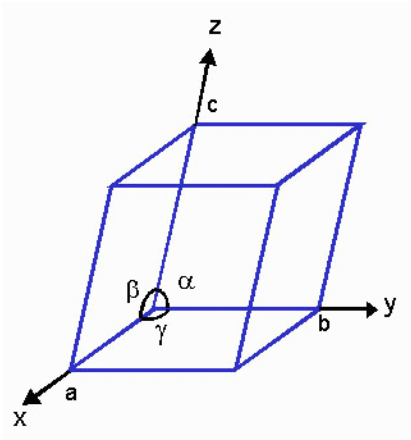
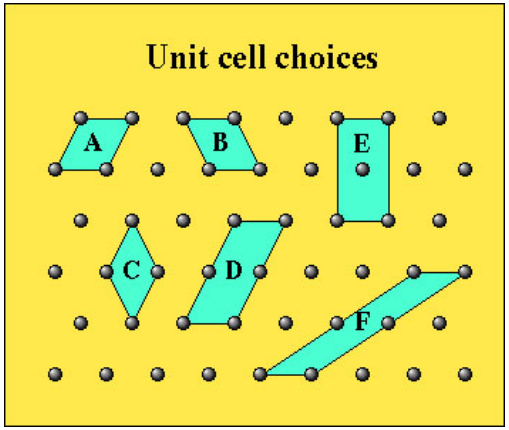
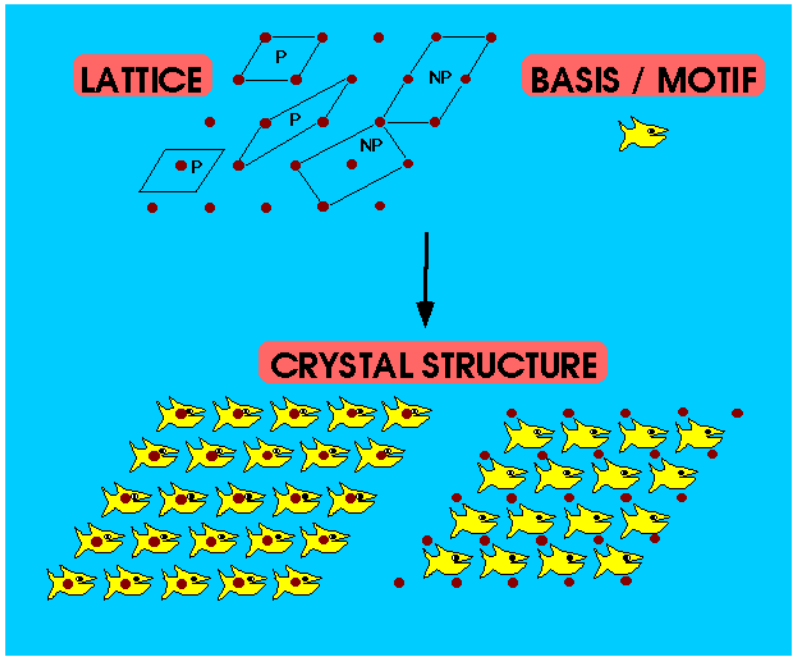
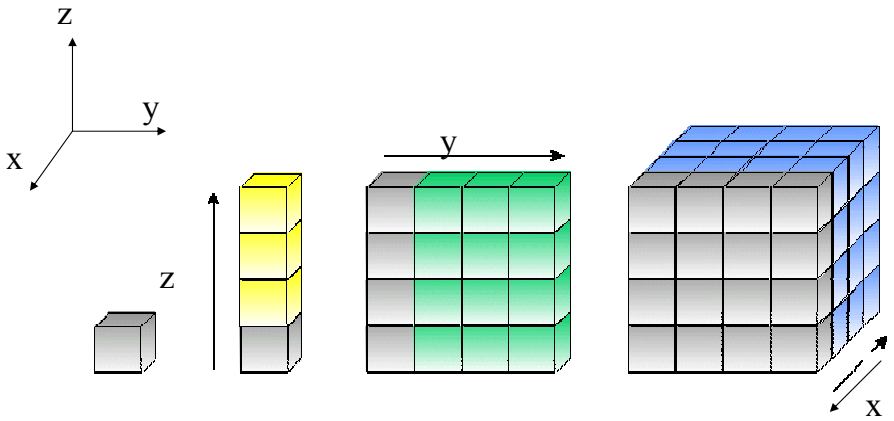
Kap. 5
Crystallography and crystal structures

Unit cell



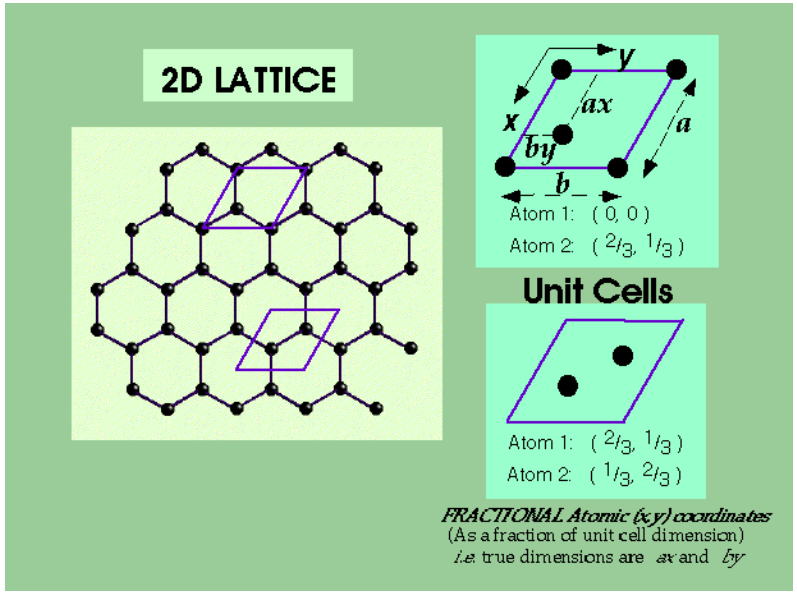


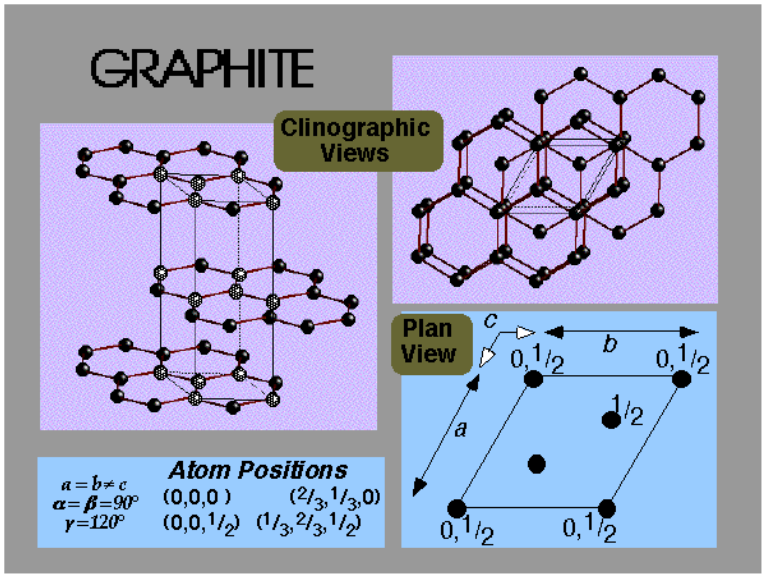


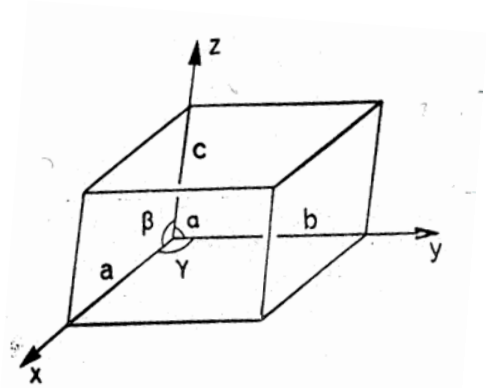


Unitcell

Transtaltion along x, y, z



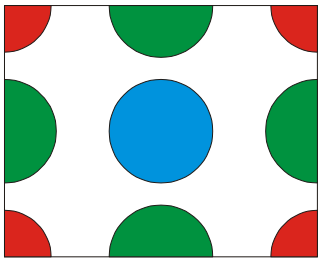




$$V = a \cdot (b \times c)$$

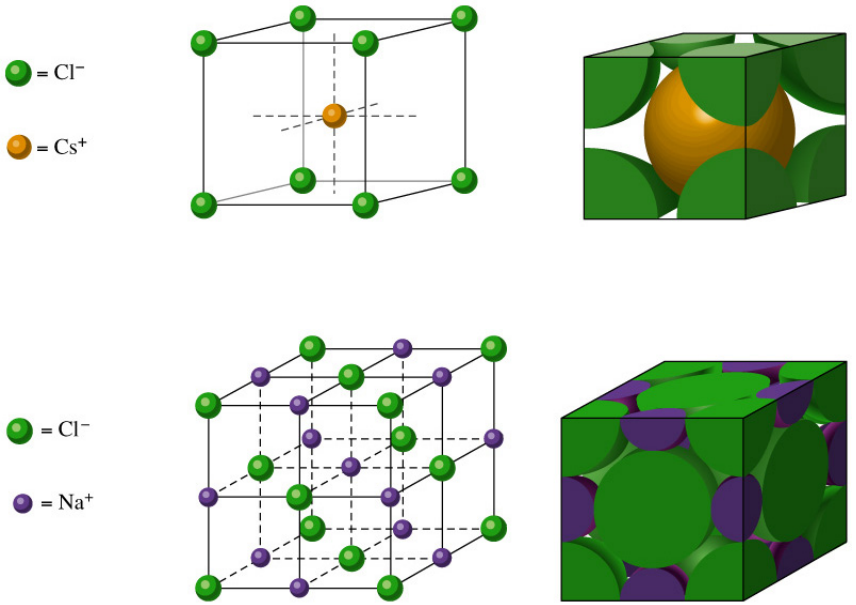
Counting of atoms in 2D

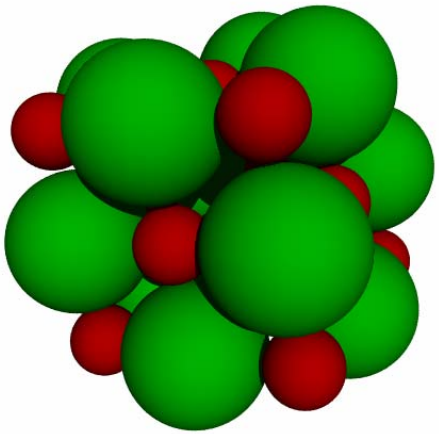
- Atoms in a corner = ¼
- Atoms on an edge = $^1/_2$
- Atoms inside the cell = 1

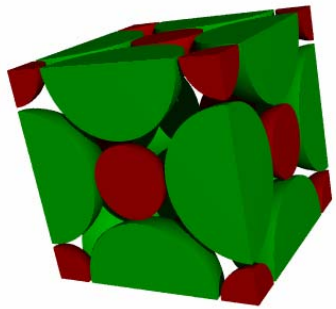


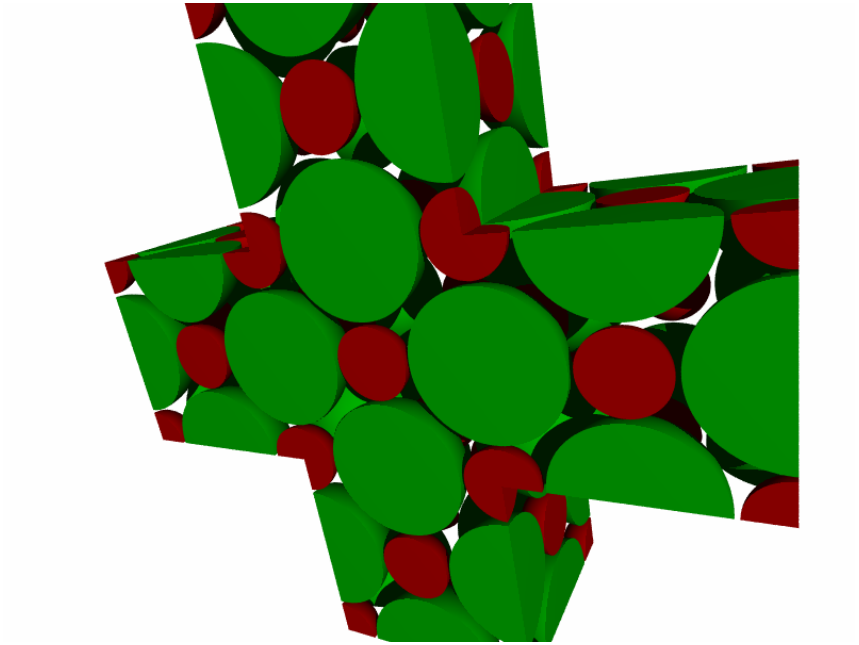
Counting of atoms in 3D

- A corner-atom is shared between **8** cells ⇒ $^1/_8$ atoms pr. cell
- An edge-atom is shared between mellom **4** cells ⇒ $^1/_4$ atom pr cell
- A surface-atom is shared between **2** cells ⇒ $^1/_2$ atom pr cell
- A atom inside one cell ⇒ **1** atom pr cell

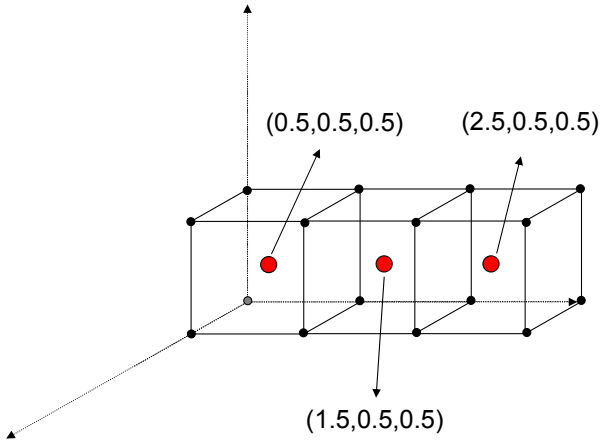








Positioning of atoms



Can add and subtract whole numbers at will.

Crystal plane and crystal directions

A plane (h k l)

A set of equivalent planes {h k l}

A direction [h k l]

A set of equivalent directions <h k l>

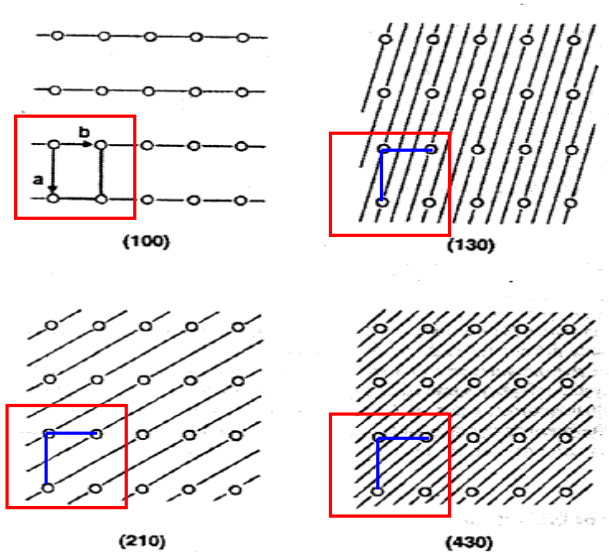
The equivalent planes and directions are a result of the systems symmetry

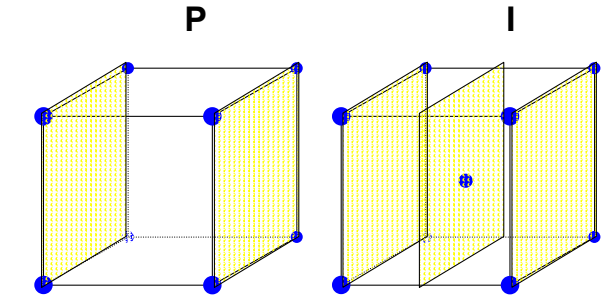
e.g. fcc <111>

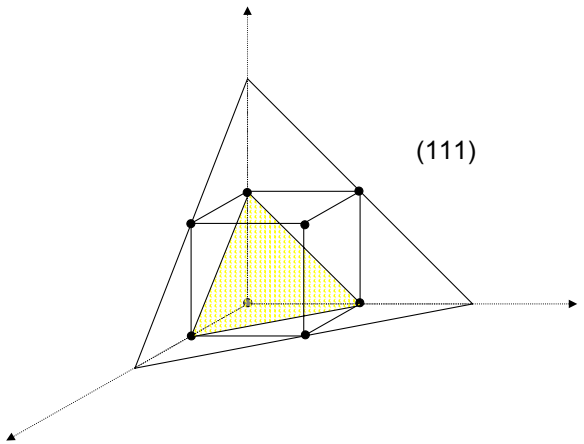
[111] [$\bar{1}$11] [$\bar{1}\bar{1}$1] [1$\bar{1}$1]

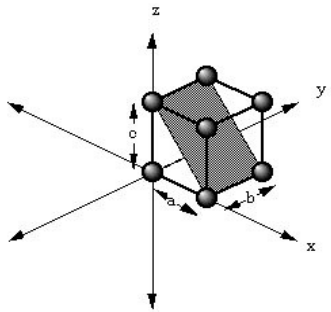
[$\bar{1}\bar{1}\bar{1}$] [1$\bar{1}\bar{1}$] [11$\bar{1}$] [$\bar{1}$1$\bar{1}$]

Miller indices, 2D



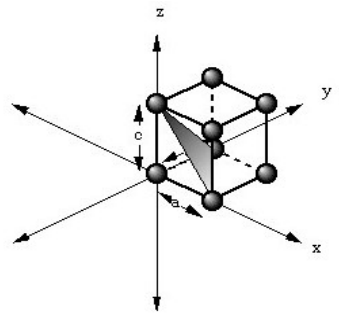






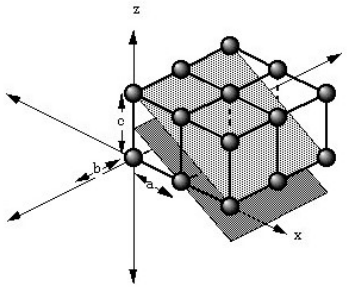
	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1

Miller indice (101)



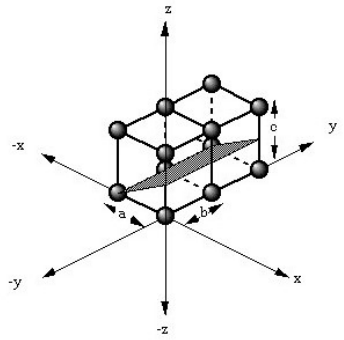
	a	b	c
intercept length	1	1	1
reciprocal	$\frac{1}{1}$	$\frac{1}{1}$	$\frac{1}{1}$
cleared fraction	1	1	1

Miller indice (111)



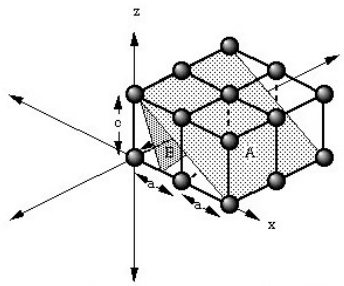
	a	b	c
intercept length	1	∞	1/2
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2

Miller indice (102)

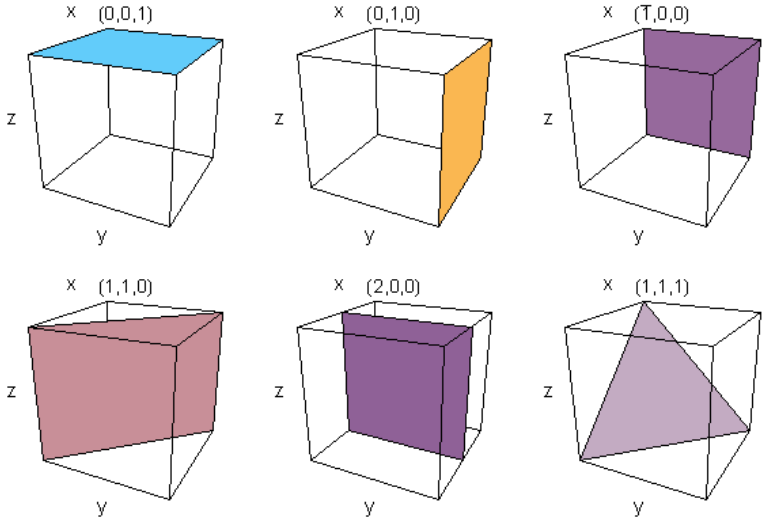


	a	b	c
intercept length	-1	∞	$\frac{1}{2}$
reciprocal	$\frac{1}{-1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	-1	0	2

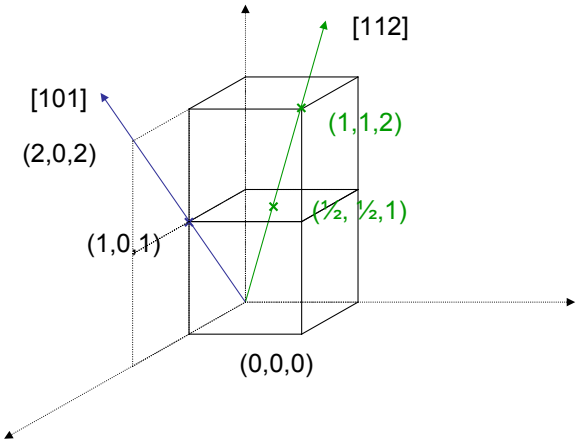
Miller indice ($\bar{1}02$)



	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	∞	$\frac{1}{2}$	$\frac{1}{2}$	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	(102)			(201)		



Directions



[½ 0 ½] = [101] = [202] = n[101]

Parallel directions have same index

Crystal plane and crystal directions

A plane	(h k l)
A set of equivalent planes	{h k l}
A direction	[h k l]
A set of equivalent directions	<h k l>

The equivalent planes and directions are a result of the systems symmetry

e.g. fcc <111>

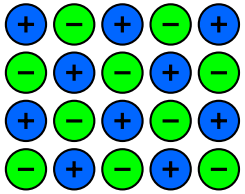
[111] [$\bar{1}$11] [$\bar{1}\bar{1}$1] [1$\bar{1}$1]

[$\bar{1}\bar{1}\bar{1}$] [1$\bar{1}\bar{1}$] [11$\bar{1}$] [$\bar{1}$1$\bar{1}$]

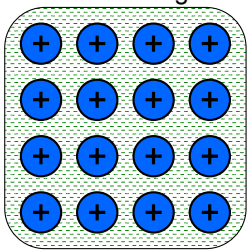
Kulepakking

Atoms as spheres:
- ions
- metal atoms
- molecules

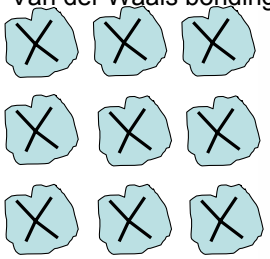
Ionic bonding

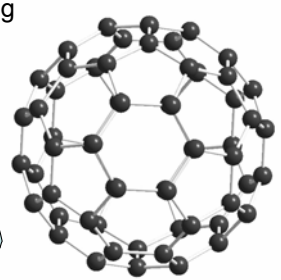


Metal bonding

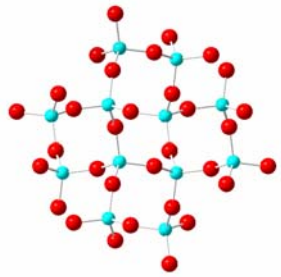


Van der Waals bonding





Covalent bonding



Spherepacking

The entities have to be:

•Spherical
•Of same type (size)
•Non-compressible
•Non-repulsive / contractive

Ideal sphere packing model

Any observed deviation from the ideal model will be explained by that the requirements are not fully met.

Closest (densest) packing of spheres:

74% of the volume is filled by the spheres

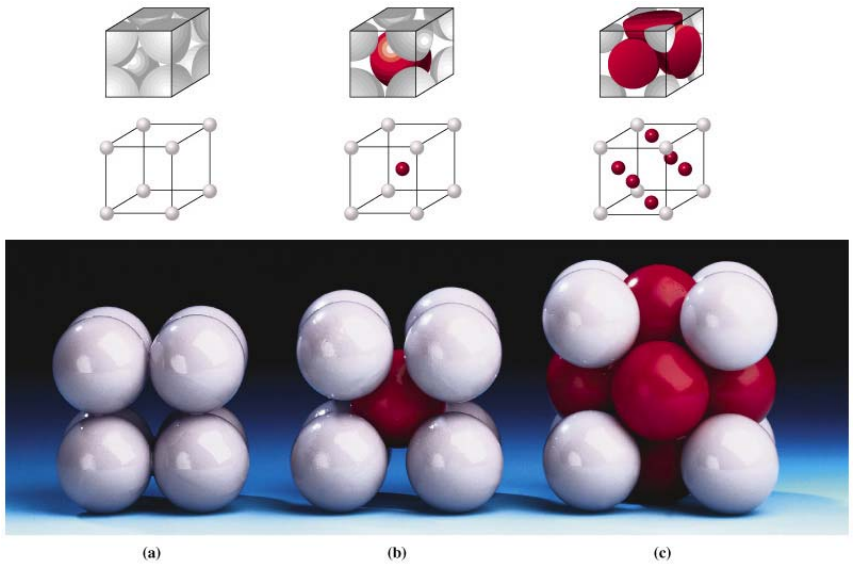
26% voids / vacant space

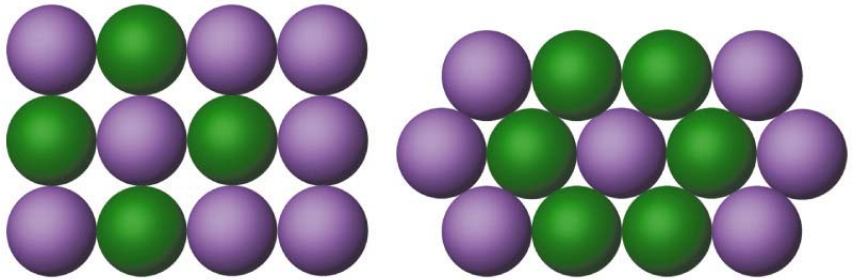
The voids/holes will have different appearance:
•Octahedral shape
•Tetrahedral shape
•(Trigonal prismatic holes)
•(Trigonal bipyramidale holes)

The voids/holes may be filled with atoms
•of the same type as the packing spheres
•of different type

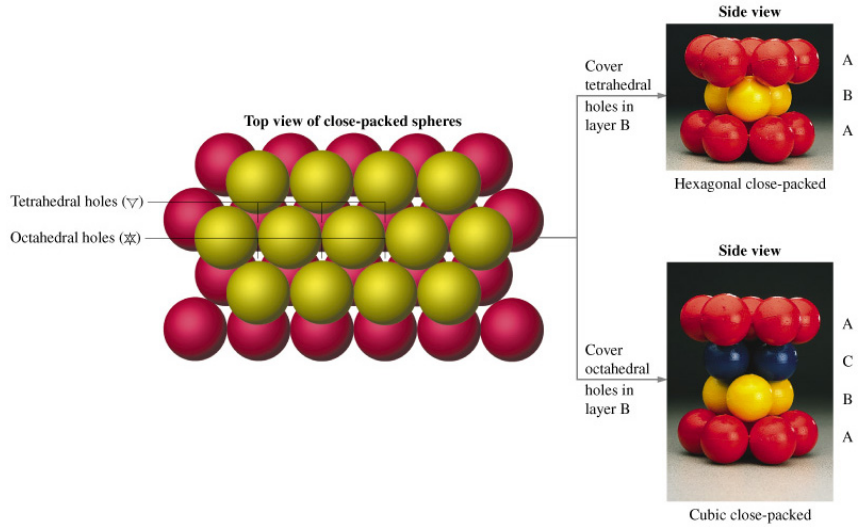
Density of packing

Coordination number (CN)	Name	Density
6	Simple cubic	0.5236
8	Simple hexagonal	0.6046
8	Body-centred cubic	0.6802
10	Body-centred tetragonal	0.6981
12	Closest packing	0.7405

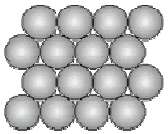



(a) An "open" packing

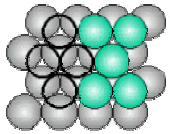
(b) Close packing



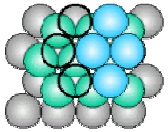
Dense sphere packing



A

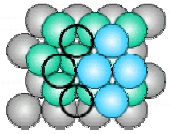


AB



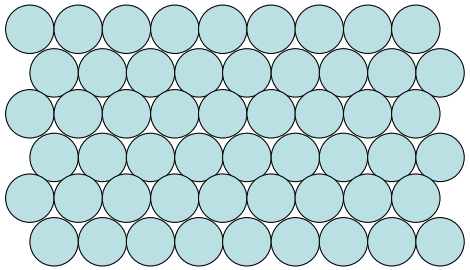
ABA

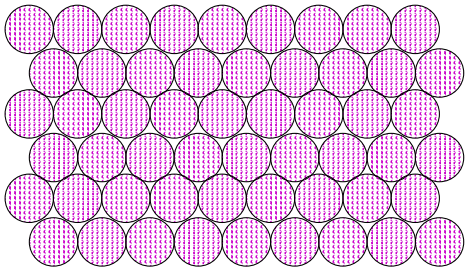
hcp

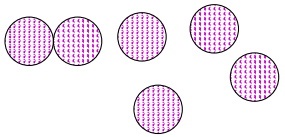


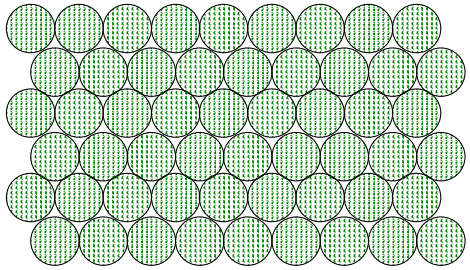
ABC

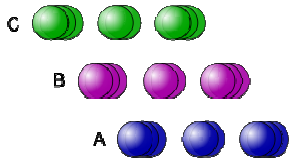
ccp

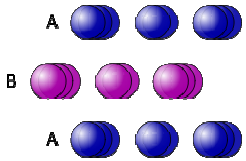


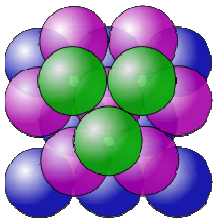




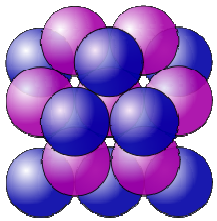




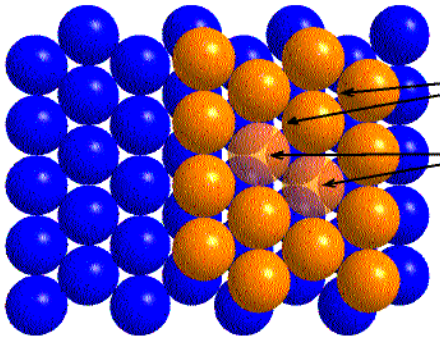


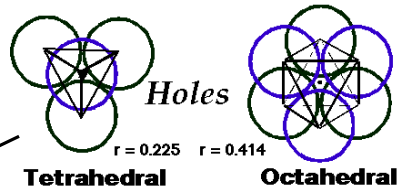


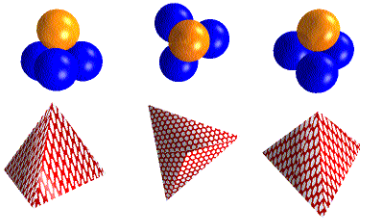
Cubique à faces centrées ABC

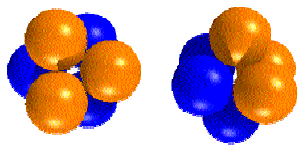


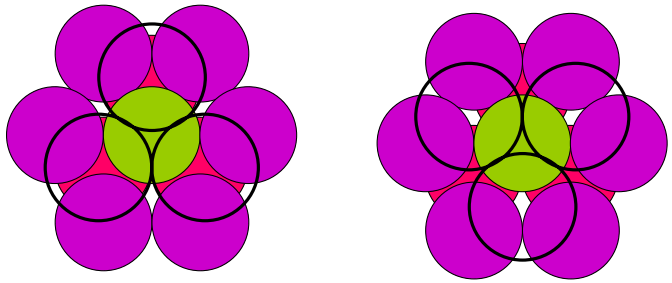
Hexagonal compact ABA







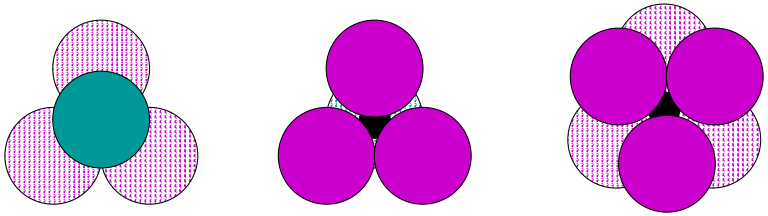




Tetraeder hole +

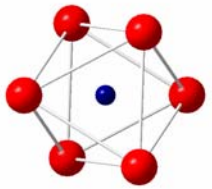
Tetraeder hole -

Octaeder hole



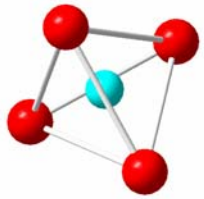
Octahedra holes

CN = 6



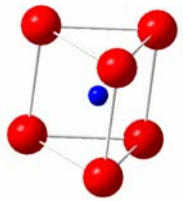
Tetrahedra holes

CN = 4



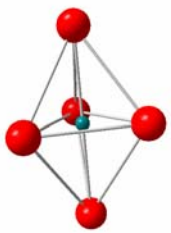
Hexagonal packing (AA..)
Trigonal prismatic holes

CN = 6

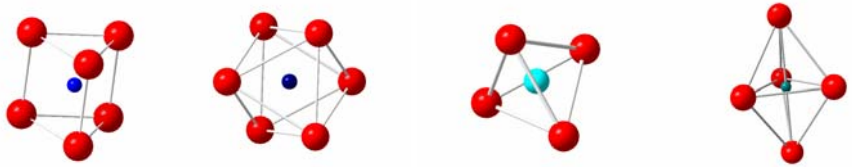


Hexagonal closepacked (AB..)
Trigonal bipyramidal

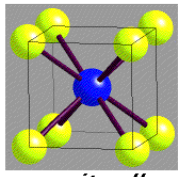
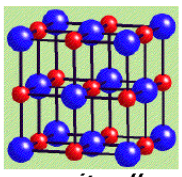
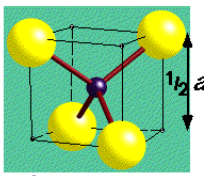
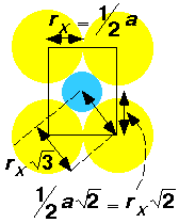
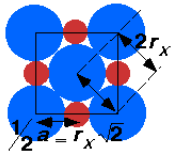
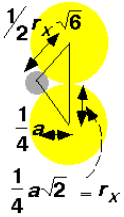
CN = 5

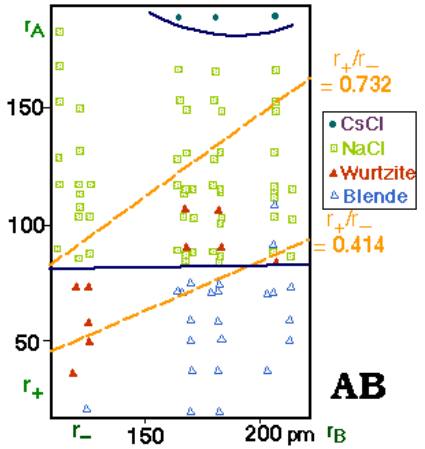


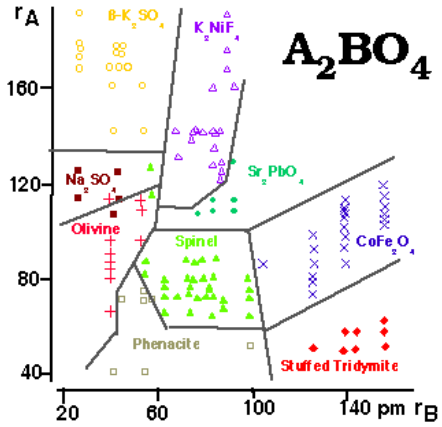
Type of hole	*Number*	*Max. radius*
Cuboctahedron	N	1
Cube	N	0.732
Trigonal prismatic	2N	0.528
Octahedral	N	0.414
Tetragonal	2N	0.225
Triangle	N	0.155

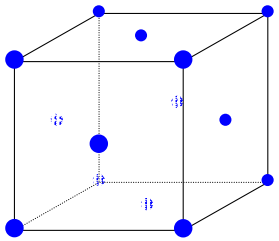


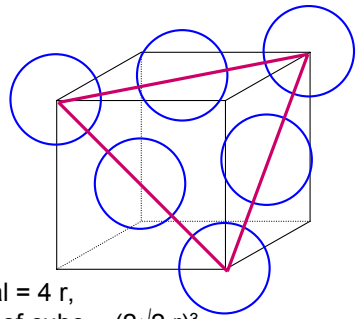
Limiting Radius Ratios

CsCl 8:8	NaCl 6:6	ZnS 4:4
		
unit cell	*unit cell*	*1/8th unit cell*
cell side a	face diagonal $a\sqrt{2}$	body diagonal $a\sqrt{3}$
		
$r_M + r_X = r_X\sqrt{3}$	$r_M + r_X = r_X\sqrt{2}$	$r_M + r_X = \frac{1}{2}r_X\sqrt{6}$
$r_M / r_X = \sqrt{3} - 1$	$r_M / r_X = \sqrt{2} - 1$	$r_M / r_X = \frac{1}{2}\sqrt{6} - 1$
= 0.732	= 0.414	= 0.225



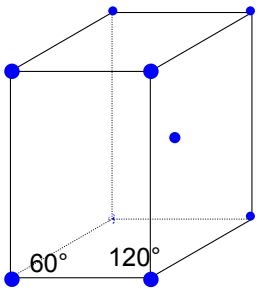


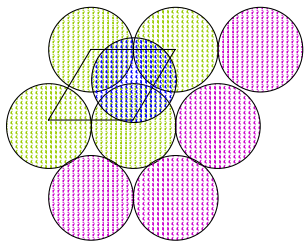


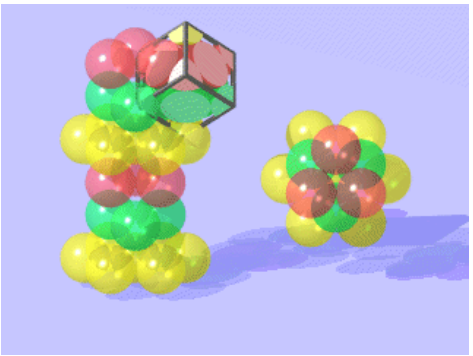


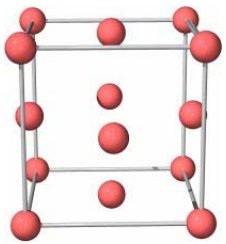
(111)

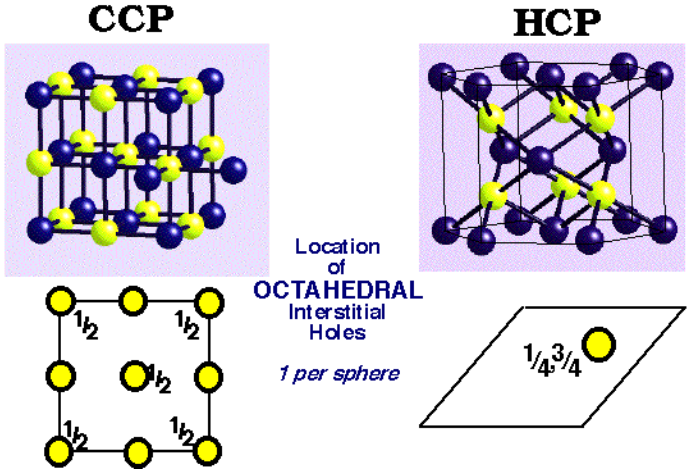
Diagonal = 4 r,
Volume of cube = $(2\sqrt{2}\ r)^3$
Volume of 4 spheres = $4*\pi*4/3\ r^3$
Density = $16\pi/3\ /\ (2\sqrt{2})^3 = 0.7405$

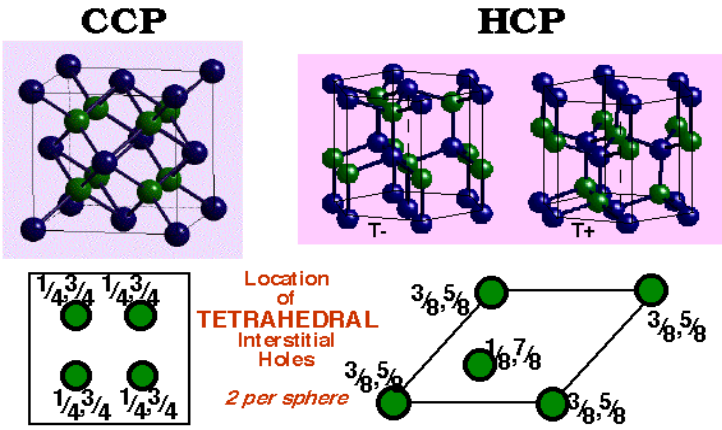


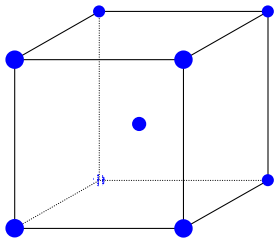




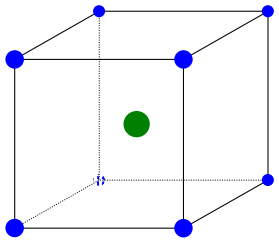




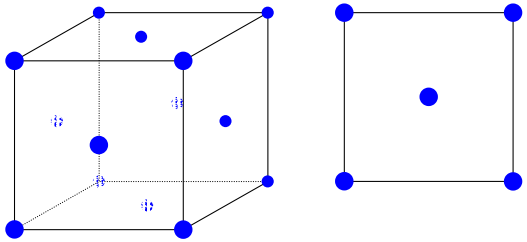




bcc, cucic, I-centered
(0,0,0) + (1/2,1/2,1/2)
CN = 8



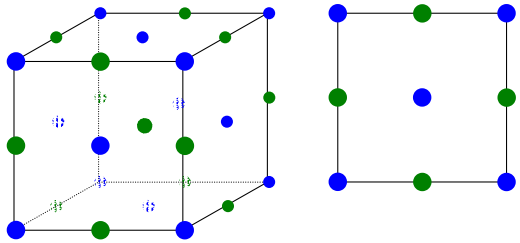
CsCl-type structure, CN = 8
M in (0,0,0)
X in (1/2,1/2,1/2)
Not I-centered, -> P



fcc, Cubic F-centered lattice

Structure = lattice + basis (motif)

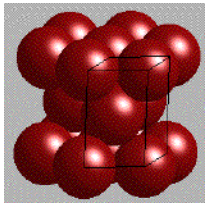
F-centered lattice with metal in (0,0,0)



NaCl-type structure = cubic + basis

F-centered lattice:
Na in (0,0,0)
Cl in (1/2,0,0)

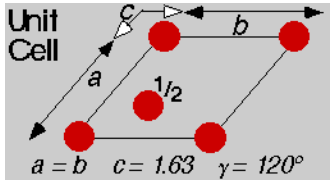
hcp (hexagonal close packed)

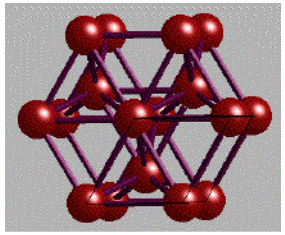


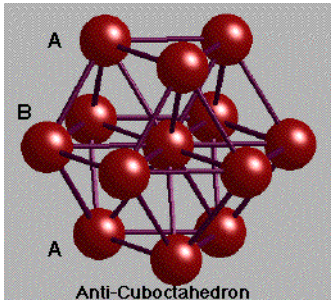
Z = 2

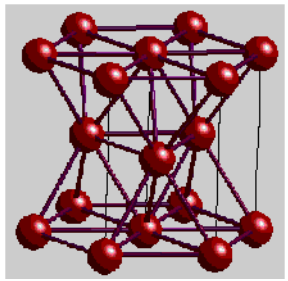
2 atoms in unitcell:

(0, 0, 0), ($^2/_3$, $^1/_3$, $^1/_2$)

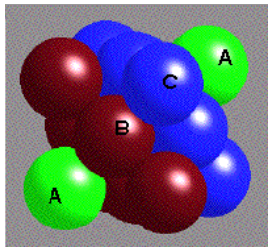








ccp (cubic close packed)

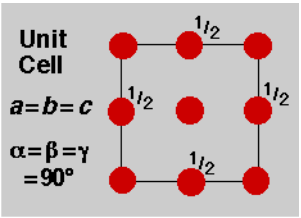


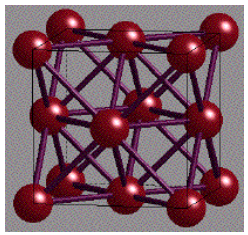
Z=4

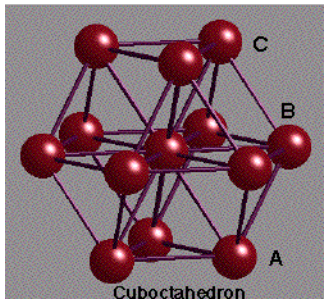
4 atoms in unitcell:

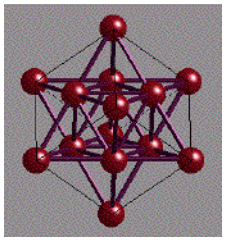
(0, 0, 0) (0, $^1/_2$, $^1/_2$)

($^1/_2$, 0, $^1/_2$) ($^1/_2$, $^1/_2$, 0)

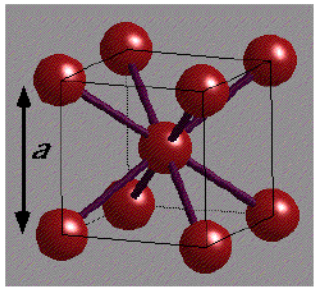




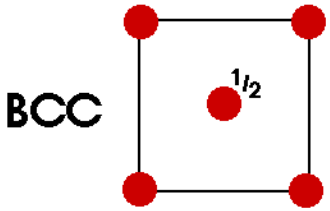


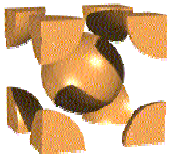


bcc



Body-Centred Cubic





Z=2

2 atoms in unitcell:

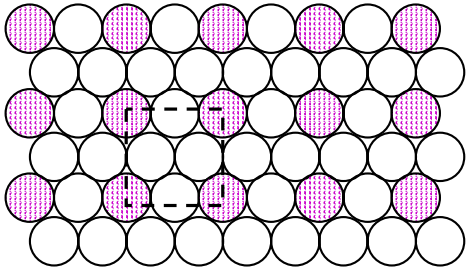
(0, 0, 0) ($^1/_2$, $^1/_2$, $^1/_2$)

Structure (types) derived from dense closepacking of spheres

Principe:

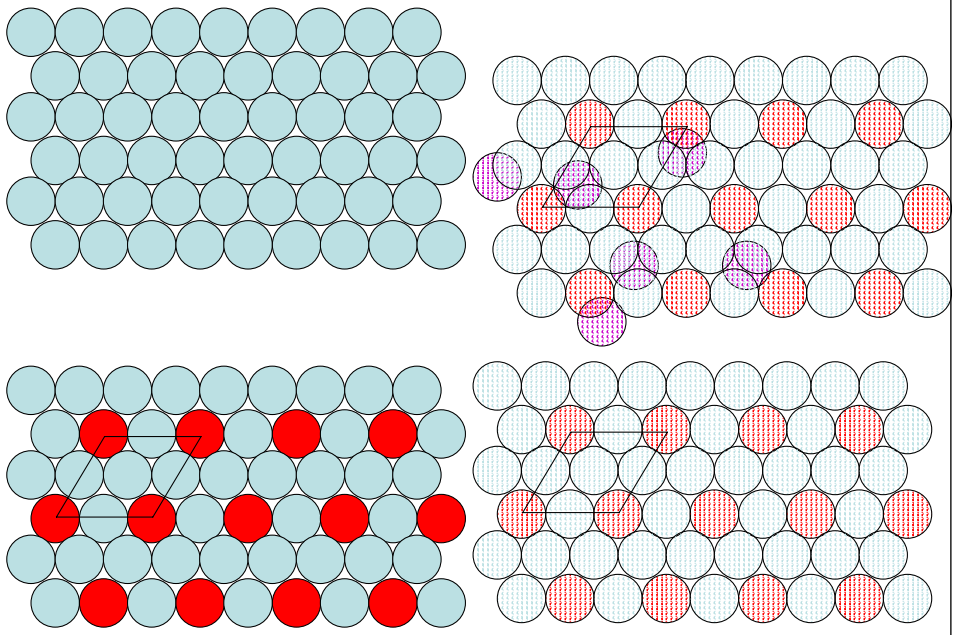
- **A** Closepacked layers of different types of spheres
- **B** Filling of holes with smaller spheres (octahedra-, tetrahedra-, trig. bipyramidal.- holes)
- **C** Combinations of **A** and **B**

A



$TiAl_3$

$WAl_5 = WAl_3 + Al_2$



B

Filling of holes (interstitial possitions)

AB_n M_mX

X = Packing sphere

Filling degree	AB_n	M_mX	Spherepacking ccp		hcp
All octaederholes		AB	MX	NaCl	NiAs
All tetraederholes		AB_2	M_2X	CaF_2	
½ teraederholes	AB	MX	ZnS(bl.)		ZnS(wu.)
½ octaederholes	AB_2	$M_{1/2}X$	$CdCl_2$		$CdI_2[Cd(OH)_2]$
$^1/_3$ octaeerholes	AB_3	$M_{1/3}X$	$CrCl_3$		BiI_3, β-$ZrCl_3$

C

Mixed spheres in dense packed layers + filling of interstitial holes

A, B cations
X anion

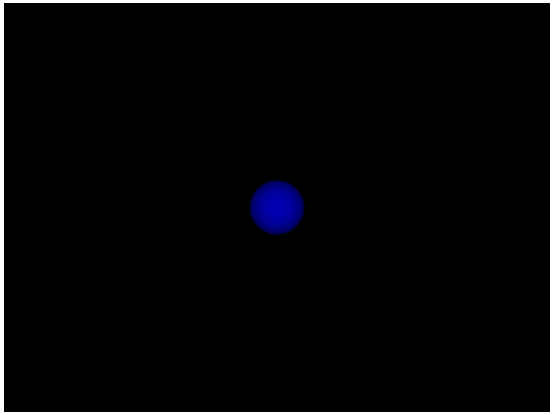
A and X of similar size
B is so small that it fits into octaeder holes

AX_3 densepacked layers

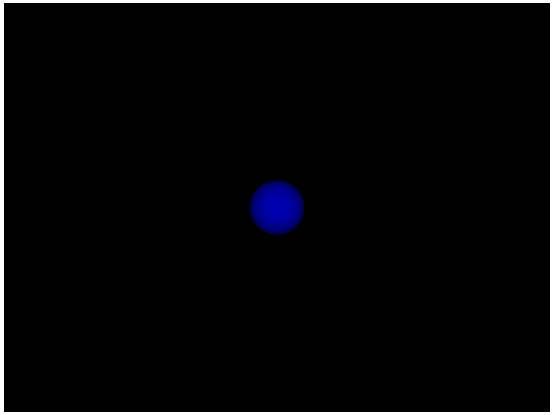
Those octahedra holes with 6 neighbours of X type is filled with B

ABX_3 perovskite type structure

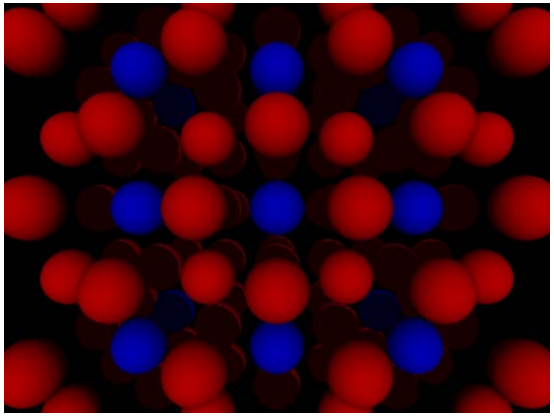
Perovskite



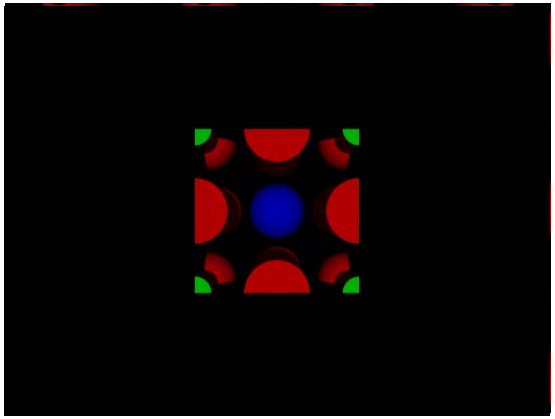
Perovskite



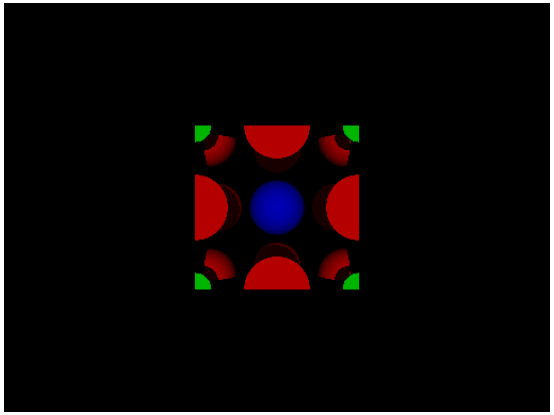
Perovskite



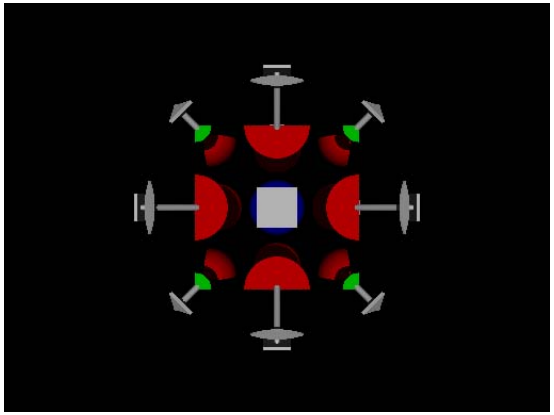
Perovskite



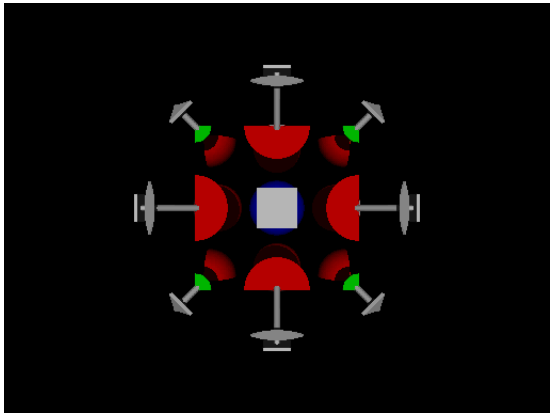
Perovskite



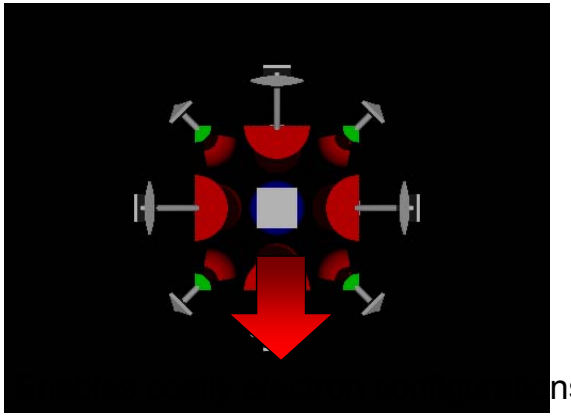
Perovskite



Perovskite



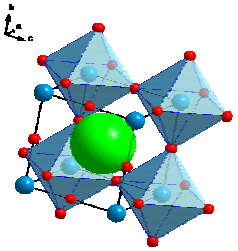
Perovskite



ns

Interesting properties

Perovskite



Property	Compound examples
Insulator	$LaGaO_3$, $LaAlO_3$, $LaCrO_3$, $LaFeO_3$
High-K dielectric	$BaTiO_3$, $Ba_2EuZrO_{5.5}$, $CaCu_3Ti_4O_{12}$
Semiconductivity	$LaMnO_3$, $PbCrO_3$, $RTiO_3$ (R = La...Tm)
Half metallicity	$LaBaMn_2O_{5.5}$, $YBaMn_2O_{5.5}$ Sr_2FeMoO_6, Ba_2FeMoO_6, Ca_2FeMoO_6, Ca_2FeReO_6
Metallic conductivity	$LaNiO_3$
Superconductivity	$YBa_2Cu_3O_7$, $HgBa_2CuO_4$, $La_{1.5}Nd_{0.5}CaBa_2Cu_5O_z$, $Bi_2Sr_2Ca_2Cu_3O_{10-d}$, $HgBa_2Ca_2Cu_3O_{8+d}$
Colossal magnetoresistance	$A_{0.3}La_{0.7}MnO_3$ (A = Ca, Sr, Pr, Pb)
Multi ferroics	$BiMnO_3$, $BiFeO_3$,
Ferroelacticity	$LaCoO_3$
Ferromagnetic	$SrRuO_3$, $LaMnO_{3.15}$, $La_{1-x}Ca_xMnO_3$, $Sr_{1-x}LaMnO_3$
Anti ferro	$BiMnO_3$, $LaFeO_3$, $LaMnO_3$
Piezoelectricity	$PbZr_{0.47}Ti_{0.53}O_3$
Spin glass	$CaRuO_3$
Multi valence materials	$Ca_3Co_2O_6$, $Sr_4Fe_4O_{11}$, $YBaMn_2O_{5.5}$

Space filling of polyhedra

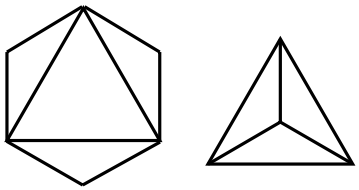
Structures can be described as connections of polyhedra that share:

- **Corners**
- **Edges**
- **Faces**

The polyhedra are simplified for visual clarity.

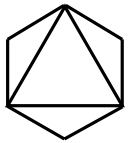
Type of polyhedra:

- **Tetrahedra**
- **Octahedra**
- **Trigonal prismatic**
- **…**

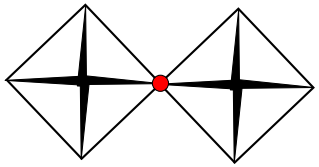


Basically the same types of polyhedra as mention for sphere packing

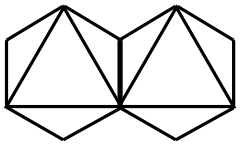
Limited units, Octahedra



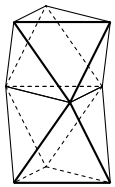
Isolated octahedra — MX_6



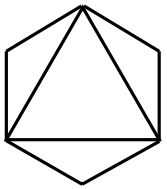
Dimer — M_2X_{11} ($Nb_2F_{11}^-$)



Dimer — M_2X_{10} (Nb_2Cl_{10}) (U_2Cl_{10})

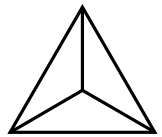


Dimer — M_2X_9 ($Fe_2(CO)_9$) ($I_2O_9^{4-}$)



Octahedra

Connected by:
Corners
Edges
(Faces)

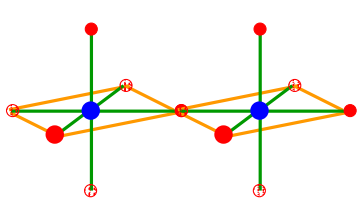


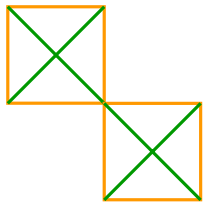
Tetrahedra

Connected by:
Corners
(Edges)

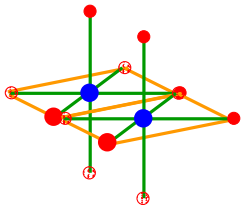
How these units connect will affect the chemical composition, and vice versa.

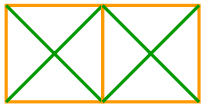
Polymerization of MX_6 octahedra



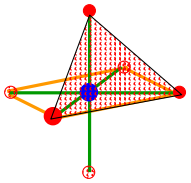


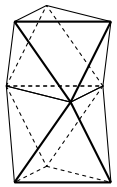
Corner sharing:
d(M-M) = 2*d(M-X)





Edge sharing:
d(M-M) = √2*d(M-X)





Face sharing:
d(M-M) = 1.16*d(M-X)

Calculation of interatomic distances in some simple structures

Structure type	Distance	Number of such distances	Magnitude of separation in terms of unit cell dimensions
Rock salt (cubic)	Na–Cl	6	$a/2 = 0.5a$
	Cl–Cl	12	$a/\sqrt{2} = 0.707a$
	Na–Na	12	$a/\sqrt{2} = 0.707a$
Zinc blende (cubic)	Zn–S	4	$a\frac{\sqrt{3}}{4} = 0.433a$
	Zn–Zn	12	$a/\sqrt{2} = 0.707a$
	S–S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca–F	4 or 8	$a\frac{\sqrt{3}}{4} = 0.433a$
	Ca–Ca	12	$a/\sqrt{2} = 0.707a$
	F–F	6	$a/2 = 0.5a$
Wurtzite* (hexagonal)	Zn–S	4	$a\sqrt{\frac{3}{8}} = 0.612a = \frac{3c}{8} = 0.375c$
	Zn–Zn	12	$a = 0.612c$
	S–S	12	$a = 0.612c$
Nickel arsenide* (hexagonal)	Ni–As	6	$a/\sqrt{2} = 0.707a = 0.433c$
	As–As	12	$a = 0.612c$
	Ni–Ni	2	$c/2 = 0.5c = 0.816a$
	Ni–Ni	6	$a = 0.612c$
Cesium chloride (cubic)	Cs–Cl	8	$a\frac{\sqrt{3}}{2} = 0.866a$
	Cs–Cs	6	a
	Cl–Cl	6	a
Cadmium iodide (hexagonal)	Cd–I	6	$a/\sqrt{2} = 0.707a = 0.433c$
	I–I	12	$a = 0.612c$
	Cd–Cd	6	$a = 0.612c$

*These formulae do not necessarily apply when c/a is different from the ideal value of 1.633.

Infinite structures built from octahedral AX_6 groups

Vertices only shared — HJØRNER

2 AX_5 chains:
cis: VF_5, CrF_5
trans: BiF_5, $(CrF_5)^{2-}$, α-UF_5

4 AX_4 layers:
cis: $BaMnF_4$
trans: SnF_4, K_2NiF_4

6 AX_3 frameworks:
ReO_3, $Sc(OH)_3$,
FeF_3 etc.,
Perovskite,
W bronzes,
pyrochlore

Vertices and edges shared — H + K

AX_2, A_3X_8, A_2X_5 layers (V oxyhydroxides)
AX_2 frameworks
Rutile structure
α-AlO . OH
Eu_3O_4
$CaTi_2O_4$
α-MnO_2
(Table 5.5)
BeY_2O_4
AX_3 layer: MoO_3
AX_3 framework: $CaTa_2O_6$

Edges only shared — KANTER

2 AX_4 chains: $TeCl_4$, NbI_4
3 AX_3 layer: YCl_3, BiI_3
4 AX_3 double chain: NH_4CdCl_3
AX_3 layer: NH_4HgCl_3
A_3X_8 layer: Nb_3Cl_8
6 AX_2 layer: CdI_2, $CdCl_2$
AX_2 double layer: MOCl, γ-MO . OH
AX_2 framework: $Cu_2(OH)_3Cl$

Vertices, edges, and faces shared

α-Al_2O_3 (corundum)
γ-$Cd(OH)_2$

Vertices and faces shared

ABO_3 structures: hexagonal $BaTiO_3$; high-$BaMnO_3$, $BaRuO_3$ (Table 5.6)

Faces and edges shared

Nb_3S_4

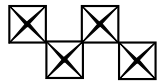
Faces only shared — FLATER

2 AX_3 chain: ZrI_3, Ba NiO_3, Cs $NiCl_3$

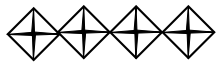
Infinite systems; octahedra by cornersharing

Number of corners shared in a given octahedra:
2, (3), 4, (5), 6

AX_5 chains: (cis-, trans-)

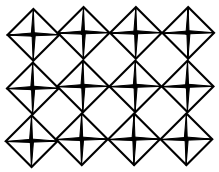


cis- VF_5



trans- BiF_5

AX_4 layers:



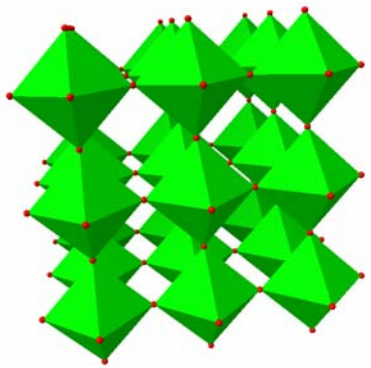
SnF_4
K_2NiF_4

AX_3 3D network:

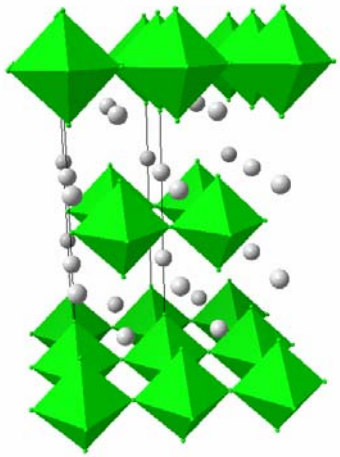
ReO_3
FeF_3

ABX_3 perovskite

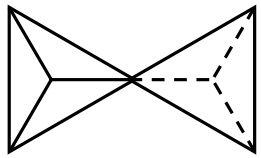
ReO_3



K_2NiF_4

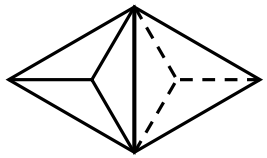


Polymerization of MX_4 tetrahedra

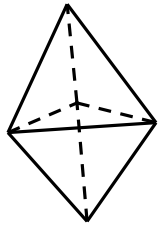


Corner sharing:
d(M-M) = 2*d(M-X)

2.0 only observed for SiO_4
Si^{4+} - Si^{4+} repulsions



Edge sharing:
d(M-M) = 1.16*d(M-X)



Face sharing:
d(M-M) = **0.67***d(M-X)

Structures based on tetrahedas

Vertices only shared, Vertices common to two tetrahedra

No. shared vertices	Formula	Type of complex	Examples
1	A_2X_7	Finite molecule or pyro ion	Cl_2O_7, $S_2O_7^{2-}$, etc.
2	$(AX_3)_n$	Cyclic molecule, or meta-ion infinite chain	S_3O_9, Se_4O_{12}, $(PNCl_2)_n$ $(P_4O_{12})^{4-}$, $(Si_3O_9)^{6-}$, $(SO_3)_n$, $(PO_3)_n^{n-}$
3	$(A_2X_5)_n$	Finite polyhedral, double chain, layer or 3D structure	P_4O_{10} $Al[AlSiO_5]$ P_2O_5, $Li_2Si_2O_5$ P_2O_5, $La_2[Be_2O_5]$
4	$(AX_2)_n$	Layer, double layer, or 3D structure	HgI_2 (red) $CaSi_2Al_2O_8$ (hexag.) SiO_2 structures, GeS_2

Vertices common to three tetrahedra

3	$(AX_2)_n$	Infinite layer	AlOCl, GaOCl

Structures based on tetrahedas

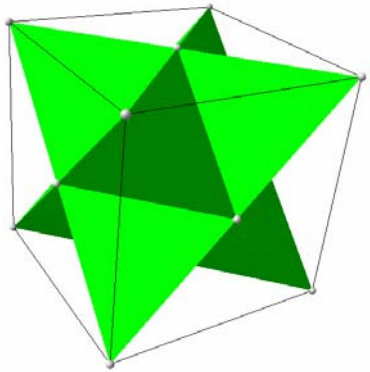
Edges only shared, Edges common to two tetrahedra

No. shared edges	Formula	Type of complex	Examples
1	A_2X_6	Finite dimer	Al_2Cl_6, Fe_2Cl_6
2	$(AX_2)_n$	Infinite chain	$BeCl_2$, SiS_2, $Be(CH_3)_2$
3	$(A_2X_3)_n$	Infinite double chain	$Cs(Cu_2Cl_3)$
4	$(AX)_n$	Infinite layer	LiOH, PbO
6	$(A_2X)_n$	3D structures	Li_2O, F_2Ca

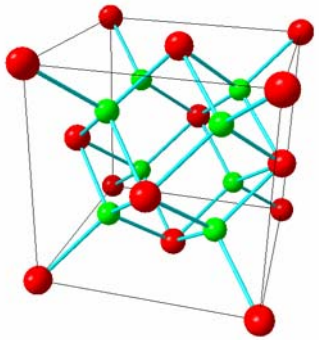
Vertices and edges shared

	$(AX)_n$	Double layer	La_2O_3, Ce_2O_2S, U_2N_2Sb
	$(AX)_n$	3D structure	β-BeO

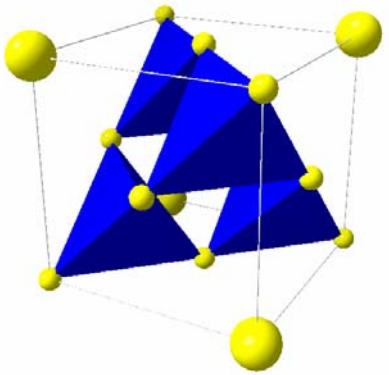
CaF_2
FCa_4 - tetraheda



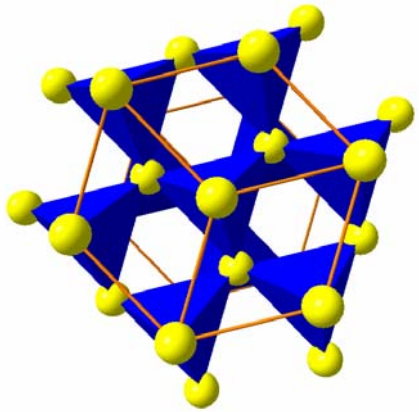
Na_2O
NaO_4 - tetraheda

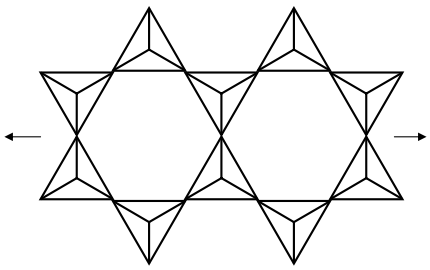


Sink blende
ZnS_4, SZn_4

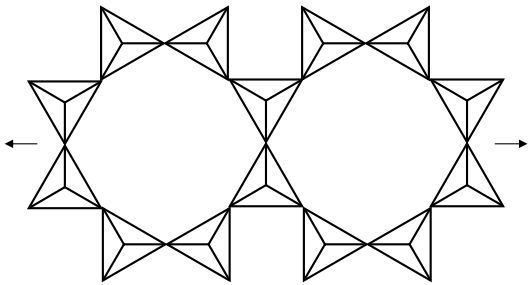


Wurtsitt
ZnS_4, SZn_4

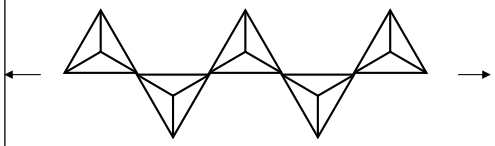




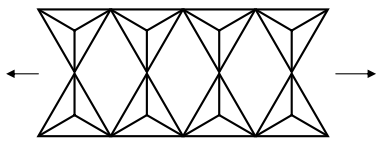
A_4X_{11}



A_6X_{17}



AX_3



A_2X_5

Silicates:

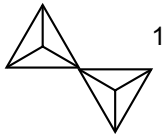
SiO_4 tetrahedas

Corner (vertice) sharing, never edge or face (too strong Si^{4+}-Si^{4+} repulsions)

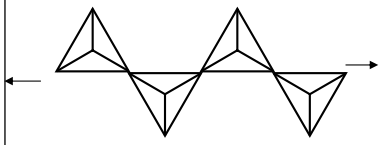
Only two SiO4 tetrahedra share a common corner

Bridging oxygens count ½
Non-bridging count 1

1:4



1:3.5



1:3

Rings	1:3
Double rings	1:2.5
Layer	1:2.5
Double layer	…
3D	1:2

Relation between chemical formula and silicate anion structure.

Si:O ratio	Number of oxygens per Si: bridging	Number of oxygens per Si: non-bridging	Type of silicate anion	Examples
1:4	0	4	isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	dimer $Si_2O_7^{6-}$	$Ca_3Si_2O_7$ rankinite, $Sc_2Si_2O_7$ thortveite
1:3	2	2	chains $(SiO_3)_n^{2n-}$	Na_2SiO_3, $MgSiO_3$ pyroxene
			rings, eg $Si_3O_9^{6-}$	$CaSiO_3$*, $BaTiSi_3O_9$ benitoite
			$Si_6O_{18}^{12-}$	$Be_3Al_2Si_6O_{18}$ beryl
1:2.5	3	1	infinite sheets $(Si_2O_5)_n^{2n-}$	$Na_2Si_2O_5$
1:2	4	0	3D framework	SiO_2†

* $CaSiO_3$ is dimorphic. One polymorph has $Si_3O_9^{6-}$ rings. The other polymorph has infinite $(SiO_3)_n^{2n-}$ chains.
† The three main polymorphs of silica, quartz, tridymite and cristobalite each have a different kind of 3D framework structure.