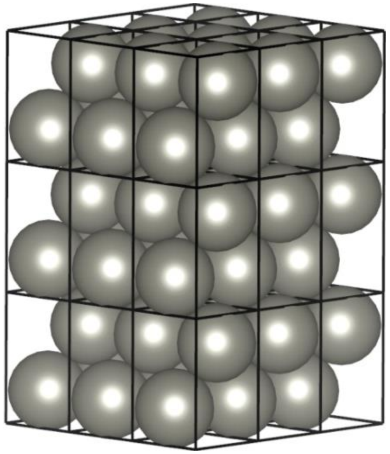
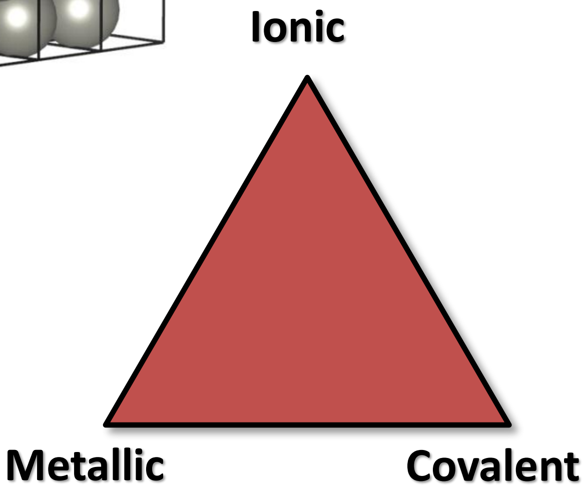
Lecture 3: Bonding in solids and description of crystal structures

- 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**

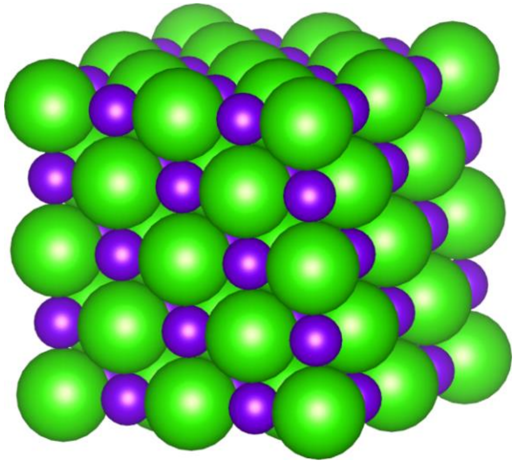


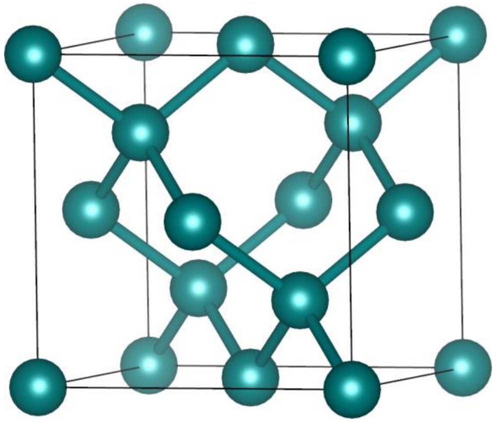


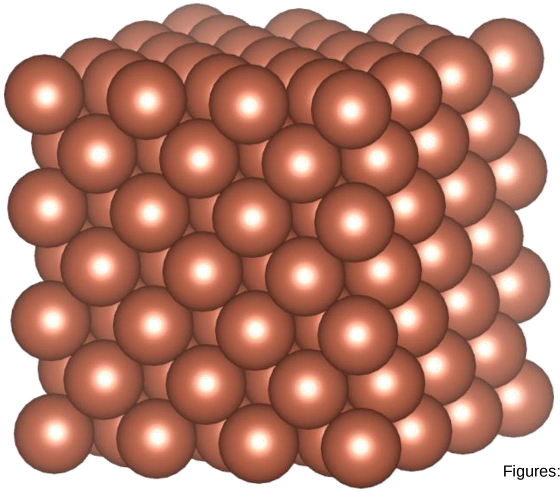
Figures: AJK

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







Figures: AJK

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.

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

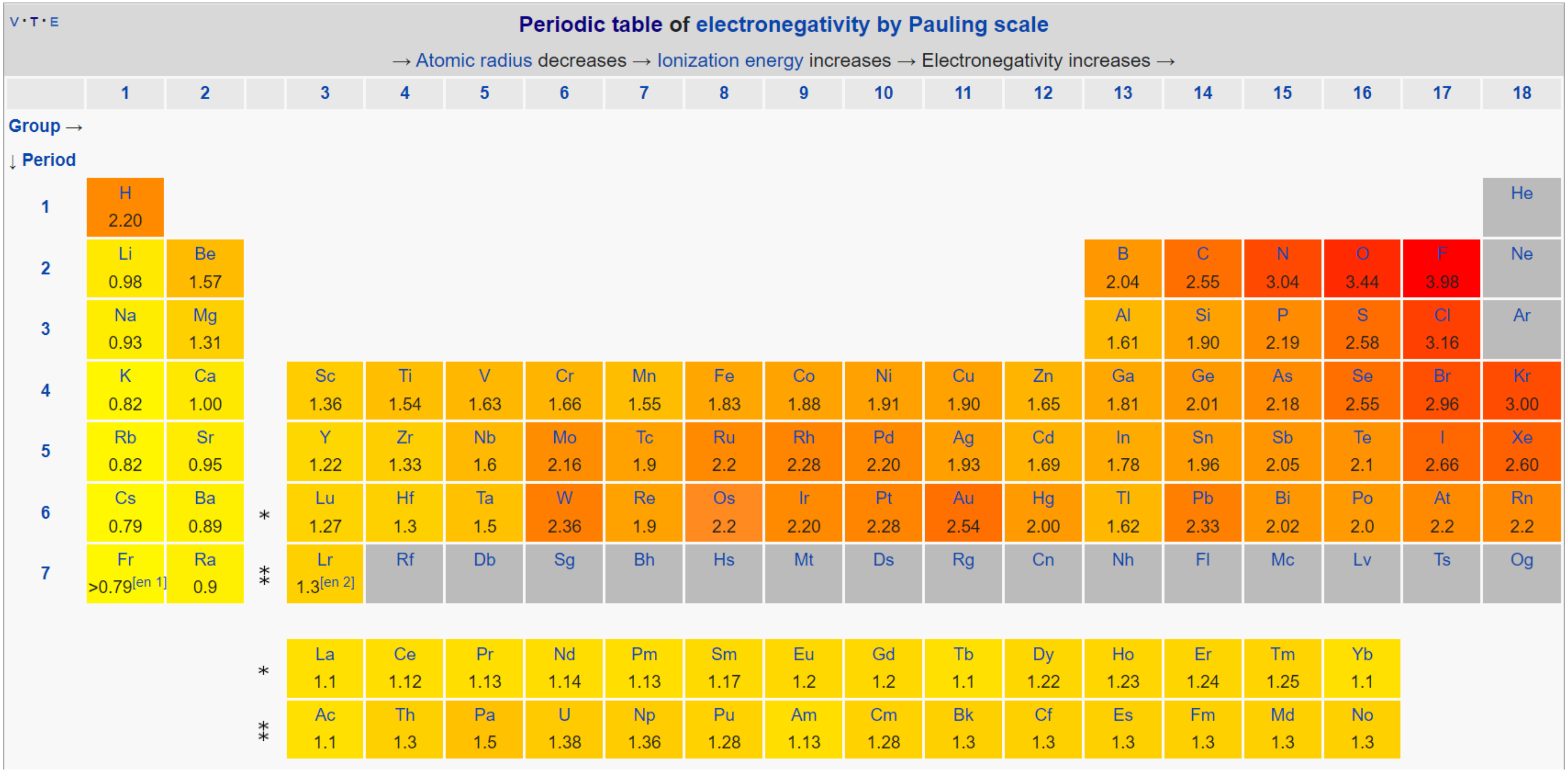
- Pauling defined the difference of two electronegativities χ_A and χ_B in terms of bond dissociation energies, D_0:

  $$|\chi_A - \chi_B| = \{D_0(AB) - \tfrac{1}{2}[D_0(AA) + D_0(BB)]\}^{1/2}$$

- $D_0(AA)$ 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)

Ref: Atkins' Physical Chemistry, 9th ed. p. 389

Pauling Electronegativities



V · T · E

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	*	Lu 1.27	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 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr >0.79[en 1]	Ra 0.9	**	Lr 1.3[en 2]	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
			*	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		
			**	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		

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 for the s- and p-block elements, but somewhat ambiguous for *d*- and *f*-metals

Electronegativity using the Allen scale

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.300																	He 4.160
2	Li 0.912	Be 1.576											B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
3	Na 0.869	Mg 1.293											Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
4	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 1.588	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
5	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 1.58	Ag 1.87	Cd 1.521	In 1.656	Sn 1.824	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
6	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 1.765	Tl 1.789	Pb 1.854	Bi 2.01	Po 2.19	At 2.39	Rn 2.60
7	Fr 0.67	Ra 0.89																

Figure: Wikipedia

Using electronegativities (χ)

- 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	
Zn–S	0.93	
C–H	0.35	**Covalent**

van Arkel-Ketalaar Triangles

- The electronegativies can be used to arrange binary compounds into so-called ***van Arkel-Ketalaar Triangles***
- Very illustrative concept for estimating the nature of a chemical bond

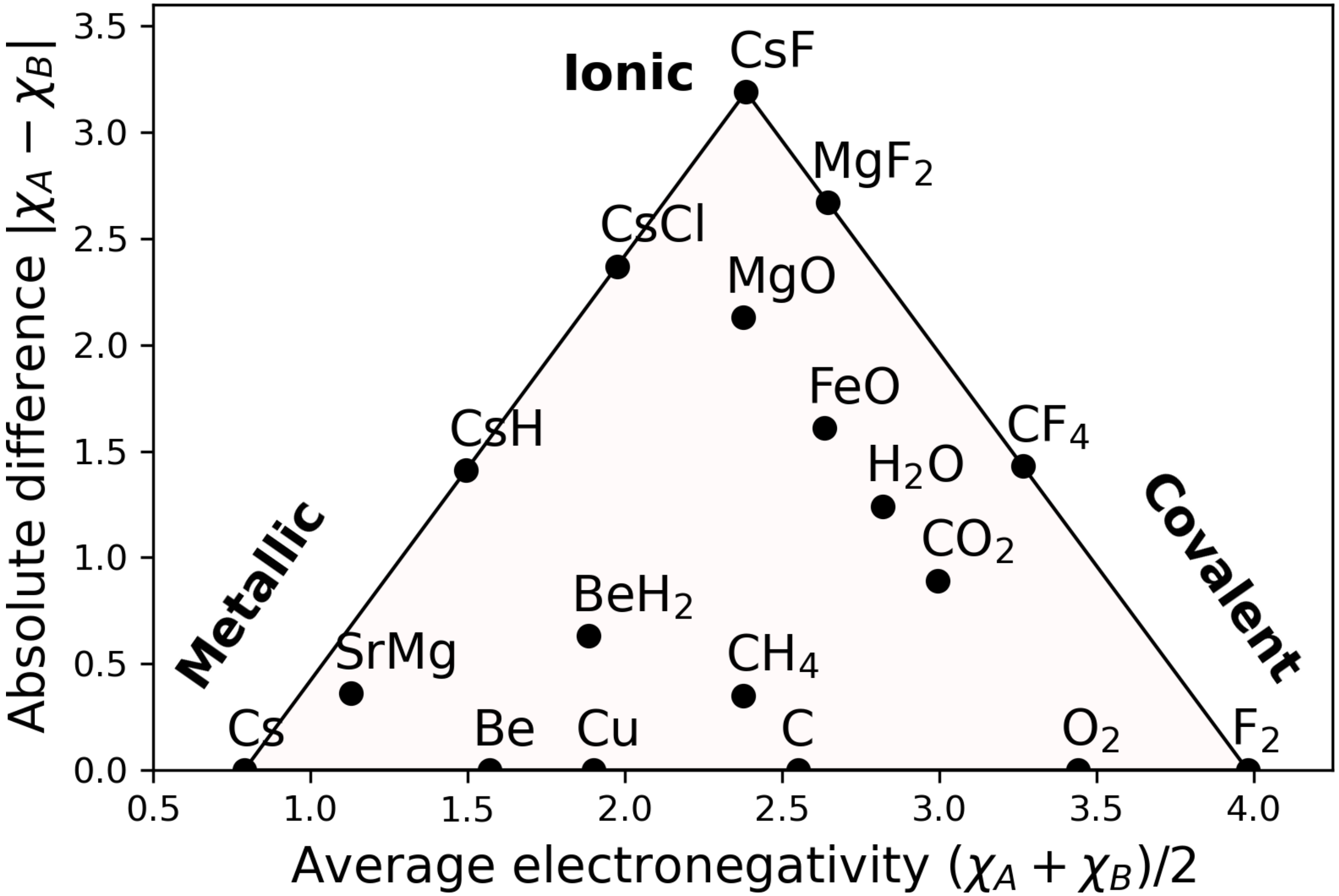


Figure: AJK

What really determines χ?

- Pauling determined the χ 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_{eff} experienced by the valence electrons
- $Z_{eff} = Z - \sigma$, where Z is the atomic number and σ 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_{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_{eff}	1.28	1.91	2.42	3.14	3.83	4.45	5.10	5.76
χ	0.98	1.57	2.04	2.55	3.04	3.44	3.98	(4.8)*

* Allen electronegativity

χ vs. Z_{eff} for the 2nd period

- χ 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}(Cl) = 6.1 e^-), while electronegativity ***decreases***
- Full consideration of orbital shapes *etc.* required to understand the χ values
- The moral of the story: simple explanations of complex many-electron systems may sound nice, but are probably not right

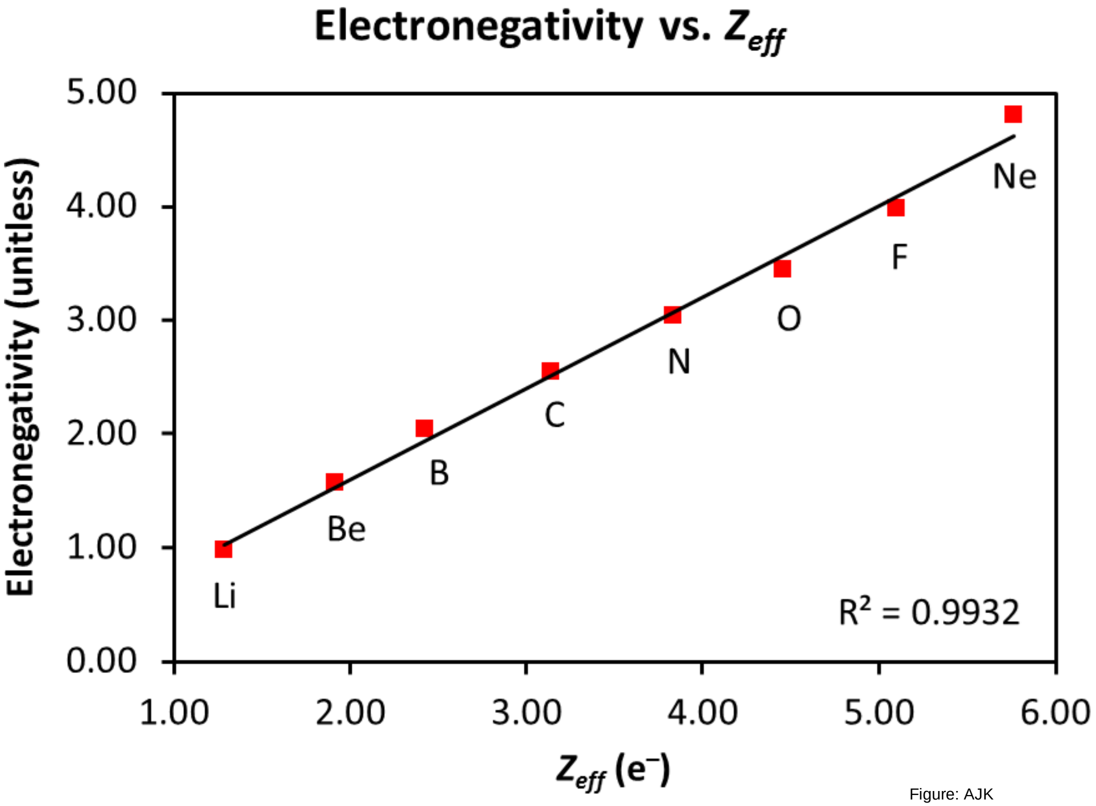


Figure: AJK

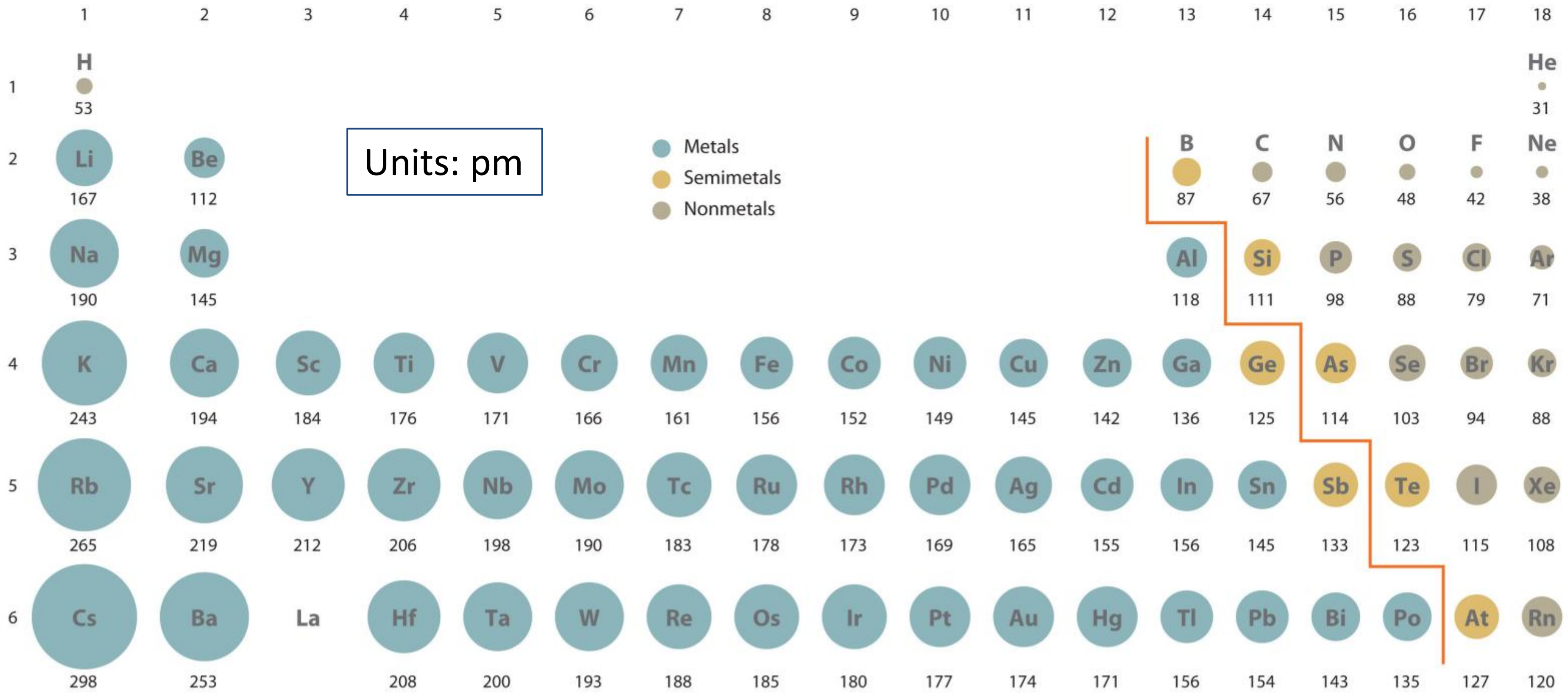
Atomic radii

Atomic radii

- When the crystal structure of a material 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 discussed:
  - 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, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186)
  - 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

- 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)
- Useful for the illustration of periodic trends, but not that valuable otherwise



Units: pm

● Metals
● Semimetals
● Nonmetals

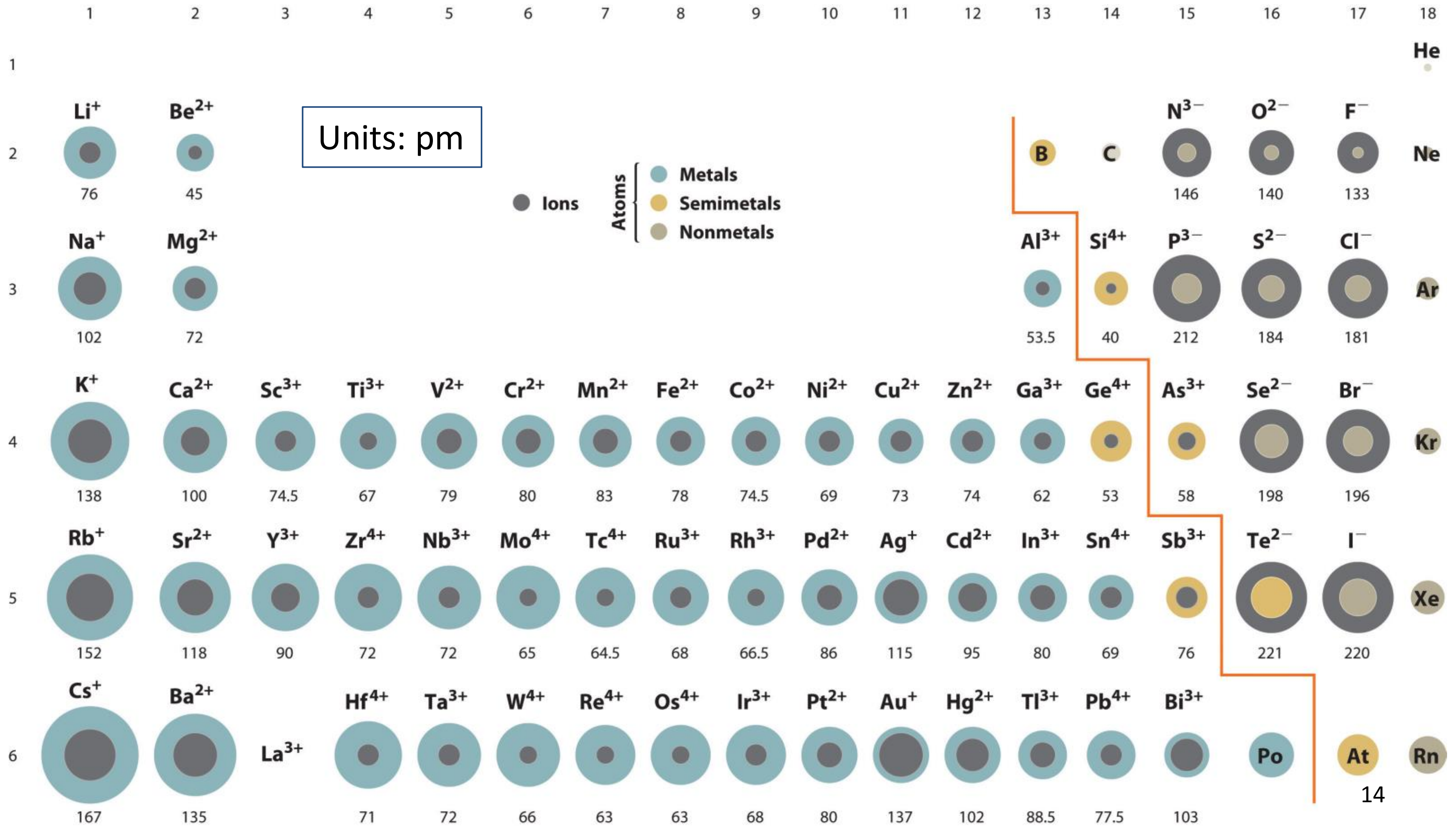
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 53																	He 31
2	Li 167	Be 112											B 87	C 67	N 56	O 48	F 42	Ne 38
3	Na 190	Mg 145											Al 118	Si 111	P 98	S 88	Cl 79	Ar 71
4	K 243	Ca 194	Sc 184	Ti 176	V 171	Cr 166	Mn 161	Fe 156	Co 152	Ni 149	Cu 145	Zn 142	Ga 136	Ge 125	As 114	Se 103	Br 94	Kr 88
5	Rb 265	Sr 219	Y 212	Zr 206	Nb 198	Mo 190	Tc 183	Ru 178	Rh 173	Pd 169	Ag 165	Cd 155	In 156	Sn 145	Sb 133	Te 123	I 115	Xe 108
6	Cs 298	Ba 253	La	Hf 208	Ta 200	W 193	Re 188	Os 185	Ir 180	Pt 177	Au 174	Hg 171	Tl 156	Pb 154	Bi 143	Po 135	At 127	Rn 120

Figure: chem.libretexts.org

Shannon ionic radii

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. Data available at: http://abulafia.mt.ic.ac.uk/shannon/ptable.php).

Figure: chem.libretexts.org



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 Na^+ (102 pm) and 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.

Pyykkö Self-Consistent Covalent radii

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H **32** - -																	2 He **46** - -
3 Li **133** **124** -	4 Be **102** **90** **85**				Z Radius, r_n: Symbol r_1 r_2 r_3							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**

Source: http://www.chem.helsinki.fi/~pyykko/Radii12.pdf

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

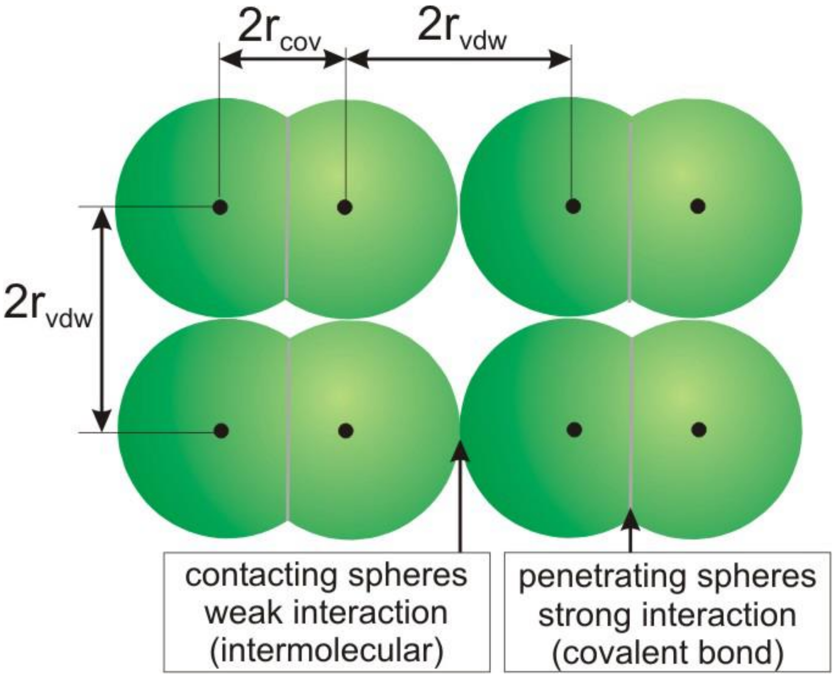


Figure: http://www.webassign.net/question_assets/wertzcams3/ch_8/manual.html

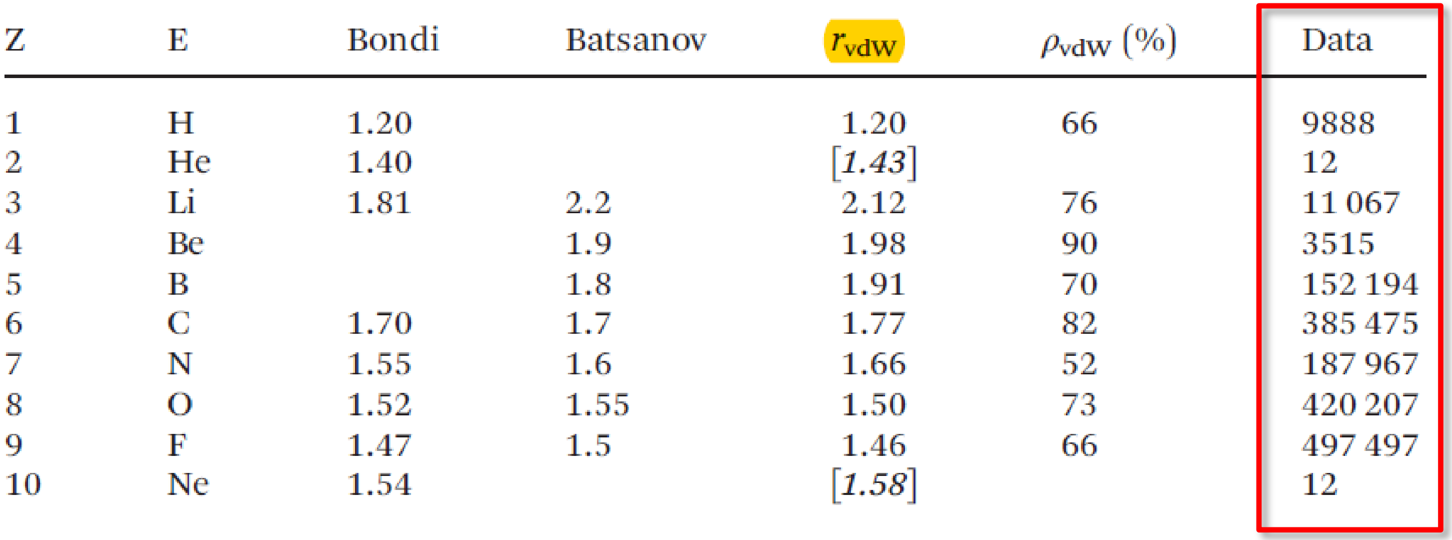
TABLE 12: Consistent van der Waals Radii for All Main-Group Elements[a]

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

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}	ρ_{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

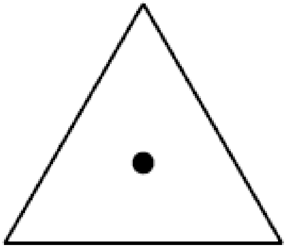
- Typical concepts used in descriptive structural chemistry
  - Coordination
  - Linked (coordination) polyhedra
  - Close-packed structures (possibly with interstitial sites)
- Whenever possible, solid state structures are assigned to some **structure type**
  - Some examples of structure types: rock salt, zinc blende, wurtzite, …
  - Summary of structure types: https://wiki.aalto.fi/display/SSC/Structure+types

Coordination (1)

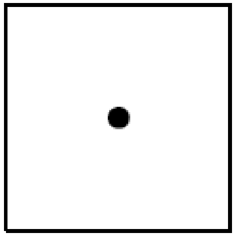
The central atom of the coordination polyhedron is shown with black dot.

2: linear arrangement [2*l*]

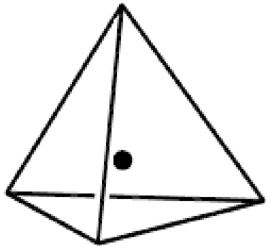
2: angular arrangement [2*n*]



3: triangle [3*l*]

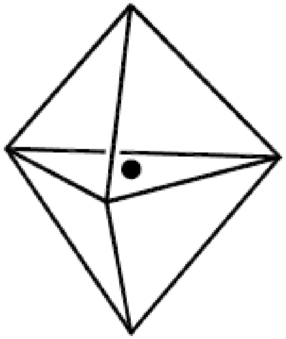


4: square [4*l*] or [*s*]

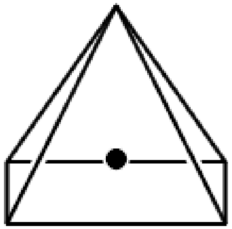


4: tetrahedron [4*t*] or [*t*]

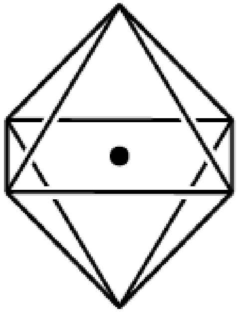
The most common ones



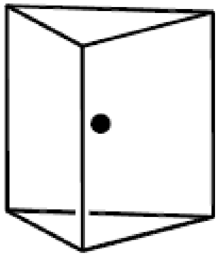
5: trigonal bi-pyramid [5*by*]



5: tetragonal pyramid [5*y*]



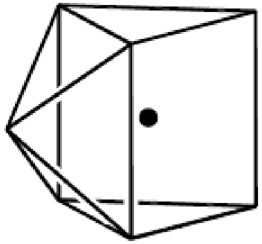
6: octahedron [6*o*] or [*o*]



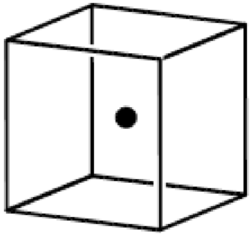
6: trigonal prism [6*p*]

Ref: Müller p. 5

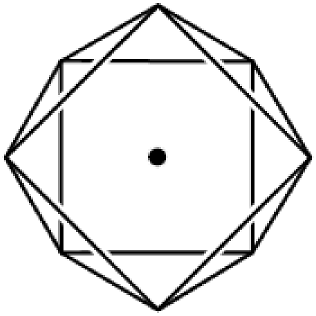
Coordination (2)



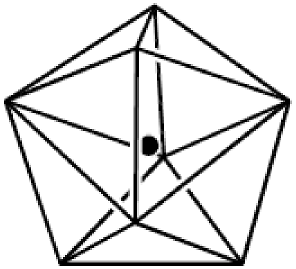
7: capped trigonal
prism [6*p*1*c*]



8: cube
[8*cb*] or [*cb*]

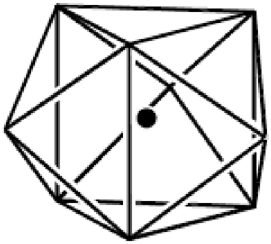


8: square anti-
prism [8*acb*]

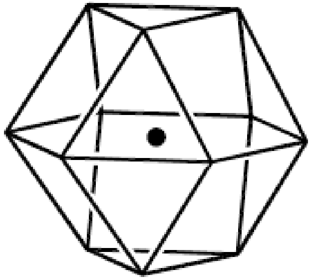


8: dodecahedron
[8*do*] or [*do*]

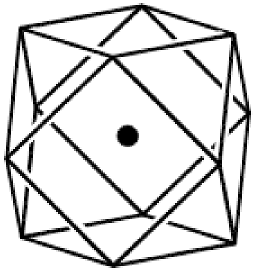
(dodecahedral = 12 faces. The polyhedron shown is actually a *snub disphenoid*)



9: triply-capped tri-
gonal prism [6*p*3*c*]



12: anticuboctahedron
[12*aco*] or [*aco*]

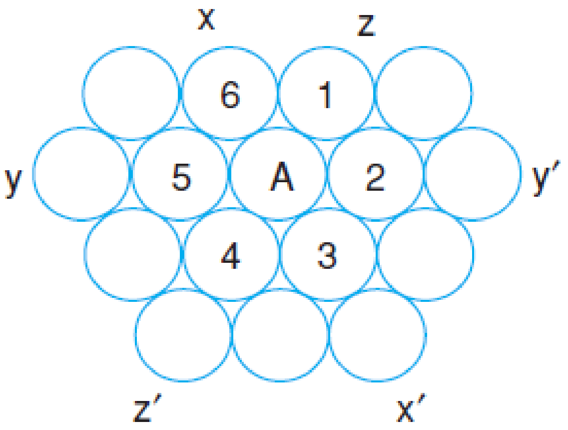


12: cuboctahedron
[12*co*] or [*co*]

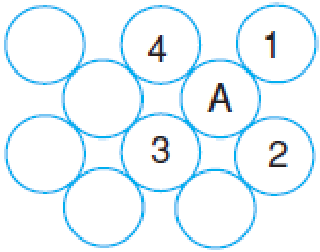
Ref: Müller p. 5

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 *close-packed* layer of equal-sized spheres. Three close packed directions xx′, yy′, and zz′ occur.

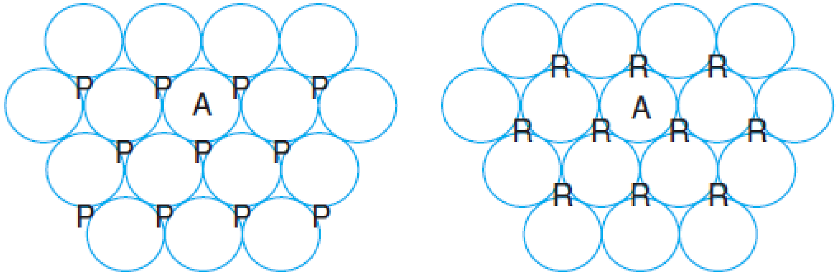


A non-*close-packed* layer with coordination number 4

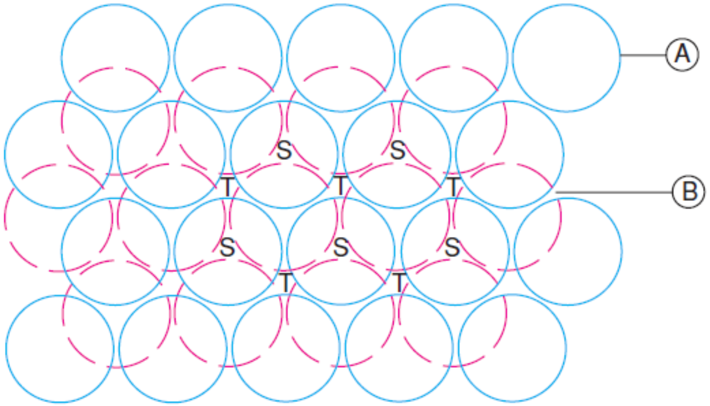
Ref: West p. 19

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…



Alternative positions **P** and **R** for a second *cp* layer

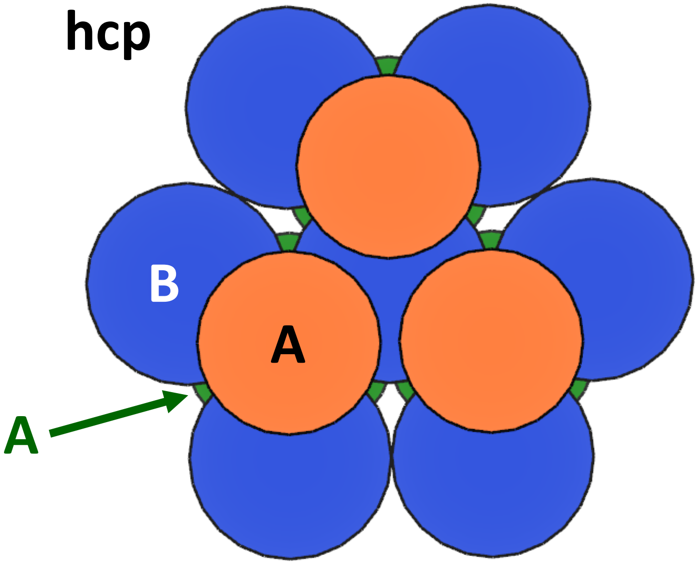


Two cp layers A and B. The B layer occupies the **P** positions

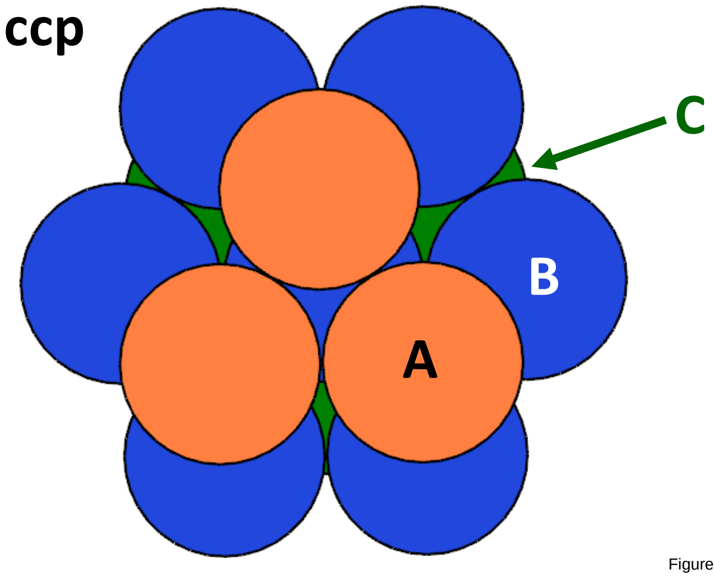
Ref: West p. 20

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)

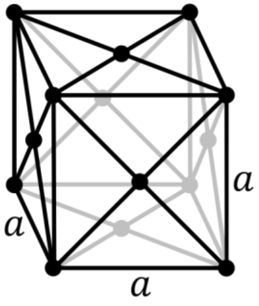


Top A-layer radius smaller and bottom A-layer radius larger to improve clarity

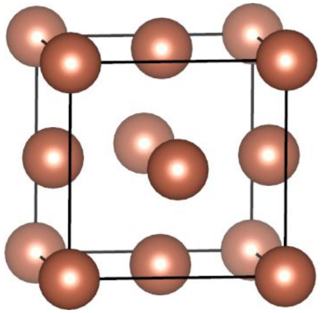


Figures: AJK

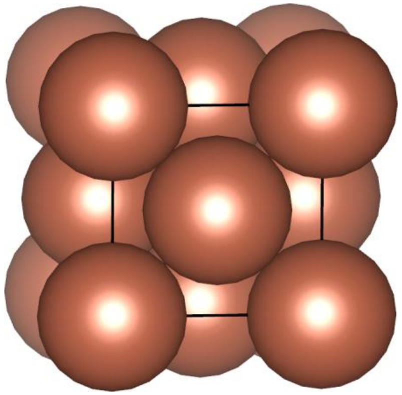
ccp arrangement corresponds to face-centered cubic Bravais lattice



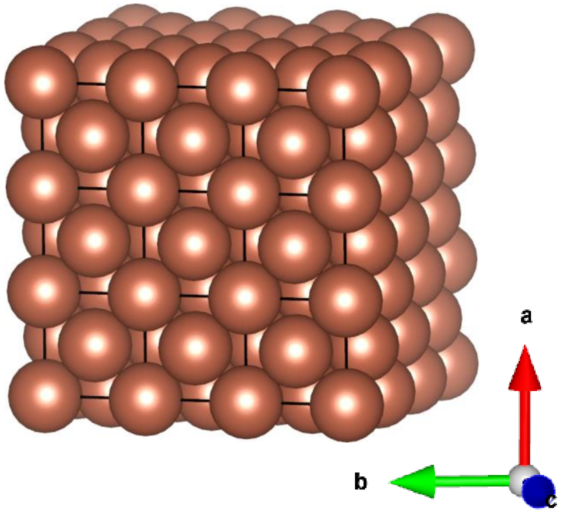
F (fcc)



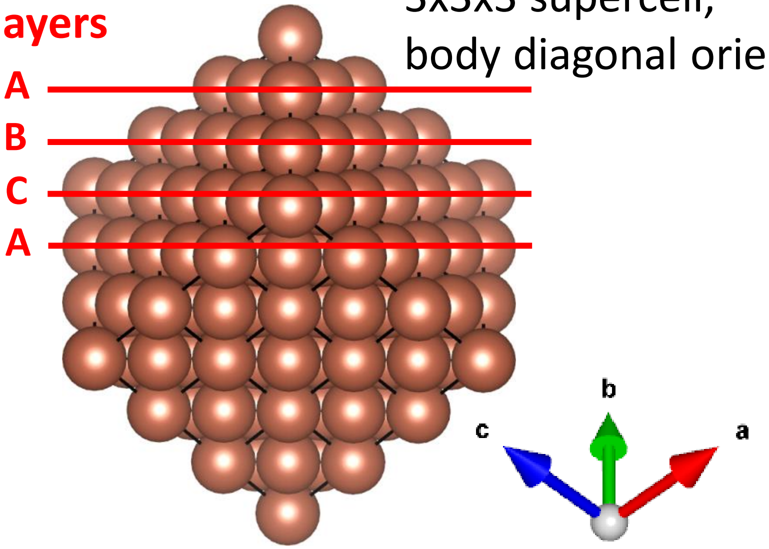
Cu (fcc metal)



3x3x3 supercell



3x3x3 supercell,
body diagonal orientation



Figures: AJK

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

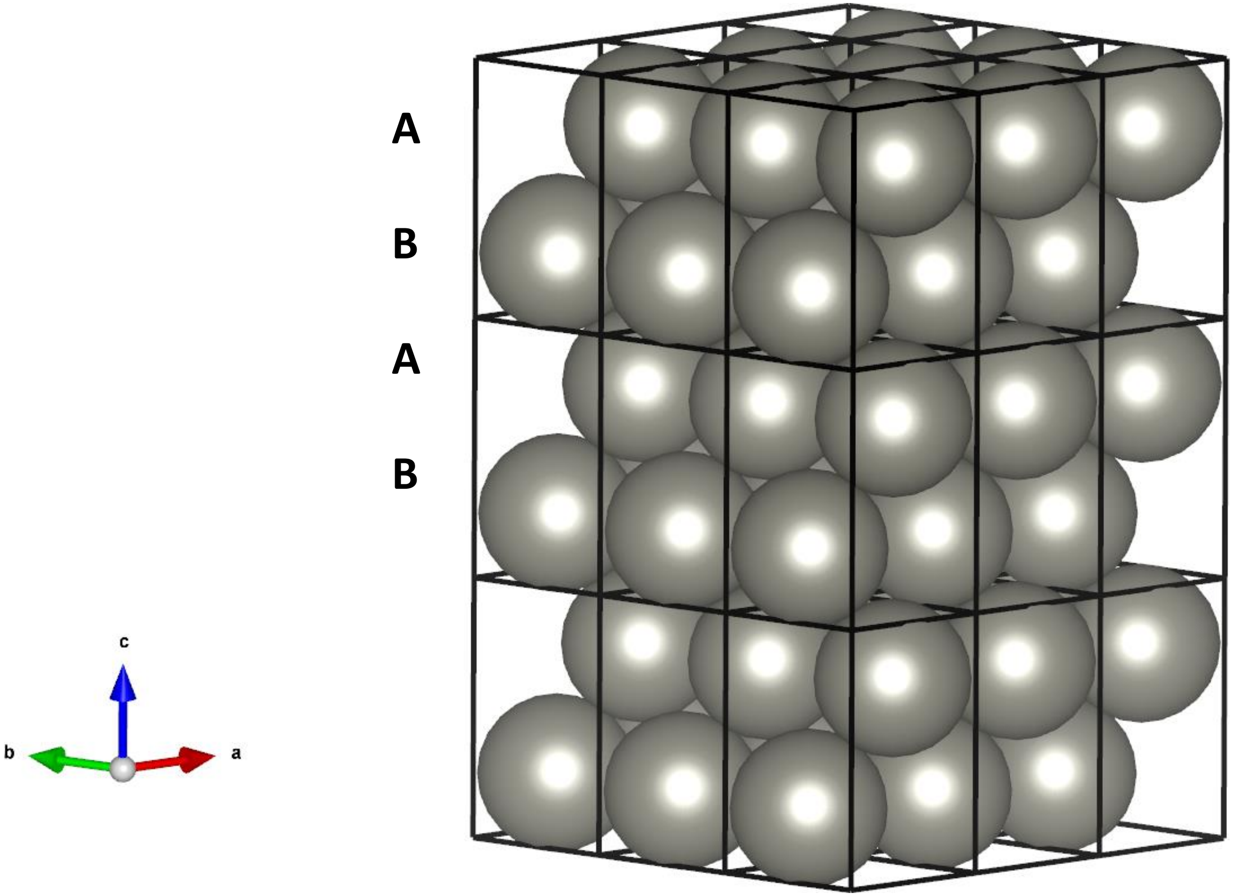


Figure: AJK

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

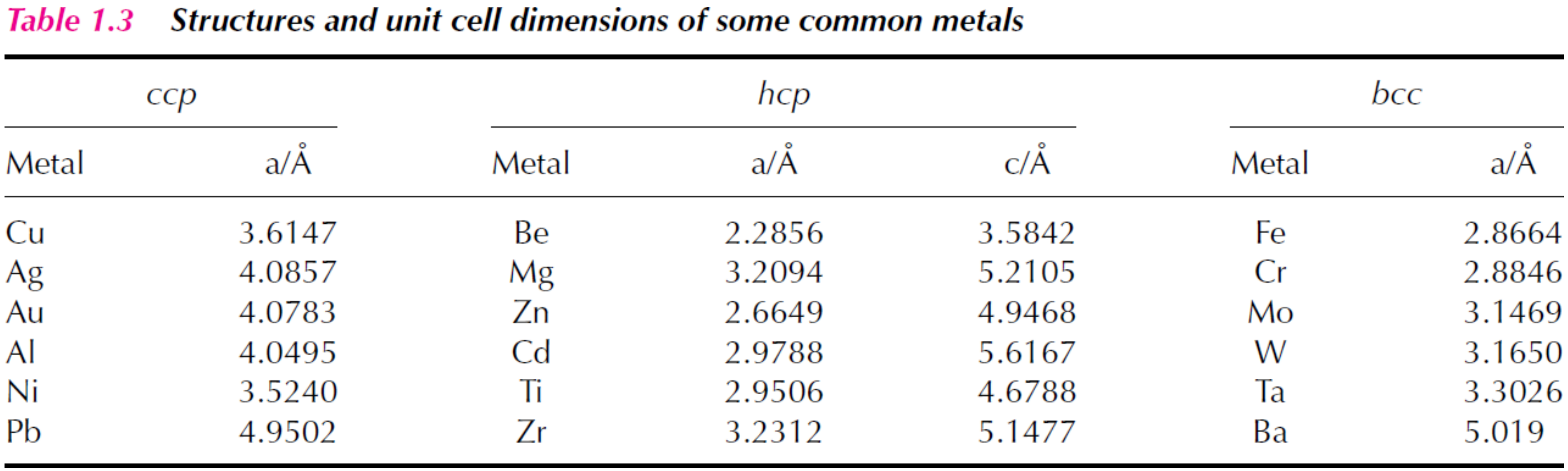
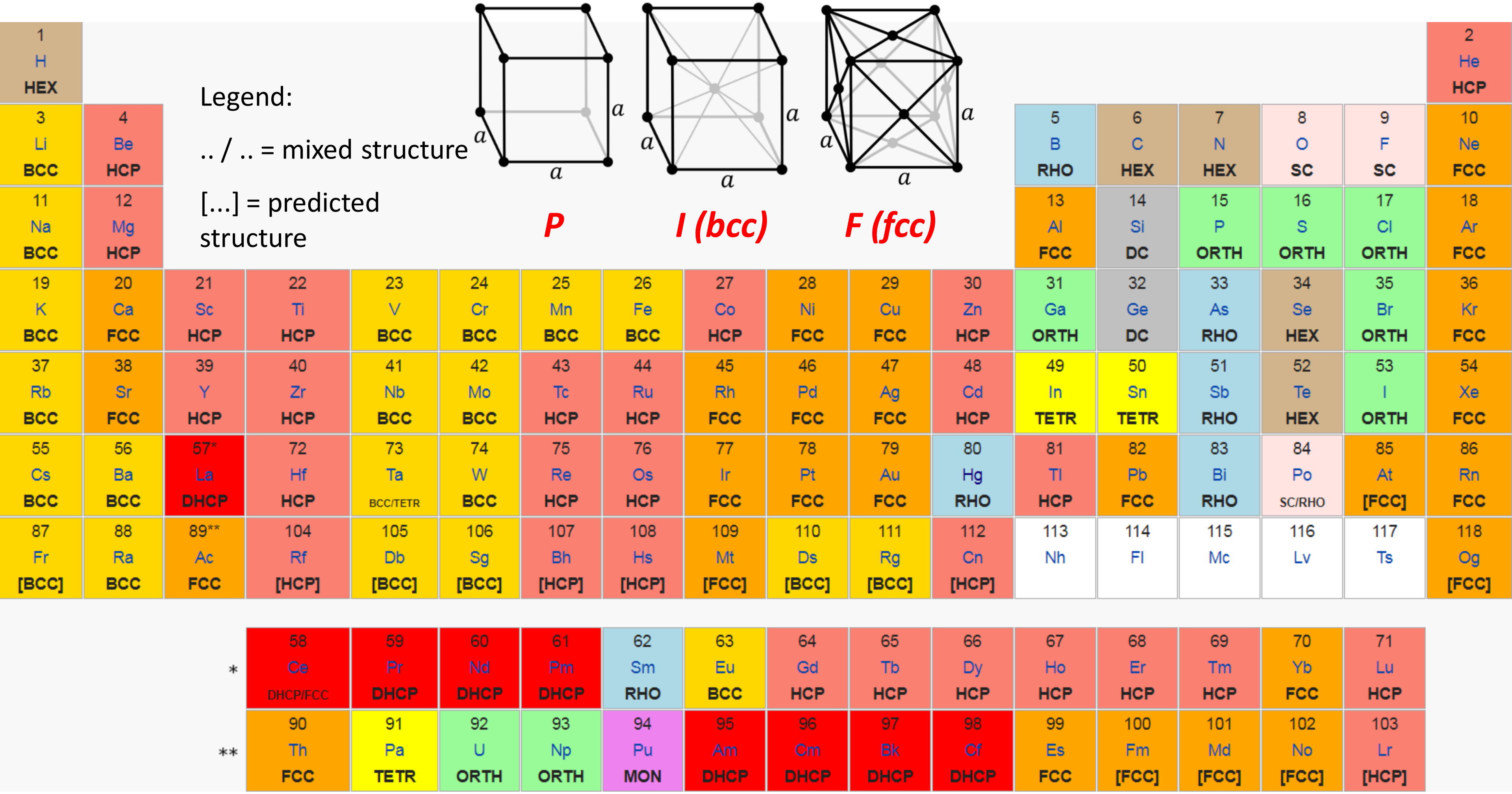


Table 1.3 ***Structures and unit cell dimensions of some common metals***

ccp		*hcp*			*bcc*	
Metal	a/Å	Metal	a/Å	c/Å	Metal	a/Å
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

Ref: West p. 25

Periodic table of crystal structures



Legend:

.. / .. = mixed structure

[...] = predicted structure

1 H HEX																	2 He HCP
3 Li BCC	4 Be HCP											5 B RHO	6 C HEX	7 N HEX	8 O SC	9 F SC	10 Ne FCC
11 Na BCC	12 Mg HCP											13 Al FCC	14 Si DC	15 P ORTH	16 S ORTH	17 Cl ORTH	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]
		*	58 Ce DHCP/FCC	59 Pr DHCP	60 Nd DHCP	61 Pm DHCP	62 Sm RHO	63 Eu BCC	64 Gd HCP	65 Tb HCP	66 Dy HCP	67 Ho HCP	68 Er HCP	69 Tm HCP	70 Yb FCC	71 Lu HCP	
		**	90 Th FCC	91 Pa TETR	92 U ORTH	93 Np ORTH	94 Pu MON	95 Am DHCP	96 Cm DHCP	97 Bk DHCP	98 Cf DHCP	99 Es FCC	100 Fm [FCC]	101 Md [FCC]	102 No [FCC]	103 Lr [HCP]	

Figures: Wikipedia

Close packing in ionic materials

- When the anion is larger than the cation in an ionic material:
  - The structures often contain **close-packed layers of anions**
  - The cations occupy **interstitial sites** between the close-packed layers
- For example: NaCl, Al_2O_3, Na_2O, 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

Ref: West p. 26

T_+, T_-, and O sites

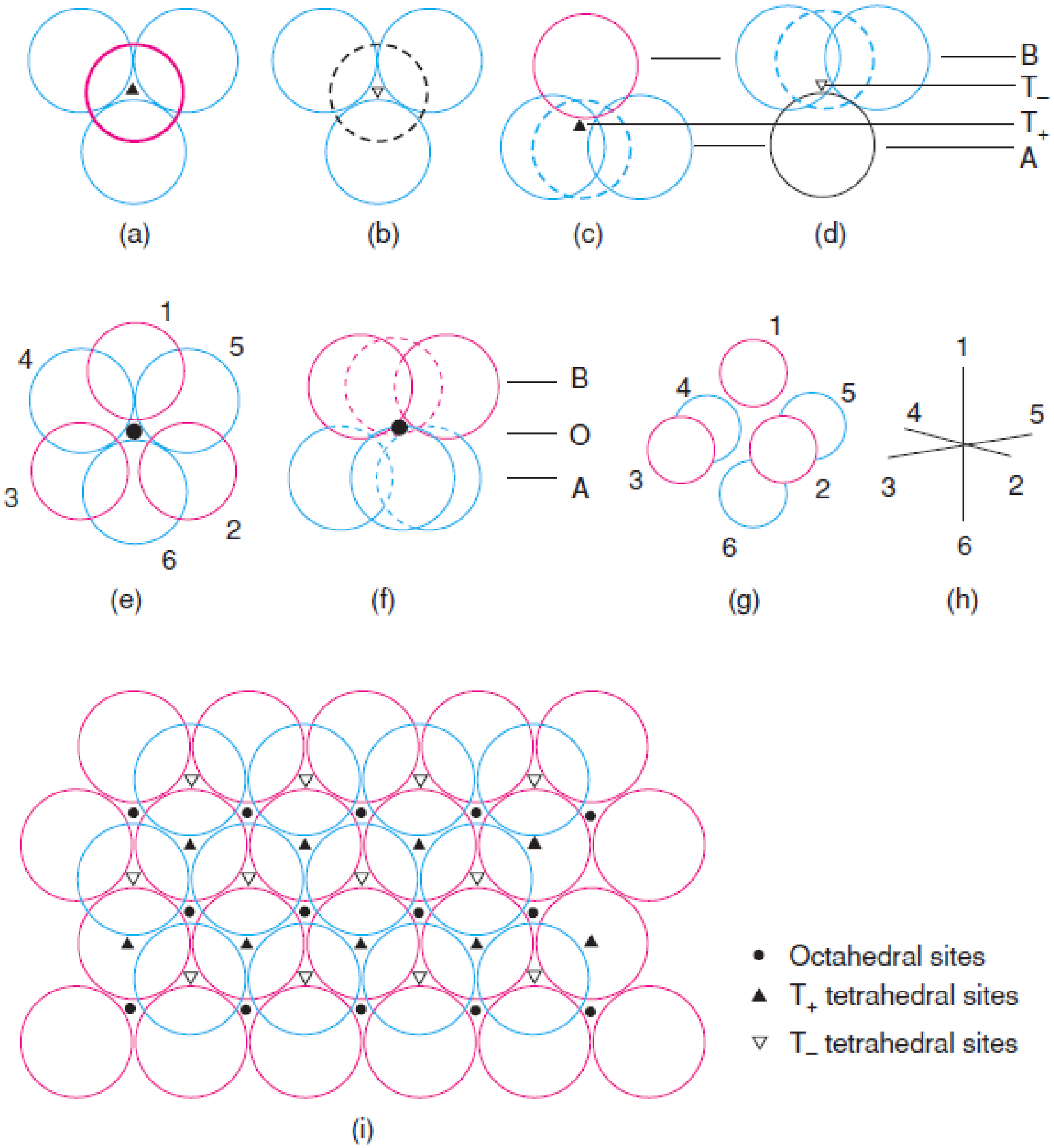
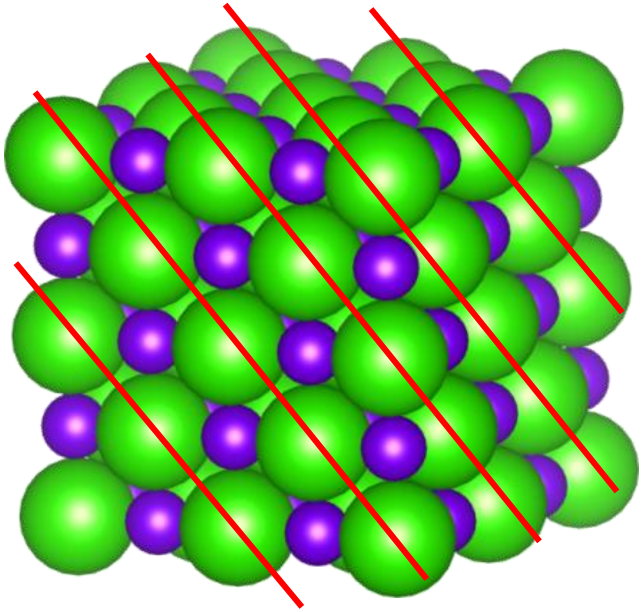


Figure 1.23 Tetrahedral and octahedral sites between two cp anion layers, seen from different perspectives. (a, b) Projection down threefold axis of T_+, T_- sites. (c, d) Tetrahedral sites edge-on. (e) Projection down threefold axis of octahedral site and (f) seen edge-on. (g, h) Conventional representation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

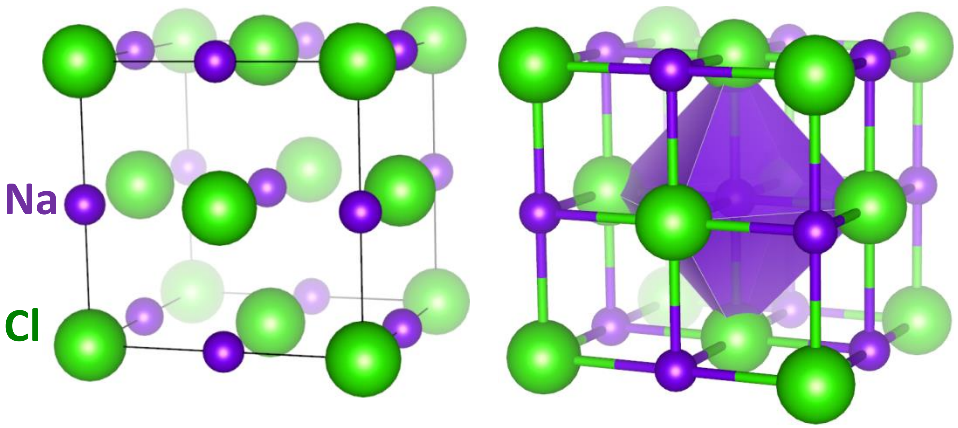
Ref: West p. 27

Octahedral interstitials in NaCl structure

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



Close-packed anion layers



Figures: AJK

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

Ref: West p. 28

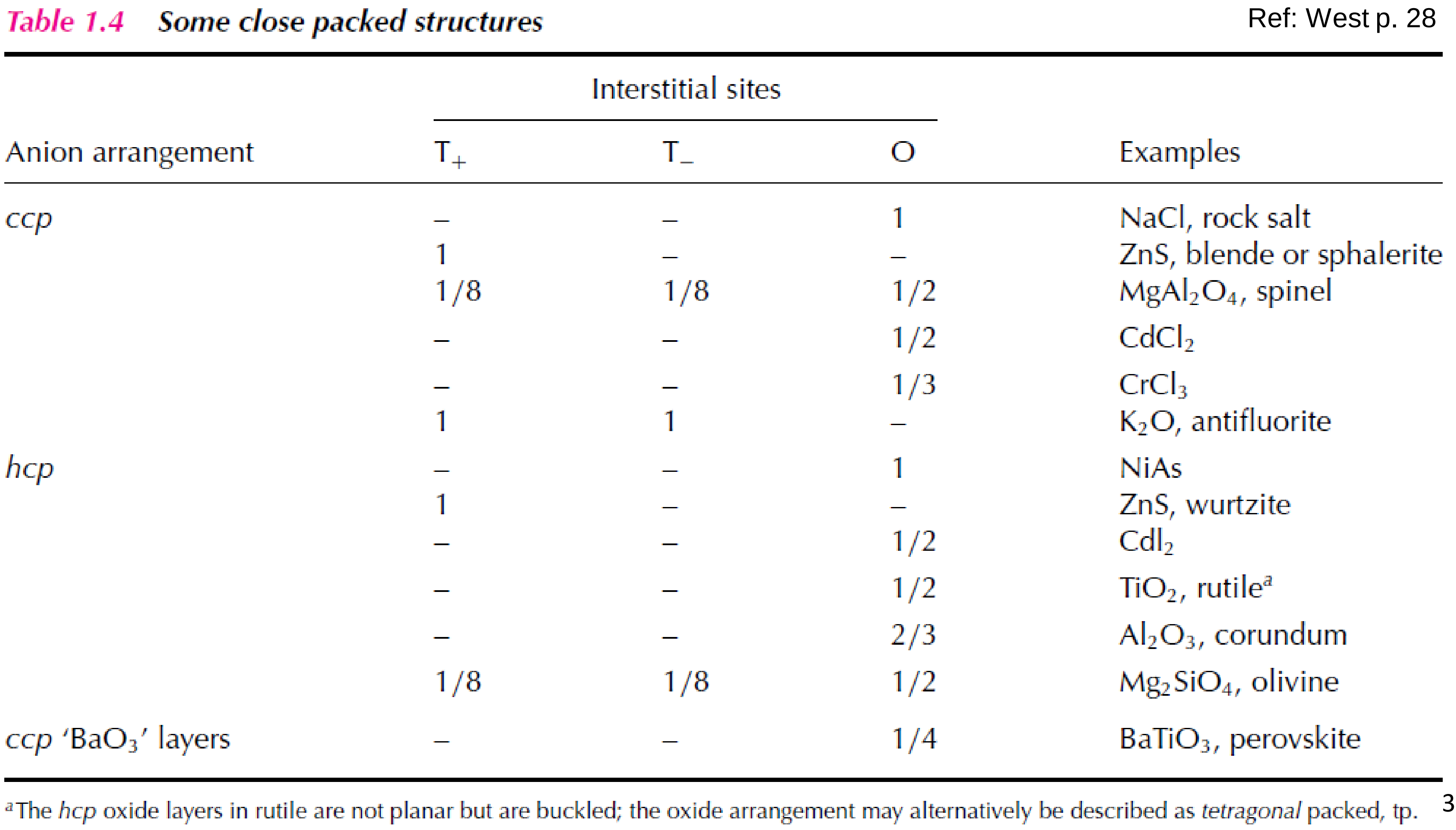
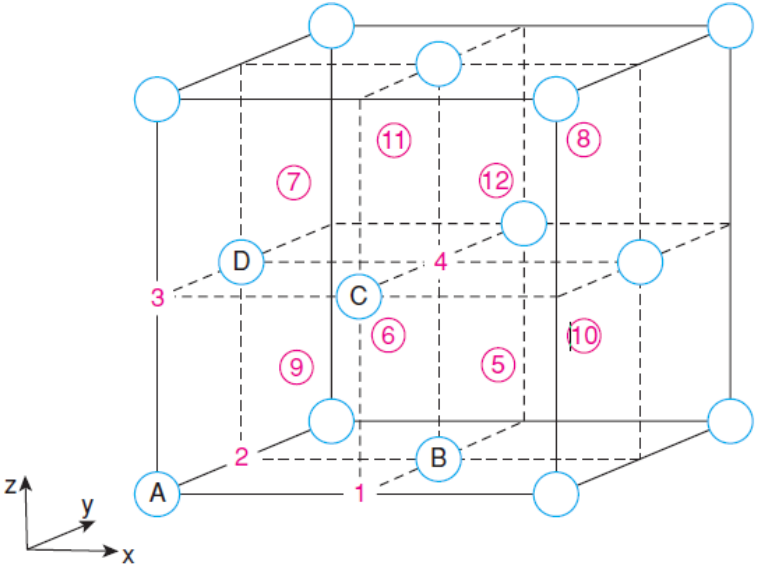


Table 1.4 ***Some close packed structures***

Anion arrangement	Interstitial sites			Examples
	T_+	T_-	O	
ccp	–	–	1	NaCl, rock salt
	1	–	–	ZnS, blende or sphalerite
	1/8	1/8	1/2	$MgAl_2O_4$, spinel
	–	–	1/2	$CdCl_2$
	–	–	1/3	$CrCl_3$
	1	1	–	K_2O, antifluorite
hcp	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI_2
	–	–	1/2	TiO_2, rutile[a]
	–	–	2/3	Al_2O_3, corundum
	1/8	1/8	1/2	Mg_2SiO_4, olivine
ccp 'BaO_3' layers	–	–	1/4	$BaTiO_3$, perovskite

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

Cation sites in an *fcc* anion array



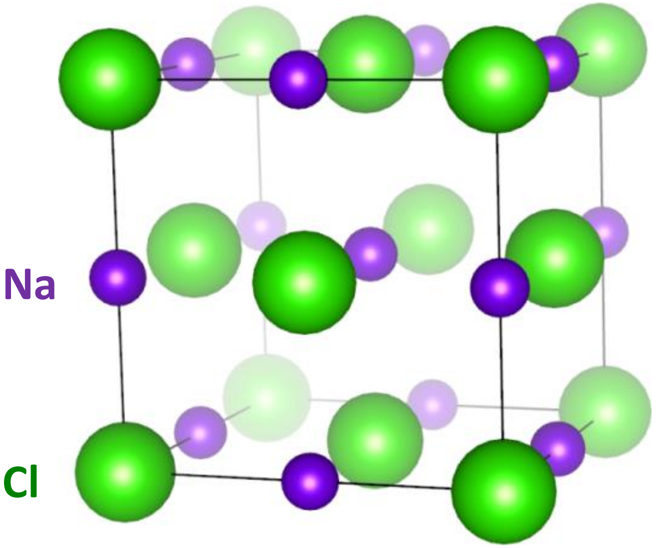


Figure 1.24 *Available cation sites, 1–12, in an fcc anion array.*

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

octahedral	1: $^1/_2 00$	2: $0 ^1/_2 0$	3: $00 ^1/_2$	4: $^1/_2\, ^1/_2\, ^1/_2$
tetrahedral, T_+	5: $^3/_4\, ^1/_4\, ^1/_4$	6: $^1/_4\, ^3/_4\, ^1/_4$	7: $^1/_4\, ^1/_4\, ^3/_4$	8: $^3/_4\, ^3/_4\, ^3/_4$
tetrahedral, T_-	9: $^1/_4\, ^1/_4\, ^1/_4$	10: $^3/_4\, ^3/_4\, ^1/_4$	11: $^1/_4\, ^3/_4\, ^3/_4$	12: $^3/_4\, ^1/_4\, ^3/_4$

Ref: West p. 29