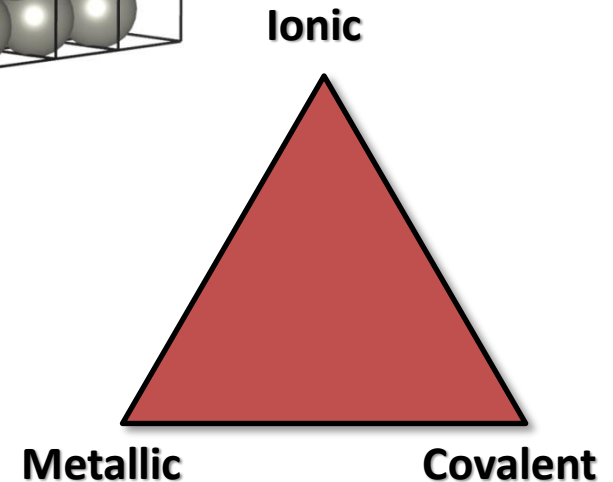
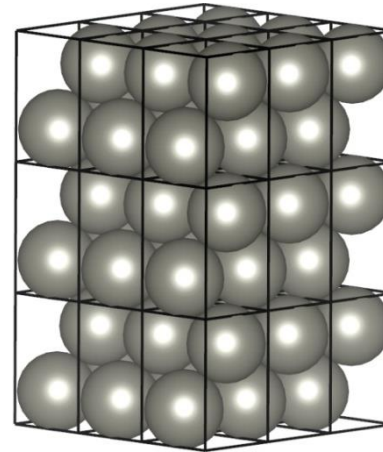


Lecture 3: Bonding in solids and description of crystal structures

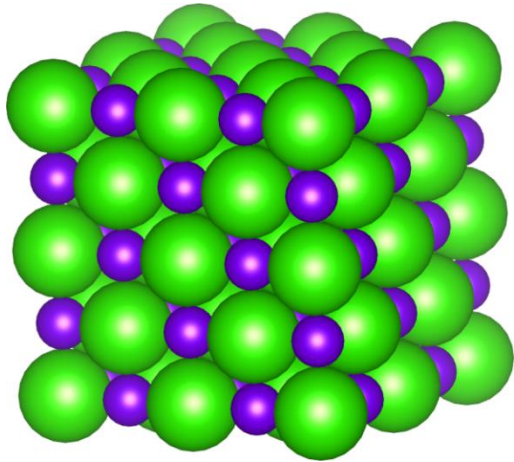
- Bonding in solids
 - Electronegativity
 - Atomic and ionic radii
 - (*Band theory in Lecture 4*)
- Description of crystal structures
 - Coordination
 - Close packed structures
 - Metallic structures
 - Ionic structures with interstitial sites
- Concept of a **structure type**



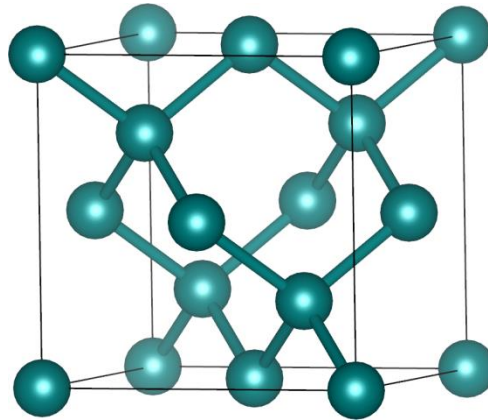
Figures: AJK

Strong chemical bonding

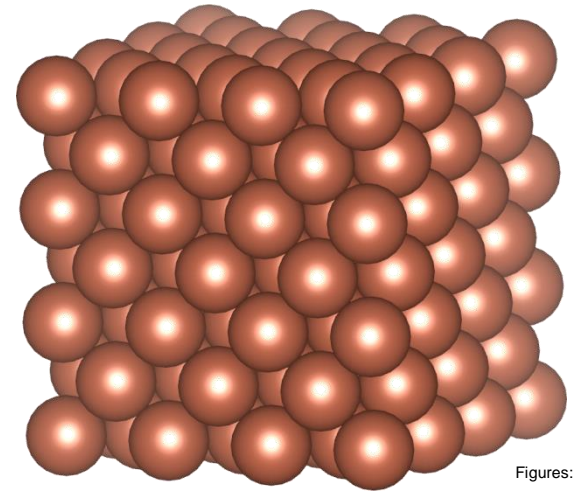
- The chemical bonds in solids are usually classified as **ionic**, **covalent**, or **metallic**.
 - The focus of the lecture is on these bonding types.
- Examples of weaker (non-covalent) bond types: **hydrogen bonds**, **halogen bonds**.



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 χ_A and χ_B in terms of bond dissociation energies, D_0 :
$$|\chi_A - \chi_B| = \{D_0(AB) - \frac{1}{2}[D_0(AA) + D_0(BB)]\}^{1/2}$$
- $D_0(AA)$ 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

V · T · E

Periodic table of electronegativity by Pauling scale

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

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
↓ 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	*	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 →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
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](#)

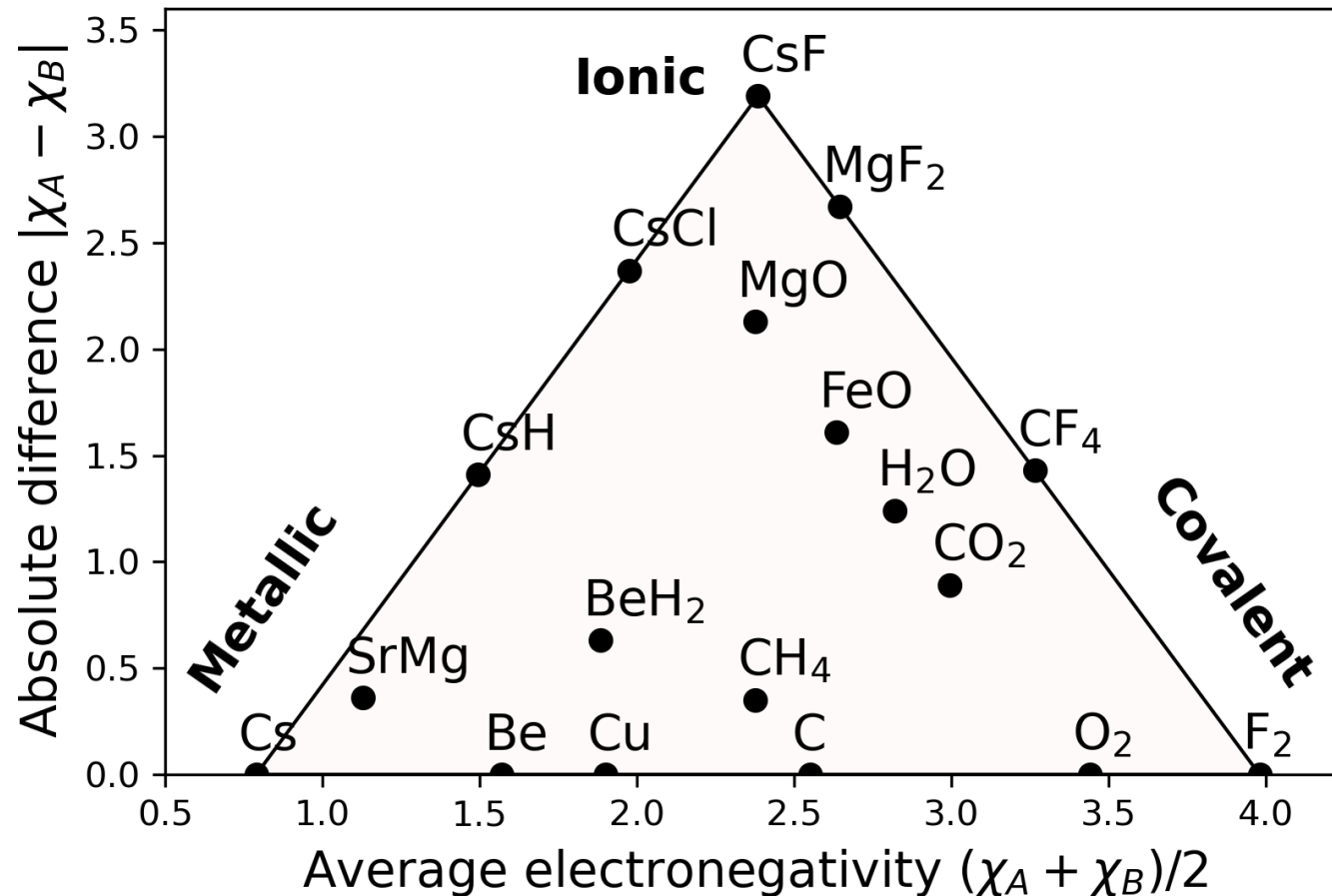
Using electronegativities (χ)

- 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	Polar covalent
Fe–O	1.61	
Si–O	1.54	
Zn–S	0.93	Covalent
C–H	0.35	

van Arkel-Ketelaar Triangles

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



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. $Z_{eff}(\text{Cl}) = 6.1 e^-$), 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

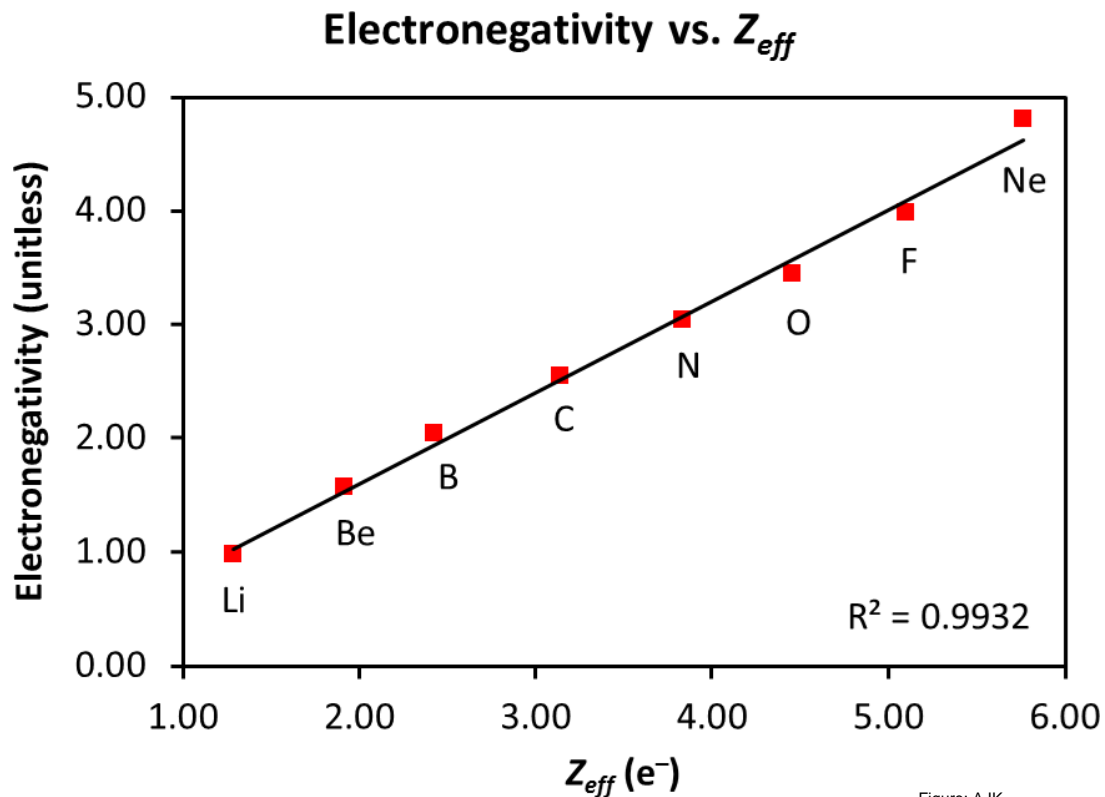


Figure: AJK

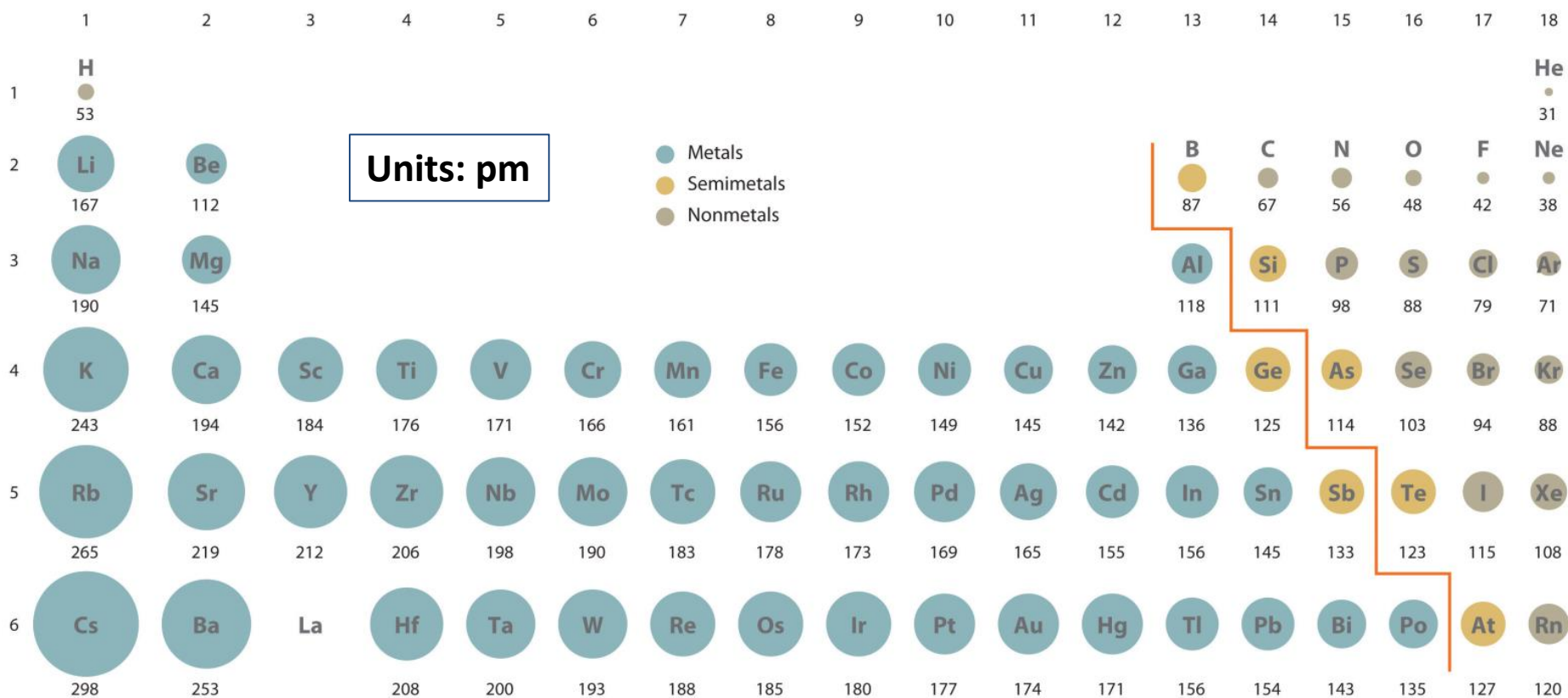
Atomic radii

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

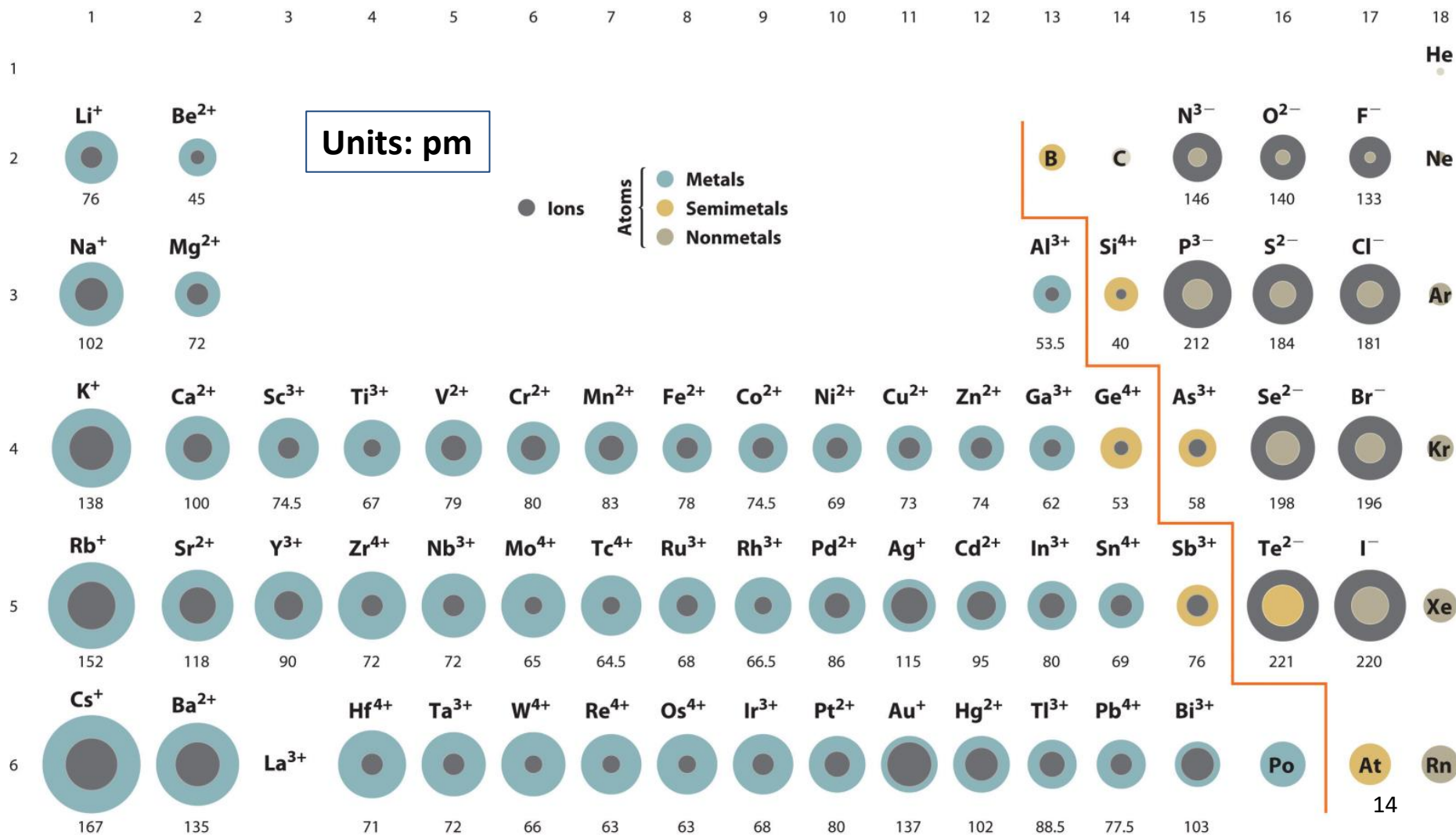


Shannon ionic radii

Ionic Radii 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
- 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.

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

<h1 style="text-align: center;">Pyykkö Self-Consistent Covalent radii</h1>																	1 H 32 - -	2 He 46 - -																				
3 Li 133 124 -			4 Be 102 90 85		<table border="1" style="margin: auto;"> <tr> <td>Z</td> <td>Radius, r_n:</td> <td>Symbol</td> </tr> <tr> <td></td> <td>r_1</td> <td></td> </tr> <tr> <td></td> <td>r_2</td> <td></td> </tr> <tr> <td></td> <td>r_3</td> <td></td> </tr> </table>										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 -	
Z	Radius, r_n :	Symbol																																				
	r_1																																					
	r_2																																					
	r_3																																					
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

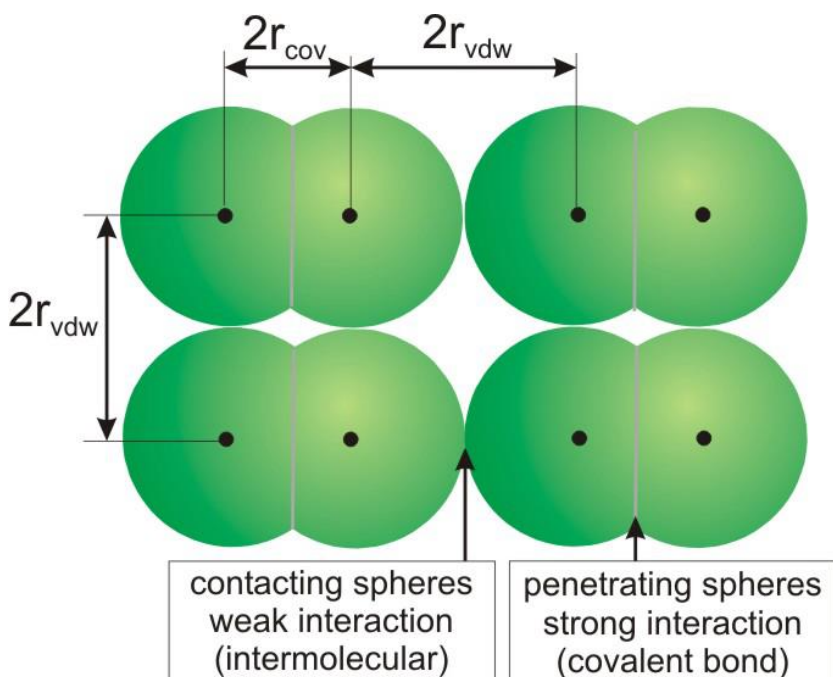


TABLE 12: Consistent van der Waals Radii for All Main-Group Elements^a

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)

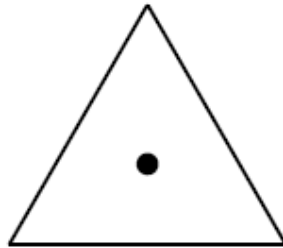
The central atom of the coordination polyhedron is shown with a black dot.



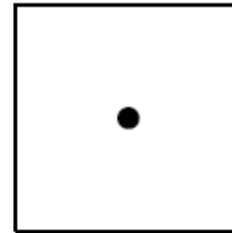
2: linear arrangement
[2l]



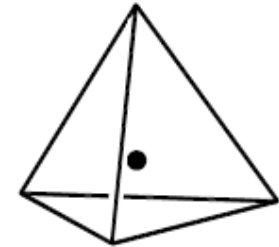
2: angular arrangement [2n]



3: triangle
[3l]

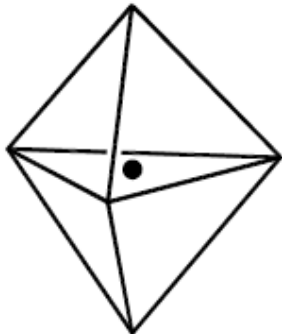


4: square
[4l] or [s]

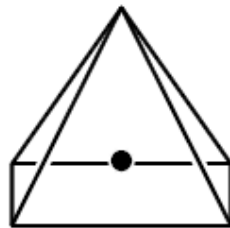


4: tetrahedron
[4t] or [t]

The most common ones



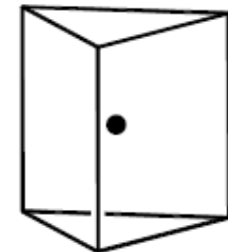
5: trigonal bi-
pyramid [5by]



5: tetragonal
pyramid [5y]

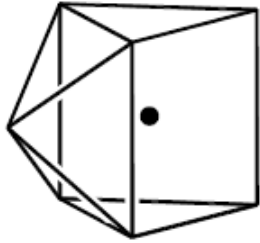


6: octahedron
[6o] or [o]

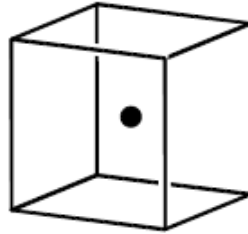


6: trigonal
prism [6p]

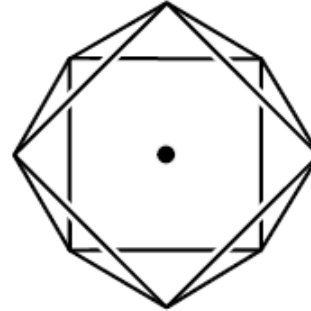
Coordination (2)



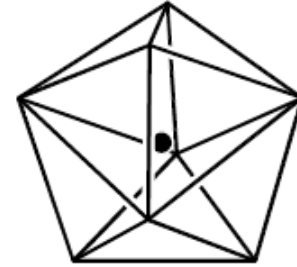
7: capped trigonal prism $[6p1c]$



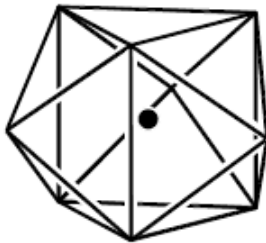
8: cube $[8cb]$ or $[cb]$



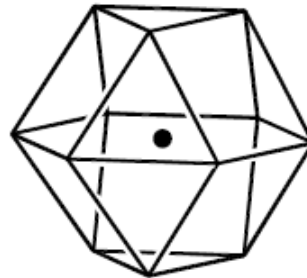
8: square anti-prism $[8acb]$



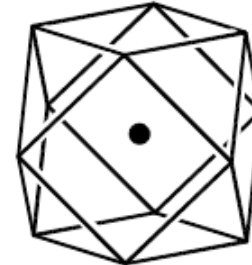
8: dodecahedron $[8do]$ or $[do]$
(dodecahedral = 12 faces. The polyhedron shown is actually a *snub disphenoid*)



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



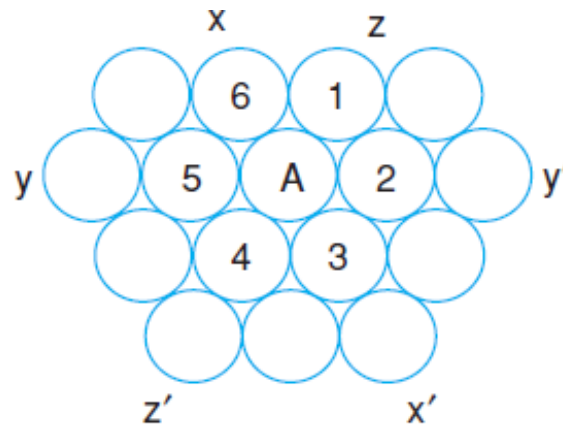
12: anticuboctahedron $[12aco]$ or $[aco]$



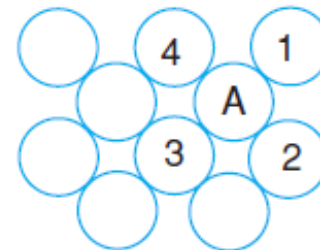
12: cuboctahedron $[12co]$ or $[co]$

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



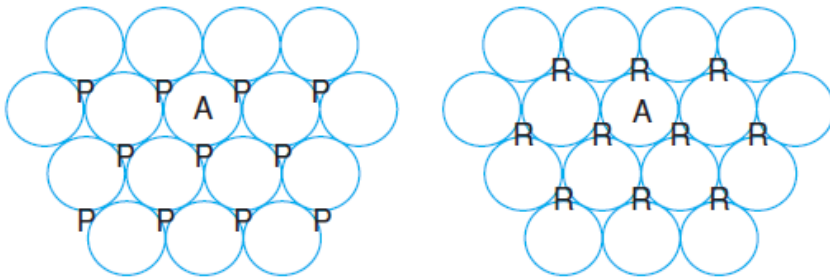
A close-packed layer of equal-sized spheres. Three close packed directions xx' , yy' , and zz' occur.



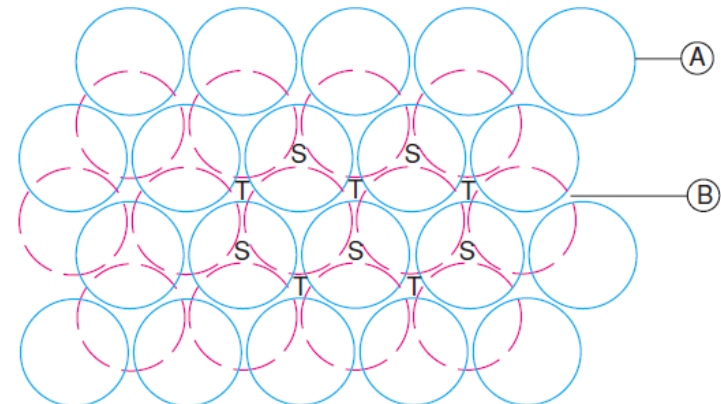
A non-close-packed layer with coordination number 4

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...



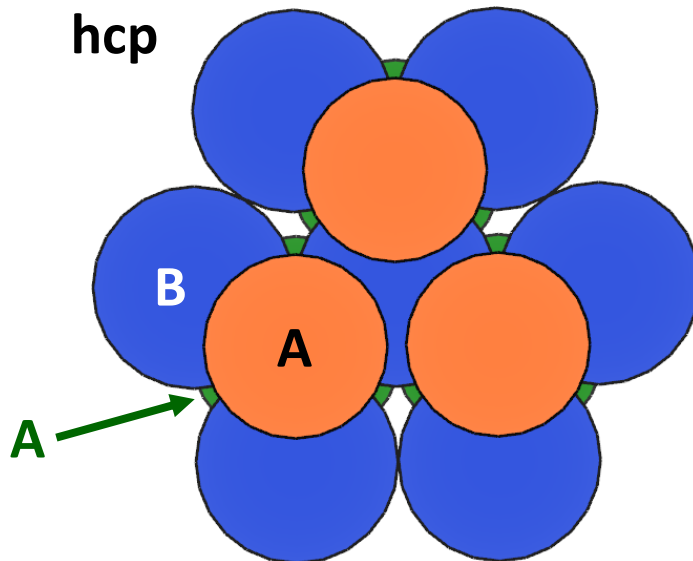
Alternative positions **P** and **R** for a second *cp* layer



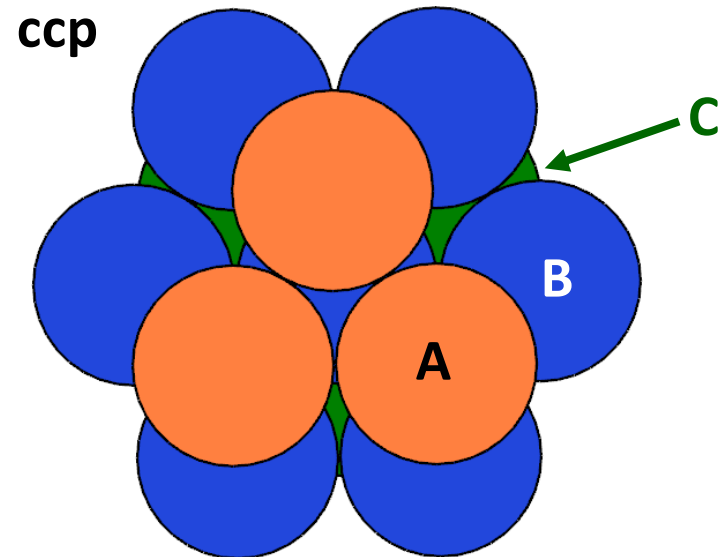
Two *cp* layers A and B. The B layer occupies the **P** positions

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)

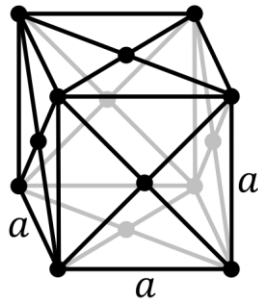


Top A-layer radius smaller and bottom A-layer radius larger to improve clarity

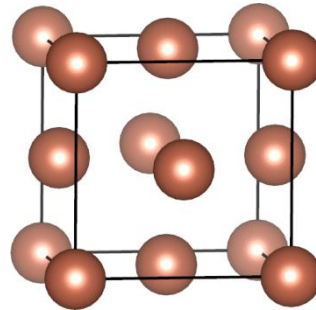


Figures: AJK

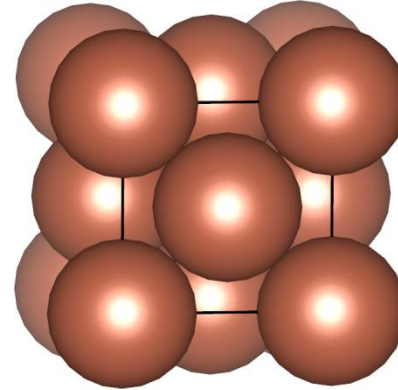
ccp arrangement corresponds to face-centered cubic Bravais lattice



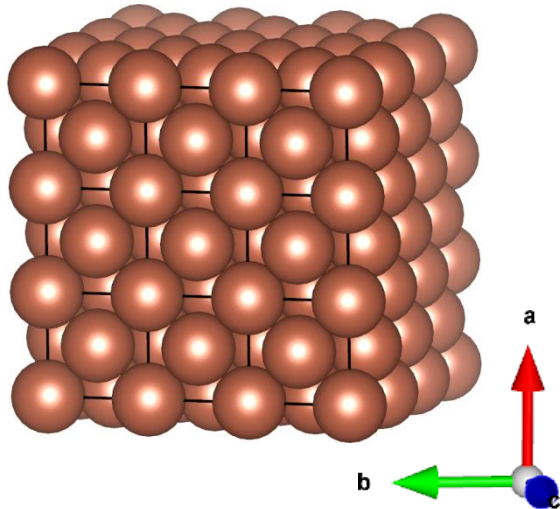
F (fcc)



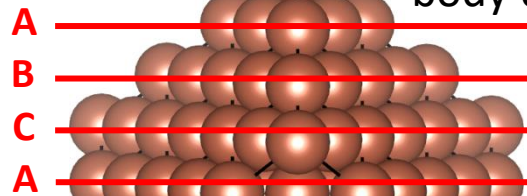
Cu (fcc metal)



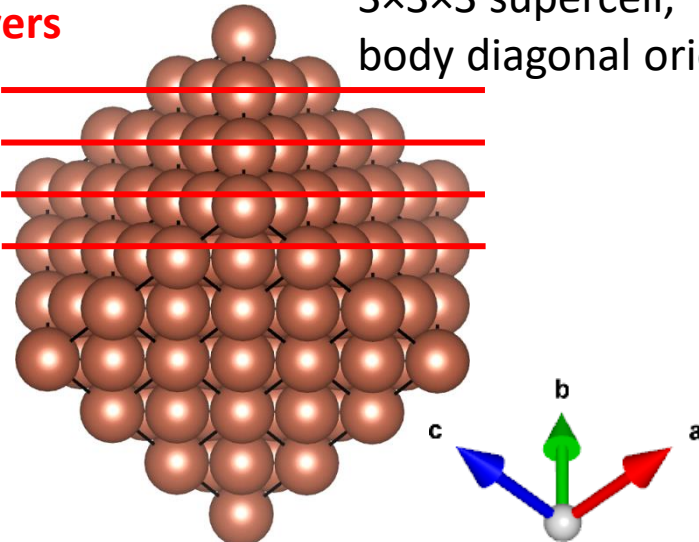
3x3x3 supercell



cp layers



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

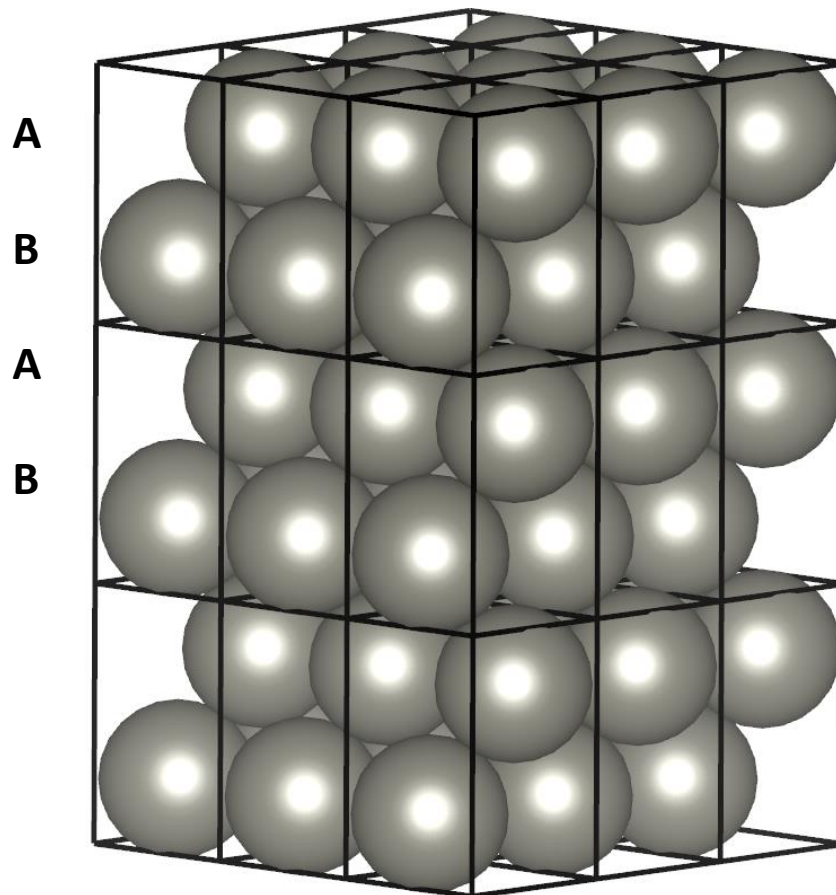
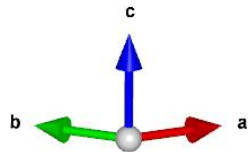


Figure: AJK

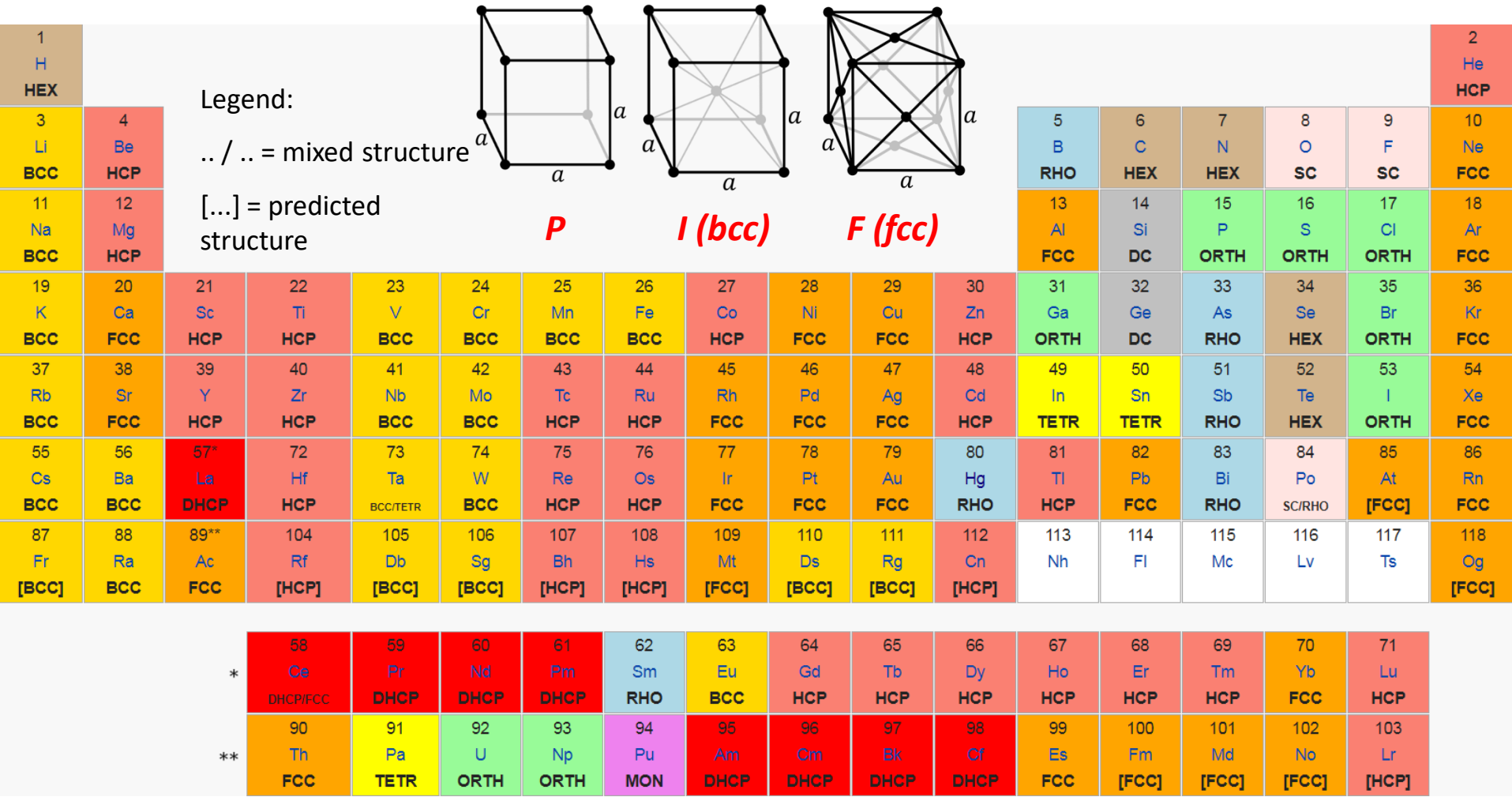
Structures of common metals

- 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



Figures: [Wikipedia](https://en.wikipedia.org/wiki/Periodic_table_of_crystal_structures)

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, Al₂O₃, Na₂O, 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

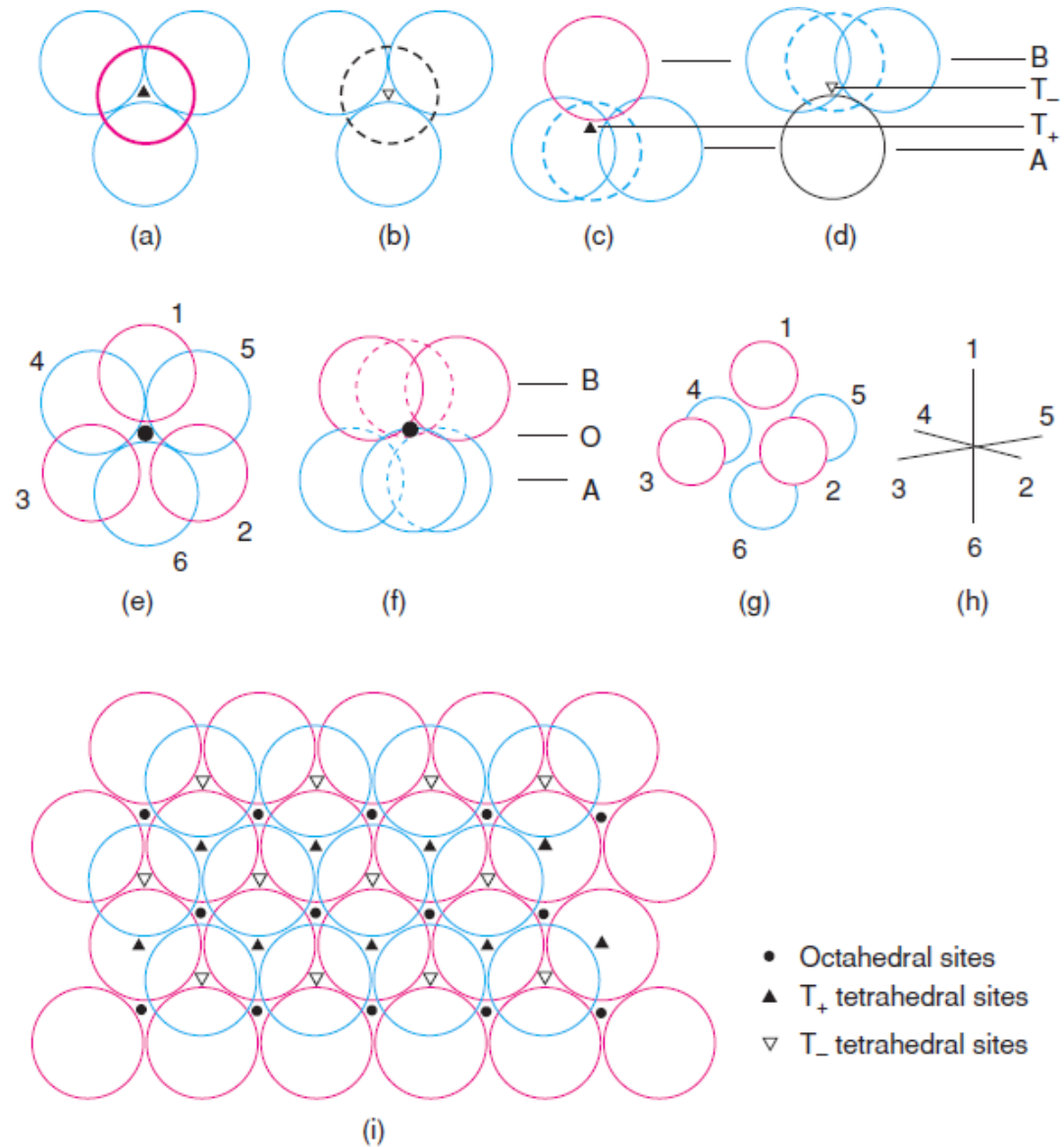
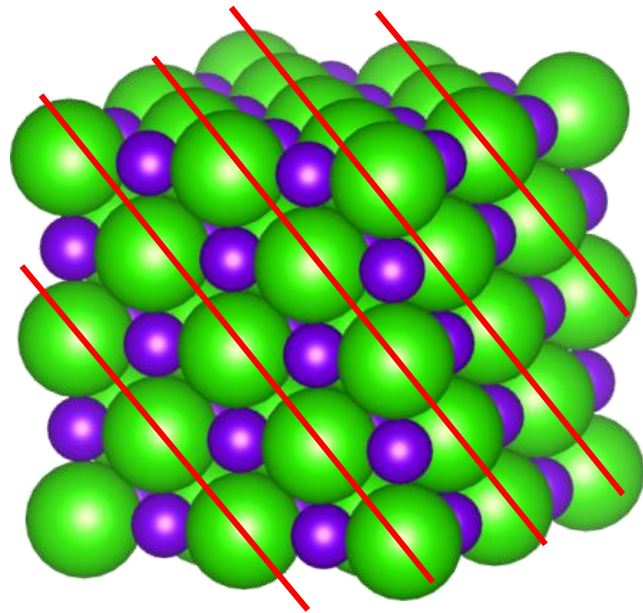


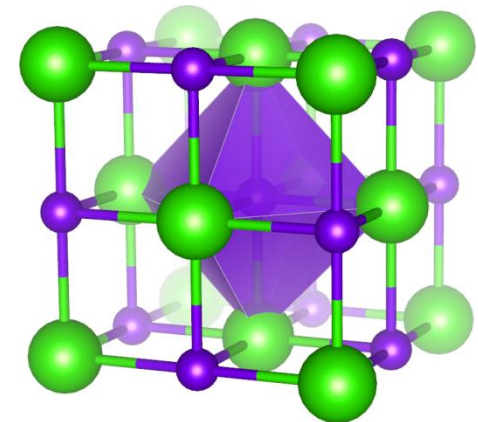
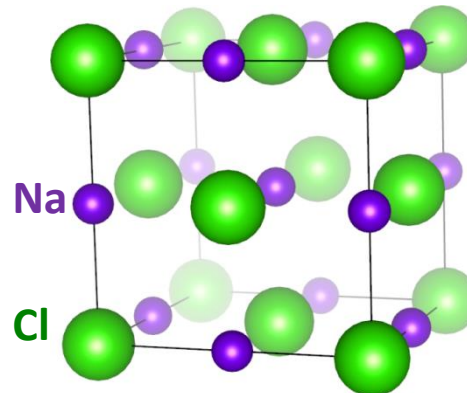
Figure 1.23 Tetrahedral and octahedral sites between two cp anion layers, seen from different perspectives. (a, b) Projection down threefold axis of T_+ , T_- sites. (c, d) Tetrahedral sites edge-on. (e) Projection down threefold axis of octahedral site and (f) seen edge-on. (g, h) Conventional representation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

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

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 ₂ O ₄ , spinel
	–	–	1/2	CdCl ₂
	–	–	1/3	CrCl ₃
	1	1	–	K ₂ O, antifluorite
<i>hcp</i>	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI ₂
	–	–	1/2	TiO ₂ , rutile ^a
	–	–	2/3	Al ₂ O ₃ , corundum
	1/8	1/8	1/2	Mg ₂ SiO ₄ , olivine
<i>ccp</i> 'BaO ₃ ' layers	–	–	1/4	BaTiO ₃ , perovskite

^aThe *hcp* oxide layers in rutile are not planar but are buckled; the oxide arrangement may alternatively be described as *tetragonal* packed, tp. 34

Cation sites in an *fcc* anion array

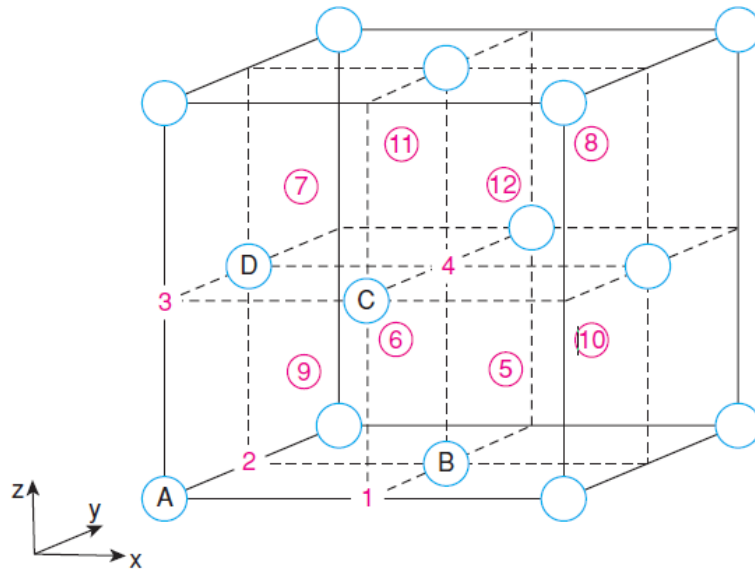
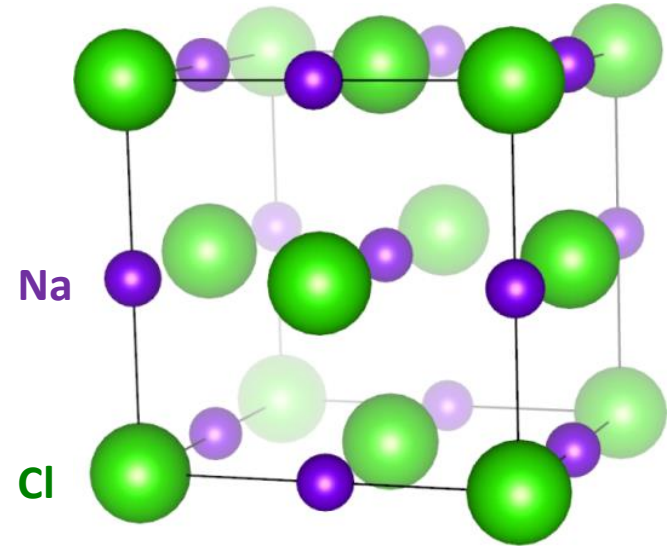


Figure 1.24 Available cation sites, 1–12, in an fcc anion array.



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: $\frac{3}{4} \frac{1}{4} \frac{3}{4}$