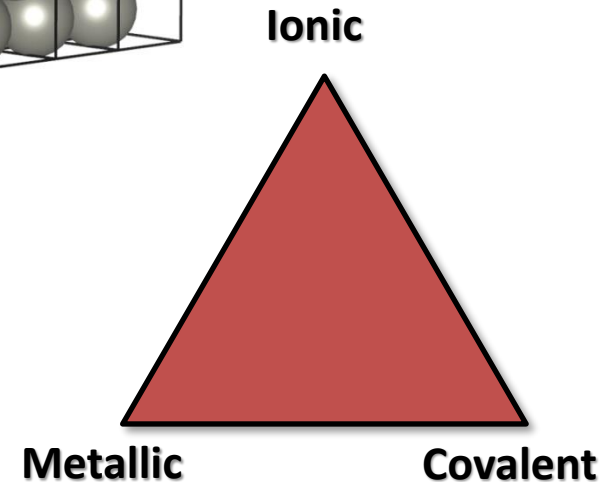
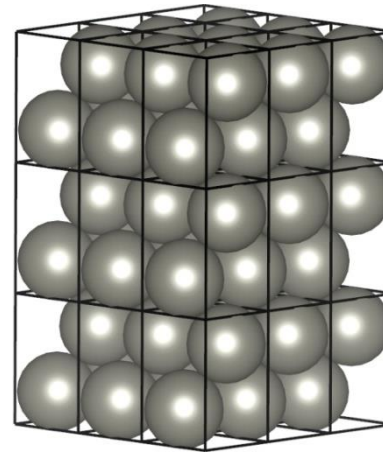


# Lecture 3: Bonding in solids and description of crystal structures

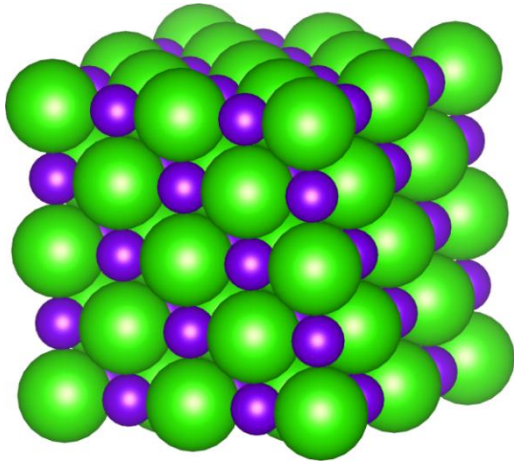
- Bonding in solids
  - Electronegativity
  - Atomic and ionic radii
  - (*Band theory in Lecture 4*)
- Description of crystal structures
  - Coordination
  - Close packed structures
  - Metallic structures
  - Ionic structures with interstitial sites
- Concept of a **structure type**



Figures: AJK

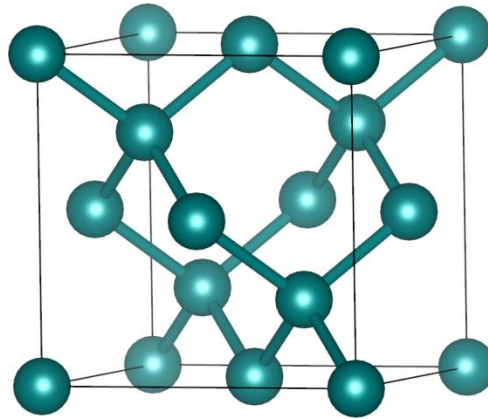
# Strong chemical bonding

- The chemical bonds in solids are usually classified as **ionic**, **covalent**, or **metallic**
  - The focus of the lecture is on these bonding types
- Examples of weaker (non-covalent) bond types: hydrogen bonds, halogen bonds



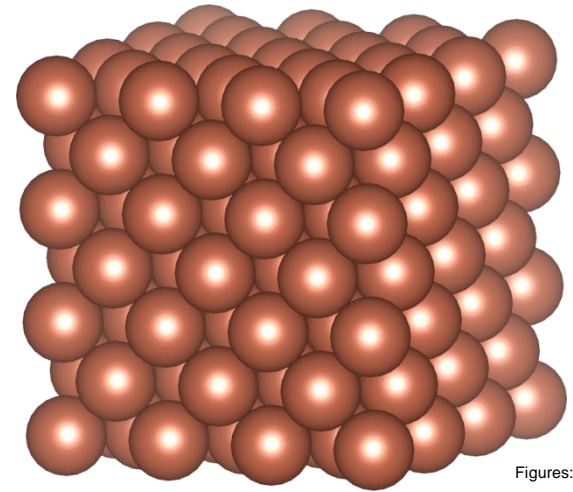
***Ionic bonding*** (e.g. NaCl)

Typically high symmetry and high coordination numbers.



***Covalent bonding*** (e.g. Si)

Typically highly directional bonds. Smaller coordination numbers than for ionic structures.



Figures: AJK

***Metallic bonding*** (e.g. Cu)

Delocalized valence electrons. Can result in high coordination and close packing of atoms

# Electronegativity

# Electronegativity

- The concept of **electronegativity** is an important tool for estimating how ionic or covalent a chemical bond is
- The electronegativity is a parameter introduced by Linus Pauling as a measure of the power of an atom to attract electrons to itself when it is part of a compound
- Pauling defined the difference of two electronegativities  $\chi_A$  and  $\chi_B$  in terms of bond dissociation energies,  $D_0$ :
$$|\chi_A - \chi_B| = \{D_0(AB)\} - 1/2[D_0(AA) + D_0(BB)]^{1/2}$$
- $D_0(AA)$  and  $D_0(BB)$  are the dissociation energies of A–A and B–B bonds and  $D_0(AB)$  is the dissociation energy of an A–B bond, all in eV units
- The expression gives differences of electronegativities
- To establish an absolute scale, Pauling set the electronegativity of **fluorine** to 3.98 (unitless quantity)

# Pauling Electronegativities

Periodic table of electronegativity by Pauling scale																			
→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →																			
	1	2	3		4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Group →																			
↓ Period																			
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	La 1.1	*	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 <sup>[en 1]</sup>	Ra 0.9	Ac 1.1	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
				*															
				**															
					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	
					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 <sup>[en 2]</sup>	

Figure: [Wikipedia](#)

# Allen Electronegativities

- Pauling's electronegativity scale is the best known, but there are also others
- Allen determined his scale based on spectroscopic data (one-electron energies)
- Good correlation with Pauling electronegativities, but somewhat ambiguous for *d*- and *f*-metals

Electronegativity using the Allen scale																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.300																	He 4.160
Li 0.912	Be 1.576											B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.789
Na 0.869	Mg 1.293											Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Sc 1.19	Ti 1.38	V 1.53	Cr 1.65	Mn 1.75	Fe 1.80	Co 1.84	Ni 1.88	Cu 1.85	Zn 1.59	Ga 1.756	Ge 1.994	As 2.211	Se 2.434	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	Y 1.12	Zr 1.32	Nb 1.41	Mo 1.47	Tc 1.51	Ru 1.54	Rh 1.56	Pd 1.59	Ag 1.87	Cd 1.52	In 1.656	Sn 1.824	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
Cs 0.659	Ba 0.881	Lu 1.09	Hf 1.16	Ta 1.34	W 1.47	Re 1.60	Os 1.65	Ir 1.68	Pt 1.72	Au 1.92	Hg 1.76	Tl 1.789	Pb 1.854	Bi 2.01	Po 2.19	At 2.39	Rn 2.60
Fr 0.67	Ra 0.89																

Figure: Wikipedia

# Using electronegativities ( $\chi$ )

- Electronegativities can be used to estimate the **polarity** of a bond
- There is **no** clear-cut division between covalent and ionic bonds!
- Note that the electronegativity difference  $|\chi_A - \chi_B| = 0$  both for fully covalent (*e.g.* C–C) and fully metallic bonds (*e.g.* Li–Li)
- Quantum chemical calculations can help to understand the nature of the bonding better
  - Even then, many controversies about various analysis methods exist
  - More discussion about the analysis methods in Lecture 4

Bond A-B	$ \chi_A - \chi_B $	
Cs–F	3.19	Ionic
Na–Cl	2.23	
H–F	1.78	
Fe–O	1.61	
Si–O	1.54	Covalent
Zn–S	0.93	
C–H	0.35	

# van Arkel-Ketelaar Triangles

- The electronegativities can be used to arrange binary compounds into ***Triangles of bonding***, also known as ***van Arkel-Ketelaar Triangles***
- Very illustrative concept for estimating the nature of a chemical bond

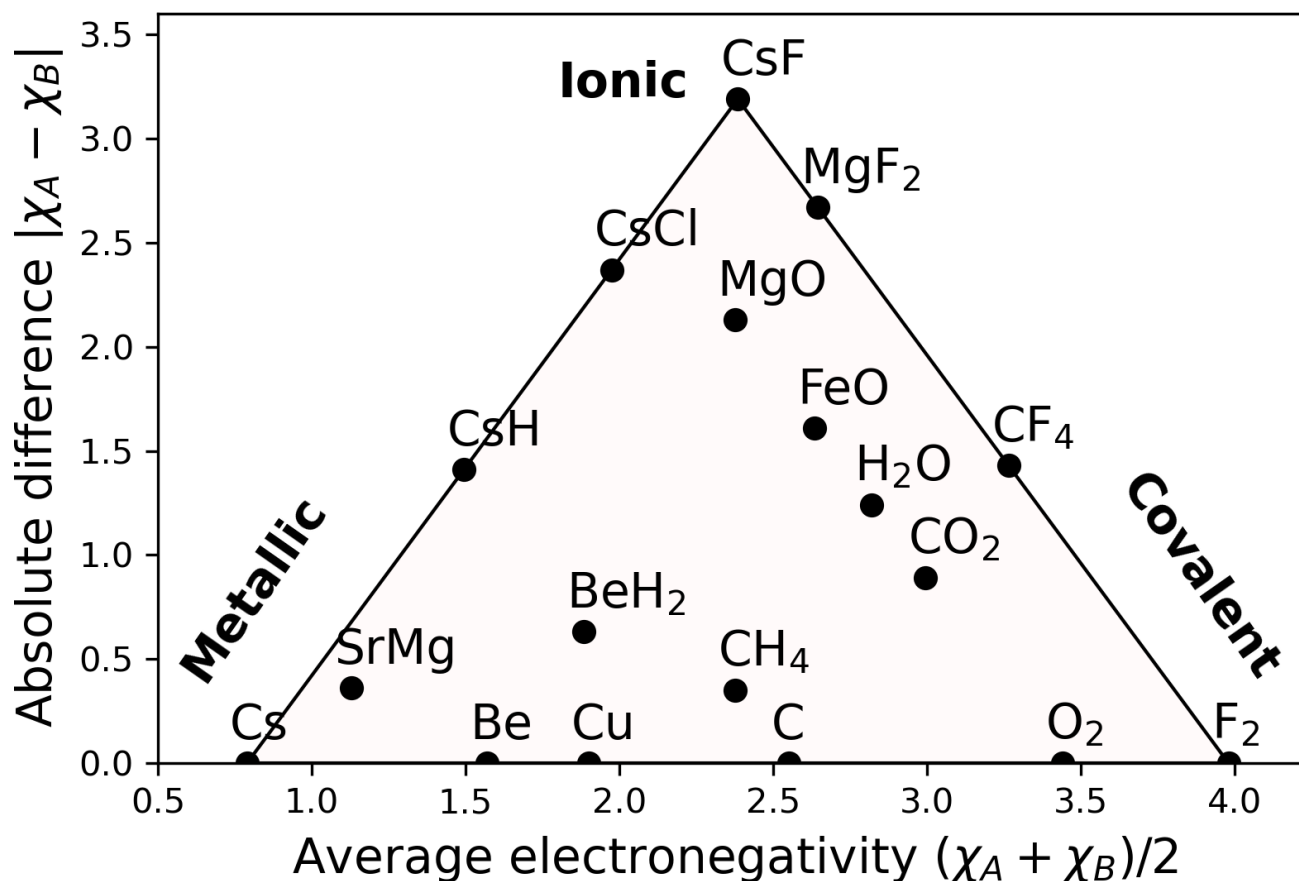


Figure: AJK



# What really determines $\chi$ ?

- Pauling determined the  $\chi$  values from bond dissociation energies
- Allen used one-electron energies from spectroscopic data
- The periodic trends of electronegativity (and chemical bonding) can be discussed in terms of **effective nuclear charge**  $Z_{\text{eff}}$  experienced by the valence electrons
- $Z_{\text{eff}} = Z - \sigma$ , where  $Z$  is the atomic number and  $\sigma$  is **shielding** by other electrons
- The shielding can be determined from simple rules such as Slater's rules or from quantum chemical calculations
  - Clementi, E.; Raimondi, D. L., "Atomic Screening Constants from SCF Functions", *J. Chem. Phys* **1963**, 38, 2686–2689
- Higher the  $Z_{\text{eff}}$ , the tighter the valence electrons are "bound" to the atom

Element	Li	Be	B	C	N	O	F	Ne
$Z$	3	4	5	6	7	8	9	10
$Z_{\text{eff}}$	1.28	1.91	2.42	3.14	3.83	4.45	5.10	5.76
$\chi$	0.98	1.57	2.04	2.55	3.04	3.44	3.98	(4.8)*

\* Allen electronegativity

# $\chi$ vs. $Z_{eff}$ for the 2nd period

- $\chi$  and  $Z_{eff}$  do actually show a beautiful correlation when moving from left to right in the periodic table
- However,  $Z_{eff}$  of the valence electrons actually **increases** when moving down in periodic table (e.g.  $Z_{eff}(\text{Cl}) = 6.1 e^-$ ), while electronegativity **decreases**
- Full consideration of orbital shapes *etc.* required to understand the  $\chi$  values
- The moral of the story: simple explanations of complex many-electron systems may sound nice, but are probably not right

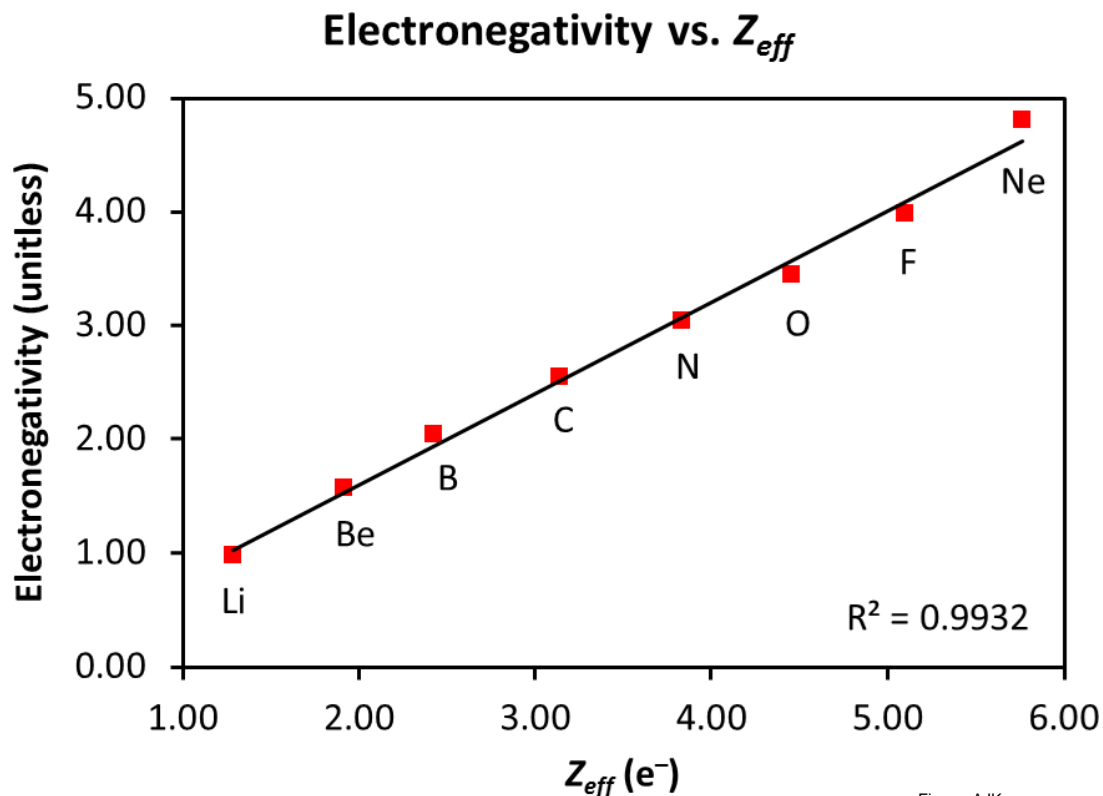


Figure: AJK

# Atomic radii

# Atomic radii

- When a crystal structure is available, the distances between atoms are often a very useful measure of the possible bonding between them
- However, the size of an atom or ion is not easy to define because there is not clear-cut definition for the "border" of an atom
- Various definitions for **atomic**, **ionic**, **covalent**, and **van der Waals** radii exist, here the following datasets are included:
  - Atomic radii of neutral atoms from quantum chemical calculations (E. Clementi *et al.* *J. Chem. Phys.* **1967**, 47, 1300).
  - Ionic radii from experimental data (R. D. Shannon, *Acta Cryst.* **1976**, 32, 751)
  - Covalent radii from quantum chemical calculations (P. Pyykkö)
  - van der Waals radii from experimental and quantum chemical data (Bondi, A. *J. Phys. Chem.* **1964**, 68, 441; Truhlar *et al.* *J. Phys. Chem. A*, **2009**, 113, 5806; S. Alvarez, *Dalton Trans.* **2013**, 42, 8617).

# Atomic radii for neutral atoms

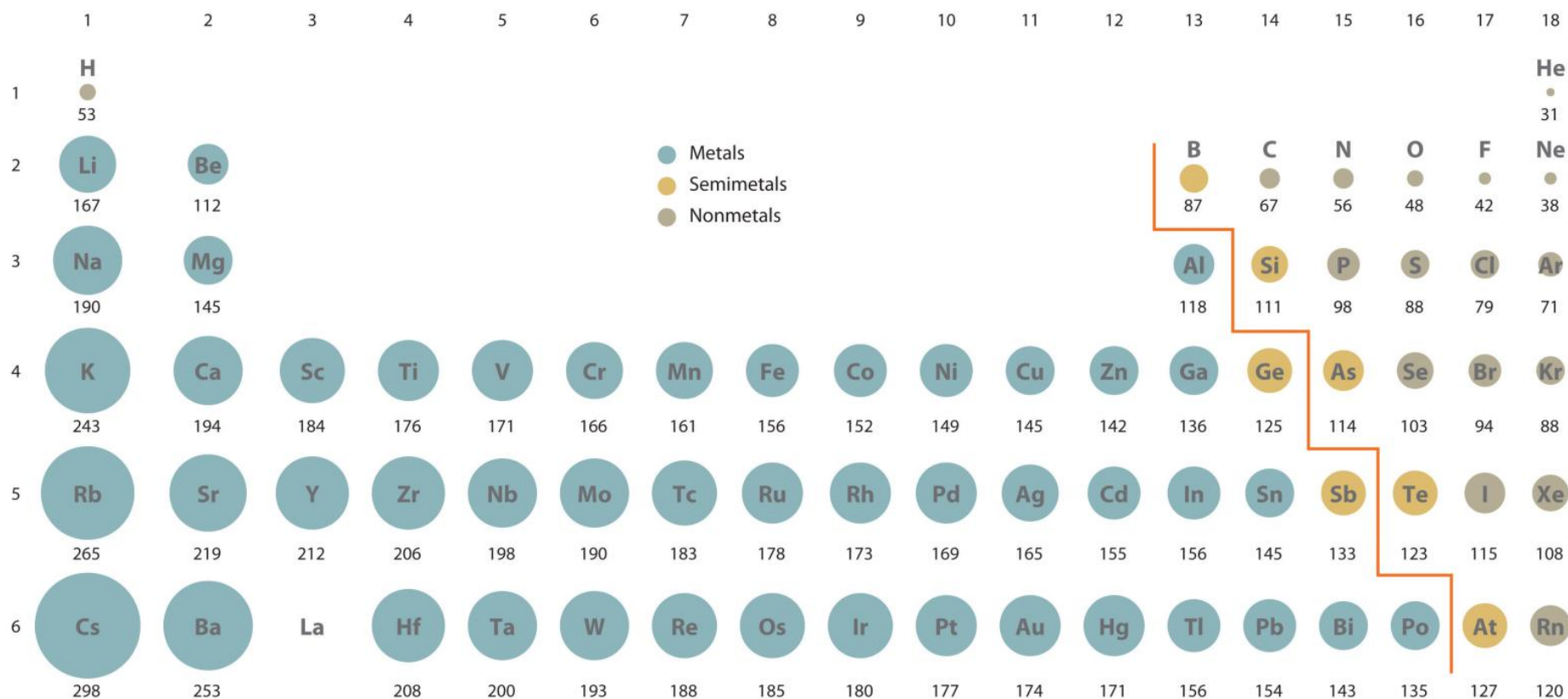
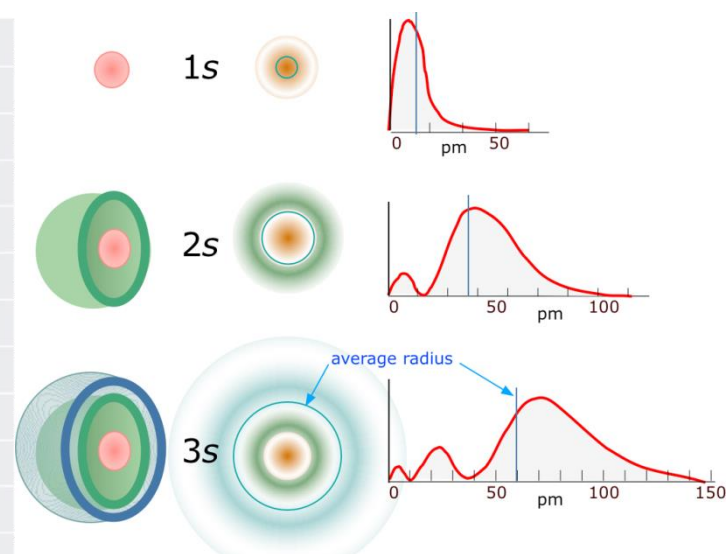
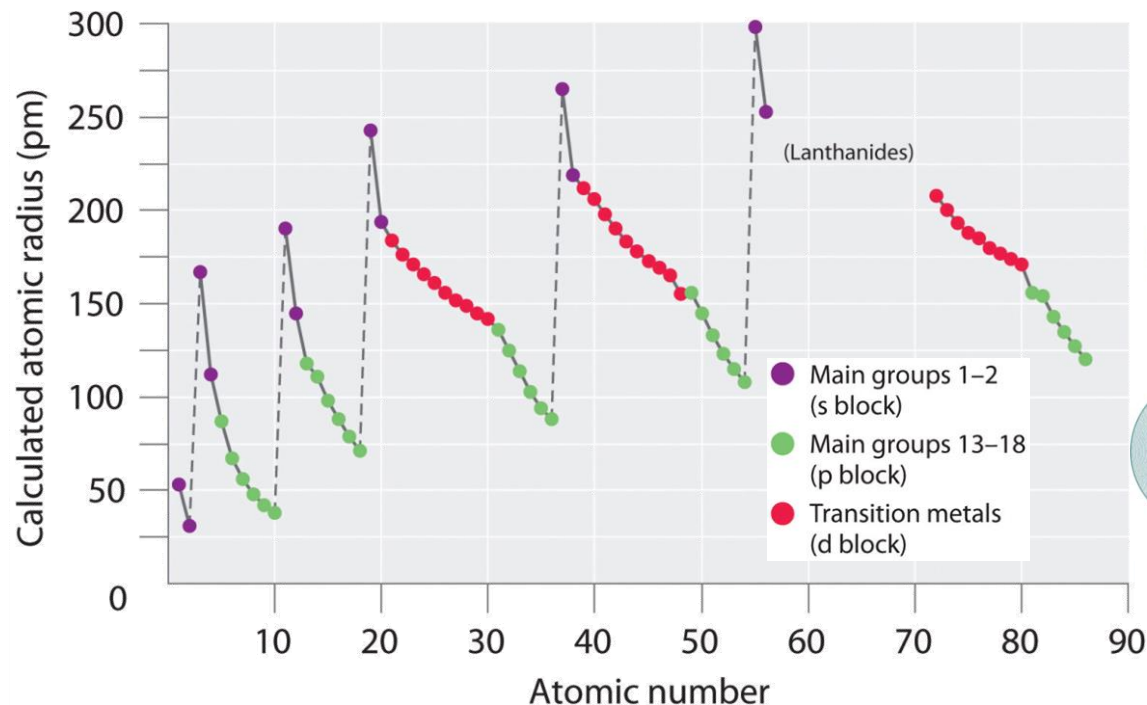


Figure: [chem.libretexts.org](http://chem.libretexts.org)

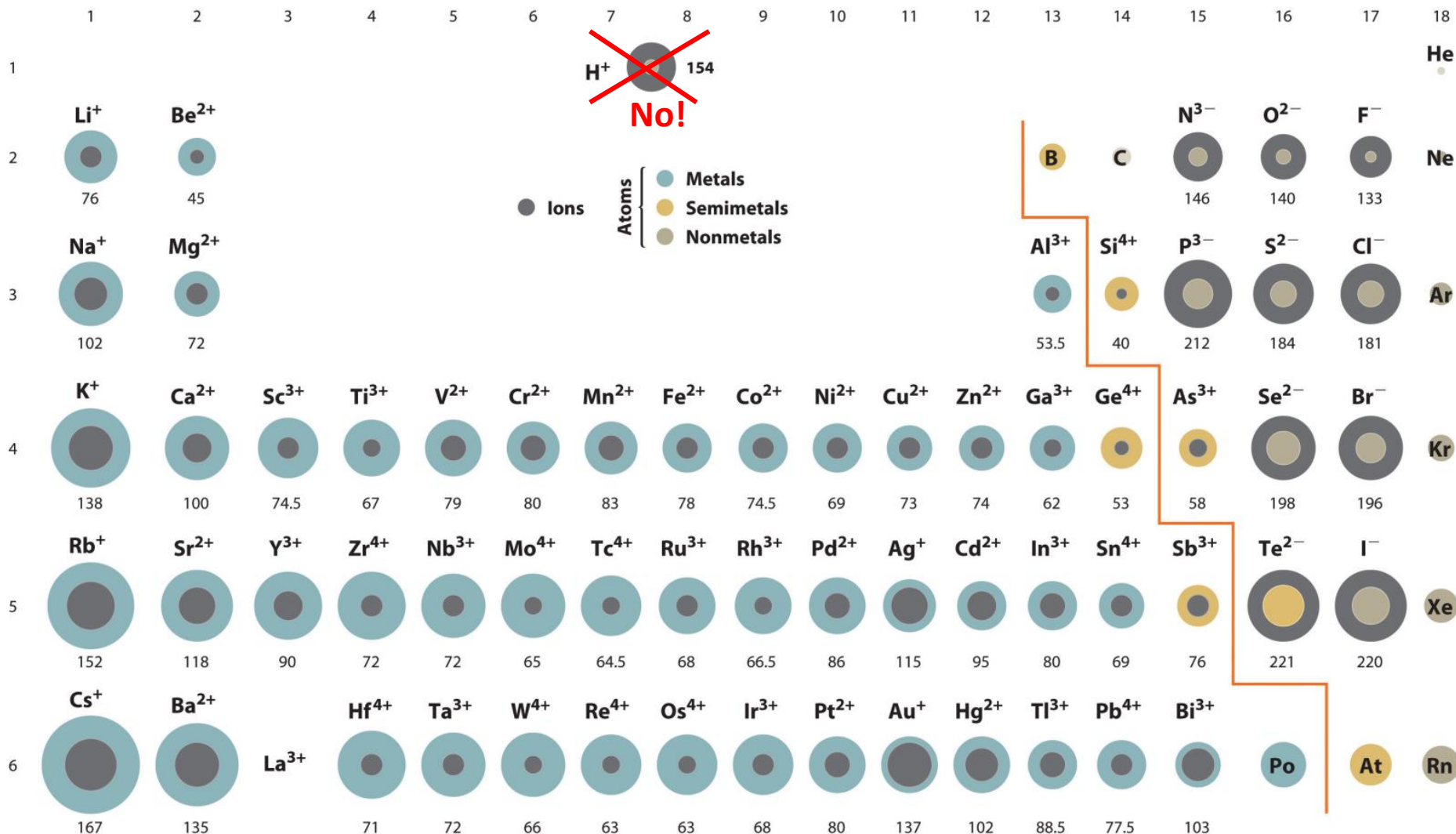
# Periodic trends of atomic radii

- Radii decrease when moving from left to right ( $Z_{eff}$  increases)
- Radii increase when moving down in the group (principal quantum number  $n$  increases, orbitals become more expanded)
- The atomic radii are useful for the illustration of periodic trends, but not that valuable otherwise



# Shannon ionic radii

Figure: [chem.libretexts.org](http://chem.libretexts.org)



Ionic Radii (in pm units) of the most common ionic states of the s-, p-, and d-block elements. **Gray** circles indicate the sizes of the ions shown; **colored** circles indicate the sizes of the neutral atoms. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Cryst. **1976**, 32, 751. Full radii data available at: <http://abulafia.mt.ic.ac.uk/shannon/ptable.php>.

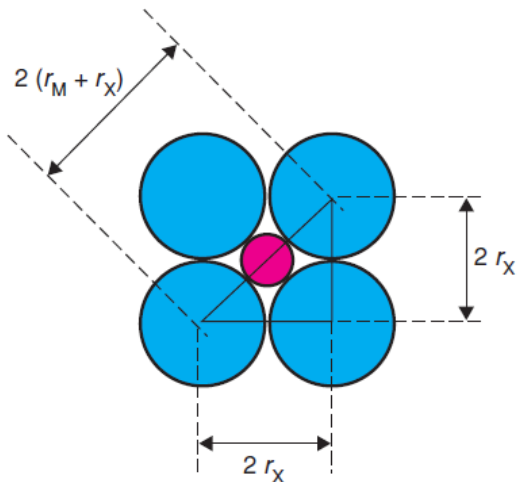
# Applications of the ionic radii

- The ionic radii have been derived from a large number of experimental data
- They can be used for example:
  - To investigate whether a new crystal structure shows ionic bonding
  - To investigate whether a bond that is expected to be ionic has a reasonable length (even pointing out possible problems with the crystal structure)
- For example: The Na-Cl distance in solid NaCl is 282 pm, this compares well with the sum of the ionic radii: of  $\text{Na}^+$  (102 pm) and  $\text{Cl}^-$  (181 pm) = 283 pm
- Another application is the ***radius ratio rules*** for ionic structures (next slide)
- Note that the radii depend on the formal charge and the coordination of the ion!
  - The charge is more important than the coordination (there is not data for all coordination numbers)
  - Figure on the previous slide shows only the most common ionic state. The full dataset at <http://abulafia.mt.ic.ac.uk/shannon/ptable.php> has more details.



# Radius ratio rules

- Cations surround themselves with as many anions as possible, and vice versa.
  - A cation must be in contact with its anionic neighbors (otherwise unstable)
  - Neighboring anions may or may not be in contact
- With simple trigonometry, one can then derive minimum radius ratios for different coordination numbers
- For example, NaCl: 102 pm/181 pm = 0.56 -> **octahedral** coordination.
- Nice qualitative tool, but not highly predictive (lots of exceptions to the rule exist)



**Table 3.3** Minimum radius ratios

Coordination	Minimum $r_M:r_X$
Linear, 2	–
Trigonal, 3	0.155
Tetrahedral, 4	0.225
Octahedral, 6	0.414
Cubic, 8	0.732
Dodecahedral, 12	1.000

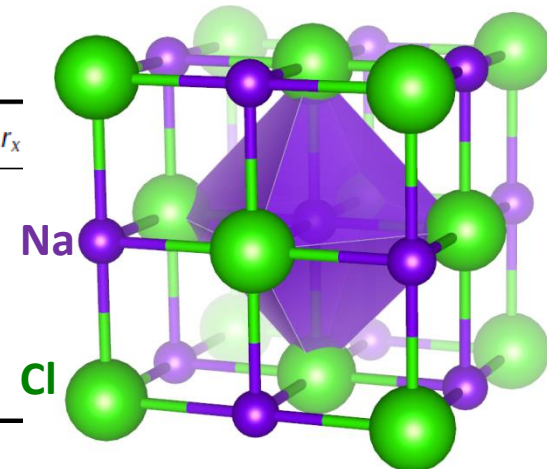


Figure:AJK

**Figure 3.4** Radius ratio calculation for octahedral coordination.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
---	---	---	---	---	---	---	---	---	----	----	----	----	----	----	----	----	----

Pyykkö Self-Consistent Covalent radii																		2 He 46 - -																	
3 Li 133 124 -		4 Be 102 90 85		<div><div>Z</div><div>Radius, r<sub>n</sub>:</div><div>Symbol</div><div>r<sub>1</sub></div><div>r<sub>2</sub></div><div>r<sub>3</sub></div></div>										5 B 85 78 73		6 C 75 67 60		7 N 71 60 54		8 O 63 57 53		9 F 64 59 53		10 Ne 67 96 -											
11 Na 155 160 -		12 Mg 139 132 127												13 Al 126 113 111		14 Si 116 107 102		15 P 111 102 94		16 S 103 94 95		17 Cl 99 95 93		18 Ar 96 107 96											
19 K 196 193 -		20 Ca 171 147 133		21 Sc 148 116 114		22 Ti 136 117 108		23 V 134 112 106		24 Cr 122 111 103		25 Mn 119 105 103		26 Fe 116 109 102		27 Co 111 103 96		28 Ni 110 101 101		29 Cu 112 115 120		30 Zn 118 120 -		31 Ga 124 117 121		32 Ge 121 111 114		33 As 121 114 106		34 Se 116 107 107		35 Br 114 109 110		36 Kr 117 121 108	
37 Rb 210 202 -		38 Sr 185 157 139		39 Y 163 130 124		40 Zr 154 127 121		41 Nb 147 125 116		42 Mo 138 121 113		43 Tc 128 120 110		44 Ru 125 114 103		45 Rh 125 110 106		46 Pd 120 117 112		47 Ag 128 139 137		48 Cd 136 144 -		49 In 142 136 146		50 Sn 140 130 132		51 Sb 140 133 127		52 Te 136 128 121		53 I 133 129 125		54 Xe 131 135 122	
55 Cs 232 209 -		56 Ba 196 161 149		La–Lu		72 Hf 152 128 122		73 Ta 146 126 119		74 W 137 120 115		75 Re 131 119 110		76 Os 129 116 109		77 Ir 122 115 107		78 Pt 123 112 110		79 Au 124 121 123		80 Hg 133 142 -		81 Tl 144 142 150		82 Pb 144 135 137		83 Bi 151 141 135		84 Po 145 135 129		85 At 147 138 138		86 Rn 142 145 133	
87 Fr 223 218 -		88 Ra 201 173 159		Ac–Lr		104 Rf 157 140 131		105 Db 149 136 126		106 Sg 143 128 121		107 Bh 141 128 119		108 Hs 134 125 118		109 Mt 129 125 113		110 Ds 128 116 112		111 Rg 121 116 118		112 122 137 130		113 136		114 143		115 162		116 175		117 165		118 157	

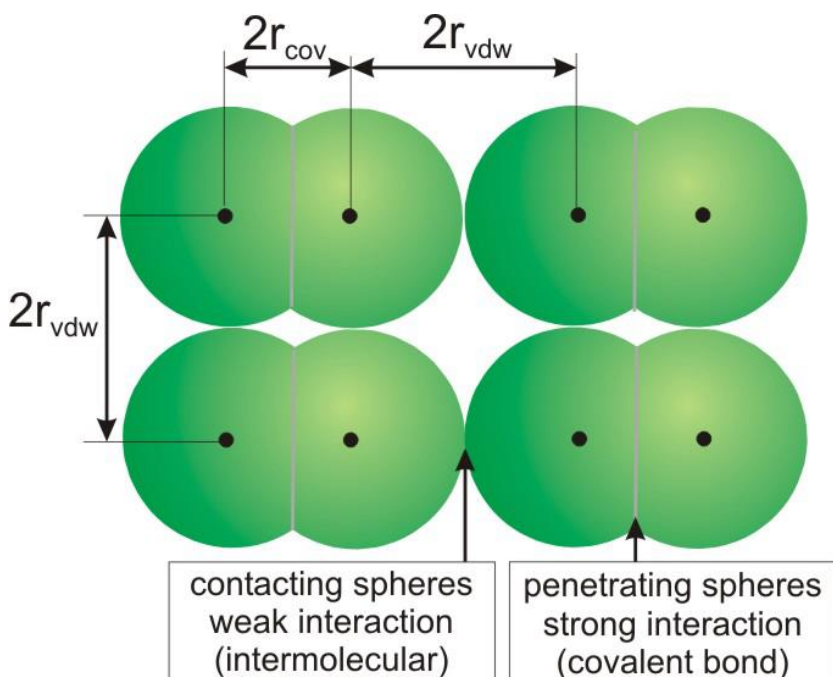
57 La 180 139 139	58 Ce 163 137 131	59 Pr 176 138 128	60 Nd 174 137	61 Pm 173 135	62 Sm 172 134	63 Eu 168 134	64 Gd 169 135 132	65 Tb 168 135	66 Dy 167 133	67 Ho 166 133	68 Er 165 133	69 Tm 164 131	70 Yb 170 129	71 Lu 162 131 131
89 Ac 186 153 140	90 Th 175 143 136	91 Pa 169 138 129	92 U 170 134 118	93 Np 171 136 116	94 Pu 172 135	95 Am 166 135	96 Cm 166 136	97 Bk 168 139	98 Cf 168 140	99 Es 165 140	100 Fm 167	101 Md 173 139	102 No 176 159	103 Lr 161 141

# Self-Consistent Covalent Radii

- The Pyykkö Self-Consistent Covalent radii have been derived from a large number of experimental and computational data
- Similar to ionic radii, the covalent radii can be used for example:
  - To check whether a new crystal structure shows covalent bonding
  - To check whether an bond that is expected to be covalent has a reasonable length (even pointing out possible problems with the crystal structure)
- For example: The C-C distance in diamond is 154 pm, this compares well with the sum of the single-bond covalent radii  $75 + 75 = 150$  pm
- The availability of double and triple bond radii makes the data set useful for interpreting new crystal structures
- Original papers:
  - P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186.
  - P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770.
  - P. Pyykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511.
- Another (experimental) set of radii: Alvarez *et al.* *Dalton Trans.*, **2008**, 2832.

# van der Waals radii

- Significantly larger than covalent radii
- Can be used to check for weak interactions / contacts in a crystal structure
- The dataset of A. Bondi (*J. Phys. Chem.* **1964**, 68, 441) was a major milestone
- Historically vdW radii have been rather difficult to determine for *d*-/*f*-metals
- The values below are a combination of experimental and quantum chemical values



**TABLE 12: Consistent van der Waals Radii for All Main-Group Elements<sup>a</sup>**

1	2	13	14	15	16	17	18
H 1.10							He 1.40
Li 1.81	Be <b>1.53</b>	B <b>1.92</b>	C 1.70	N 1.55	O 1.52	F 1.47	Ne 1.54
Na 2.27	Mg 1.73	Al <b>1.84</b>	Si 2.10	P 1.80	S 1.80	Cl 1.75	Ar 1.88
K 2.75	Ca <b>2.31</b>	Ga 1.87	Ge <b>2.11</b>	As 1.85	Se 1.90	Br 1.83	Kr 2.02
Rb <b>3.03</b>	Sr <b>2.49</b>	In 1.93	Sn 2.17	Sb <b>2.06</b>	Te 2.06	I 1.98	Xe 2.16
Cs <b>3.43</b>	Ba <b>2.68</b>	Tl 1.96	Pb 2.02	Bi <b>2.07</b>	Po <b>1.97</b>	At <b>2.02</b>	Rn <b>2.20</b>
Fr <b>3.48</b>	Ra <b>2.83</b>						

Ref: Truhlar *et al.* *J. Phys. Chem. A*, **2009**, 113, 5806

# Alvarez van der Waals radii

- S. Alvarez, A cartography of the van der Waals territories, *Dalton Trans.* **2013**, 42, 8617 ([link](#)).
- The most recent and the most comprehensive set of vdW radii
- Analysis of more than five million interatomic “non-bonded” distances in the Cambridge Structural Database
- Proposal of a consistent set of vdW radii for most naturally occurring elements
- Paper available in MyCourses (Materials -> Scientific papers)
- See  $r_{vdW}$  values in Table 1. Bondi values are given for comparison:

Z	E	Bondi	Batsanov	$r_{vdW}$	$\rho_{vdW}$ (%)	Data
1	H	1.20		1.20	66	9888
2	He	1.40		[1.43]		12
3	Li	1.81	2.2	2.12	76	11 067
4	Be		1.9	1.98	90	3515
5	B		1.8	1.91	70	152 194
6	C	1.70	1.7	1.77	82	385 475
7	N	1.55	1.6	1.66	52	187 967
8	O	1.52	1.55	1.50	73	420 207
9	F	1.47	1.5	1.46	66	497 497
10	Ne	1.54		[1.58]		12

# Descriptive structural chemistry and structure types

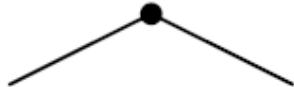
# Descriptive structural chemistry and structure types

- We have already discussed the structure of crystalline materials from the perspective of the unit cell and lattice parameters (Lecture 1)
- The nature of the chemical bonding affects how a certain structure is described
  - For example, structures with metal cations can typically be described using **coordination polyhedra**
  - This also works the other way around: the local structure of a solid can immediately suggest a certain type of chemical bonding
- Typical concepts used in descriptive structural chemistry
  - Coordination
  - Linked (coordination) polyhedra
  - Close-packed structures (possibly with interstitial sites)
- Whenever possible, solid state structures are assigned to some **structure type**
  - Some examples of structure types: rock salt, zinc blende, wurtzite, ...
  - Summary of structure types: <https://wiki.aalto.fi/display/SSC/Structure+types>

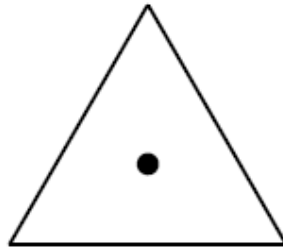
# Coordination (1)



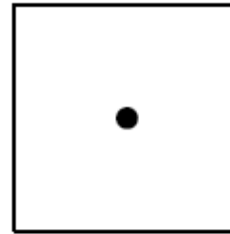
2: linear arrangement  
[2l]



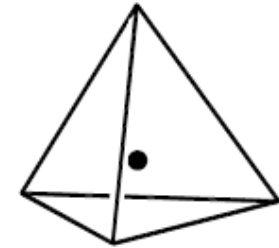
2: angular  
arrangement [2n]



3: triangle  
[3l]

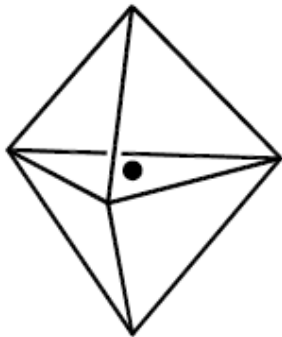


4: square  
[4l] or [s]

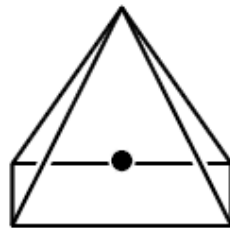


4: tetrahedron  
[4t] or [t]

**The most common ones**



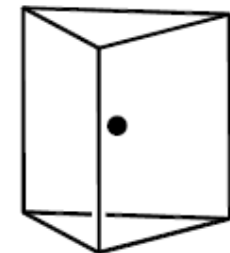
5: trigonal bi-  
pyramid [5by]



5: tetragonal  
pyramid [5y]



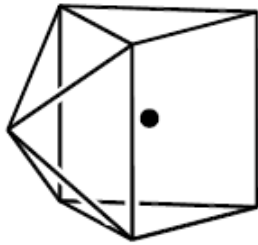
6: octahedron  
[6o] or [o]



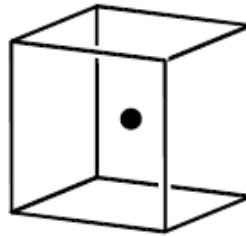
6: trigonal  
prism [6p]



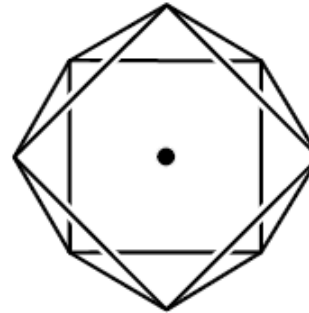
# Coordination (2)



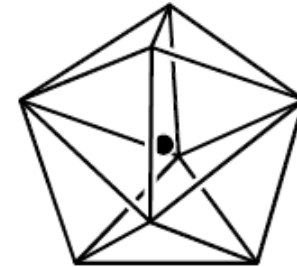
7: capped trigonal prism  $[6p1c]$



8: cube  $[8cb]$  or  $[cb]$

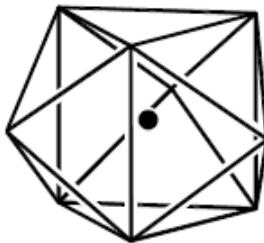


8: square anti-prism  $[8acb]$

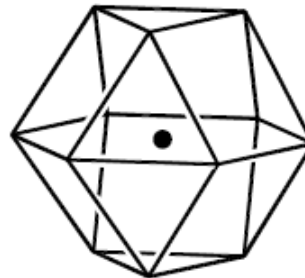


8: dodecahedron  $[8do]$  or  $[do]$

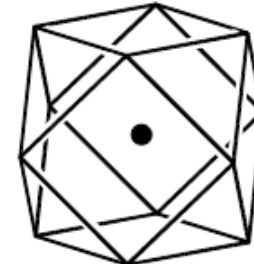
(dodecahedral = 12 faces. The polyhedron shown is actually a *snub disphenoid*)



9: triply-capped trigonal prism  $[6p3c]$



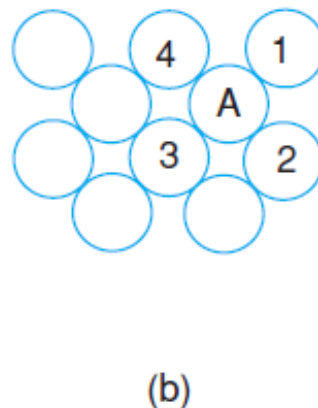
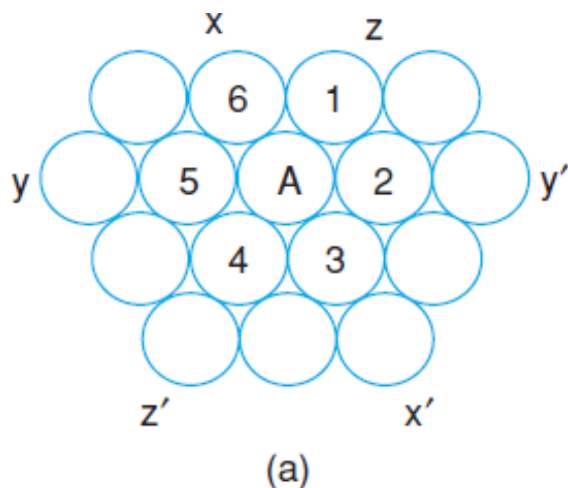
12: anticuboctahedron  $[12aco]$  or  $[aco]$



12: cuboctahedron  $[12co]$  or  $[co]$

# Close Packing (1)

- Many metallic, ionic, covalent, and molecular crystal structures can be described using the concept of **close packing (cp)**
- The structures are usually arranged to have the maximum density and can be understood by considering the most efficient way of packing **equal-sized spheres**
- The most efficient way to pack spheres in **two** dimensions is shown below
- Each sphere, *e.g.* **A**, is in contact with six others -> six **nearest neighbours** and the **coordination number, CN** = 6 (the largest possible for a planar arrangement)
- MyCourses -> Materials -> Data files for lectures -> Lecture 3 -> Close-packing

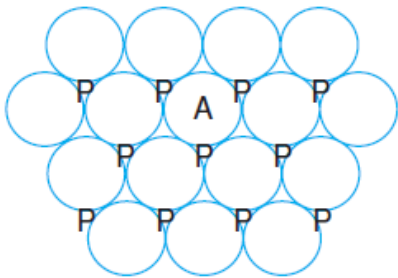


(a) a *cp* layer of equal-sized spheres;  
(b) a non-*cp* layer with coordination number 4;

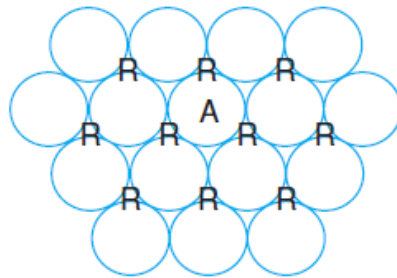
Within a *cp* layer, three close packed directions  $xx'$ ,  $yy'$ , and  $zz'$  occur

# Close Packing (2)

- The most efficient way to pack spheres in **three** dimensions is to stack *cp* layers on top of each other
- There are two simple ways to do this, resulting in **hexagonal close packed** and **cubic close packed** structures
- The most efficient way for two *cp* layers A and B to be in contact is for each sphere of one layer to rest in a hollow between three spheres in the other layer (**P** or **R**)
- Addition of a third *cp* layer can also be done in two ways:
  - Hexagonal close packing (*hcp*): Third layer at **S**, layer sequence ...ABABAB...
  - Cubic close packing (*ccp*): Third layer at **T**, layer sequence ...ABCABC...



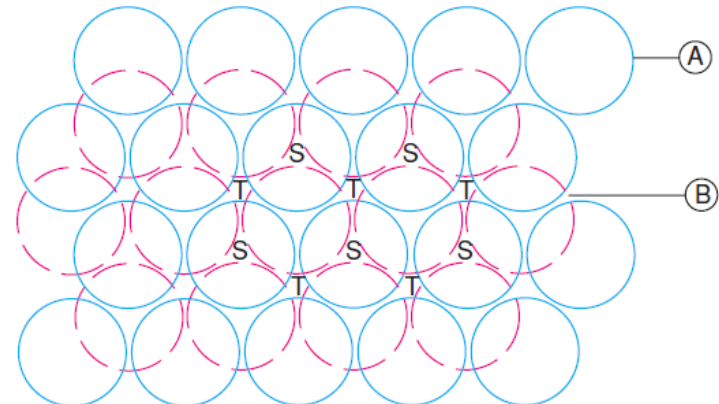
(c)



(d)

(c, d) alternative positions **P** and **R** for a second *cp* layer

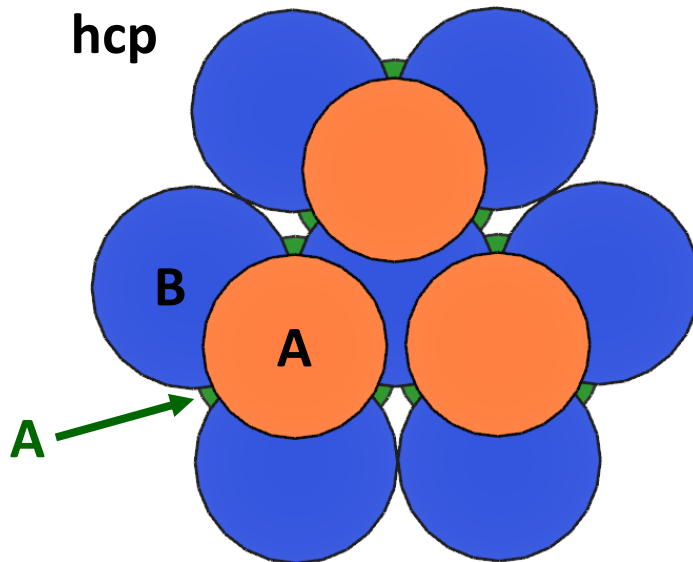
Ref: West p. 20



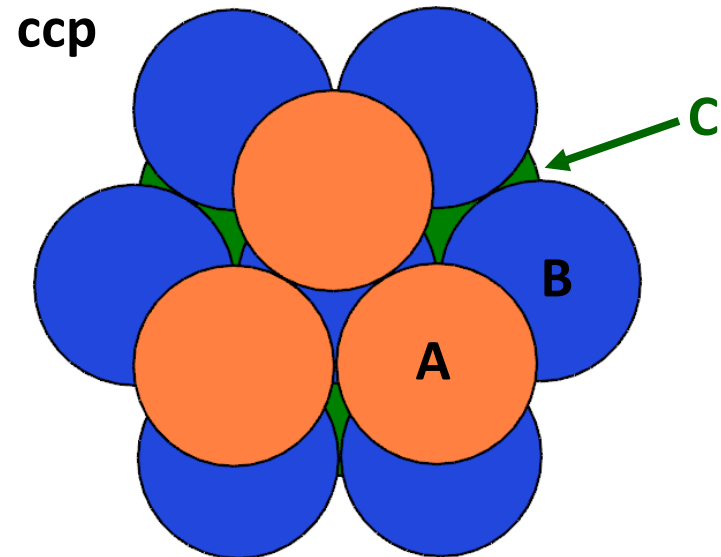
Two *cp* layers A and B. The B layer occupies the **P** positions

# Close Packing (3)

- The simplest layer stacking sequences *hcp* and *ccp* are the most important ones
- More complex sequences with larger repeat units, e.g. ABCACB or ABAC can occur and some of these give rise to the phenomenon of **polytypism**.
- Each sphere is in contact with **12** others (figure: middle atom of the B-layer)
- **74.05%** of the total volume is occupied by spheres (maximum density possible in structures constructed of spheres of only one size)

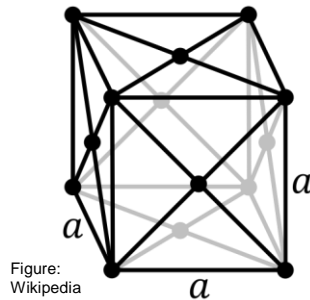


Top A-layer radius smaller and bottom A-layer radius larger to improve clarity

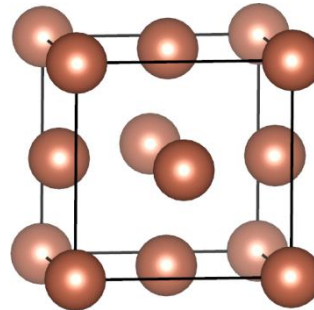


Figures: AJK

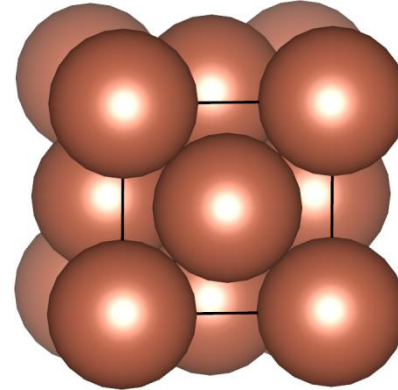
# *ccp* arrangement corresponds to face-centered cubic lattice



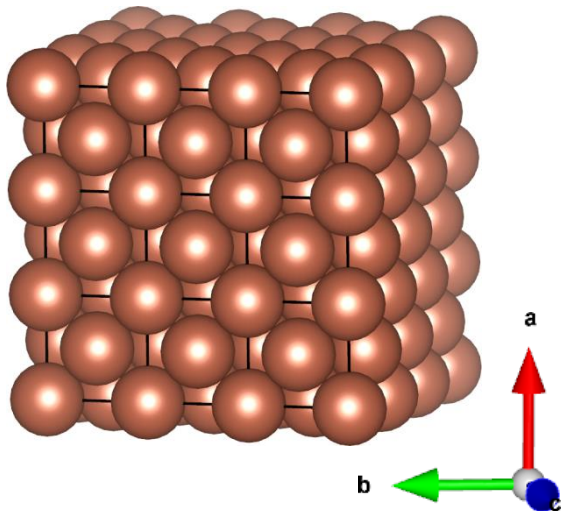
***F (fcc)***



**Cu (fcc metal)**



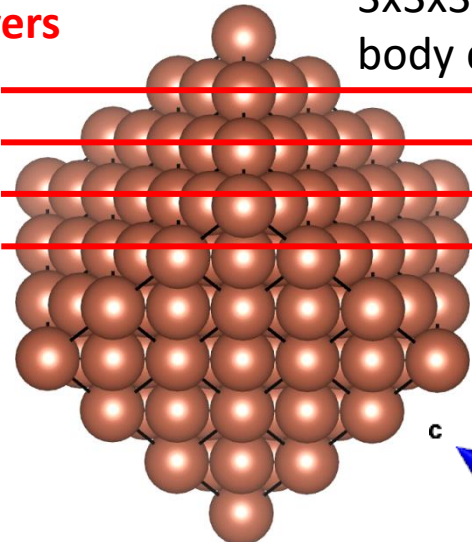
3x3x3 supercell



***cp layers***

**A** —  
**B** —  
**C** —  
**A** —

3x3x3 supercell,  
body diagonal orientation



# hcp

- *hcp* structure of Zn metal (space group  $P6_3/mmc$ )
  - The structure is slightly distorted, with 6 neighbors at 2.66 Å and 6 at 2.91 Å

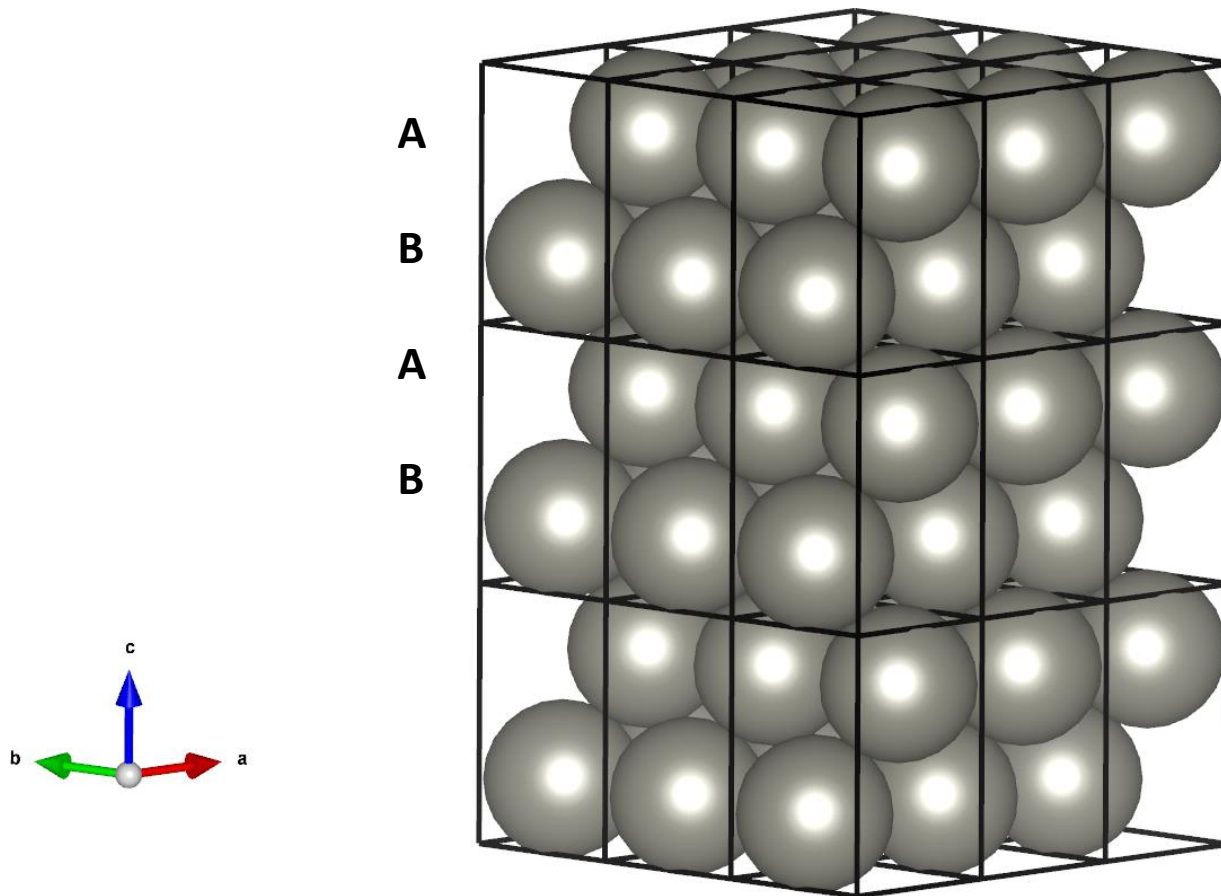


Figure: AJK

# Structures of common metals

- Most metals crystallize in one of the three arrangements: *ccp* (*fcc*), *hcp*, or *bcc*
  - *bcc* is not a close-packed structure!
- It is still not well understood why particular metals prefer one structure type to another
- Quantum chemical calculations reveal that the lattice energies of *hcp* and *ccp* metal structures are comparable
- Therefore, the structure observed in a particular case probably depends on fine details of the bonding and the band structure of the metal

**Table 1.3** Structures and unit cell dimensions of some common metals

<i>ccp</i>		<i>hcp</i>			<i>bcc</i>	
Metal	$a/\text{\AA}$	Metal	$a/\text{\AA}$	$c/\text{\AA}$	Metal	$a/\text{\AA}$
Cu	3.6147	Be	2.2856	3.5842	Fe	2.8664
Ag	4.0857	Mg	3.2094	5.2105	Cr	2.8846
Au	4.0783	Zn	2.6649	4.9468	Mo	3.1469
Al	4.0495	Cd	2.9788	5.6167	W	3.1650
Ni	3.5240	Ti	2.9506	4.6788	Ta	3.3026
Pb	4.9502	Zr	3.2312	5.1477	Ba	5.019



# Periodic table of crystal structures

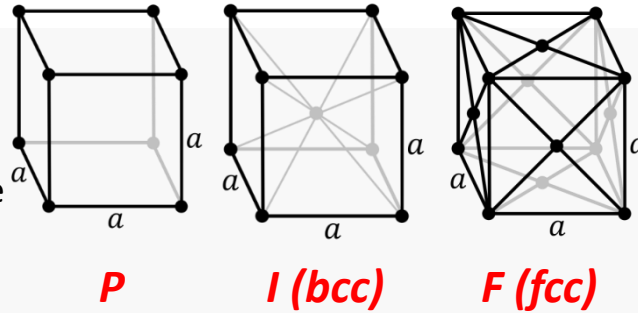
1 H HEX																2 He HCP	
3 Li BCC	4 Be HCP																10 Ne FCC
11 Na BCC	12 Mg HCP																18 Ar FCC
19 K BCC	20 Ca FCC	21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP	31 Ga ORTH	32 Ge DC	33 As RHO	34 Se HEX	35 Br ORTH	36 Kr FCC
37 Rb BCC	38 Sr FCC	39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP	49 In TETR	50 Sn TETR	51 Sb RHO	52 Te HEX	53 I ORTH	54 Xe FCC
55 Cs BCC	56 Ba BCC	57* La DHCP	72 Hf HCP	73 Ta BCC/TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO	81 Tl HCP	82 Pb FCC	83 Bi RHO	84 Po SC/RHO	85 At [FCC]	86 Rn FCC
87 Fr [BCC]	88 Ra BCC	89** Ac FCC	104 Rf [HCP]	105 Db [BCC]	106 Sg [BCC]	107 Bh [HCP]	108 Hs [HCP]	109 Mt [FCC]	110 Ds [BCC]	111 Rg [BCC]	112 Cn [HCP]	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og [FCC]

</

Legend:

.. / .. = mixed structure

[...] = predicted structure

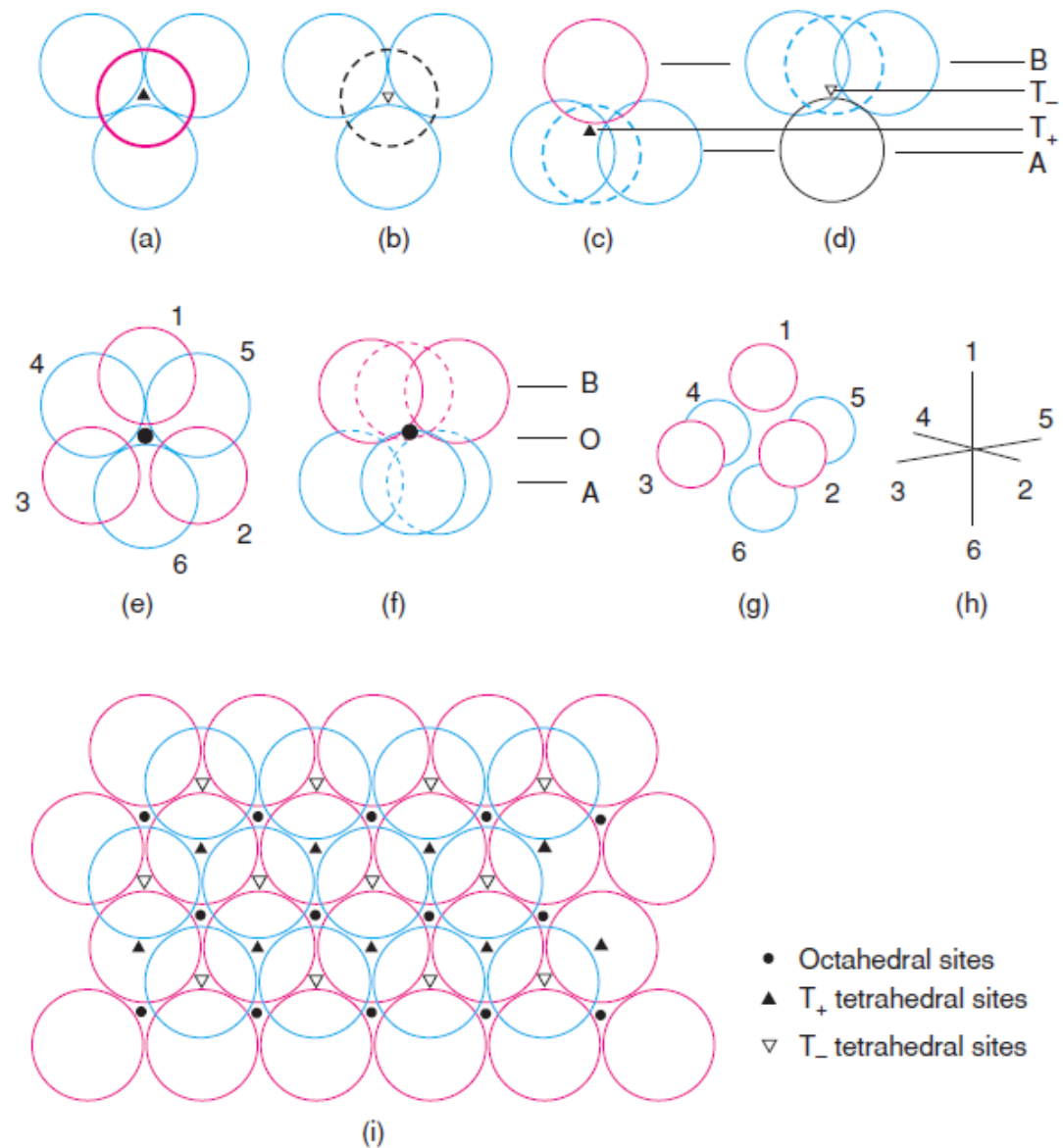




# Close packing in ionic structures

- When the anion is larger than the cation, the structures often contain ***cp* layers of anions** and the cations occupy **interstitial sites**
  - For example: NaCl, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, and ZnO.
- In such structures there are several variables:
  - Anion stacking sequence (*hcp* or *ccp*)
  - Number and type of interstitial sites occupied by cations.
  - **Tetrahedral** and **octahedral** interstitial sites are present in *cp* structures
- Summary of structure types: <https://wiki.aalto.fi/display/SSC/Structure+types>

# $T_+$ , $T_-$ , and O sites



**Figure 1.23** Tetrahedral and octahedral sites between two cp anion layers, seen from different perspectives. (a, b) Projection down threefold axis of  $T_+$ ,  $T_-$  sites. (c, d) Tetrahedral sites edge-on. (e) Projection down threefold axis of octahedral site and (f) seen edge-on. (g, h) Conventional representation of octahedral site. (i) Distribution of  $T_+$ ,  $T_-$ , O sites between two cp layers.

# Examples of interstitial sites

- It is rare that all the interstitial sites in a *cp* structure are occupied
- Often one set is full or partly occupied and the remaining sets are empty

**Table 1.4** Some close packed structures

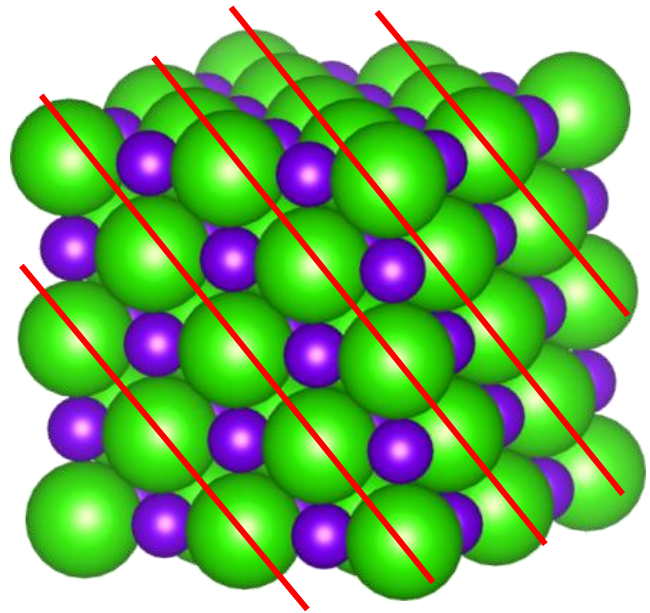
Ref: West p. 28

Anion arrangement	Interstitial sites			Examples
	$T_+$	$T_-$	O	
<i>ccp</i>	–	–	1	NaCl, rock salt
	1	–	–	ZnS, blende or sphalerite
	1/8	1/8	1/2	MgAl <sub>2</sub> O <sub>4</sub> , spinel
	–	–	1/2	CdCl <sub>2</sub>
	–	–	1/3	CrCl <sub>3</sub>
	1	1	–	K <sub>2</sub> O, antifluorite
<i>hcp</i>	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI <sub>2</sub>
	–	–	1/2	TiO <sub>2</sub> , rutile <sup>a</sup>
	–	–	2/3	Al <sub>2</sub> O <sub>3</sub> , corundum
	1/8	1/8	1/2	Mg <sub>2</sub> SiO <sub>4</sub> , olivine
<i>ccp</i> 'BaO <sub>3</sub> ' layers	–	–	1/4	BaTiO <sub>3</sub> , perovskite

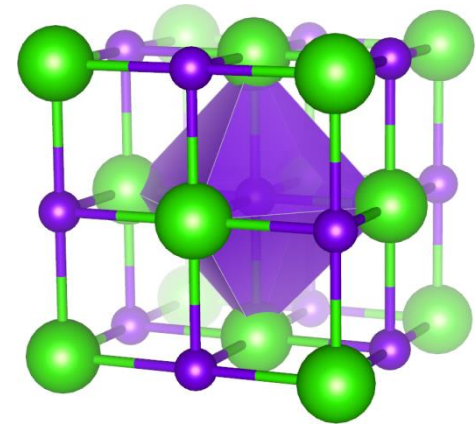
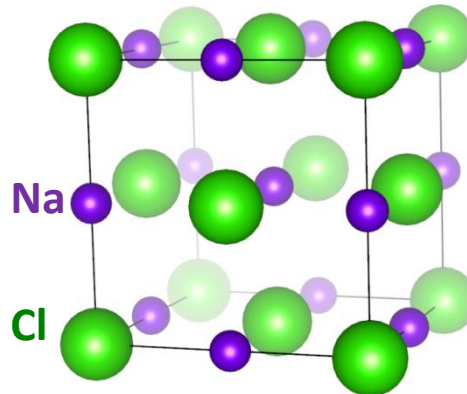
<sup>a</sup>The *hcp* oxide layers in rutile are not planar but are buckled; the oxide arrangement may alternatively be described as *tetragonal* packed, tp.

# Octahedral interstitials in NaCl structure

- Close-packed layers of  $\text{Cl}^-$  anions
- $\text{Na}^+$  cations in the octahedral interstitials
- <https://wiki.aalto.fi/pages/viewpage.action?pageId=165132721>

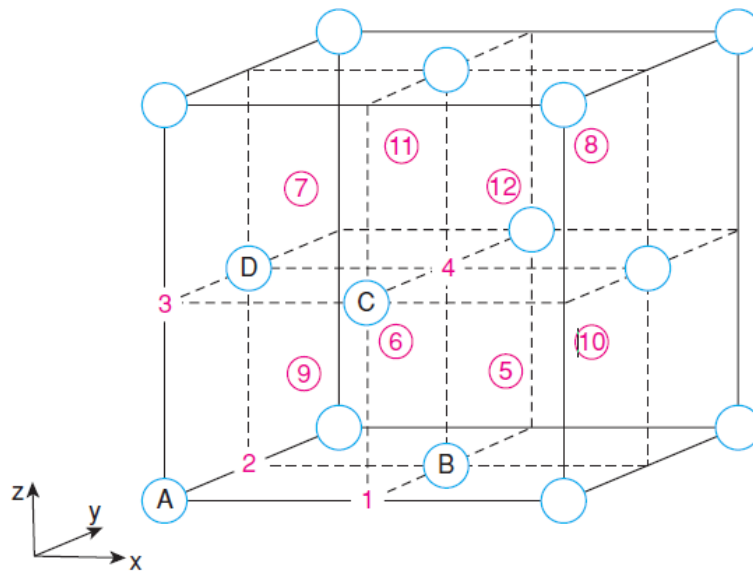


**Close-packed  
anion layers**

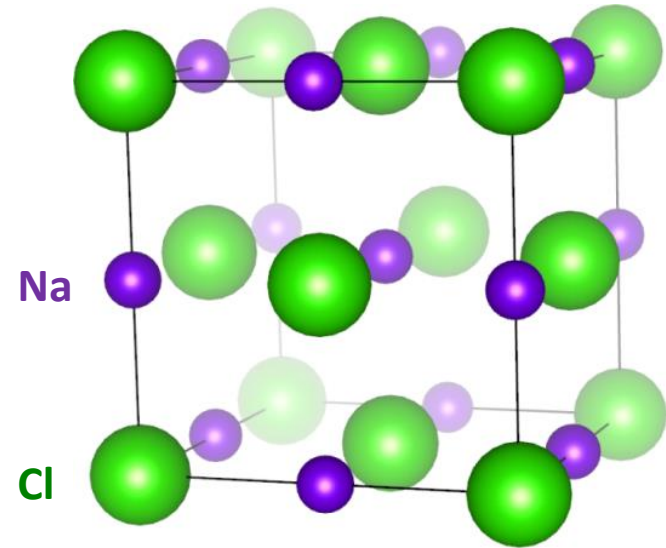


Figures: AJK

# Cation sites in an *fcc* anion array



**Figure 1.24** Available cation sites, 1–12, in an fcc anion array.



The various cation positions in Fig. 1.24 have the following coordinates:

octahedral	1: $\frac{1}{2}00$	2: $0\frac{1}{2}0$	3: $00\frac{1}{2}$	4: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
tetrahedral, $T_+$	5: $\frac{3}{4}\frac{1}{4}\frac{1}{4}$	6: $\frac{1}{4}\frac{3}{4}\frac{1}{4}$	7: $\frac{1}{4}\frac{1}{4}\frac{3}{4}$	8: $\frac{3}{4}\frac{3}{4}\frac{3}{4}$
tetrahedral, $T_-$	9: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$	10: $\frac{3}{4}\frac{3}{4}\frac{1}{4}$	11: $\frac{1}{4}\frac{3}{4}\frac{3}{4}$	12: $\frac{3}{4}\frac{1}{4}\frac{3}{4}$