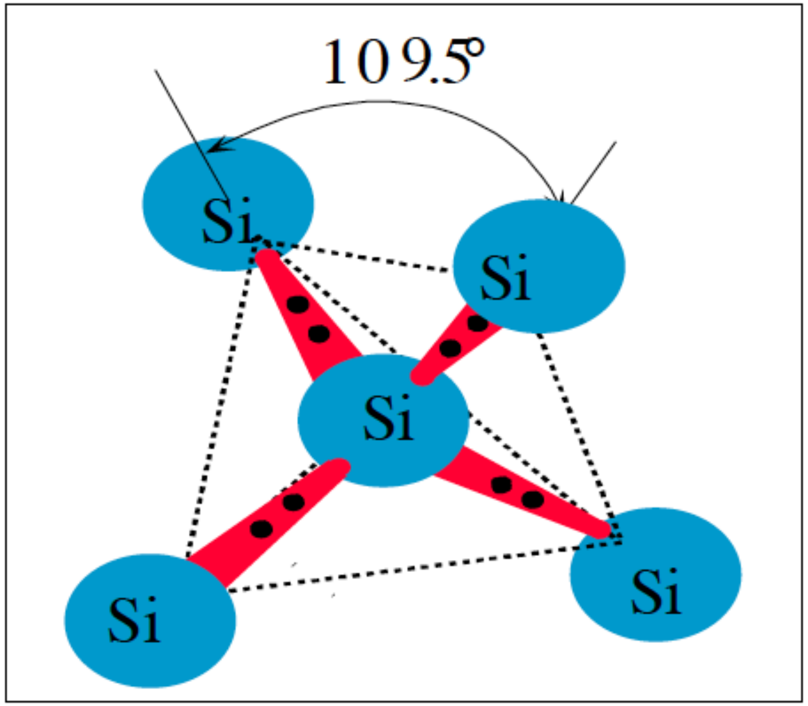
Covalent bonding

- Covalent bonding arises from sharing of electrons between two atoms.
- This bond is directional and strong

Electronic structure of Si:
Ne 3s2 3p2



By sp3 hybridization
two new bonds are formed

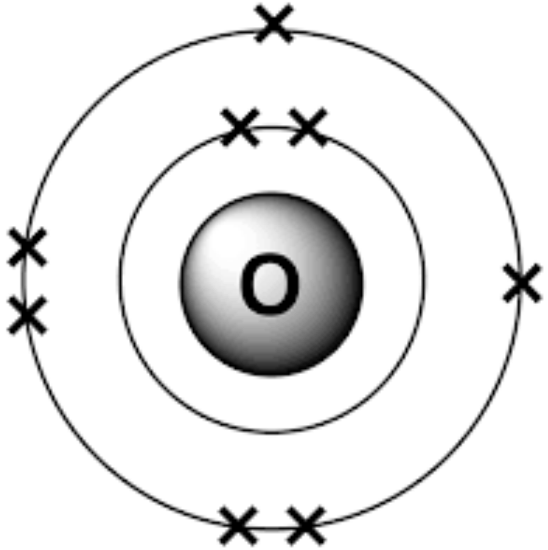


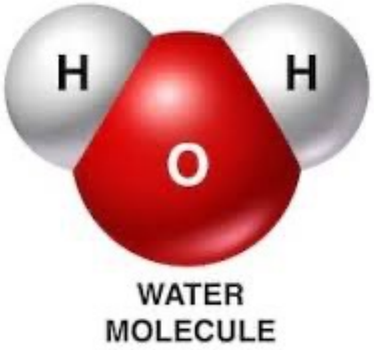
Why is angle 109.5° and the bond takes shape of tetrahedron?

Covalent bonding

- Water molecule
- O 1s2 2s2 2p4
- H 1s1

- How do H and O arrange spacially?
- What is the angle among H-O-H?





hybrid orbitals then arrange themselves in a tetrahedral geometry

Mixed bonding

- Electrons are shared, but are closer to the “anion”
- The degree of “ionicity” between atoms A and B is a function of difference of their electronegativities
- There are several attempts to describes ionicity of a bonding (**very qualitatively**):

$$ionicity = 1 - e^{-\frac{(\chi_A - \chi_B)^2}{4}}$$

(Pauling)

Calculate % of bond ionicity for:

MgO -

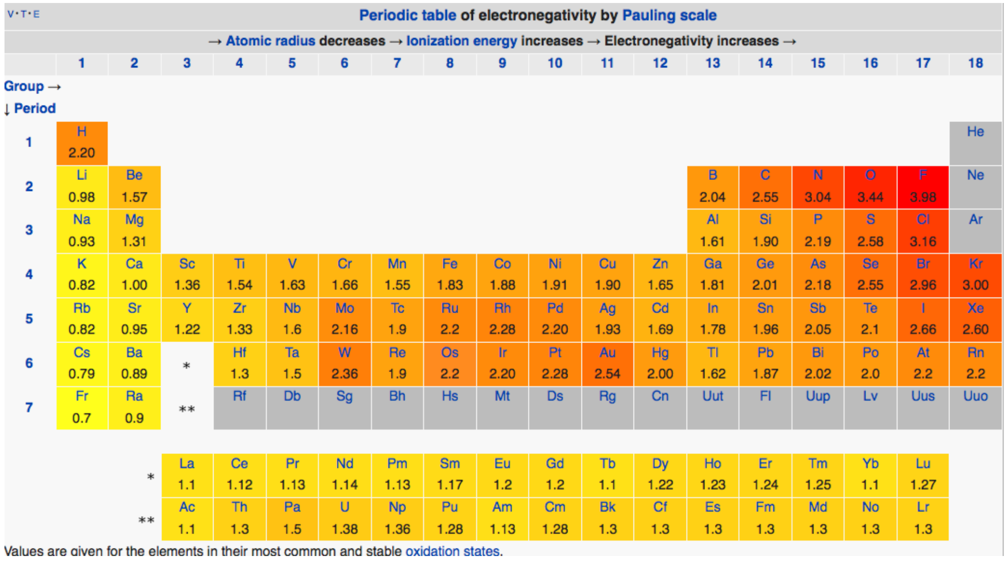
SiO2 -

AlN -

BN -

Si3N4 -

SiC -



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		*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
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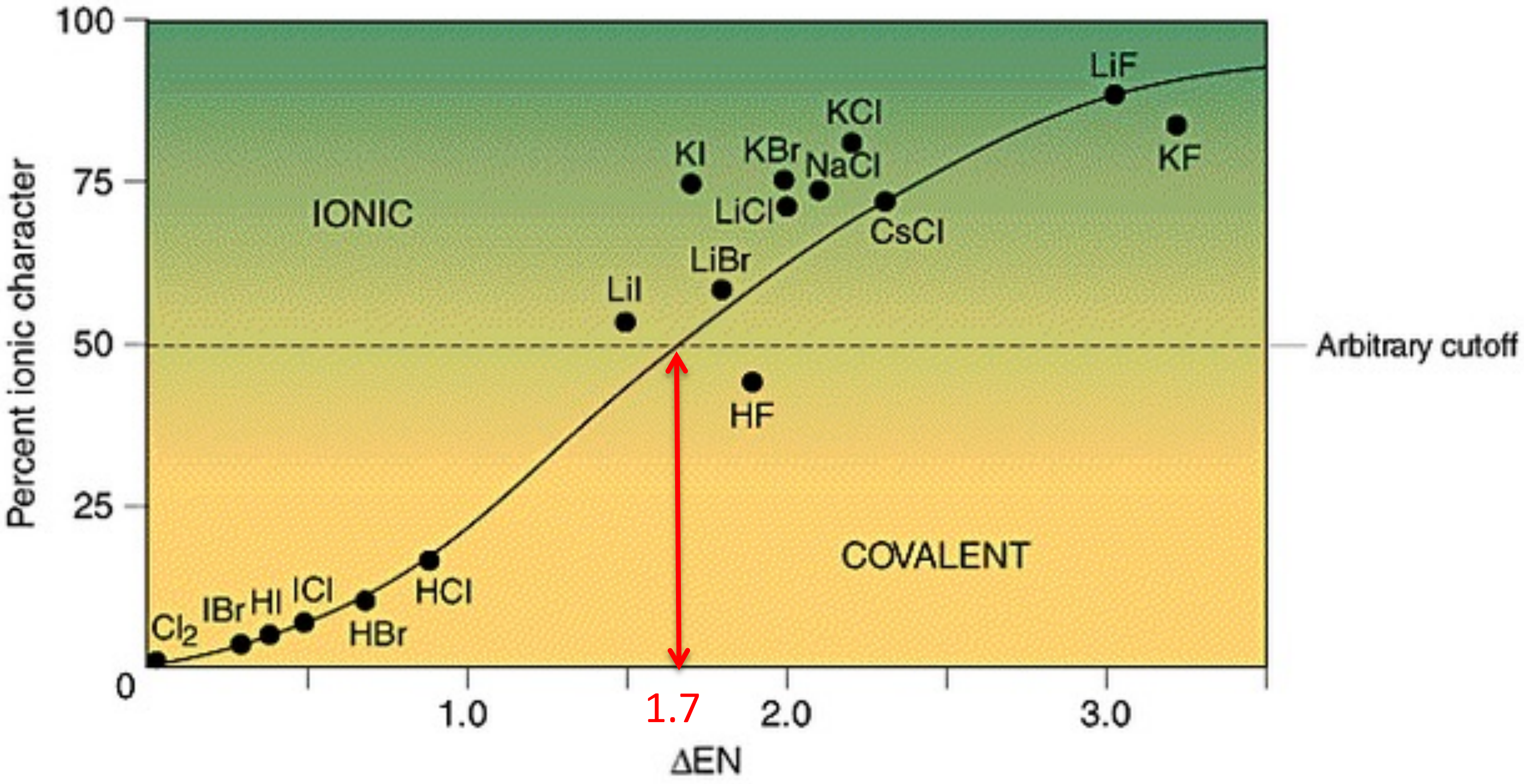
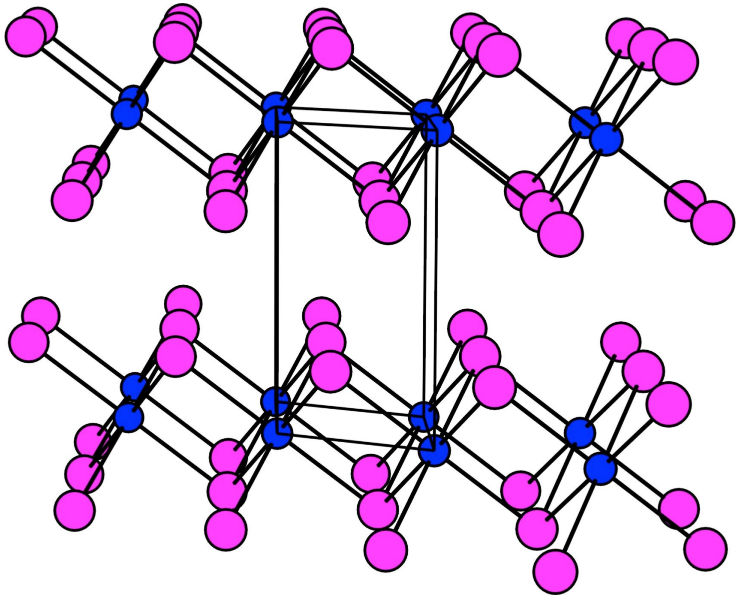
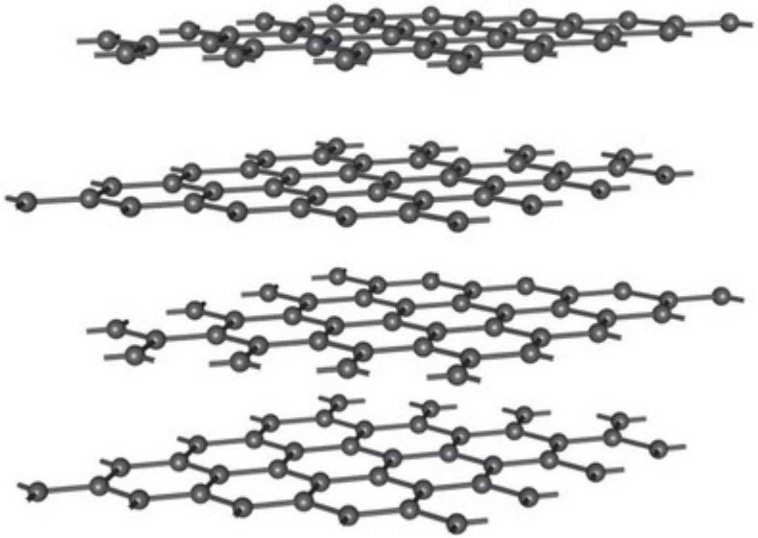
Mixed bonding



Secondary bonding: Van der Waals bond(s)

Week bond between layers or molecules due to permanent or transient dipoles





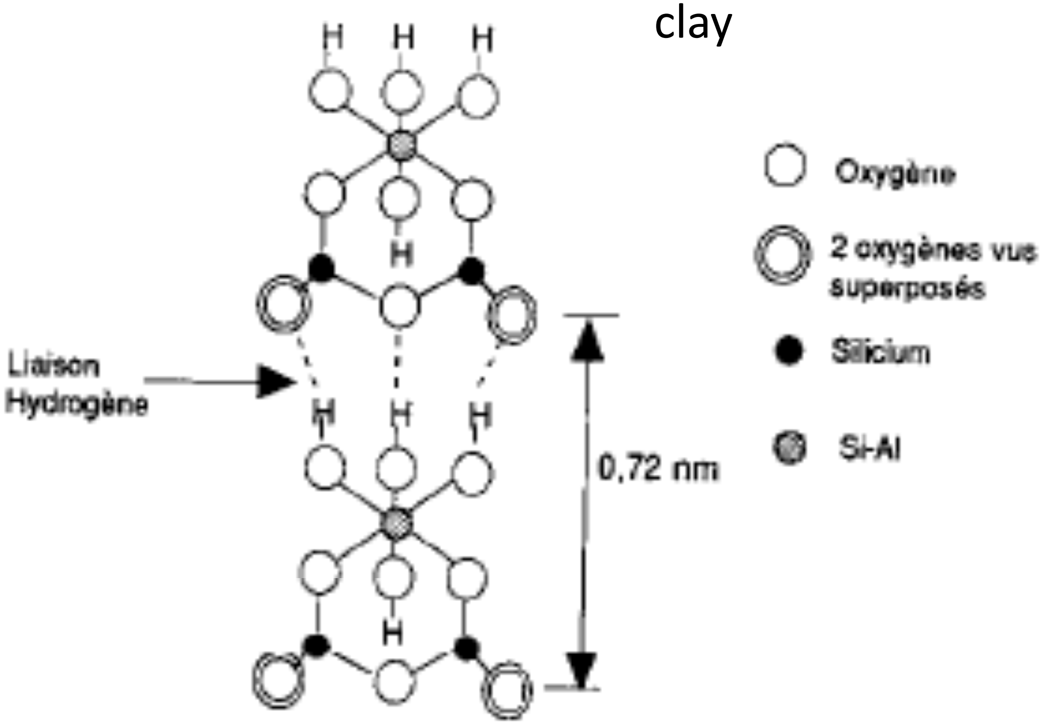
CdI_2, MoS_2,…
Some clays

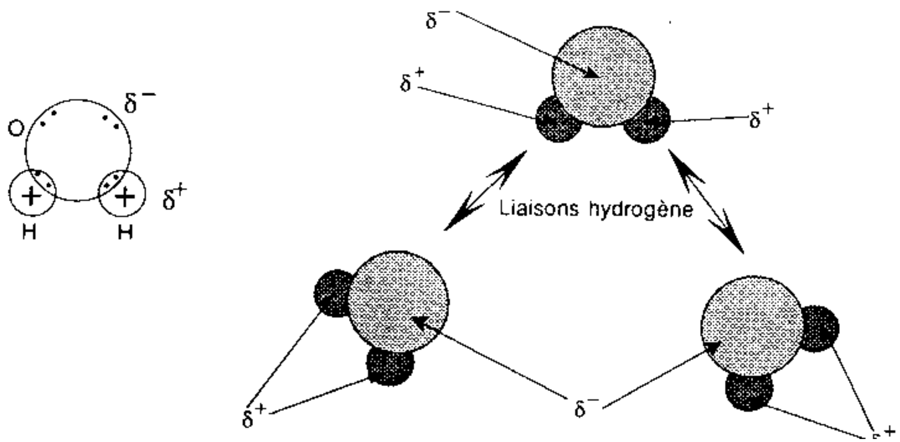
Graphite
What is the character of bond between graphene layers?

Secondary bonding: Hydrogen bonding

- Hydrogen bonding (H-”bridge”)
- The water molecule is a permanent dipole. There is electrostatic attraction between positive (H) and negative (O; N,F) extremities of neighboring dipoles

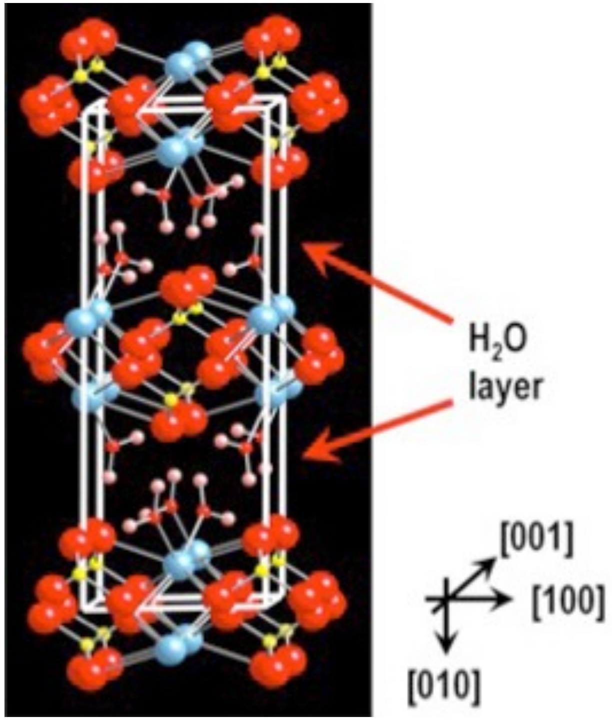
clay

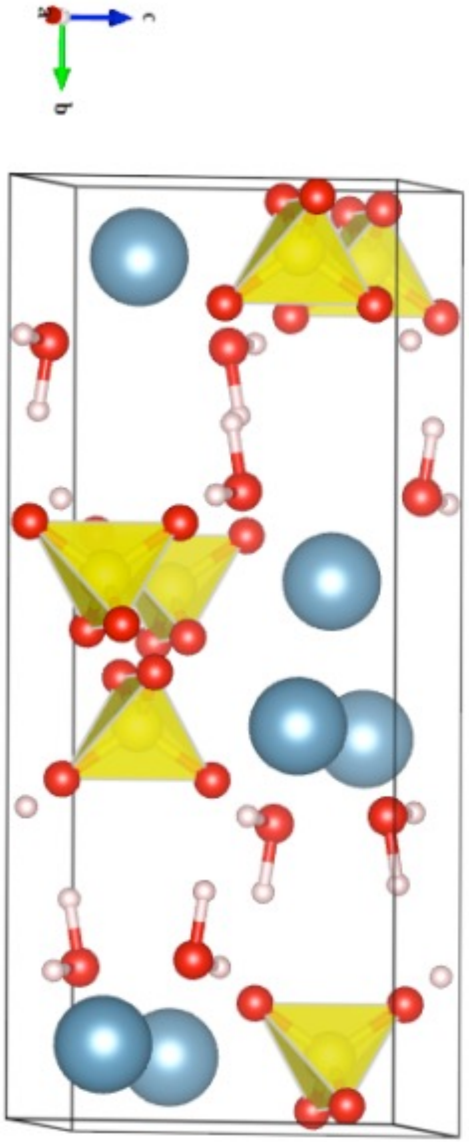




water

Gypsum - $CaSO_4 \cdot 2H_2O$

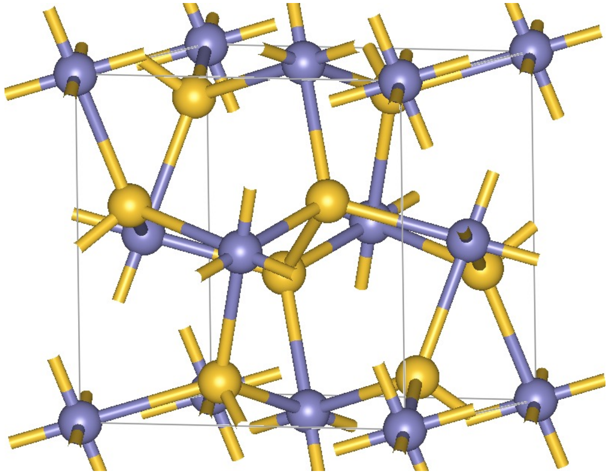


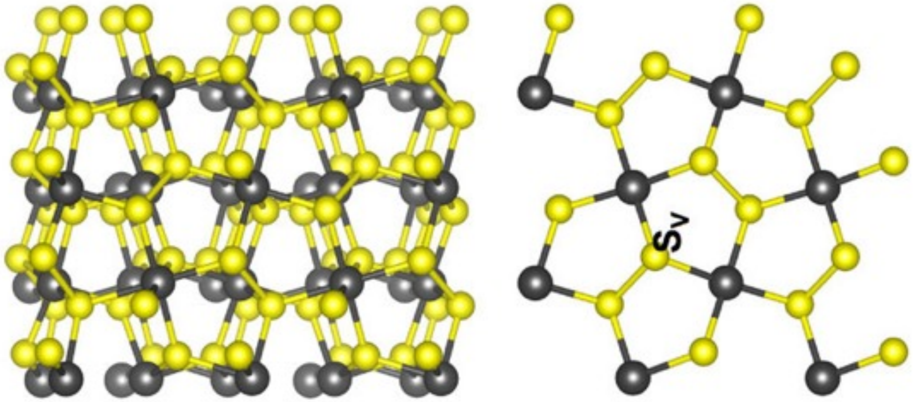


Ca blue
SO4 yellow
O red
H white

Heterodesmic structures

- More then one type of bonding exist (not same as mixed bonding)
- FeS_2: Fe-S bond is ionic, S-S bond is covalent
- Each S bonds to 3Fe and 1S; Each Fe bonds to 6 near neighbours





Pyrite

Comments on crystalline bond and properties

- The weakest bond determines mechanical properties

Dureté	Matériaux	Formula	liaisons cassés	type de liaison
10	Diamant	C **(3-dim)**	C - C	Covalente
9	Corrundum	Al_2O_3	Al - O	50% ionique
8	Topaze	$Al_2SiO_4F_2$	Al - O Al – F	50% ionique Ionique
7	Quartz	SiO_2	Si - O	50% ionique
6	Orthoclase	$KAlSi_3O_8$	Al - O Si – O K - O	50% ionique 50% ionique Ionique
5	Apatite	$Ca_5(PO_4)_3F$	Ca -O Ca - F	Ionique Ionique
4	Fluorite	CaF_2	Ca - F	Ionique
3	Calcite	$CaCO_3$	Ca - O	Ionique
2	Gypsum	$CaSO_4 \cdot 2H_2O$	OH—O	Hydrogène
1	Talc	$Mg_3Si_4O_{10}(OH)_2$	O---O	Van der Waals

Energy of an ionic structure

attraction   repulsion

$$E_{bond} = -\frac{e^2 Z_1 Z_2}{4\pi\varepsilon_0 r} + \frac{B}{r^n}$$

Bonding energy between two ions

The energy is minimal when two ions are at equilibrium distance, $r_{0:}$

$$\left(\frac{\partial E_{bond}}{\partial r}\right)_{r=r_0} = 0 \quad \Rightarrow \quad E_{bond}(r_0) = -\frac{e^2 Z_1 Z_2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

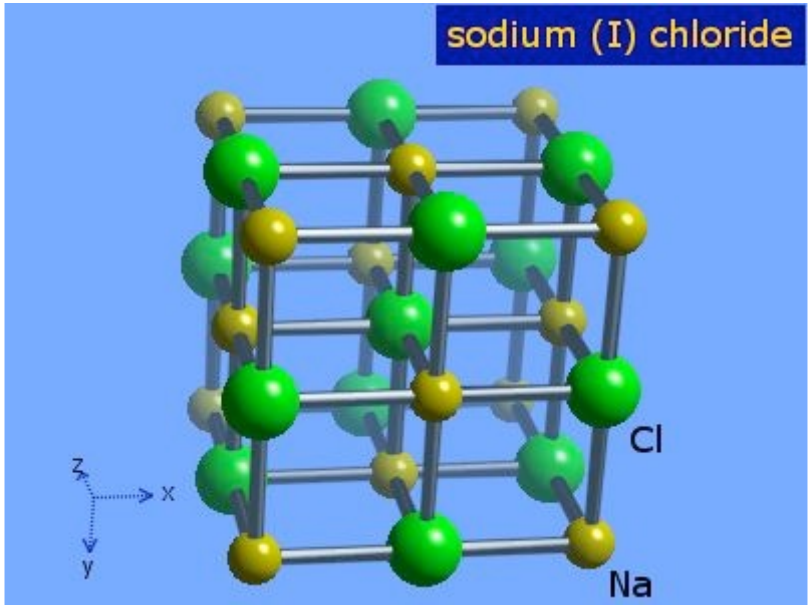
r_0 is the sum of radii of two ions
e: electron charge ($1.602\text{x}10^{-19}$ C)
ε0: permitt.of vacuum (8.85x10-12 F/m)

- Zi: valence of ion
- r: inter-ionic distance
- B: Born constant
- n: Born exponent (approx. 10)

Energy of an ionic structure

$$E_{bond}(r_0) = -\frac{e^2 Z_1 Z_2}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

Between two ions



How can equilibrium energy be described for N_A atoms?

$$E_{lattice}(r_0) = -\frac{N_A e^2 Z_1 Z_2 \alpha}{4\pi\varepsilon_0 r_0}\left(1-\frac{1}{n}\right)$$

α Madelung constant
(a geometrical factor)

Madelung constant

Structure	Madelung constant
Rocksalt	1.748
Cesium chloride	1.763
Zinc blende	1.638
Wurtzite	1.641
Fluorite	2.519
Corundum	4.040

Size of ions

- Atomic vs ionic radii

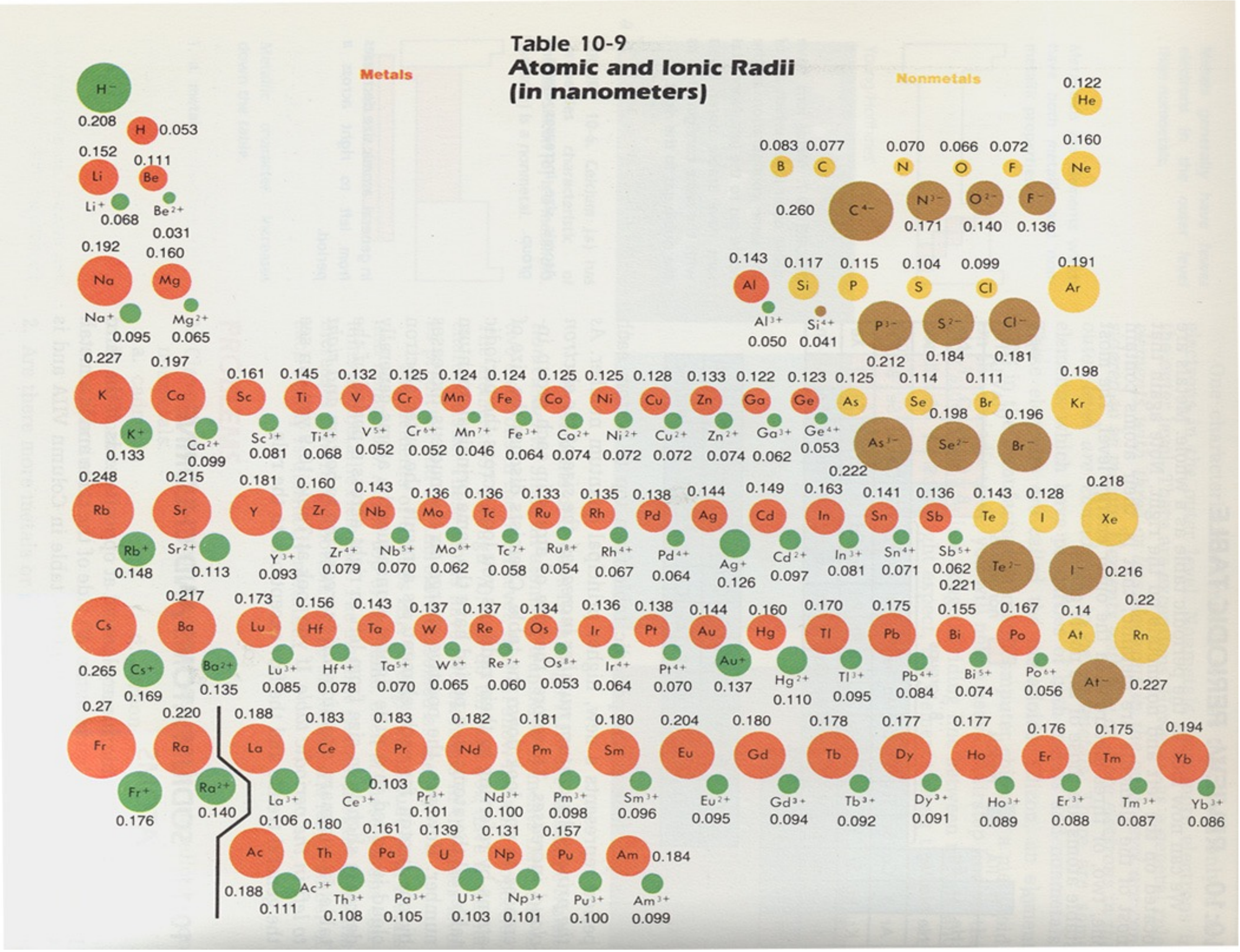
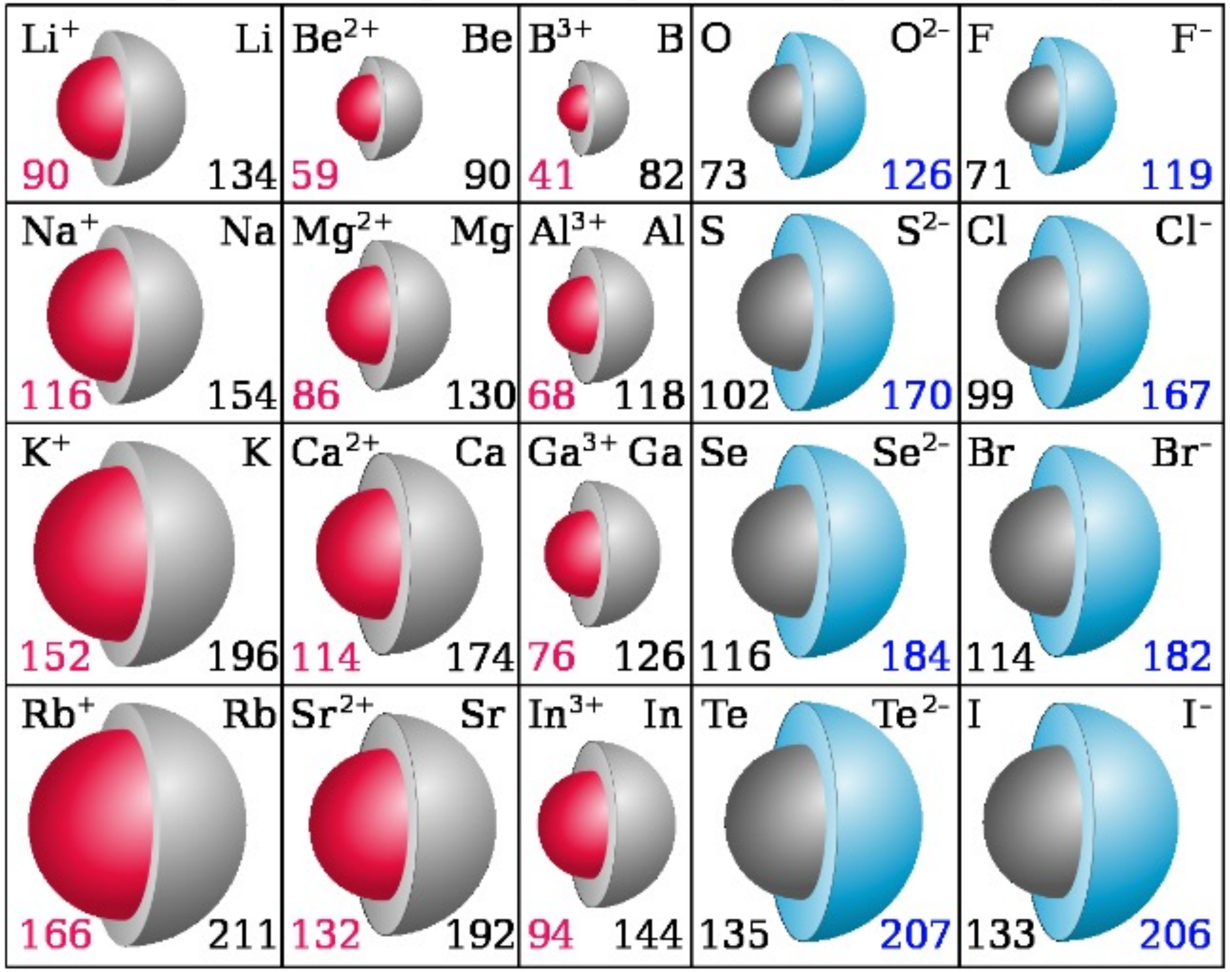


Table 10-9
Atomic and Ionic Radii
(in nanometers)

Crystal radii vs atom radii

Sizes of atoms and their ions in pm

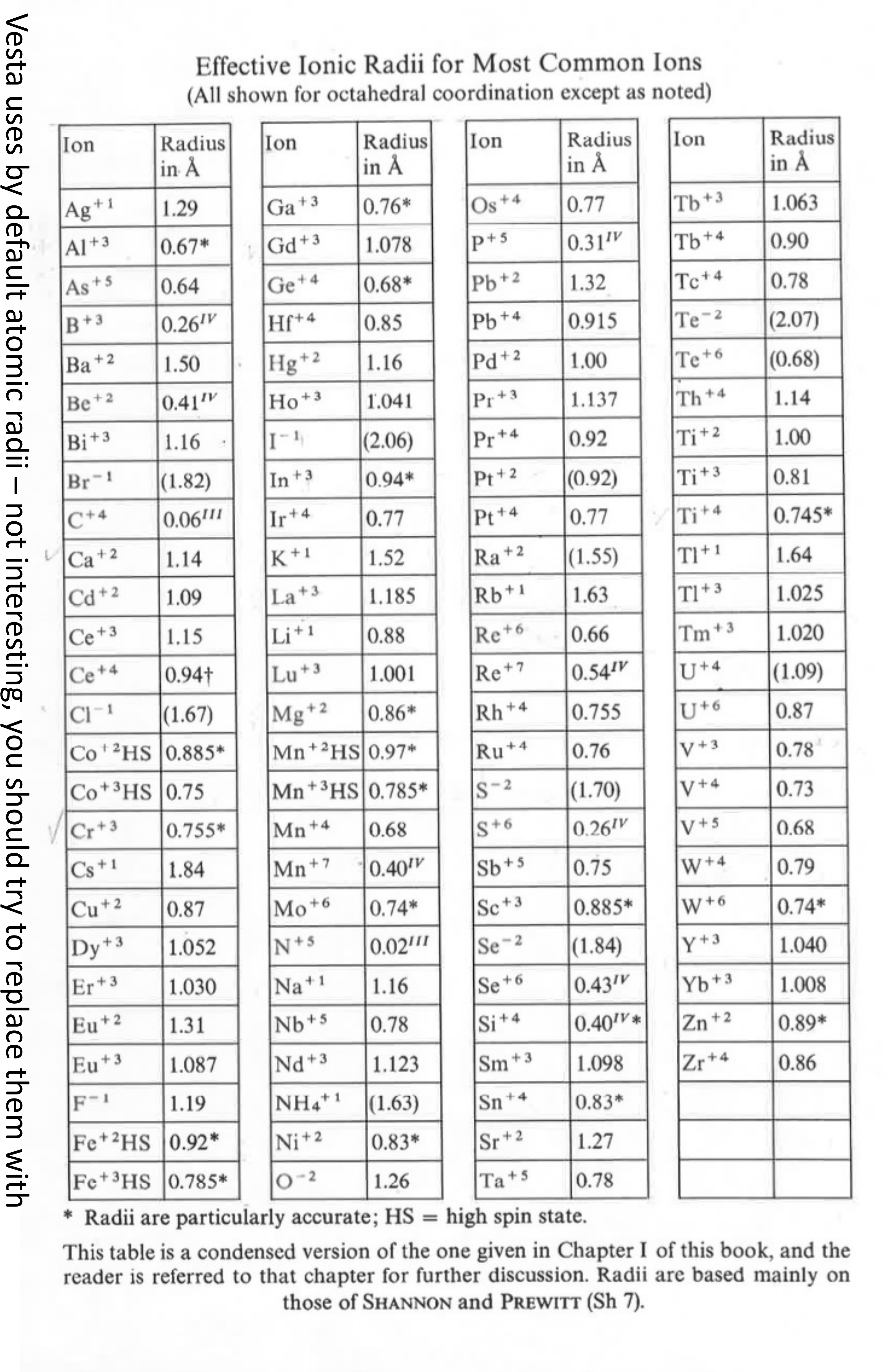


Group 1	Group 2	Group 3	Group 16	Group 17
Li^+ Li 90 134	Be^{2+} Be 59 90	B^{3+} B 41 82	O O^{2-} 73 126	F F^- 71 119
Na^+ Na 116 154	Mg^{2+} Mg 86 130	Al^{3+} Al 68 118	S S^{2-} 102 170	Cl Cl^- 99 167
K^+ K 152 196	Ca^{2+} Ca 114 174	Ga^{3+} Ga 76 126	Se Se^{2-} 116 184	Br Br^- 114 182
Rb^+ Rb 166 211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

Relative sizes of atoms and ions. The neutral atoms are colored gray, cations red, and anions blue.

http://www.knowledgedoor.com/2/elements_handbook/shannon-prewitt_crystal_radius.html

R. D. Shannon,
"Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chaleogenides,"
Acta Cryst. A, vol. 32, p. 751, 1976.



Effective Ionic Radii for Most Common Ions

(All shown for octahedral coordination except as noted)

Ion	Radius in Å	Ion	Radius in Å	Ion	Radius in Å	Ion	Radius in Å
Ag^{+1}	1.29	Ga^{+3}	0.76*	Os^{+4}	0.77	Tb^{+3}	1.063
Al^{+3}	0.67*	Gd^{+3}	1.078	P^{+5}	0.31^{IV}	Tb^{+4}	0.90
As^{+5}	0.64	Ge^{+4}	0.68*	Pb^{+2}	1.32	Tc^{+4}	0.78
B^{+3}	0.26^{IV}	Hf^{+4}	0.85	Pb^{+4}	0.915	Te^{-2}	(2.07)
Ba^{+2}	1.50	Hg^{+2}	1.16	Pd^{+2}	1.00	Te^{+6}	(0.68)
Be^{+2}	0.41^{IV}	Ho^{+3}	1.041	Pr^{+3}	1.137	Th^{+4}	1.14
Bi^{+3}	1.16	I^{-1}	(2.06)	Pr^{+4}	0.92	Ti^{+2}	1.00
Br^{-1}	(1.82)	In^{+3}	0.94*	Pt^{+2}	(0.92)	Ti^{+3}	0.81
C^{+4}	0.06^{III}	Ir^{+4}	0.77	Pt^{+4}	0.77	Ti^{+4}	0.745*
Ca^{+2}	1.14	K^{+1}	1.52	Ra^{+2}	(1.55)	Tl^{+1}	1.64
Cd^{+2}	1.09	La^{+3}	1.185	Rb^{+1}	1.63	Tl^{+3}	1.025
Ce^{+3}	1.15	Li^{+1}	0.88	Re^{+6}	0.66	Tm^{+3}	1.020
Ce^{+4}	0.94†	Lu^{+3}	1.001	Re^{+7}	0.54^{IV}	U^{+4}	(1.09)
Cl^{-1}	(1.67)	Mg^{+2}	0.86*	Rh^{+4}	0.755	U^{+6}	0.87
Co^{+2}HS	0.885*	Mn^{+2}HS	0.97*	Ru^{+4}	0.76	V^{+3}	0.78
Co^{+3}HS	0.75	Mn^{+3}HS	0.785*	S^{-2}	(1.70)	V^{+4}	0.73
Cr^{+3}	0.755*	Mn^{+4}	0.68	S^{+6}	0.26^{IV}	V^{+5}	0.68
Cs^{+1}	1.84	Mn^{+7}	0.40^{IV}	Sb^{+5}	0.75	W^{+4}	0.79
Cu^{+2}	0.87	Mo^{+6}	0.74*	Sc^{+3}	0.885*	W^{+6}	0.74*
Dy^{+3}	1.052	N^{+5}	0.02^{III}	Se^{-2}	(1.84)	Y^{+3}	1.040
Er^{+3}	1.030	Na^{+1}	1.16	Se^{+6}	0.43^{IV}	Yb^{+3}	1.008
Eu^{+2}	1.31	Nb^{+5}	0.78	Si^{+4}	0.40^{IV}*	Zn^{+2}	0.89*
Eu^{+3}	1.087	Nd^{+3}	1.123	Sm^{+3}	1.098	Zr^{+4}	0.86
F^{-1}	1.19	NH_4^{+1}	(1.63)	Sn^{+4}	0.83*		
Fe^{+2}HS	0.92*	Ni^{+2}	0.83*	Sr^{+2}	1.27		
Fe^{+3}HS	0.785*	O^{-2}	1.26	Ta^{+5}	0.78		

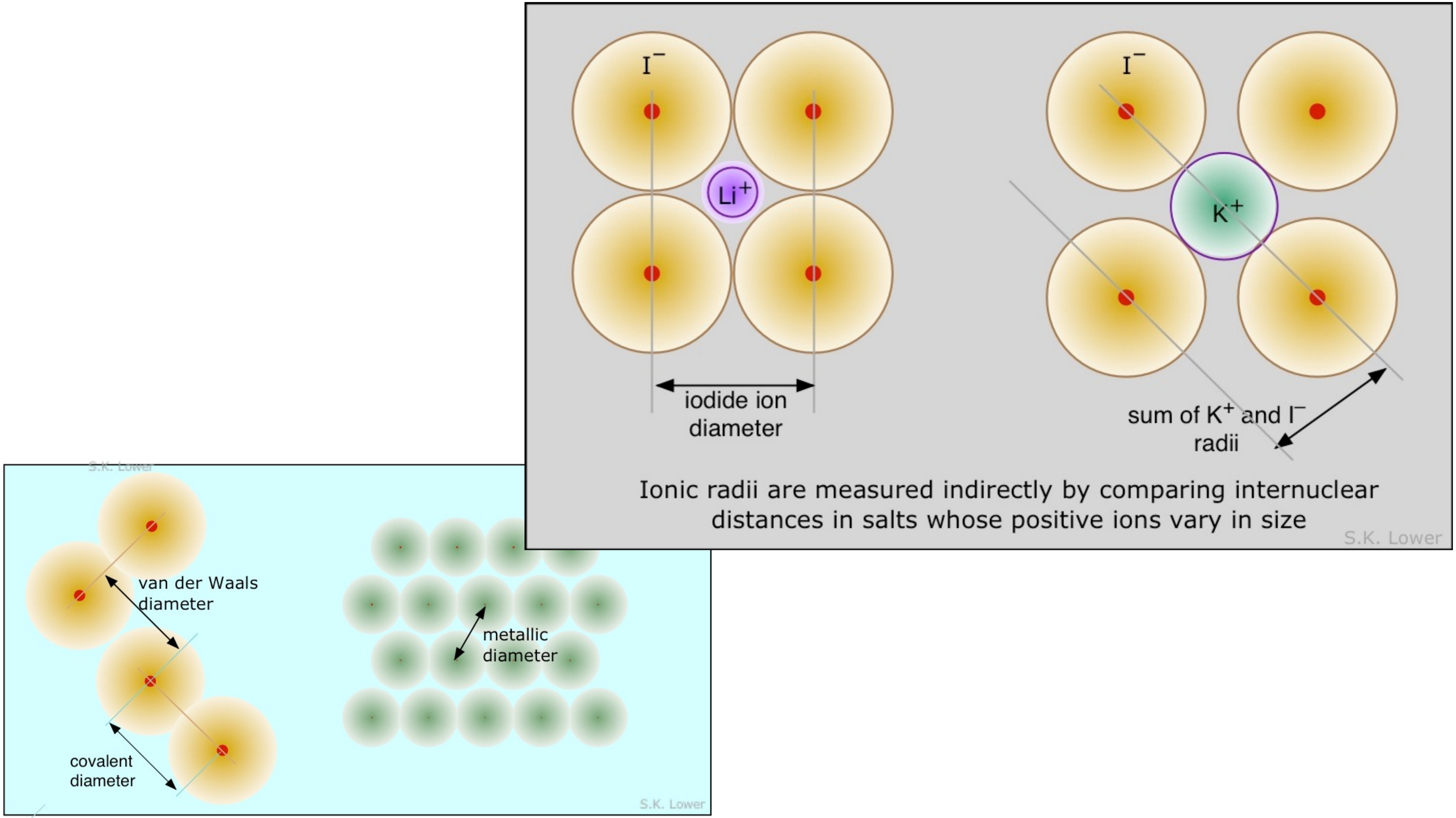
* Radii are particularly accurate; HS = high spin state.

This table is a condensed version of the one given in Chapter I of this book, and the reader is referred to that chapter for further discussion. Radii are based mainly on those of SHANNON and PREWITT (Sh 7).

Vesta uses by default atomic radii – not interesting, you should try to replace them with ionic radii

As^{+5}	0.64
B^{+3}	0.26^{IV}
Ba^{+2}	1.50
Be^{+2}	0.41^{IV}
Bi^{+3}	1.16
Br^{-1}	(1.82)
C^{+4}	0.06^{III}
Ca^{+2}	1.14
Cd^{+2}	1.09
Ce^{+3}	1.15
Ce^{+4}	0.94†
Cl^{-1}	(1.67)
Co^{+2}HS	0.885*
Ge^{+4}	0.68*
Hf^{+4}	0.85
Hg^{+2}	1.16
Ho^{+3}	1.041
I^{-1}	(2.06)
In^{+3}	0.94*
Ir^{+4}	0.77
K^{+1}	1.52
La^{+3}	1.185
Li^{+1}	0.88
Lu^{+3}	1.001
Mg^{+2}	0.86*
Mn^{+2}HS	0.97*
Pb^{+2}	1.32
Pb^{+4}	0.915
Pd^{+2}	1.00
Pr^{+3}	1.137
Pr^{+4}	0.92
Pt^{+2}	(0.92)
Pt^{+4}	0.77
Ra^{+2}	(1.55)
Rb^{+1}	1.63
Re^{+6}	0.66
Re^{+7}	0.54^{IV}
Rh^{+4}	0.755
Ru^{+4}	0.76
Tc^{+4}	0.78
Te^{-2}	(2.07)
Te^{+6}	(0.68)
Th^{+4}	1.14
Ti^{+2}	1.00
Ti^{+3}	0.81
Ti^{+4}	0.745*
Tl^{+1}	1.64
Tl^{+3}	1.025
Tm^{+3}	1.020
U^{+4}	(1.09)
U^{+6}	0.87
V^{+3}	0.78

Different definitions of sizes of elements



Ionic radii are measured indirectly by comparing internuclear distances in salts whose positive ions vary in size

Effect of ion size and valence on hardness

	BeO	MgO	CaO	SrO	BaO
Distance (Å)	1.65	2.10	2.40	2.57	2.77
Hardness	9.0	6.5	4.5	3.5	3.3

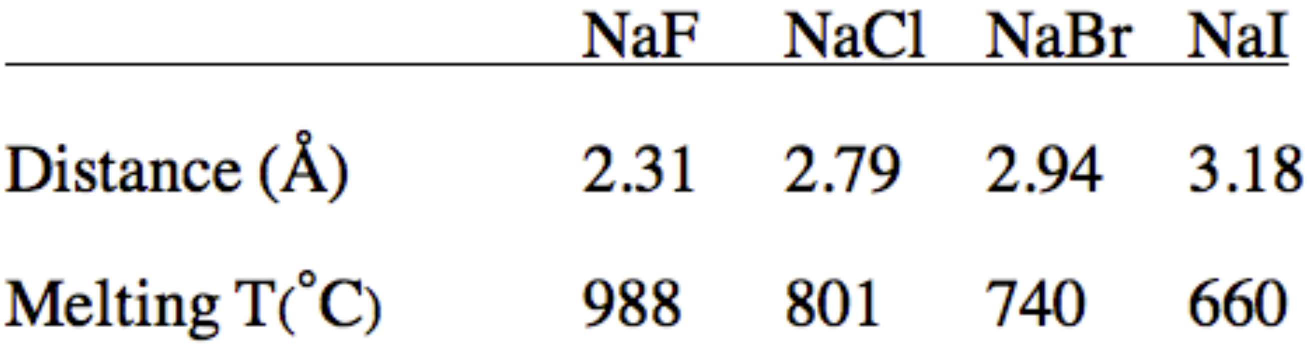
size

	NaF (1)	MgO (2)	ScN (3)	TiC (4)
Distance (Å)	2.31	2.10	2.23	2.23
Hardness	3.0	6.5	7-8	8-9

valence

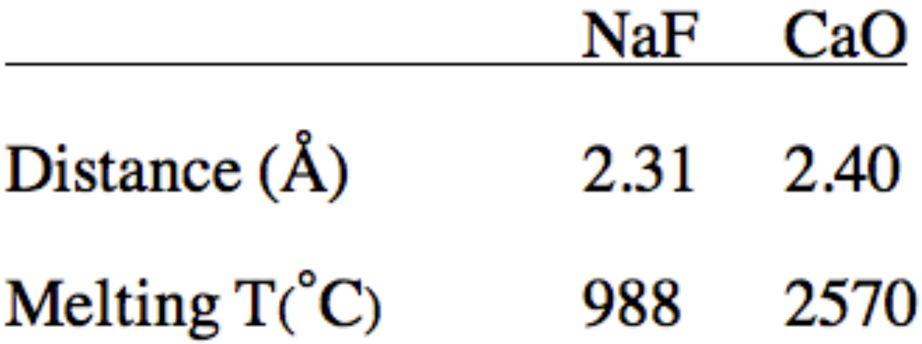
$$E_{lattice}(r_0) = -\frac{N_A e^2 Z_1 Z_2 \alpha}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

Effect of ion size and valence on melting point



	NaF	NaCl	NaBr	NaI
Distance (Å)	2.31	2.79	2.94	3.18
Melting T(°C)	988	801	740	660

size



	NaF	CaO
Distance (Å)	2.31	2.40
Melting T(°C)	988	2570

valence

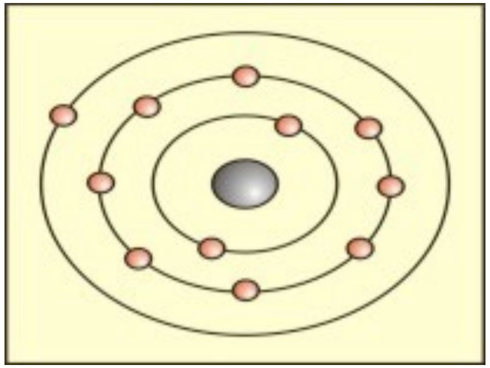
Effect of ion size and valence on thermal dilatation

valence

	NaF	NaCl	NaBr	NaI	CaF_2
Distance (10^{-10}m)	**2.31**	**2.79**	**2.94**	**3.18**	**2.43**
Expansion thermique (10-6)	**39**	**40**	**43**	**48**	**19**

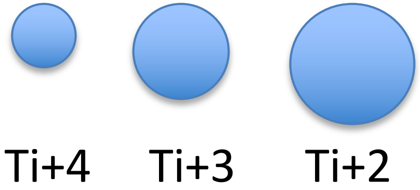
Ionic radii trends

Ionic radii are on the order of 1Å

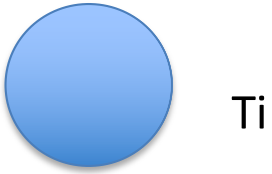


1. The radius increases with number of electron shells

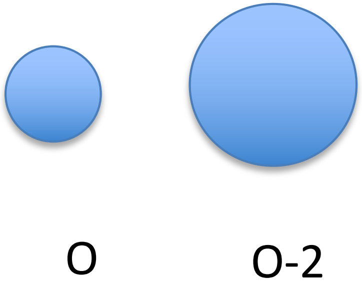
2. Positive charge of the nucleus attracts electrons.
The ionic radius decreases when valence increases



3. Cations are smaller than atoms,
and their radius decreases as valence increases



4. Anions are larger than atoms



(not in scale)

Ionic radii

- 5. Ionic radii increase when going down a column in periodic table

- 6. Along a row of periodic table (from left to right), radii decrease. The trend can be different for transition metals where radii may increase,

- 7. The bonding strength decreases as coordination number (CN) increases. As bonding strength decreases the radii of ions increase. Thus: ionic radius increases with coordination number (for example:

  Radius (CN(4)) = 0.95*Radius (CN(6))

  and Radius (CN(8)) =1.09* Radius (CN(6))

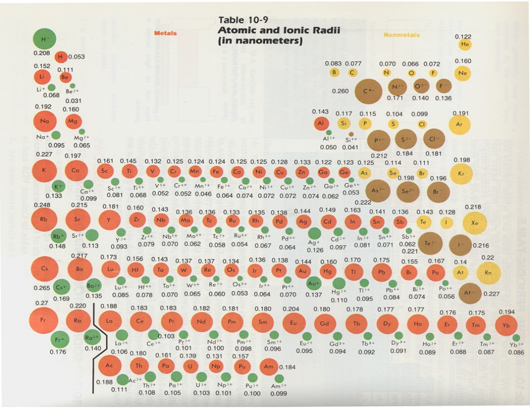
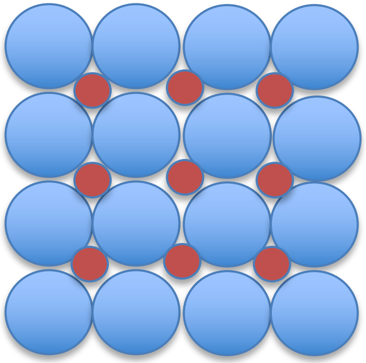


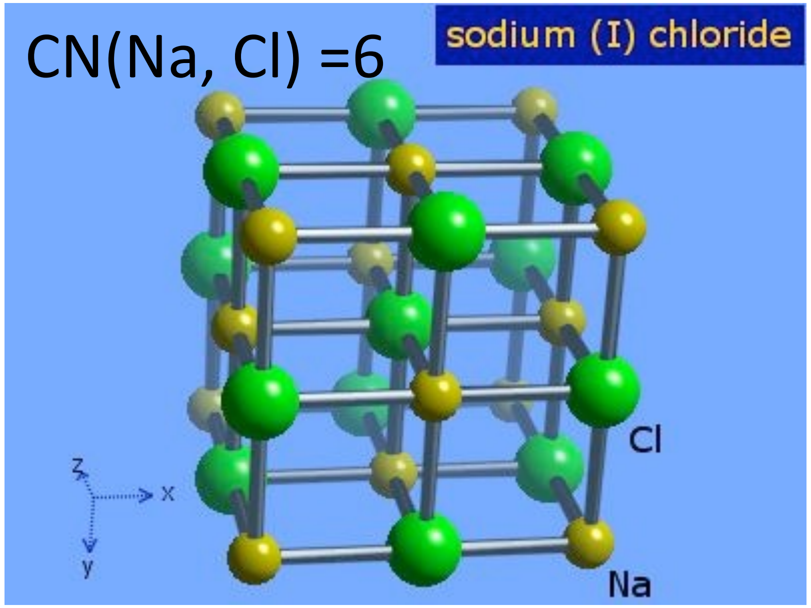
Table 10-9
Atomic and Ionic Radii
(in nanometers)

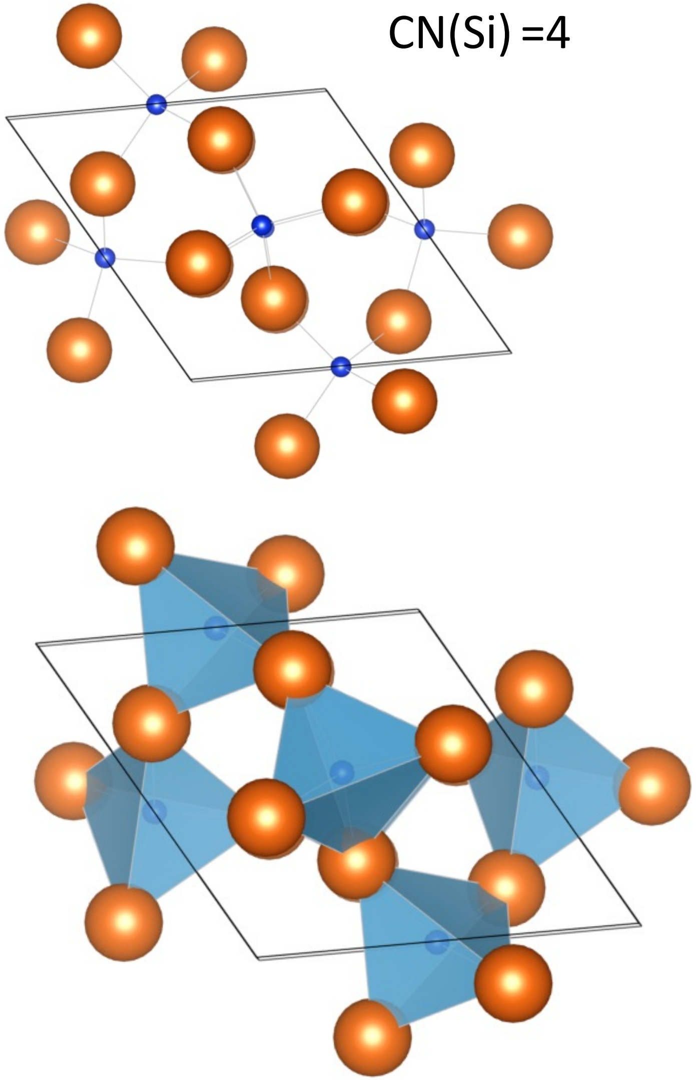
Coordination number

- The number of ions of opposite charge in the first coordination sphere around an ion is called coordination number



2dim
CN=4





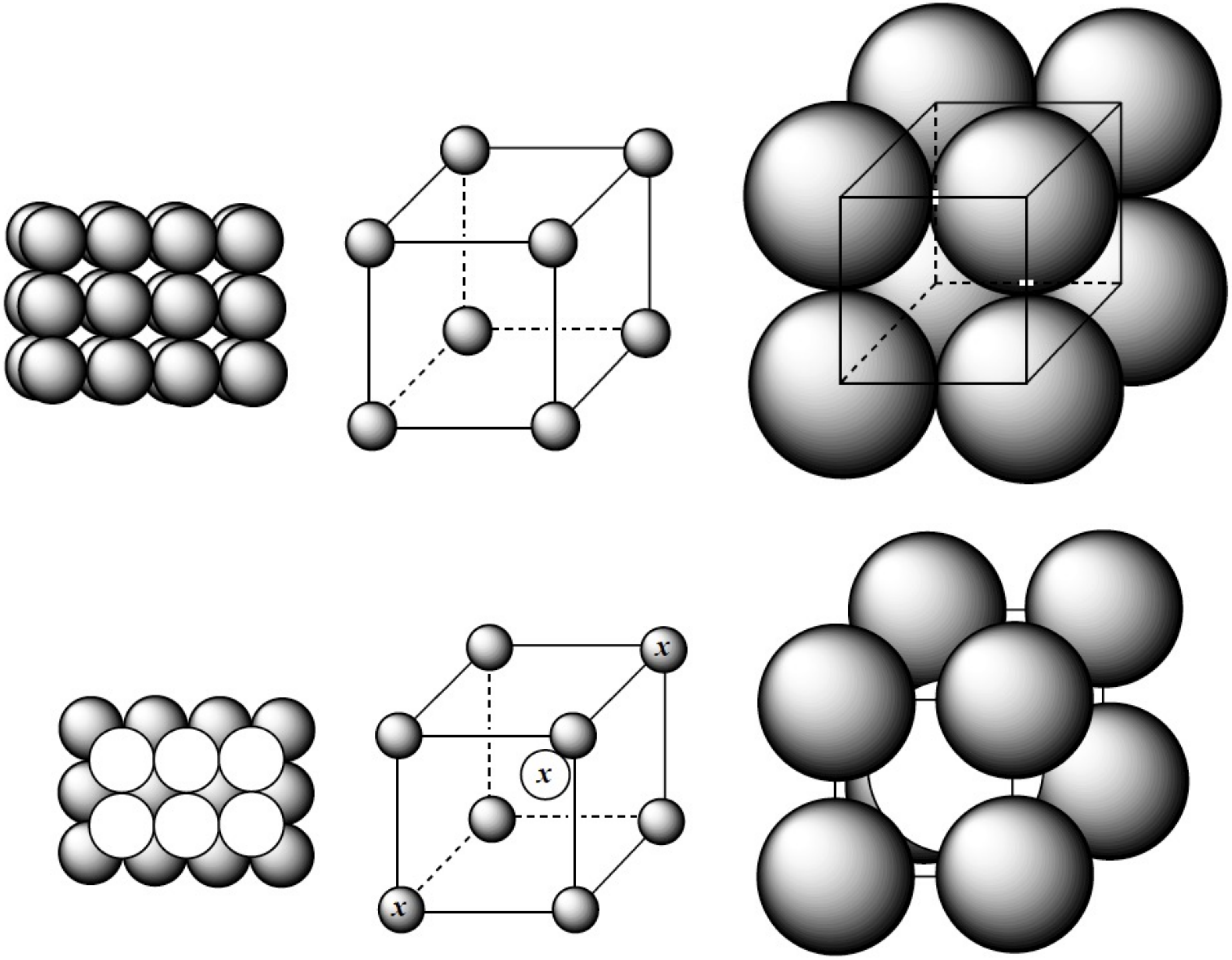
Bonding strength

$$E \propto \frac{Z_{cation} Z_{anion}}{r_0}$$

Energy of an ionic structure
Z valence
r0 distance of two ions in equilibrium

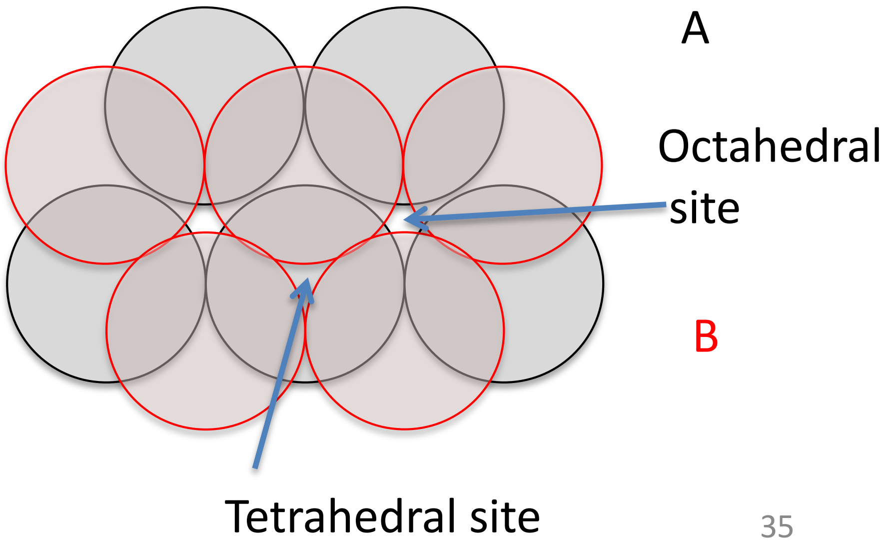
Bonding strength of a cation to each coordinated anion is defined as valence of the cation divided by its coordination number

Packing of atoms
-Primitive cubic and body centered-

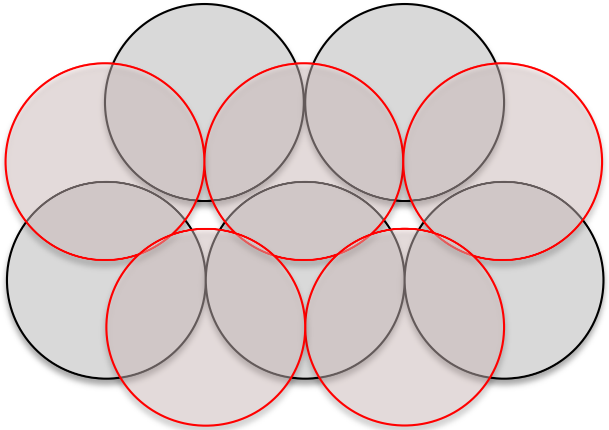


Packing of ions

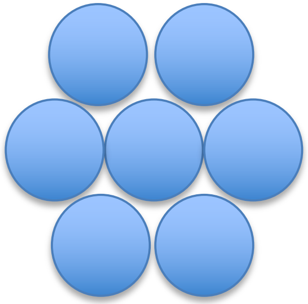
- Dense packing of large ions, while smaller ions fill up interstitial sites
- In majority of oxides anions are arranged either in hexagonal close packing (HCP) or face centered cubic (FCC) (the latter also called cubic close packing - CCP).
- Interstitial sites are octahedral or tetrahedral and are fully or partially occupied by cations.
- Occupation of interstitial sites depends on size and valence of cation



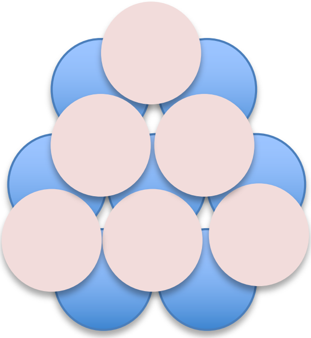
Hexagonal close packing



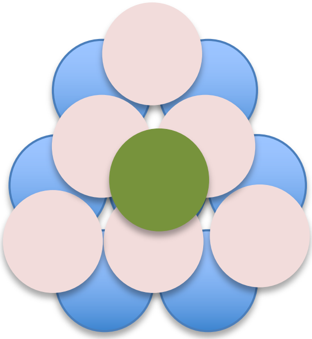
First two layers A, B
next layer is above A: therefore ABABAB… sequence



A

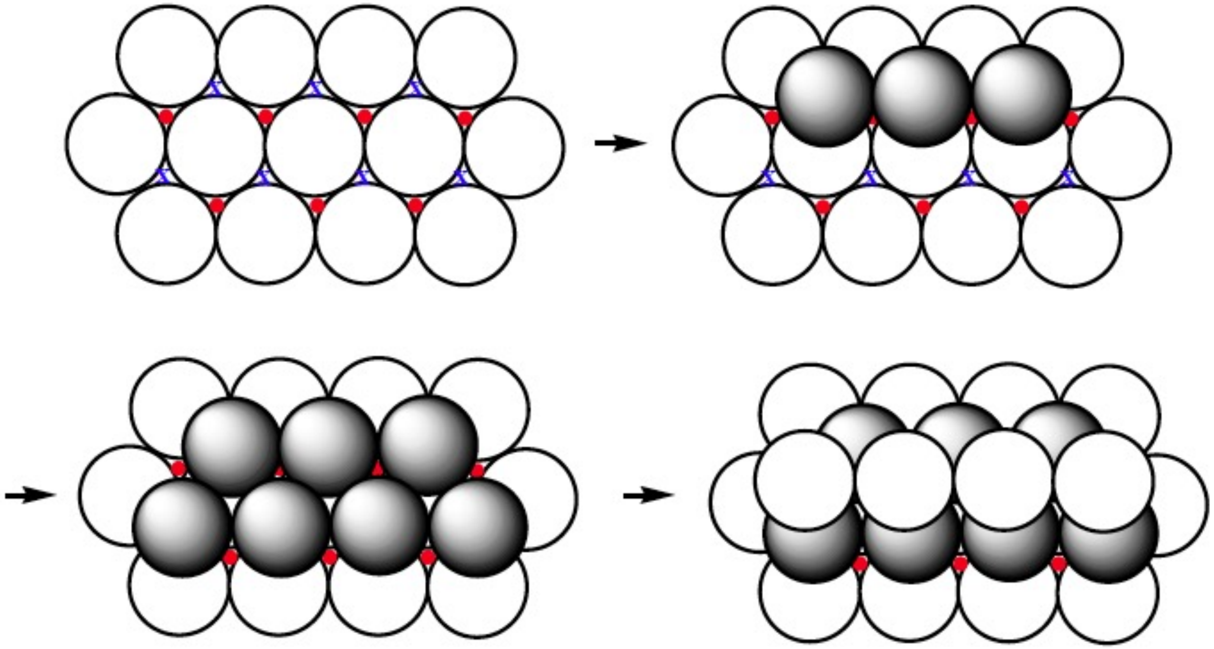


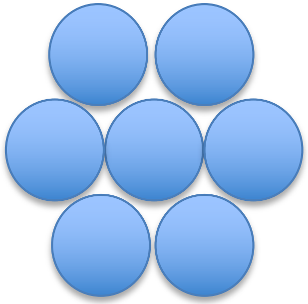
A+B



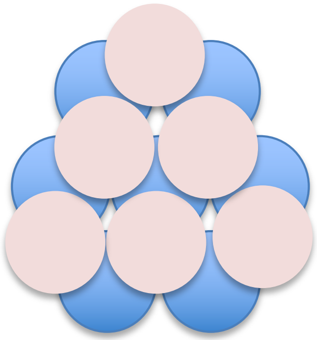
A+B+A

Cubic close packing (Face centered cubic)

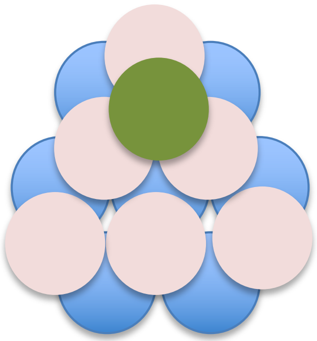




A

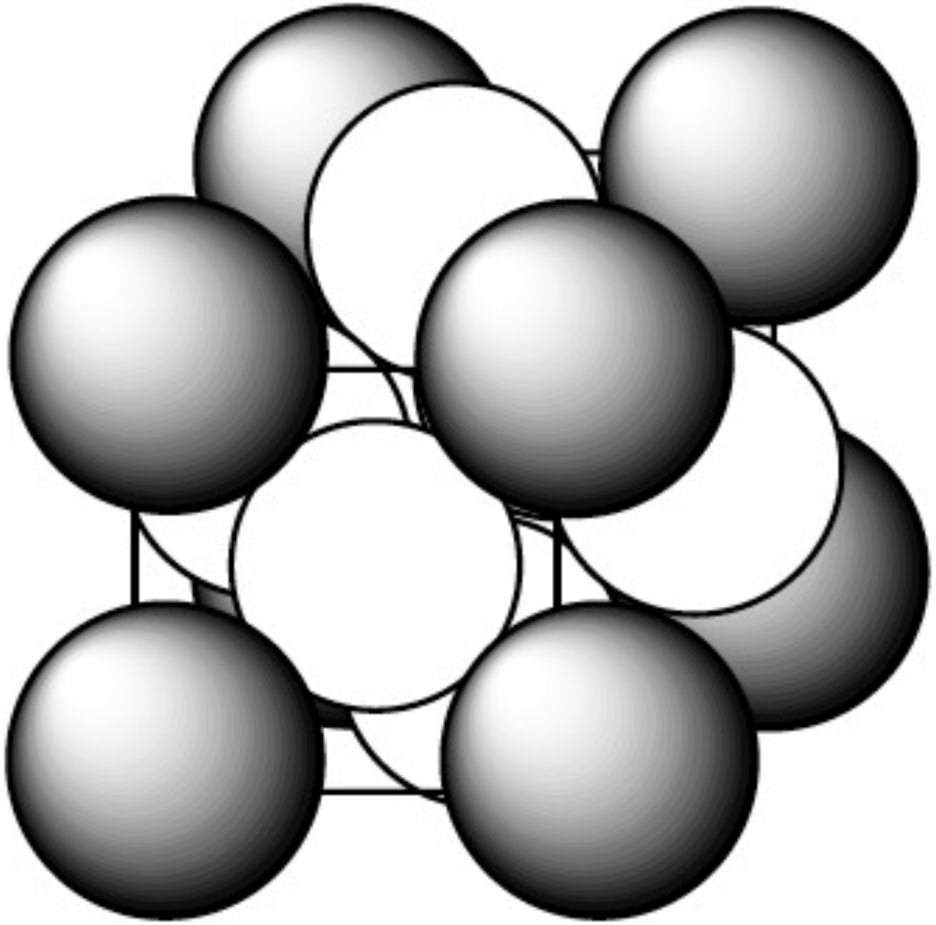


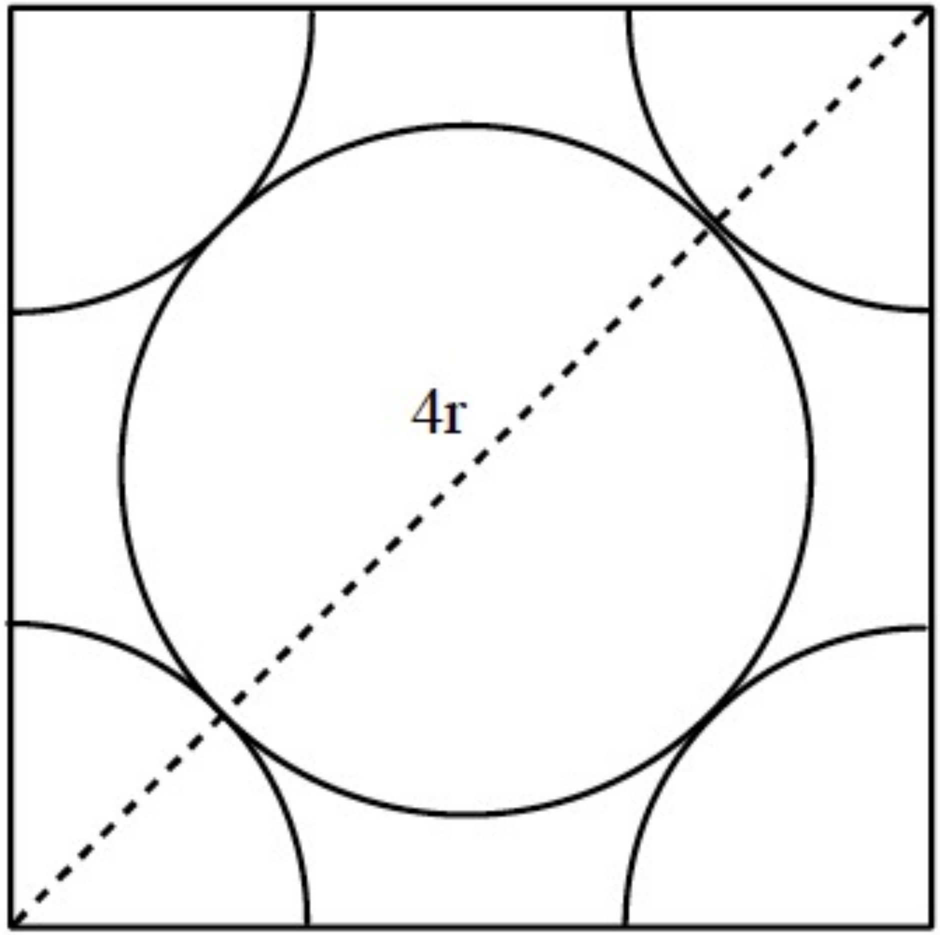
A+B



A+B+C

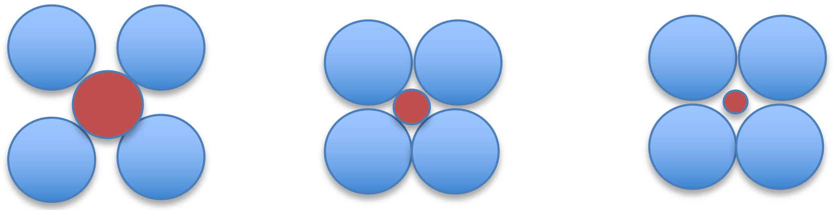
Space filling of FCC

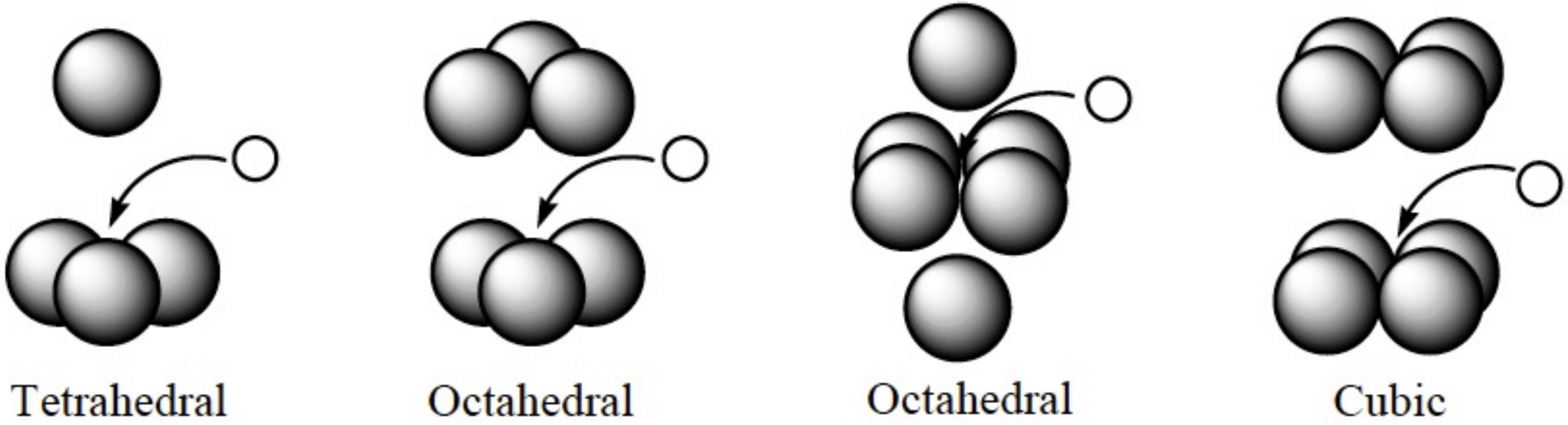




Atoms fill about 74% of the available space.

Radius ratio for various coordination numbers





Interstitial Type	Radius Ratio
Tetrahedral	0.225 – 0.414
Octahedral	0.414 – 0.732
Cubic	0.732 – 1.000

Common structures
-Pauling rules-

- At least two ions (one anion and at least one cation)
- Cation smaller, delivers electrons; anion larger, accept electrons
- Structure types: AX, A_2X, AX_2, A_2X_3, ABX_3, AB_2X_4

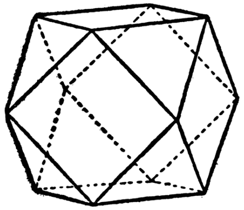
Pauling rules

Rules based on crystal chemistry arguments which permit prediction of ionic structures and coordination numbers. The rules involve ionic radii, ionic valence and electrostatic forces among ions

- **Rule 1**: Each cation is surrounded by a polyhedron of anions. The coordination number of cation is determined by the ratio of radius of cation and anion (r_{cation}/r_{anion}).

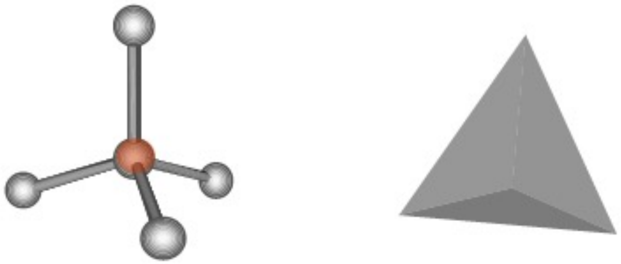
Pauling rules –Rule I : coordination number

CN	Arrangement of ions	Radio of cation/anion radii	Example
12	cuboctahedral	>1	K^+; Ba^{+2} in BaTiO3
8	cubic	>0.732	Ca^{+2} in CaF2
6	octahedral	>0.414	Mg^{+2} in MgO
4	tetrahedral	>0.225	Si^{+4} in SiO2
3	triangular	>0.155	C^{+4} in CaCO3
2	linear	>0	H^{+1}



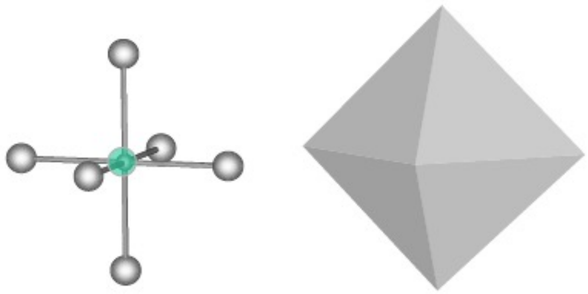
Pauling rules- polyhedra types

Tetrahedron
4 neighbors



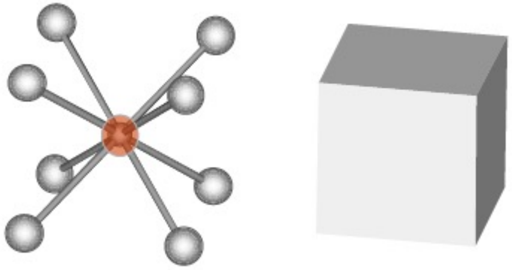
Si+4 in SiO2

Octahedron
6 neighbours



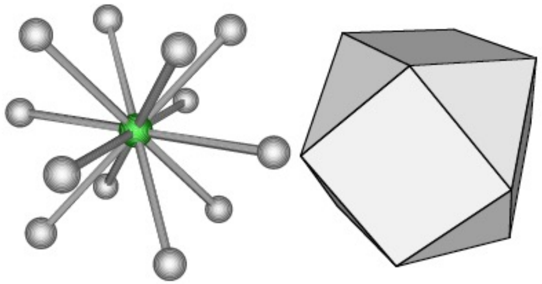
Mg+2 in MgO

Cube
8 neighbors



Th+4 in ThO2

Cuboctahedron
12 neighbours

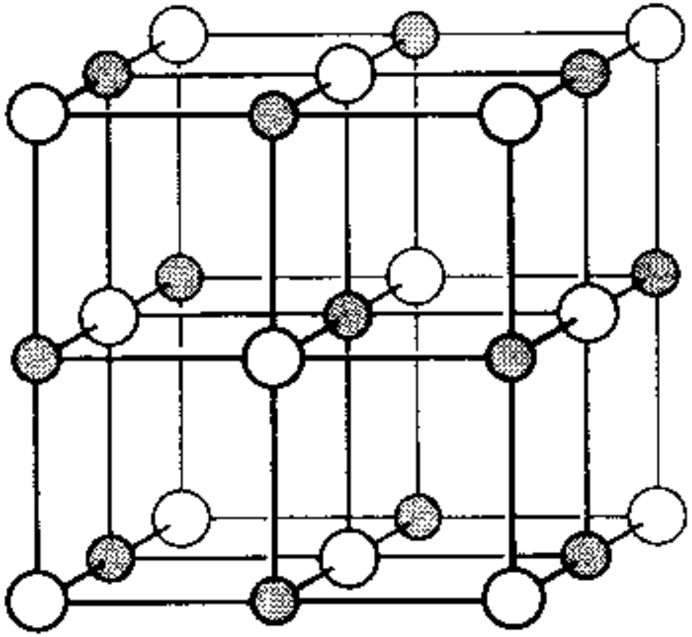


Ba+2 in BaZrO3

Pauling rules

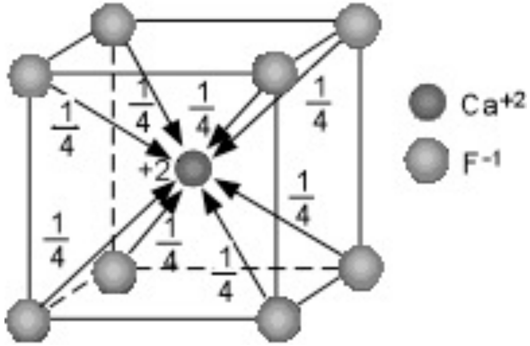
- **Rule 2:** In a stable structure, the sum of the bond strengths to an anion is equal to anion's valence (preservation of neutrality)

Bond strength =Valence of cation/cation coordination number
Valence of anion= Sum of bond strengths with cations × anion coordination number



NiO

(partial view)



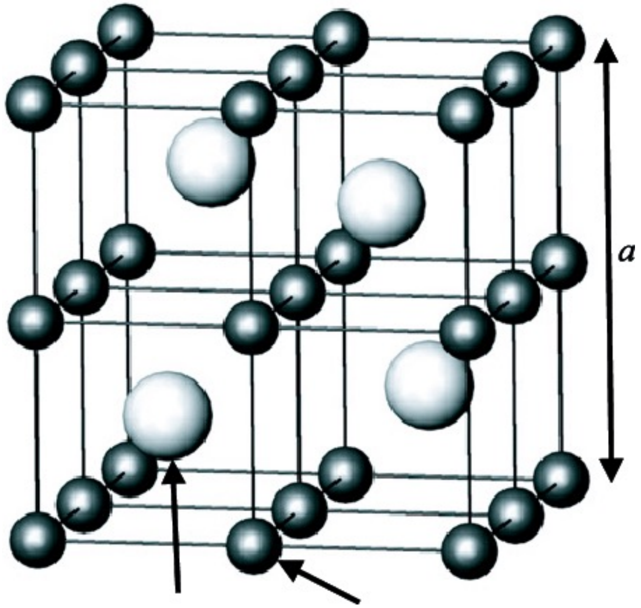
CaF_2

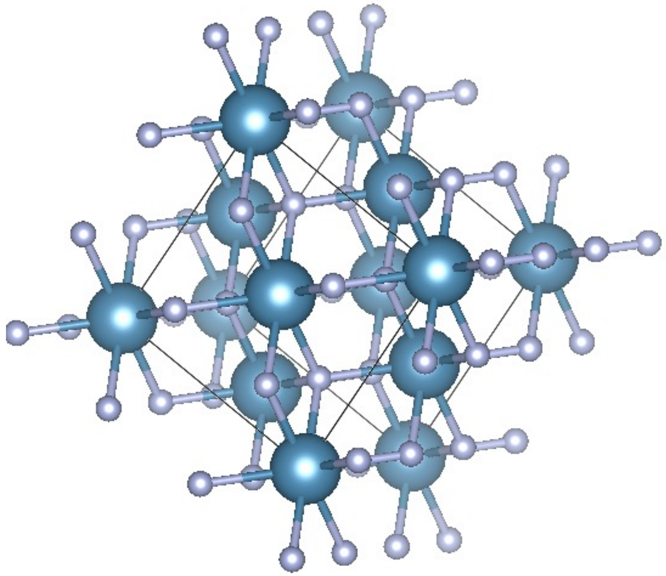
CN(Ca) of Ca^{+2} is 8.
The force strength is ¼.

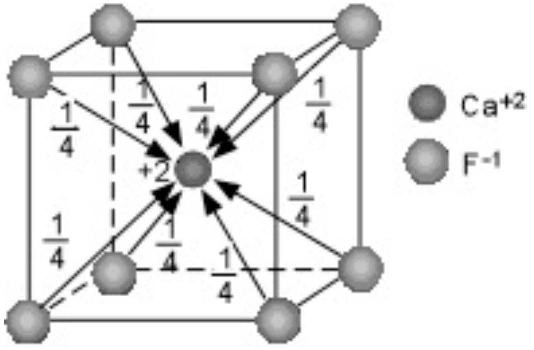
CN of F is:
CN(F)*1/4=1 → CN(F)=4

For Ni^{+2}: CN(Ni)=6
For Ni^{+2}, the bonding force or strength is: valence/CN(Ni)=2/6 =1/3
For O^{-2}, the charge (valence) is equal to the sum of bonding forces to the cation: (1/3) xCN(O) = 2: CN(O)=6

Fluorite structure







CN(Ca)=8

Pauling rules: rules 1 and 2 together

R/	CN
>.225	4
>.414	6
>.732	8
>1.00	12

- Used to predict probable structure of ionic materials:

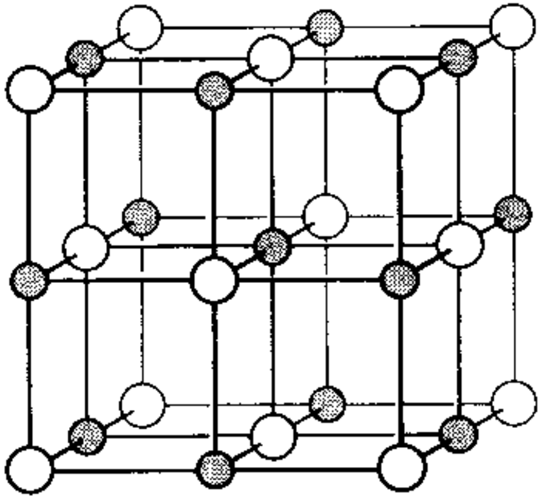
  (1) Determine coordination number of cation from its size (1st rule).

  (2) The condition that the sum of bonding strengths + valence of anion = 0, gives coordination number of anion (2^{nd} rule)

For MgO:
rMg+2 = 0.86Å, rO = 1.26Å
rMg+2/rO = 0.86/1.26 = 0.68 --> CN(Mg)= 6 for Mg2+
Bonding force around Mg+ 2: +2 / 6=1/3
Oxygen CN(O): CN(O) x 1/3 + (-2) = 0 --> CN(O) = 6

For NaCl:
rNa+1 = 1.16Å, rCl = 1.67Å
rNi+2/rO = 1.16/1.67 = 0.69 --> CN(Na)= 6 for Na1+
Bonding force around Na+ 1: +1 / 6=1/6
Chlor CN(Cl): CN(Cl) x 1/6 + (-1) = 0 --> CN(Cl) = 6

CN of Cl in NaCl and CN of O in MgO is 6



Intermediate summary: Pauling rules 1, 2

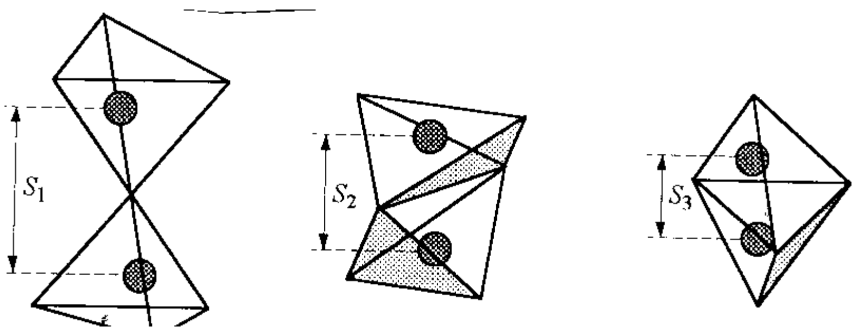
- The Pauling rules 1, 2 help making reasonable assumptions about simple structures based on electrostatics

- The first rule imposes limits based on anion repulsion + simple geometrical considerations within the model of hard spheres – coordination number of cations

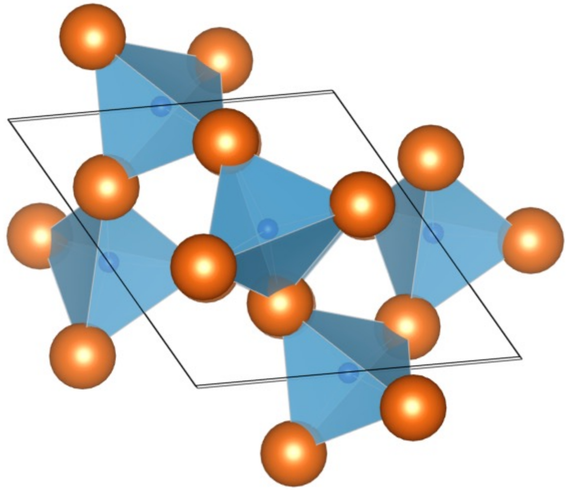
- Next, we need to find a coordination of the anion – second rule based on electrostatics

Pauling rules

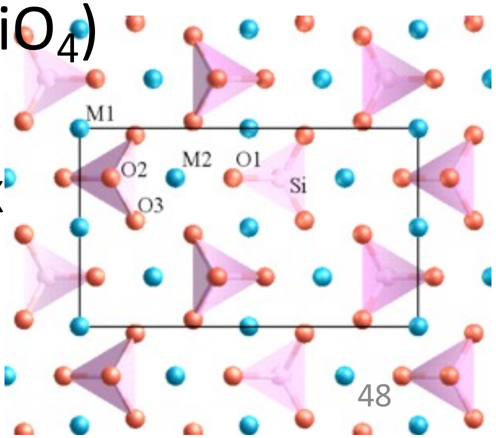
- **Rule 3:** The bond is strongest when coordination polyhedra share corners, less stable when they share edges, and least stable when they share faces.



Why?



- **Rule 4:** Coordination polyhedra of small cations with large charge tend to share corners (or not share any elements: olivine $(Mg,Fe)_2SiO_4$)



- **Rule 5:** Simpler structures are more likely than complex (the rule of parsimony)