COMMONWEALTH OF AUSTRALIA

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Solid State Materials

Lecture 6

Crystal Structures

Diffraction

Miller Indices

Bragg's Law

Lecture 7

Ionic vs. Covalent Bonding

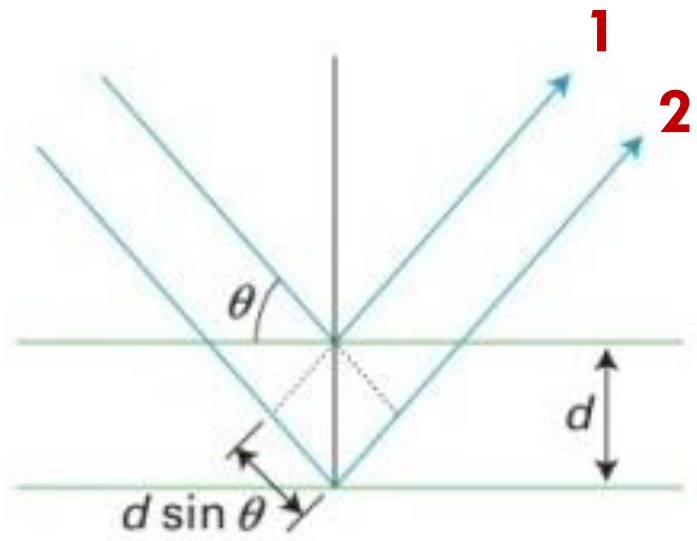
Ionic Radii

Lattice Enthalpy

Lecture 8

Electronic Structure of Materials

Bragg Diffraction



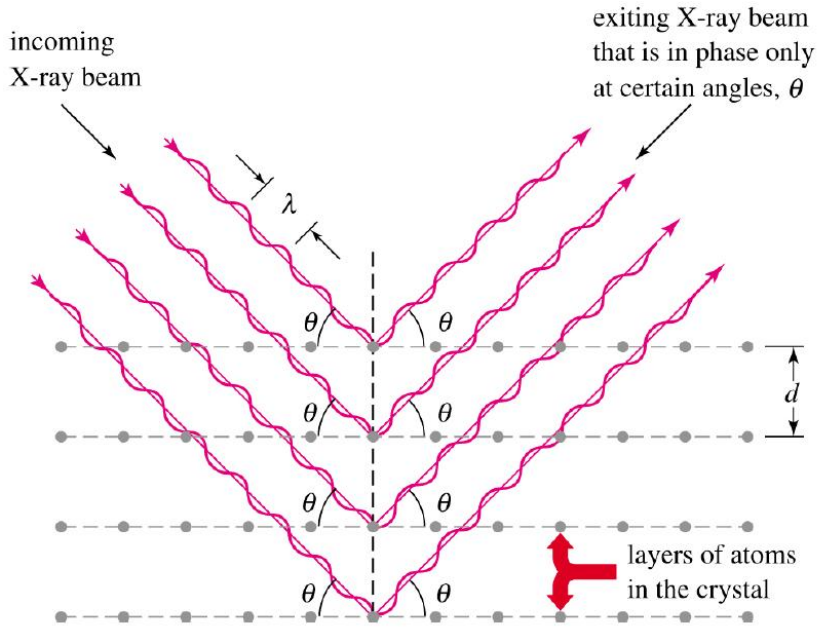
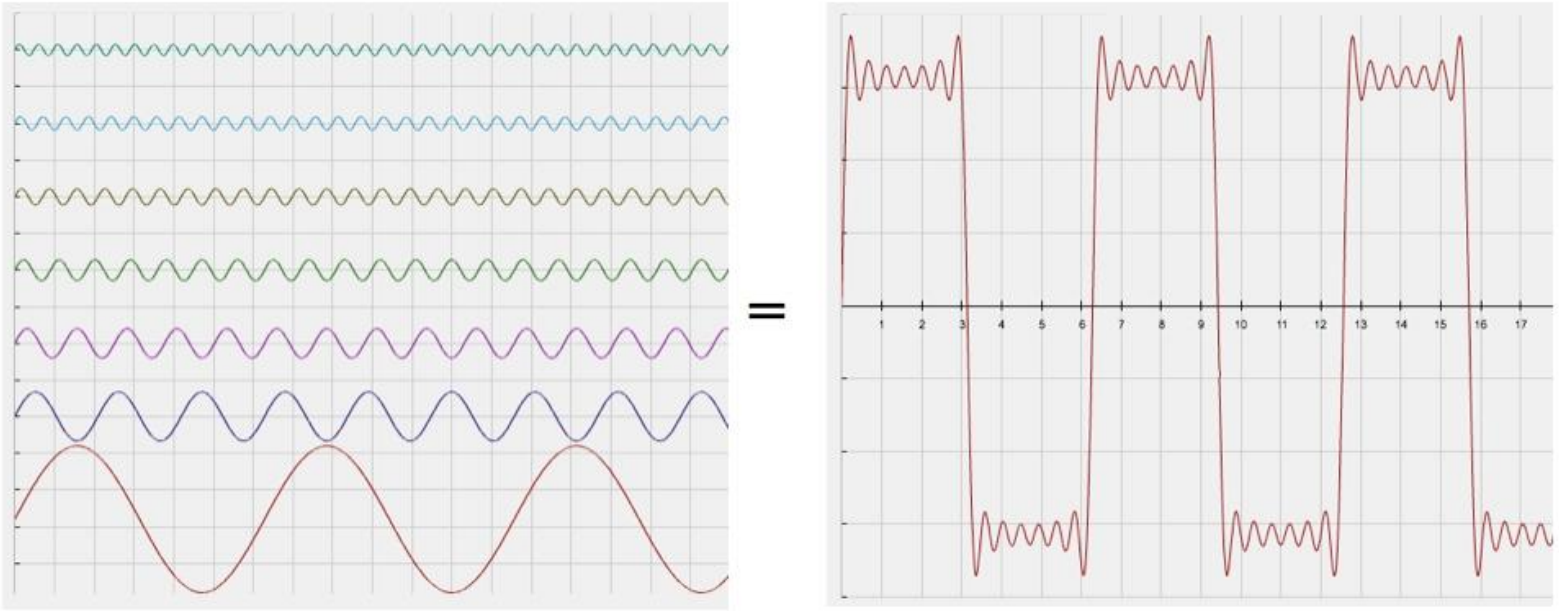


Figure from Week 4 Tutorial

The extra distance travelled by beam **2** is $2d\sin\theta$. Thus, if constructive interference is to occur then this distance must correspond to an integral number (n) of wavelengths, i.e., $n\lambda = 2d\sin\theta$.

See also https://www.youtube.com/watch?v=QHMzFUo0NL8




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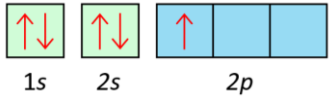
Bonding and the Implications on Structure

Number of valence electrons < number of valence atomic orbitals

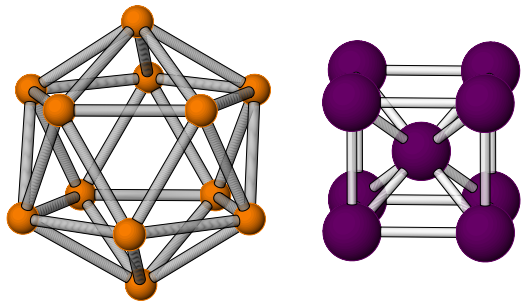
Number of valence electrons ≥ number of valence atomic orbitals

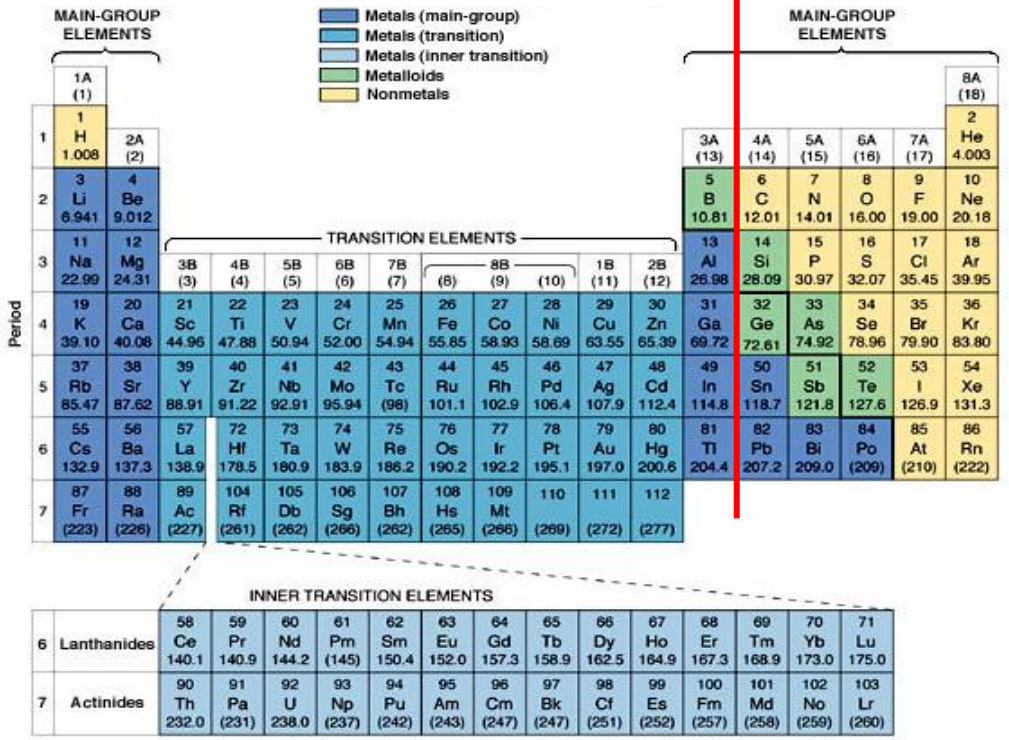
E.g., **boron**
No. of valence electrons = 3
No. of valence atomic orbitals = 4

$1s^2, 2s^2, 2p^1$



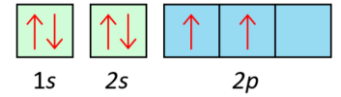
Can't achieve inert gas configuration through covalent bonding



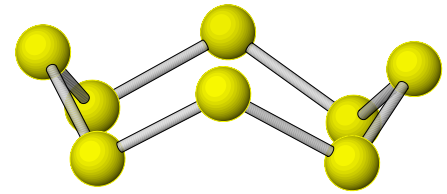


E.g., **carbon**
No. of valence electrons = 4
No. of valence atomic orbitals = 4

$1s^2, 2s^2, 2p^2$



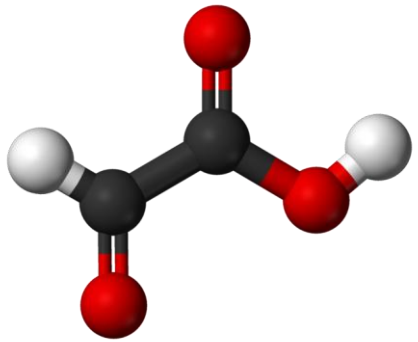
Inert gas configuration can be achieved through 2-centre, 2-electron covalent bonds (and lone pairs)



Bonding and the Implications on Structure

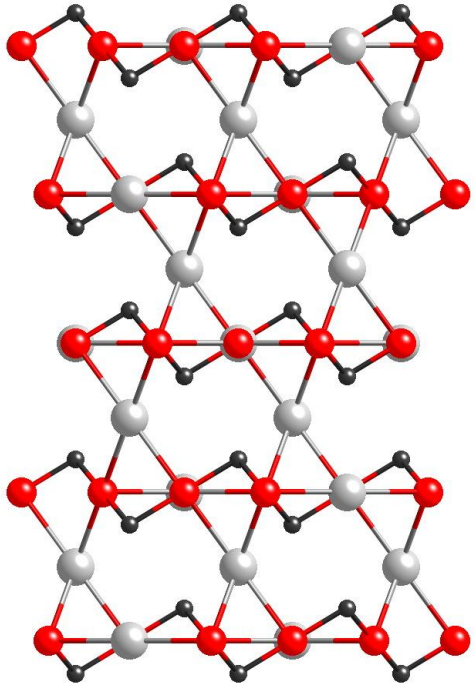
Elements in the same group near the "line" show different bonding

Consider these two compounds built of (valence) isoelectronic elements:



$C_2H_2O_3$
Glyoxylic acid

vs.



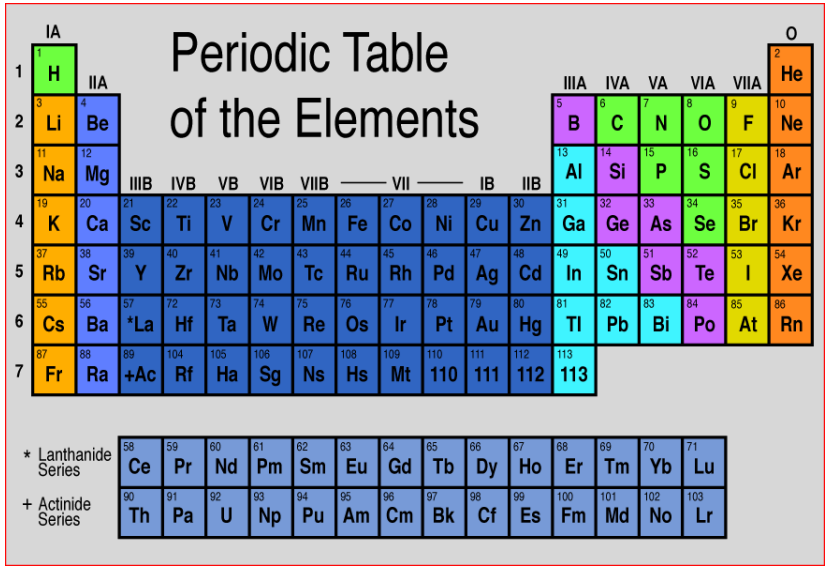
$Sn_2K_2O_3$

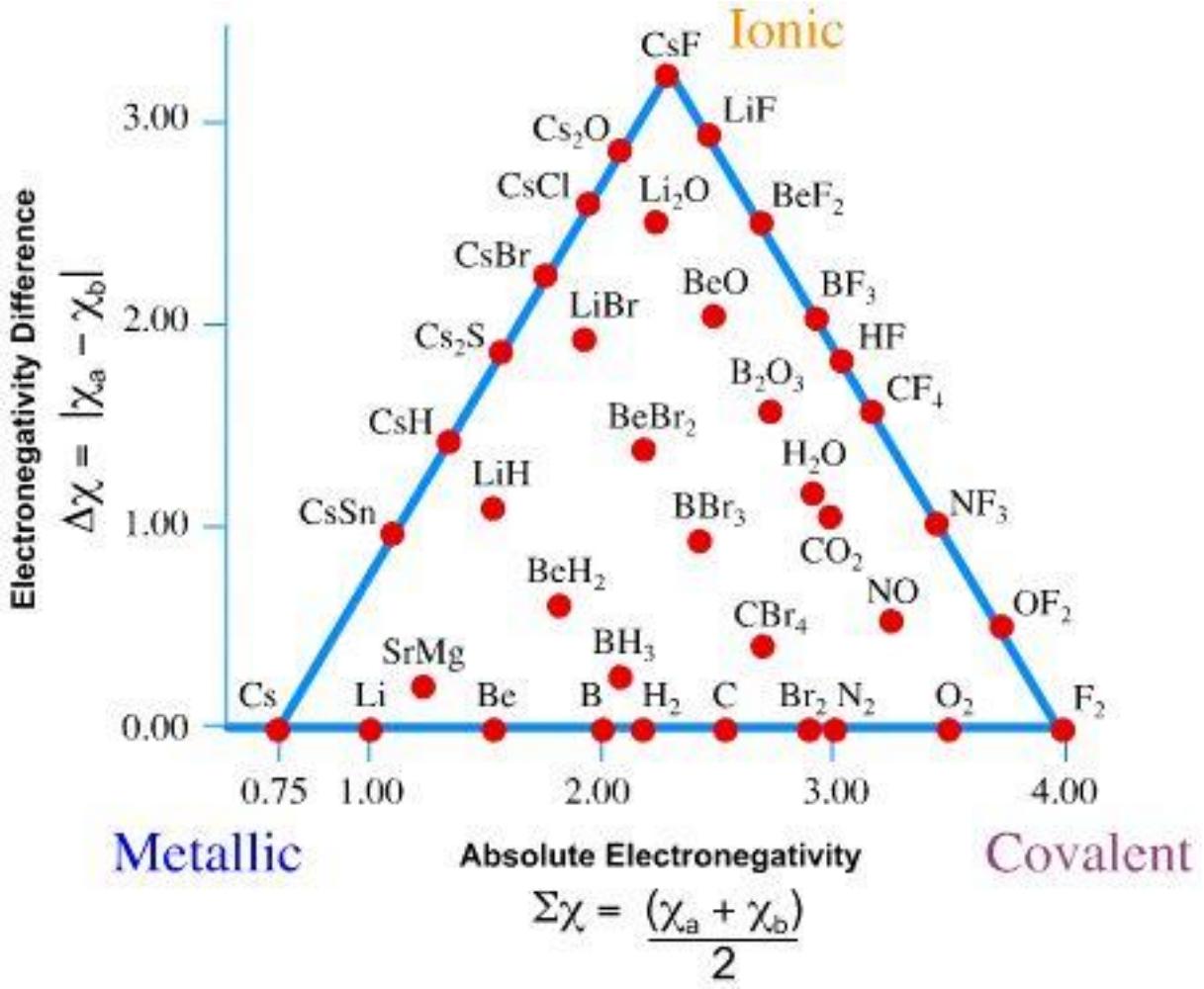
Isoelectronic elements have the same number of valence electrons. I.e., elements in the same group.

Chemical Bonding: Ionic, Covalent or Metallic?

Ketelaar's Triangle

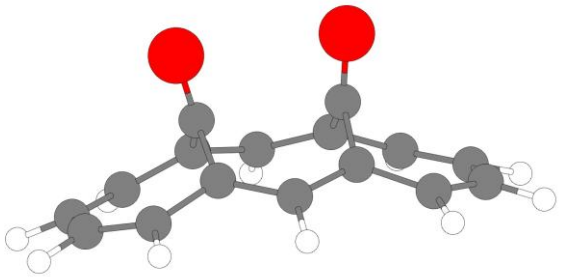
Recognises that there is a continuum of chemical bonding for compounds with intermediate electronegativities



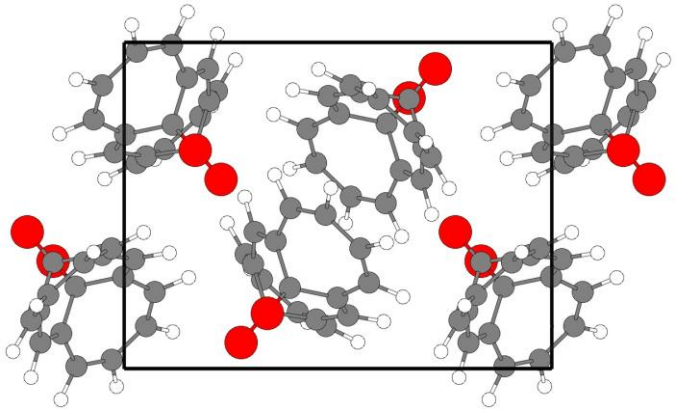


Bonding in Solids

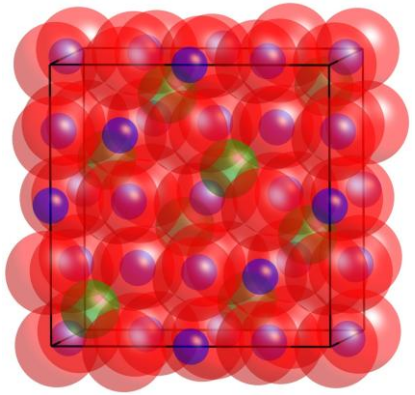
- We think of atoms in molecules as covalently bonded
  - Directional → complex shapes (low symmetry)



- We think of molecules in crystals as Van der Waals bonded
  - Non-directional → moderate symmetry (limited by the shapes of the molecules)



- We think of atoms in "solid state" compounds as ionically bonded
  - Non-directional, drive to high coordination numbers and high packing efficiency → high symmetry



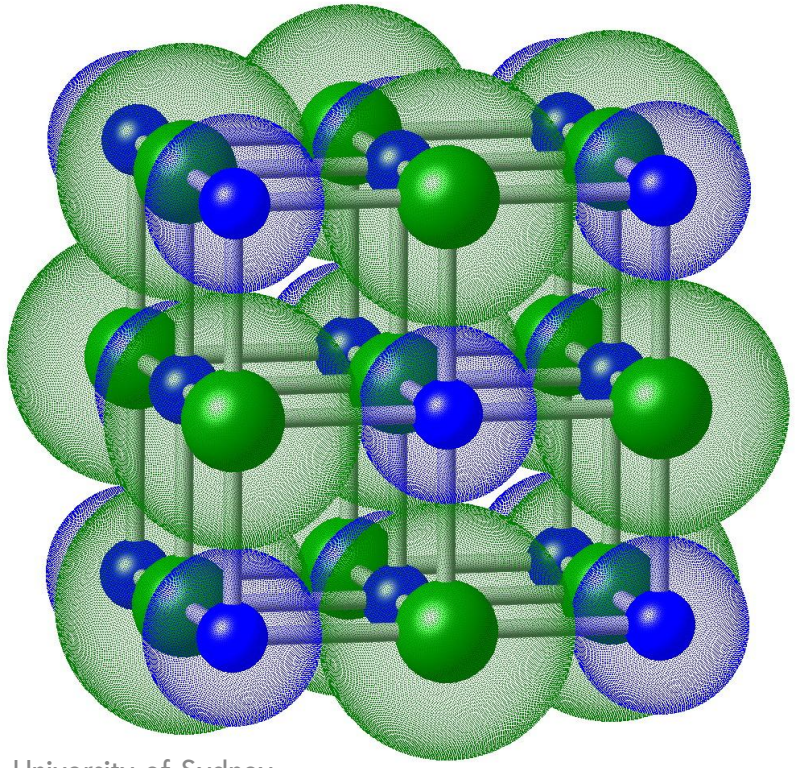
- Can also have combinations

Ionic or Covalent Bonding?

(Largely) ionic

- Large cations with low valence (groups I, II)
- Small electronegative anions (O^{2-}, F^{-})

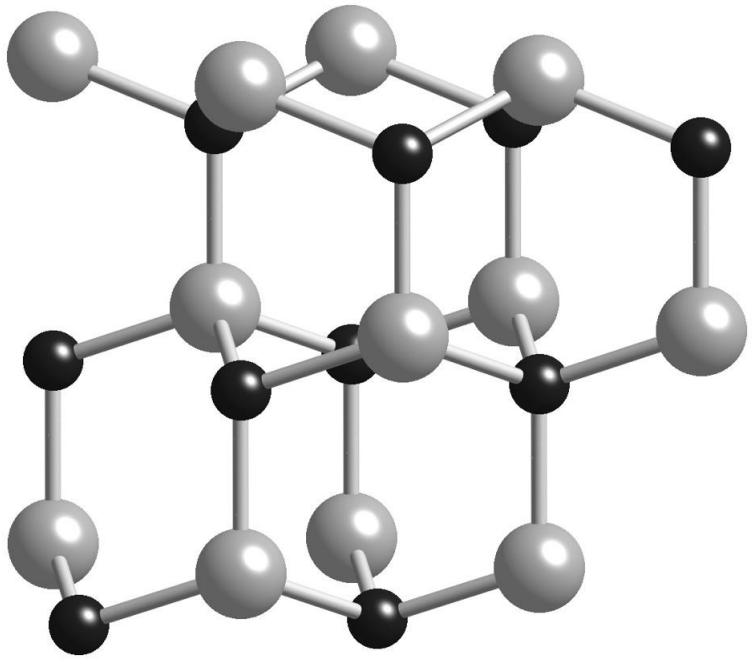
NaCl



(Largely) covalent

- Small highly polarising cations (B^{3+}, Si^{4+}, P^{5+}, S^{6+})
- Large polarisable anions (I^{-}, S^{2-})

SiC

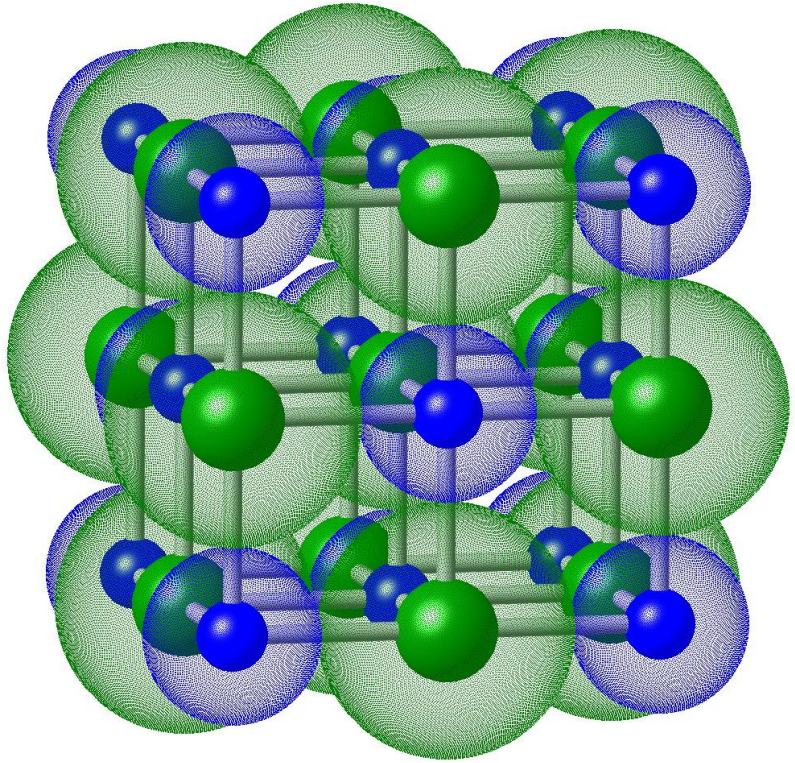


Ionic or Covalent Bonding?

Ionic

- Small formal charges such as Na^+ and Cl^- are reasonable

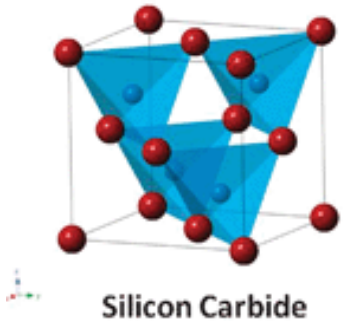
NaCl



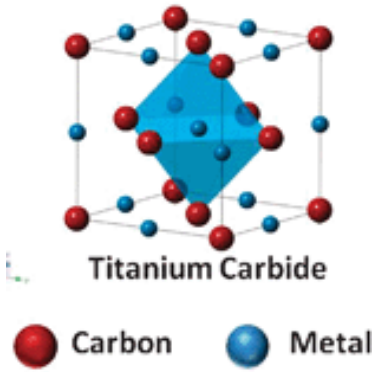
Ionic or Covalent?

- High formal charges such as Ti^{4+} and C^{4-} are unlikely to really exist
- Nevertheless, we find it convenient to classify TiC as an ionic compound…

SiC



TiC

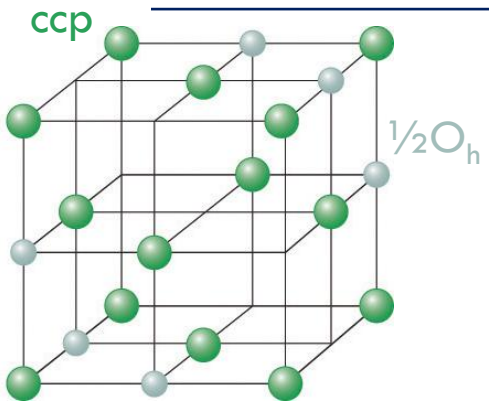


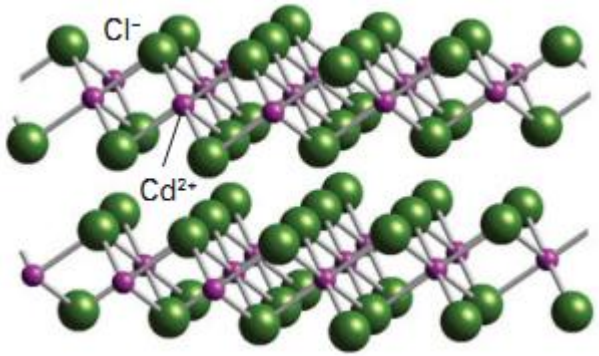
https://doi.org/10.1039/C2CS15324F

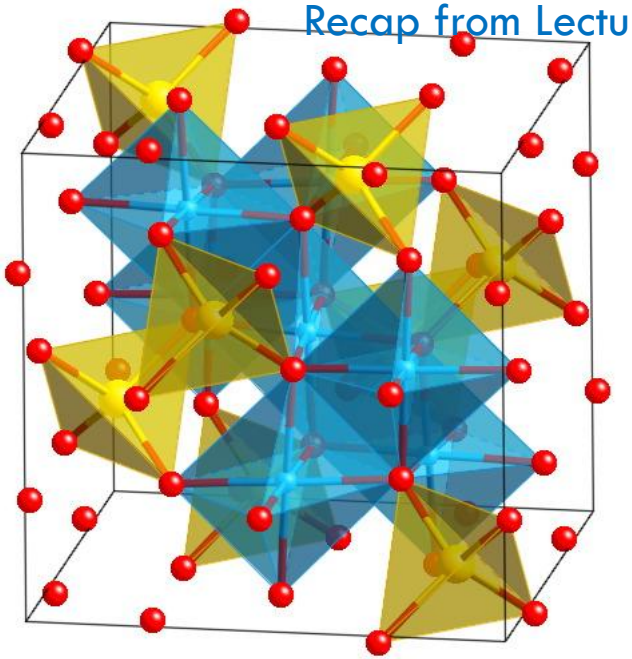
Characterising Ionic Bonding in Solids

- Effective ionic radii
- Covalency as an explanation of non-close-packed structures
- Lattice energy of ionic crystals
- Coordination spheres and Madelung constants

Octahedral and tetrahedral holes





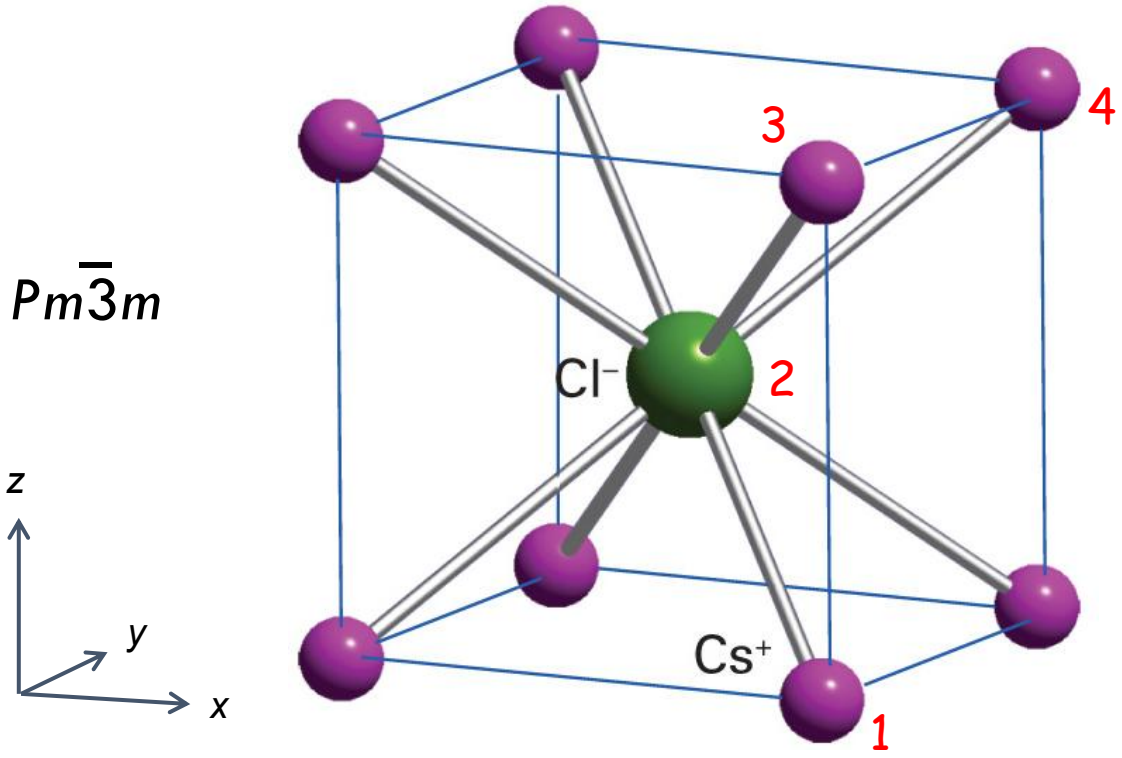


Anion	Filling of Interstitial Sites		Structure	Examples
Packing	T_d	O_h		
	-	all	rock-salt	NaCl, MgO, LaN
		1/2	cadmium chloride	$CdCl_2$, $NiCl_2$
ccp (fcc)	half	-	zinc blende (sphalerite)	ZnS, CuCl, BN
	all	-	anti-fluorite	Na_2O, Li_2S
	1/8	1/2	spinel	$MgAl_2O_4$

Ionic Structures: Caesium Chloride

Two interpenetrating simple cubic unit cells (not ccp!)

$Pm\bar{3}m$



Fractional coordinates

1: (1, 0, 0)

2: (½, ½, ½)

3: (1, 0, 1)

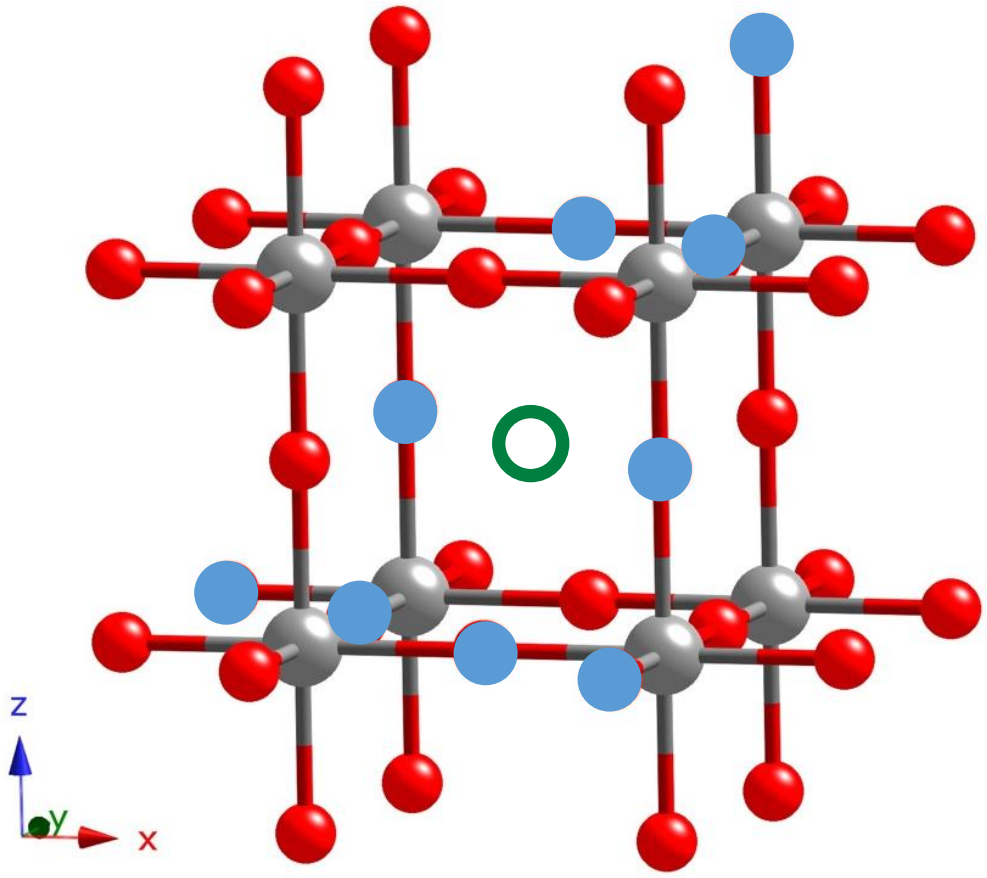
4: (1, 1, 1)

Composition = CsCl Coordination = 8 : 8

https://www.materialsproject.org/materials/mp-22865/

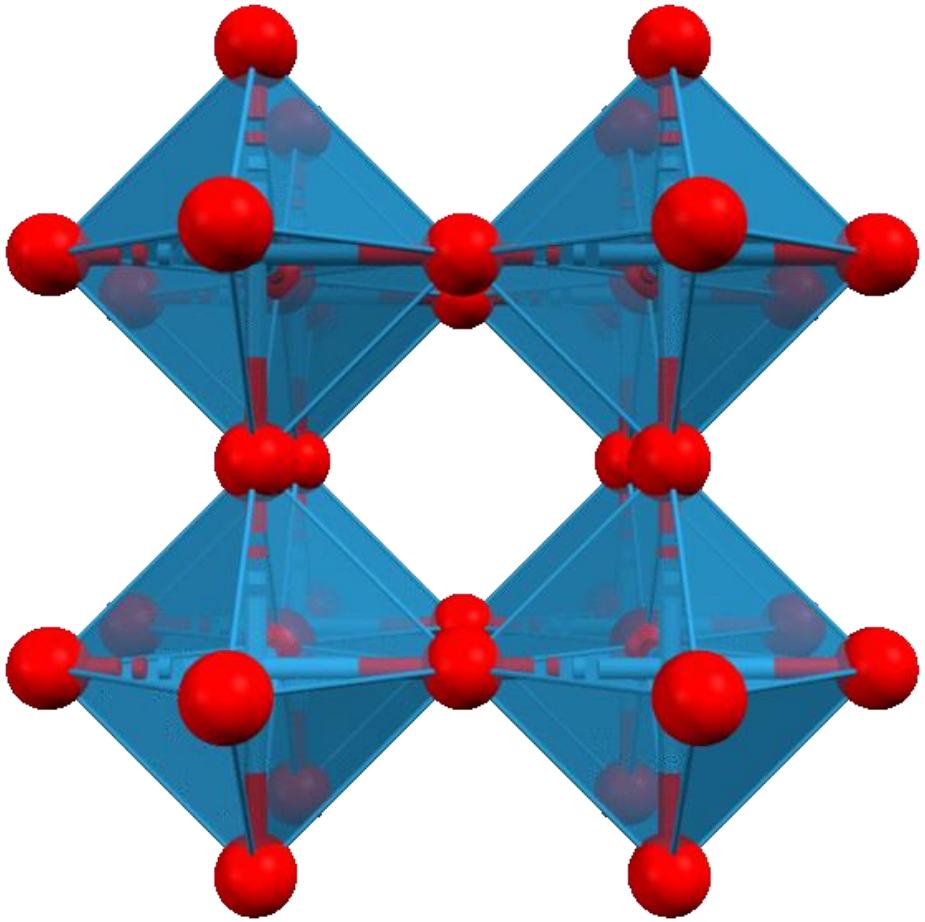
Structures of Ionic Solids

Structure of ReO_3: Almost close-packed array of O^{2-}



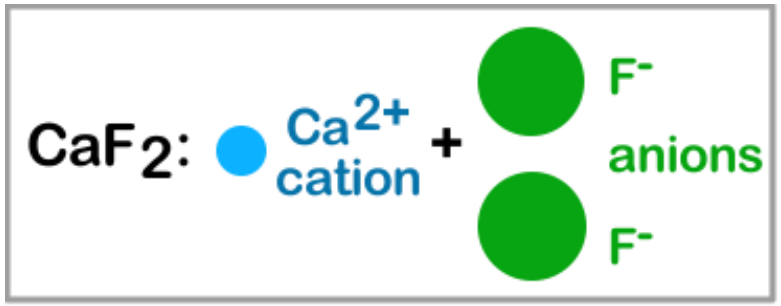
Structures of Ionic Solids

Structure of ReO_3: Almost close-packed array of O^{2-}



Ionic Bonding and Structure

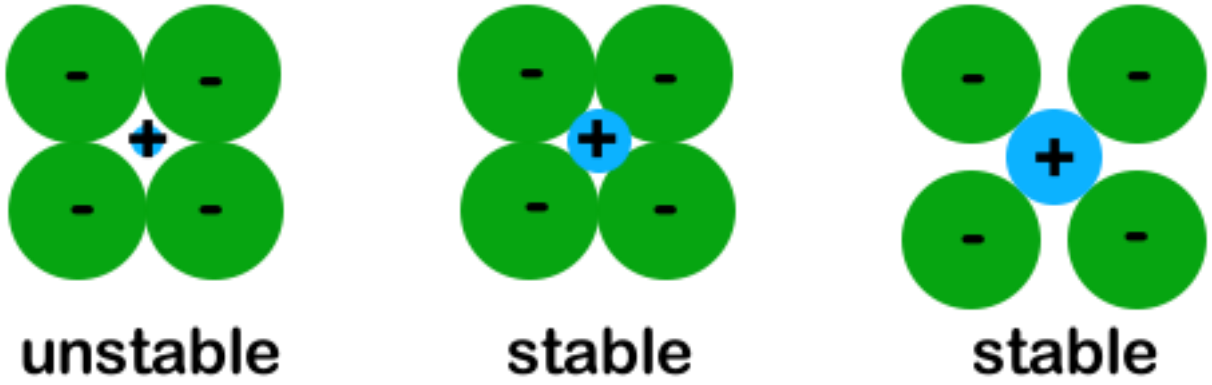
- Charge neutrality:
  - Net charge should be zero.



- General form: A_mX_p

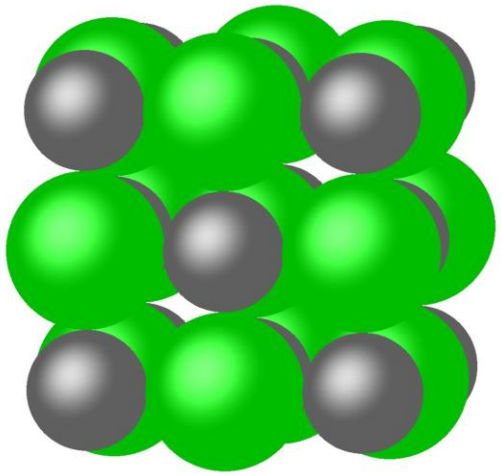
m, p determined by charge neutrality

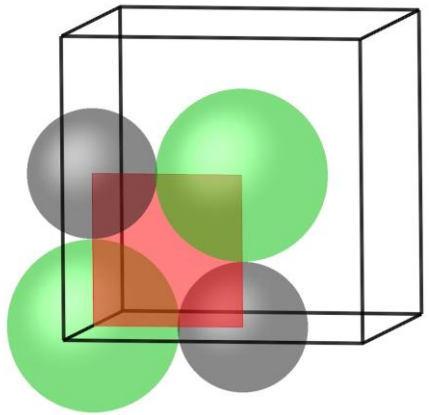
- Ionic Radii:
  - Maximise # of nearest oppositely charged neighbours.

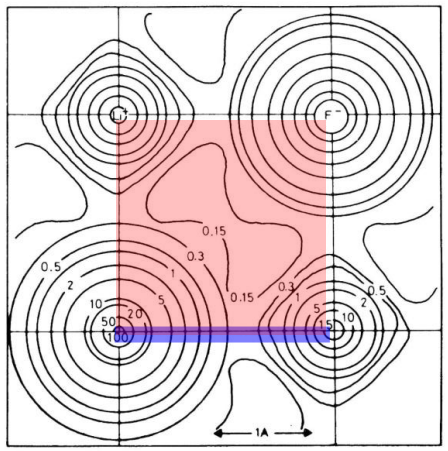


Ionic Radii

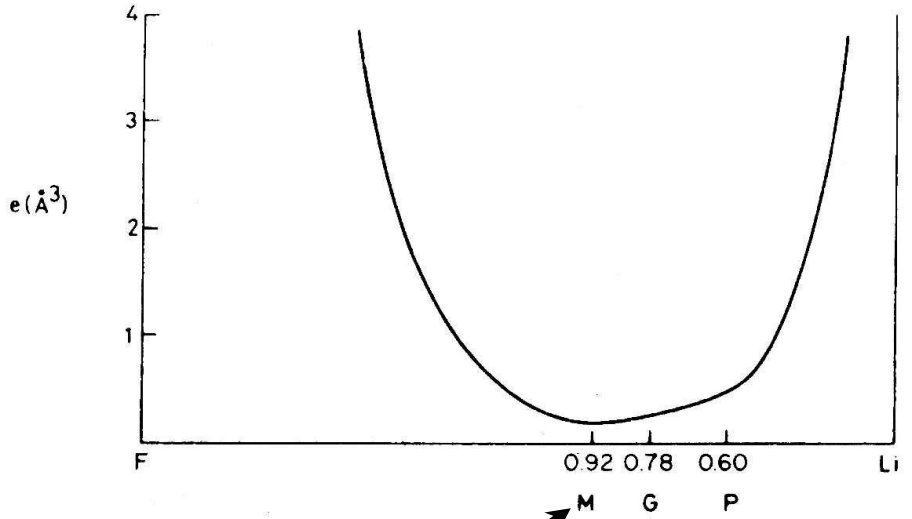
E.g., LiF (rock salt-type structure)







Electron density map



Minimum in electron density is defined as the "**effective ionic radius**"

Pauling radius

Goldschmidt radius

Figures from West "Basic Solid State Chemistry"

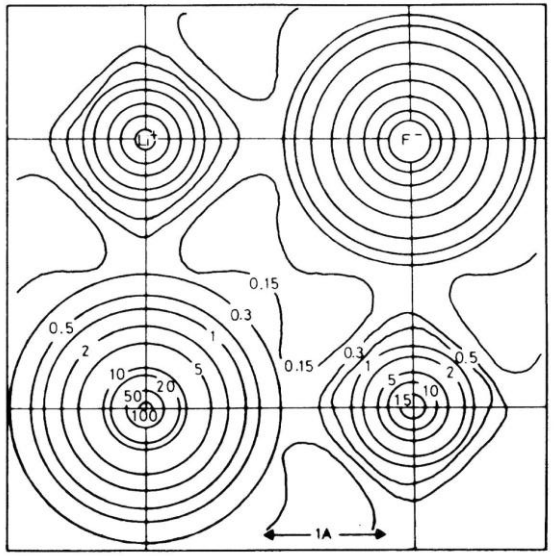
Effective Ionic Radii

Shannon and Prewitt (1969, 1970)

- Experimentally derived.
- Based on some reference radii, e.g.,:

$r\ (O^{2-}) = 1.40$ Å (similar to Pauling radii)

$r\ (O^{2-}) = 1.26$ Å (minimum in electron density)

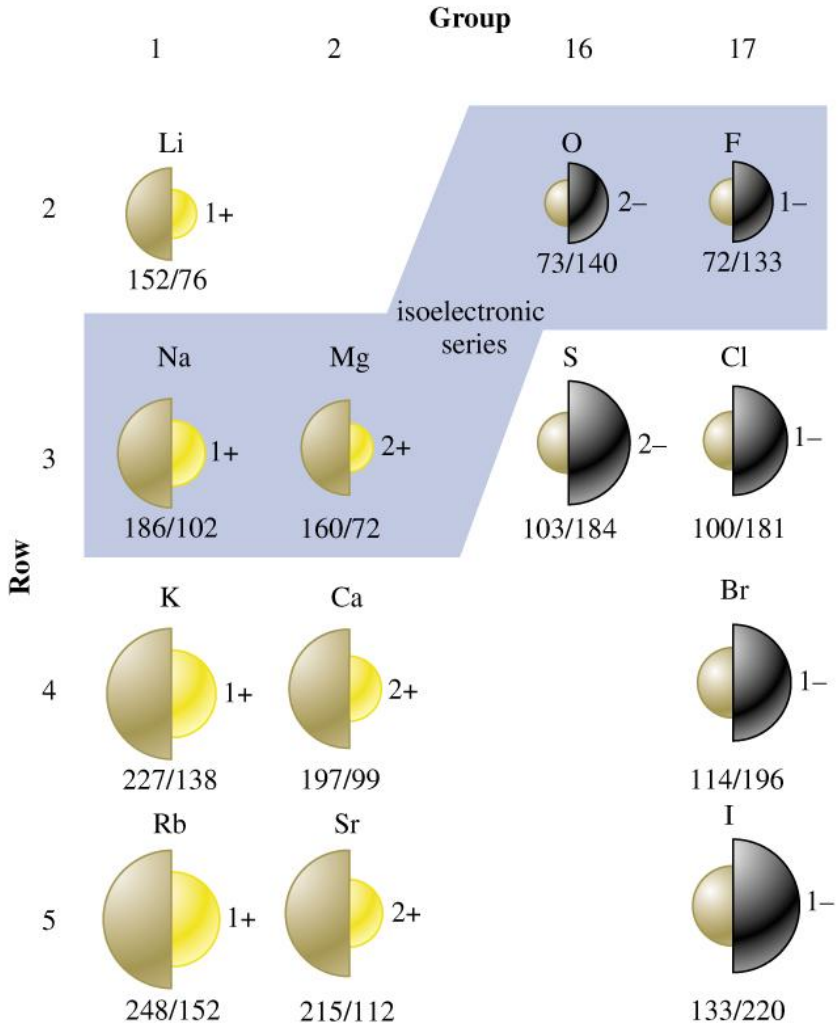


- Radii depend on coordination number! Although it is a purely ionic model, it does not treat ions as "incompressible spheres".

Figure from West "Basic Solid State Chemistry"

Trends in the Effective Ionic Radii

- For *s* and *p* block elements, *r* ↑ down a group.
- For isoelectronic cations, *r* ↓ as oxidation number ↑.
- For ions of the same charge, *r* ↓ as atomic number ↑ across a period (e.g., the "lanthanide contraction").
- For an element, *r* ↓ as oxidation number ↑.
- For an ion, *r* ↑ as coordination number ↑.



Trends in the Effective Ionic Radii

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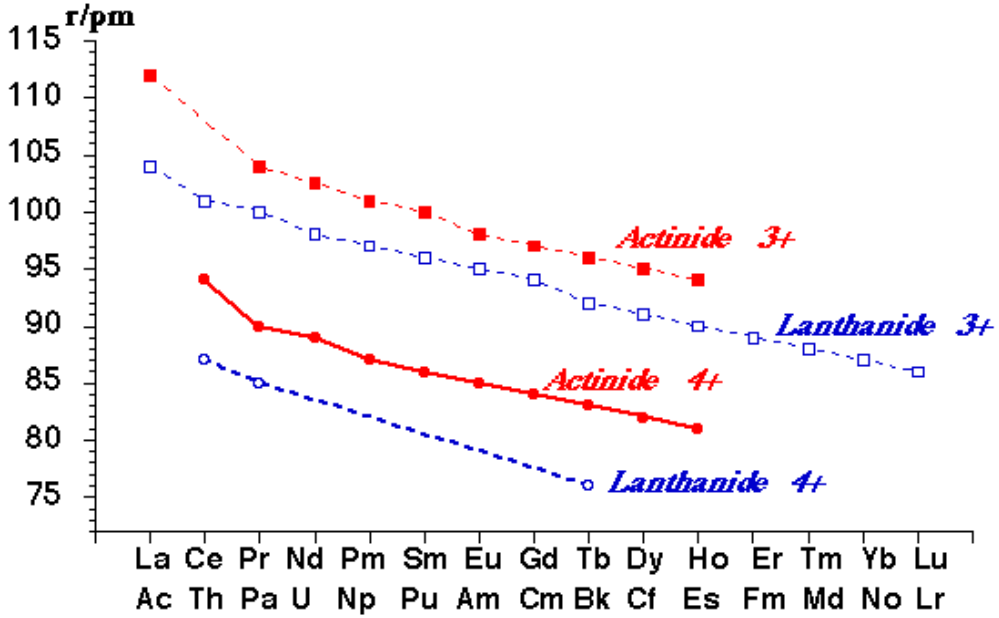


Table of Effective Ionic Radii

Ion	CN	SS	IR (Å)	Ion	CN	SS	IR (Å)	Ion	CN	SS	IR (Å)
Al +3	4		0.39	F-1	2		1.285	Mn+7	6		0.46
Al +3	5		0.48	F-1	3		1.3	N-3	4		1.46
Al +3	6		0.535	F-1	4		1.31	N+3	6		0.16
Be +2	3		0.16	F-1	6		1.33	N+5	3		-0.104
Be +2	4		0.27	F+7	6		0.08	N+5	4		0.13
Be +2	6		0.45	I-1	6		2.2	Ni+2	4		0.55
Ca +2	6		1	I+5	3		0.44	Ni+2	4		0.49
Ca +2	7		1.06	I+5	6		0.95	Ni+2	5		0.63
Ca +2	8		1.12	I+7	4		0.42	Ni+2	6		0.69
Ca +2	9		1.18	I+7	6		0.53	Ni+3	6	LS	0.56
Ca +2	10		1.23	In+3	4		0.62	Ni+3	6	HS	0.6
Ca +2	12		1.34	In+3	6		0.8	Ni+4	6	LS	0.48
Cl-1	6		1.81	In+3	8		0.92	O-2	2		1.35
Cl+5	3		0.12	Li+1	4		0.59	O-2	3		1.36
Cl+7	4		0.08	Li+1	6		0.76	O-2	4		1.38
Cl+7	6		0.27	Li+1	8		0.92	O-2	6		1.4
Cs+1	8		1.74	Mn+2	4	HS	0.66	O-2	8		1.42
Cs+1	9		1.78	Mn+2	5	HS	0.75	W+4	6		0.66
Cs+1	10		1.81	Mn+2	6	LS	0.67	W+6	4		0.42
Cs+1	11		1.85	Mn+2	6	HS	0.83	W+6	5		0.51
Cs+1	12		1.88	Mn+2	7	HS	0.90	W+6	6		0.60
Co+2	4	HS	0.58	Mn+2	8		0.96	Rb+1	6		1.52
Co+2	5		0.67	Mn+3	5		0.58	Rb+1	7		1.56
Co+2	6	LS	0.65	Mn+3	6	LS	0.58	Rb+1	8		1.61
Co+2	6	HS	0.75	Mn+3	6	HS	0.65	Rb+1	9		1.63
Co+2	8		0.90	Mn+4	4		0.39	Rb+1	10		1.66
Co+3	6	LS	0.55	Mn+4	6		0.53	Rb+1	11		1.69
Co+3	6	HS	0.61	Mn+5	4		0.33	Rb+1	12		1.72
Co+4	4		0.40	Mn+6	4		0.26	Rb+1	14		1.83
Co+4	6	HS	0.53	Mn+7	4		0.25				

"Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides" R.D. Shannon, *Acta Cryst.* (1976) **A32**, 751.

Ionic Radii and the Size of the Interstice

The size of the octahedral (or tetrahedral) interstices in fcc structures determines the size of the ion that can be accommodated

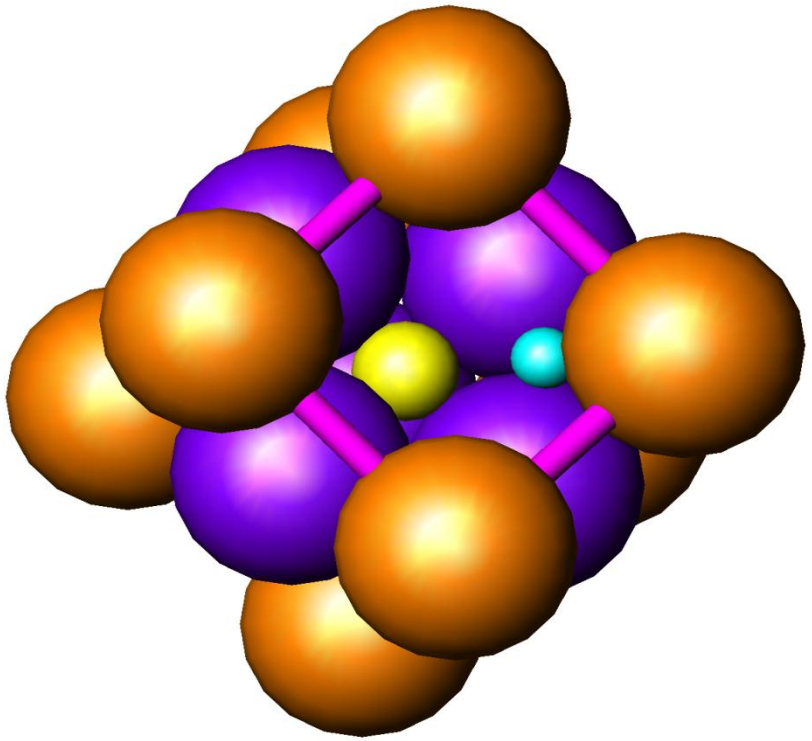
Recap from Lecture 5 pre-work

Octahedral hole:

r_{oct}/r_{sphere} = (sqrt(2)-1) = 0.414

Tetrahedral hole:

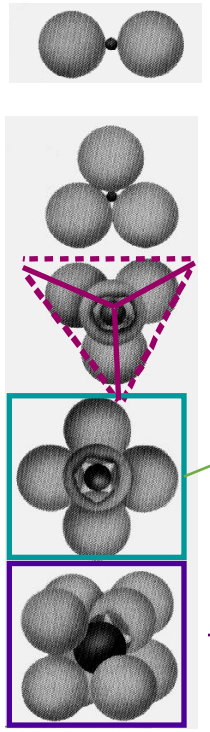
r_{tet}/r_{sphere} = {1/sin(109.47/2) – 1} = 0.225

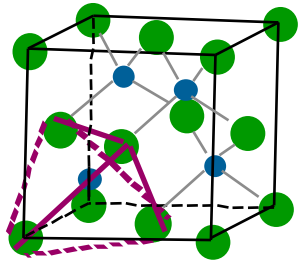


Ionic Radii and Coordination Number

Coordination number (CN) increases with r_{cation}/r_{anion}

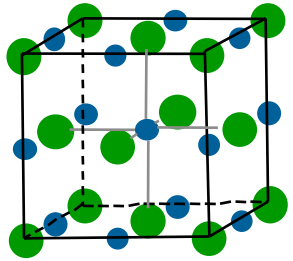
$\frac{r_{cation}}{r_{anion}}$	Coord #
< 0.155	2
0.155–0.225	3
0.225–0.414	4
0.414–0.732	6
0.732–1.000	8





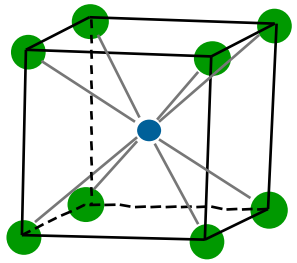
ZnS
(zinc blende)

(FCC)



NaCl
(sodium chloride)

(FCC)

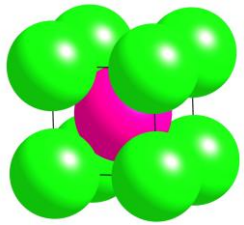


CsCl
(caesium chloride)

(Simple cubic)

Crystal Structure Maps: Covalency *vs.* Ionicity

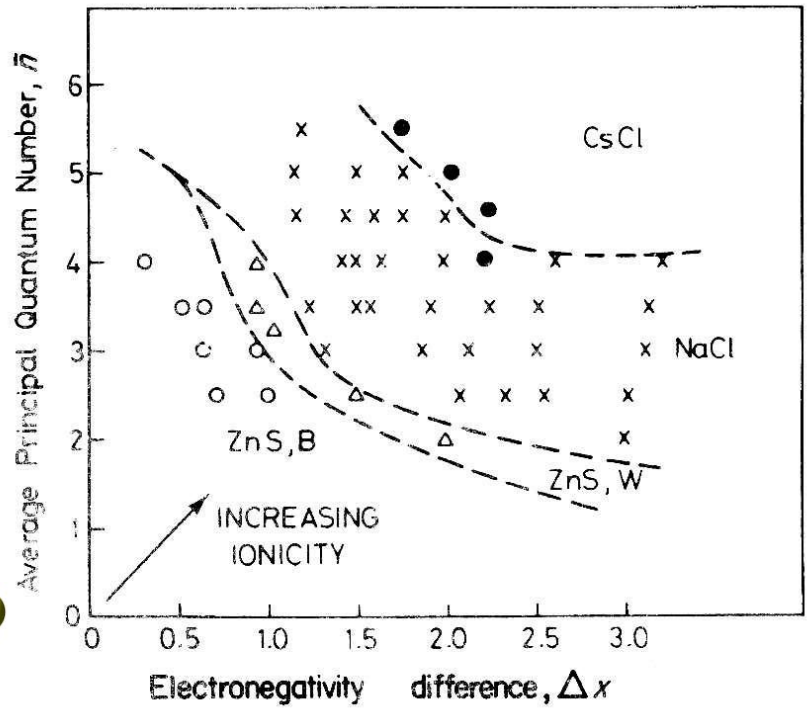
Structure maps, which incorporate properties like electronegativity, are more consistent than radius ratio rules in correctly predicting the coordination number, and hence crystal structure.



- The greater the electronegativity difference between the ions (x-axis), the more ionic is the compound. High ionicity results in higher coordination number.

- Higher principal quantum numbers (y-axis) result in less s-p hybridisation, more diffuse orbitals, less directional bonding, and therefore higher coordination number.

Mooser-Pearson diagram



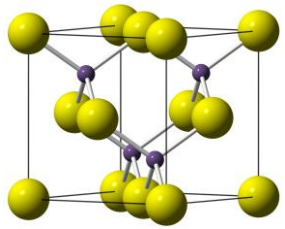


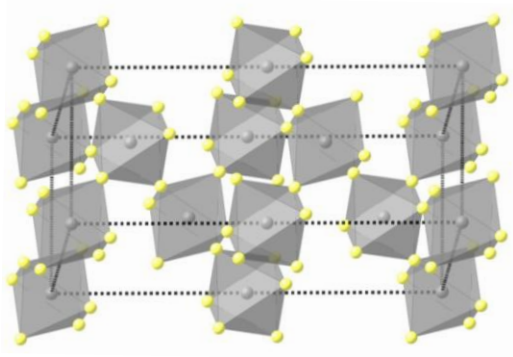
Figure from West "Basic Solid State Chemistry"

Covalency *vs.* Ionicity and Coordination Number

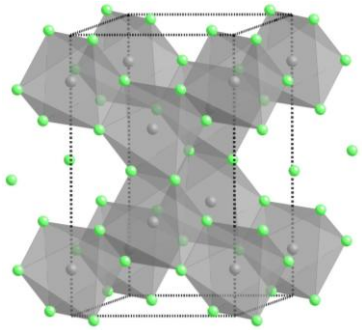
Differences between the electronegativities of ions affects covalency, and hence the coordination number and crystal structure, which can account for deviations from the ccp structure. AlX_3, where X are the halides, provides an example:

Close-packed, AlX_6 octahedra,
CN of Al = 6 (ionic)

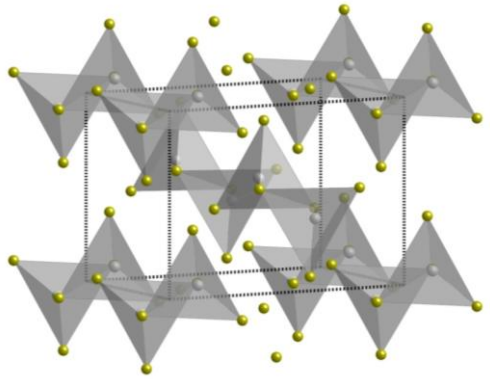
AlF_3

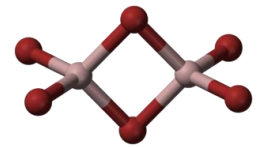


$AlCl_3$

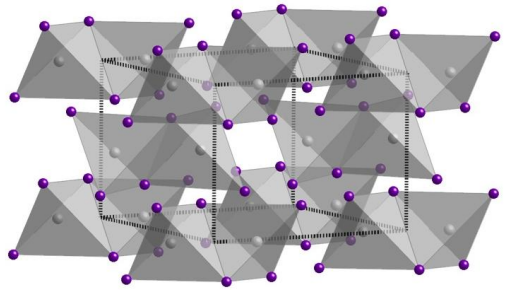


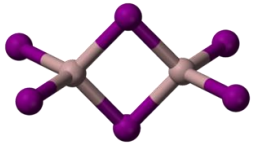
Layered, Al_2X_6 dimers,
CN of Al = 4 (covalent)





$AlBr_3$





AlI_3

Lattice Energy of Ionic Crystals

A purely ionic crystal is held together by electrostatic forces. The lattice energy ΔH^0_L is required to overcome them, e.g.:

$$NaCl\ (s) \rightarrow Na^+\ (g) + Cl^-\ (g) \qquad \Delta H = \Delta H^0_L$$

For two ions A^{z+} and B^{z-} separated by a distance $d = r_A + r_B$, lattice enthalpy ΔH^0_L is given by the Born-Mayer equation:

$$\Delta H^0_L = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)A$$

Recall from Lecture 2 that Coulomb's law describes the amount of force between two ions:

$$V(r) = -\frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

N_A is Avogadro's number

e is the fundamental electronic charge

z_A and z_B are the ionic charges on *A* and *B*

ε_0 is the vacuum permittivity

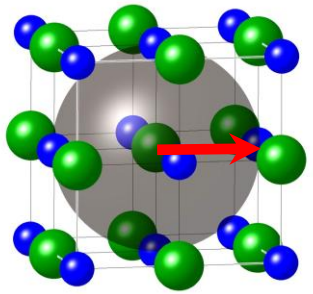
d^* is a constant representing short-range repulsion (typically 0.345 Å)

A is the Madelung constant

Madelung Constants

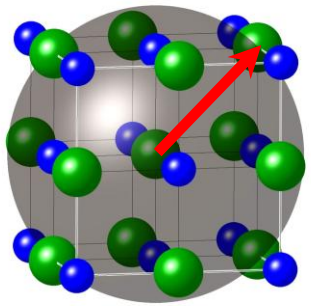
Madelung constant (A) depends on the crystal structure. It is the sum of the Coulombic attraction V between each ion and its successive coordination spheres, e.g., for NaCl:

1st coordination sphere



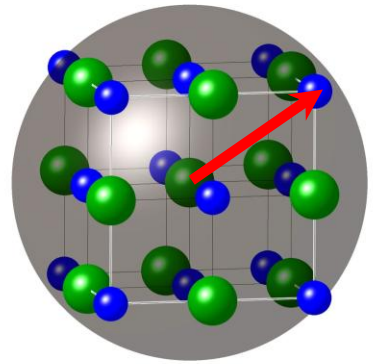
$$V = \frac{-6e^2|z_A z_B|}{d}$$

2nd coordination sphere



$$V = \frac{12e^2|z_A z_B|}{\sqrt{2}d}$$

3rd coordination sphere



$$V = \frac{-8e^2|z_A z_B|}{\sqrt{3}d}$$

$$V = \frac{-e^2|z_A z_B|}{d}\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \ldots\right)$$

$$V = \frac{-e^2|z_A z_B|}{d} \cdot A$$

Madelung constants for some simple structures			
NaCl	1.748	Sphalerite ZnS	1.638
CsCl	1.763	Fluorite CaF_2	2.520
Wurtzite (Zn,Fe)S	1.641	Rutile TiO_2	2.408

Trends in Lattice Enthalpy

$$\Delta H_L^0 = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right) A$$

For a given structure, all terms in the Born-Mayer eqn. are constant except d, z_A & z_B.

- As the size of the ion increases, d increases, and hence lattice enthalpy decreases.
- As the charge on the ion increases, lattice enthalpy increases.

Varying z_A and z_B :

- m.p. of CaO = 2572 °C
- m.p. of NaCl = 800 °C

Varying d:

- m.p. of CaO = 2572 °C
- m.p. of BaO = 1923 °C

Lattice energies (kJ mol^{-1}) for some compounds with the rock salt structure					
MgO	3938	LiF	1024	NaF	911
CaO	3566	LiCl	861	KF	815
SrO	3369	LiBr	803	RbF	777
BaO	3202	LiI	744	CsF	748

*From Ladd and Lee, Prog. Solid State Chem., **1**, 37 (1963); **2**, 378 (1965).*

Learning Outcomes

After this lecture you should be able to

- Understand the different ways in which ionic radii can be defined.
- Know how to recognise materials that are largely ionically or covalently bonded, based on their compositions and/or structures.
- Know trends in effective ionic radii as functions of atomic number, valence etc.
- Understand the origin of lattice energy of ionic crystals, how it varies for different compounds with the same structure, and how that relates to properties such as melting point.
- Complete the lecture worksheet and Q5 & 6 of Tutorial Sheet 2 (week 4).
- Complete the week 3 on-line quiz.

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5; Weller, Inorganic Materials Chemistry, OUP, 1994, Chapter 5; West, Basic Solid State Chemistry, Wiley, 1999, Chapter 2.