

# Kap. 5 Crystallography and crystal structures

## Condense phases:

- Liquids
- Solid materials
  - Amorphous materials
    - Glass
  - Crystalline materials
    - 1 Dim. phases  $\text{CrO}_3$ , carbon nanotubes
    - 2 Dim. phases  $\text{V}_2\text{O}_5$ , graphite
    - 3 Dim. phases  $\text{TiO}_2$ , diamond

## Inorganic materials / units

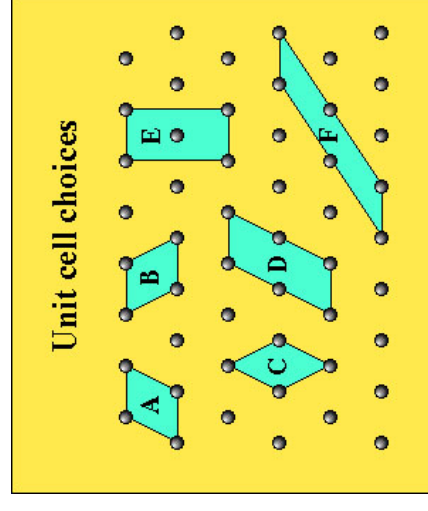
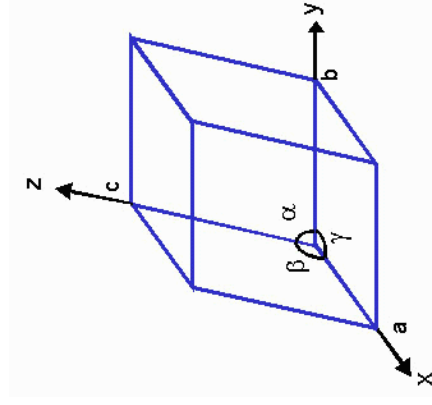
Separate units			
Elements	Molecules	Ions	Complexes
Ar(g)	$\text{CO}_2(\text{g})$	$\text{SO}_4^{2-}(\text{aq})$	$\text{PtCl}_4^{2-}(\text{aq})$
	$\text{CH}_4(\text{g})$	$\text{CO}_3^{2-}(\text{aq})$	$\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
	$\text{H}_2\text{O}(\text{g})(\text{l})$		$\text{Ag}(\text{NH}_3)_2^+(\text{aq})$
	$\text{XeOF}_4(\text{l})$		$\text{Fe}(\text{CN})_6^{3-}(\text{aq})$

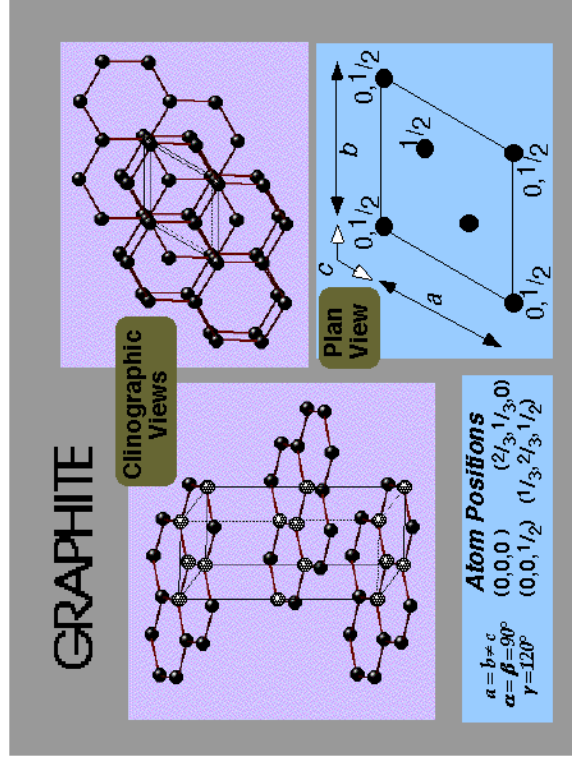
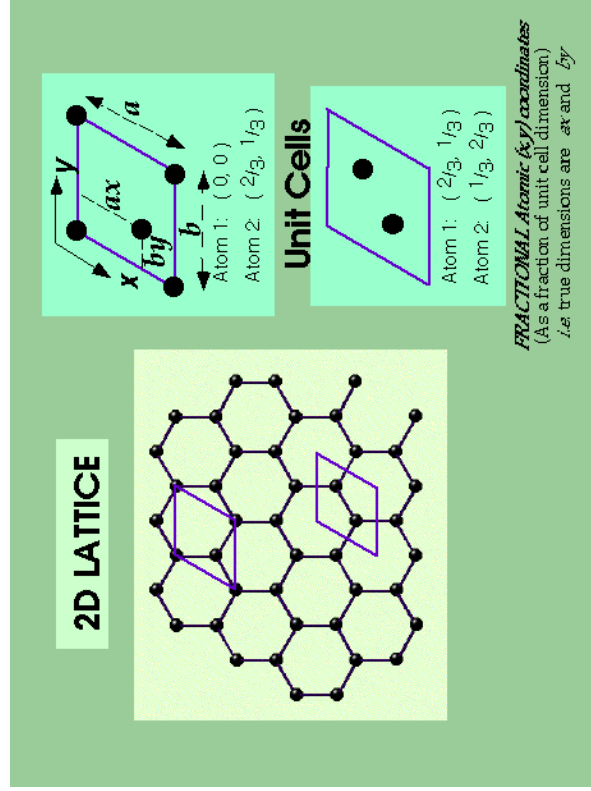
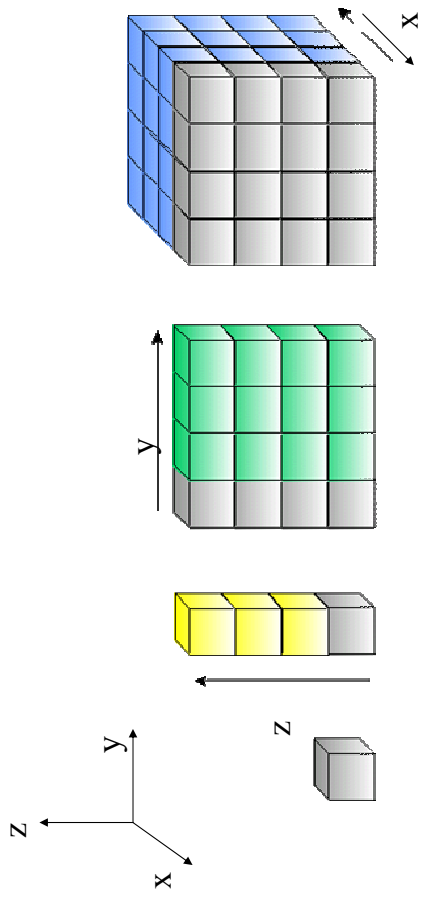
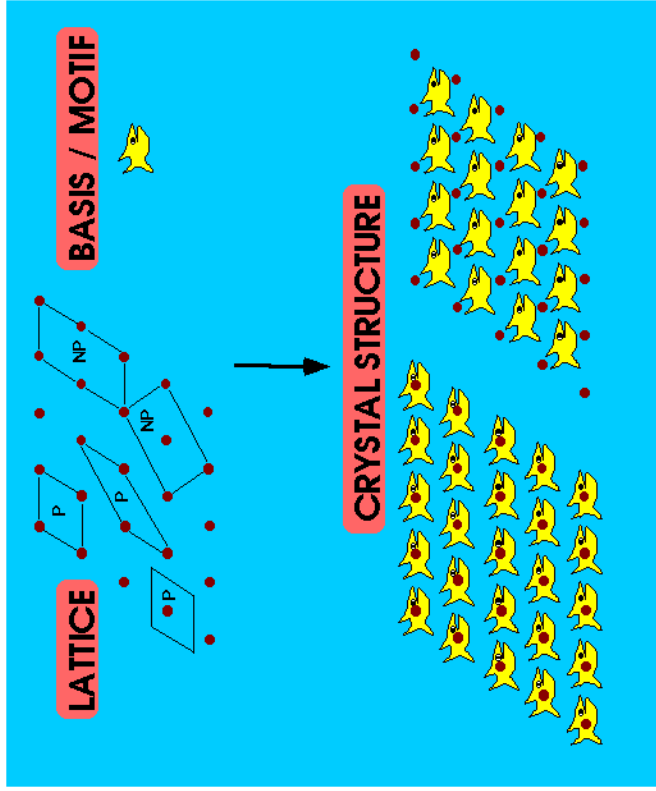
## Structur fragments in solid state

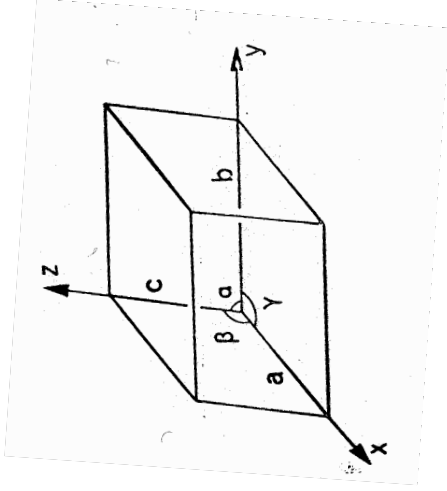
- $\text{SiO}_4^{4-}$  tetrahedral building units in silicates CN = 4 tetrahedral
- ' $\text{CuO}_2$ '-layers in high Tc-materials CN = 4 planequadratic
- ' $\text{MnO}_6$ '-octahedra in oxides CN = 6 octahedra

# Unit cell

## Unit cell







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

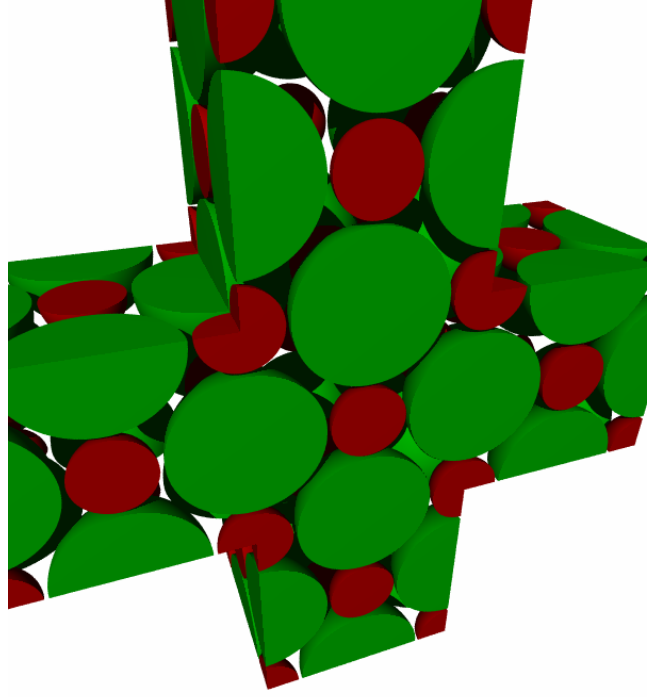
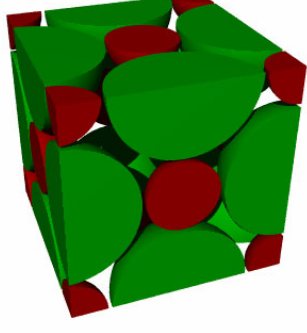
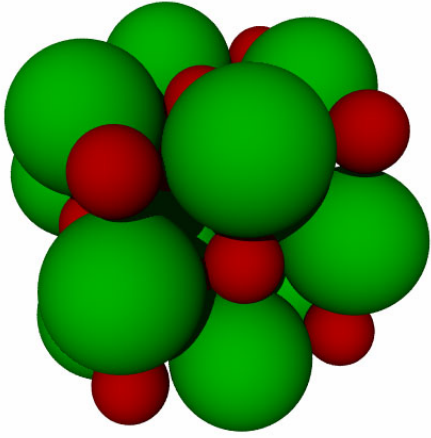
# Counting of atoms

## Counting of atoms in 2D

- ◆ Atoms in a **corner** =  $\frac{1}{4}$
- ◆ Atoms on an **edge** =  $\frac{1}{2}$
- ◆ Atoms **inside** the cell = **1**

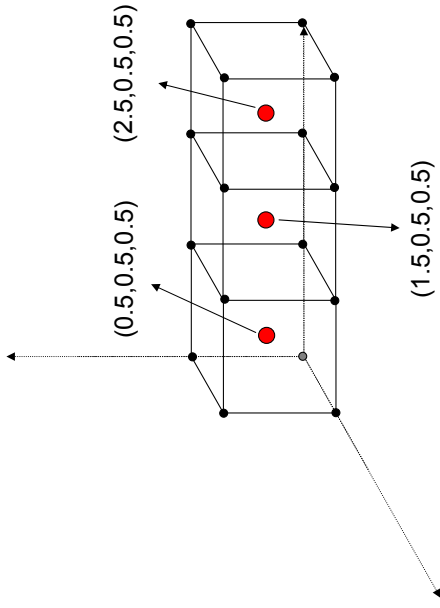
## Counting of atoms in 3D

- ◆ A **corner**-atom is shared between **8** cells  $\Rightarrow \frac{1}{8}$  atoms pr. cell
- ◆ An **edge**-atom is shared between **4** cells  $\Rightarrow \frac{1}{4}$  atom pr cell
- ◆ A **surface**-atom is shared between **2** cells  $\Rightarrow \frac{1}{2}$  atom pr cell
- ◆ A atom **inside one** cell  $\Rightarrow$  **1** atom pr cell



# Positioning of atoms

# Crystal system



## Crystal systems

A collection of point groups that in common give characteristic symmetry operations

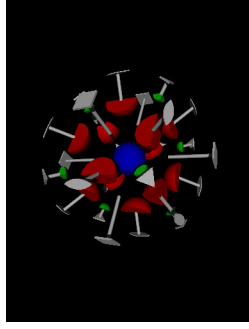


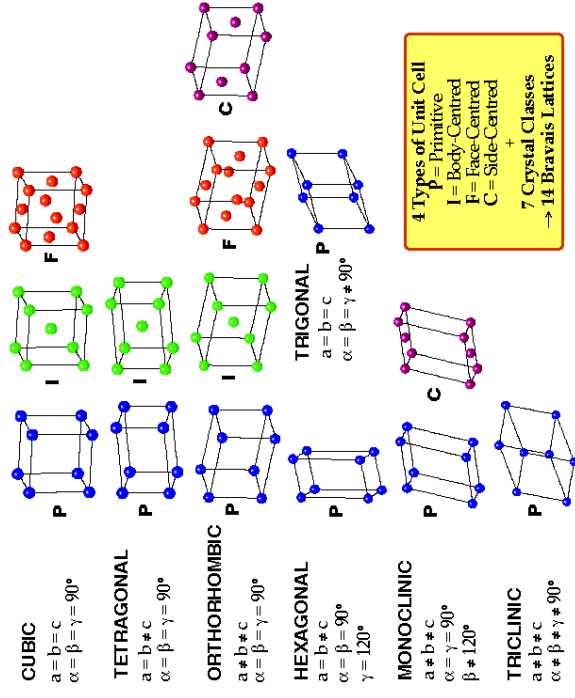
Table 1.1 The seven crystal systems

Crystal system	Unit cell shape†	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal (a)	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ, \gamma = 120^\circ$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ, \gamma = 120^\circ$	One threefold axis	R
Trigonal (b)	$a \neq b \neq c, \alpha = \beta = \gamma \neq 90^\circ$	One twofold axis or mirror plane	P, C
Monoclinic*	$a \neq b \neq c, \alpha = \beta \neq \gamma \neq 90^\circ$	None	P
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	None	P

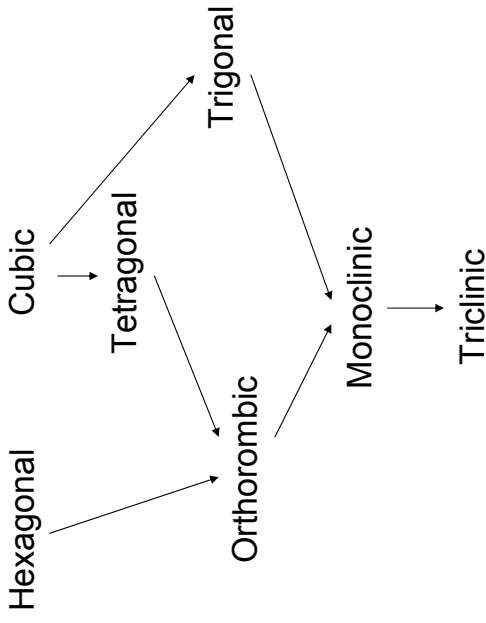
\* Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with  $b$  as the unique axis and the other with  $c$  defined as the unique axis:  $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$ . † Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

The unit cell is chosen so that the mention symmetry elements are easily observed. By describing the symmetry of the unit cell the symmetry of the condensed material is described fully.

## Bravais Lattices



4 Types of Unit Cell  
 P = Primitive  
 I = Body-Centred  
 F = Face-Centred  
 C = Side-Centred  
 +  
 7 Crystal Classes  
 → 14 Bravais Lattices

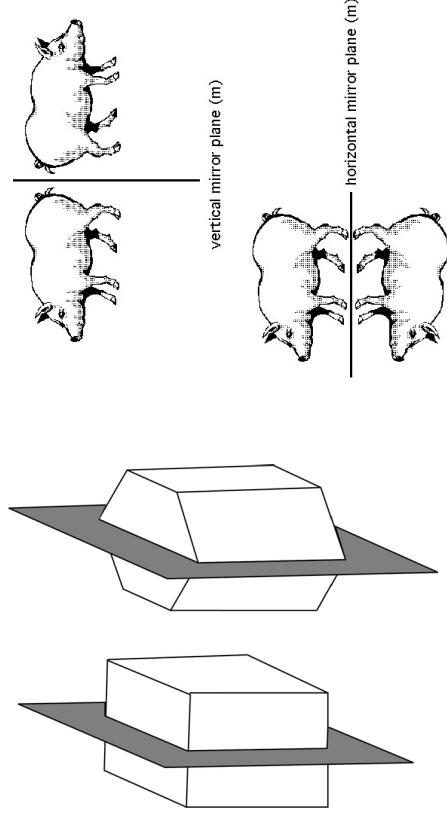


# Symmetry-operations

## Symmetry operations

- ◆ Mirrorplane  $m$
  - ◆ Rotationaxis  $n$  (2, 3, 4, 6)
  - ◆ Inversionaxis  $\bar{n}$  (1, 2, ...)
  - ◆ Sentrosymmetry  $\bar{1}$
  - ◆ Glidemirrorplane  $n, d, a, b, c$
  - ◆ Screwaxis  $2_1, 3_1, \dots, 6_3$
- Pointgroup symmetry
- Special symmetry operations

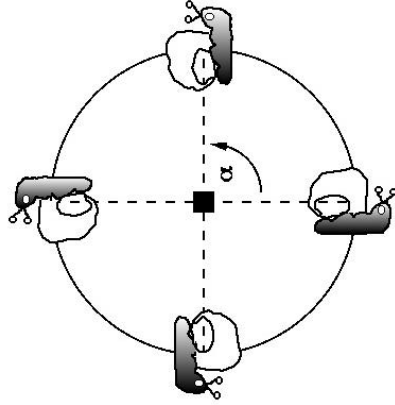
## Mirrorplane $m$



## Rotationaxis $n$

4-fold rotation axis

$$\alpha = 360^\circ/n$$



1- fold



2- fold



3- fold



4- fold



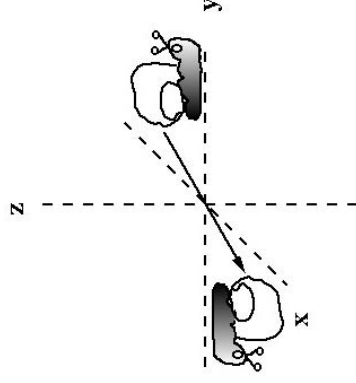
6- fold



## Inversionaxis $\bar{n}$

Rotation + inversion

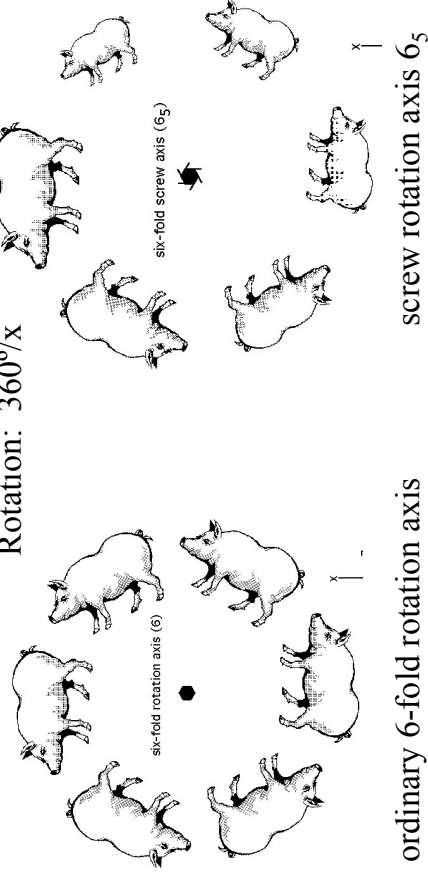
$$\alpha = 360^\circ/n$$



## Screw axis, $X_y$

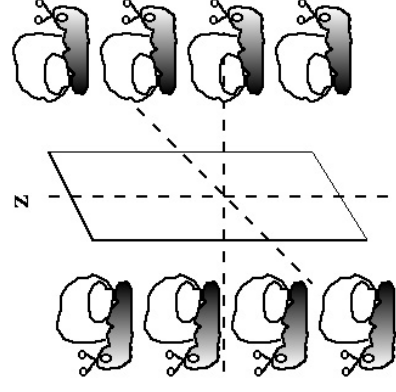
Translation:  $y/x$

Rotation:  $360^\circ/x$



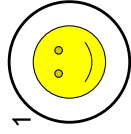
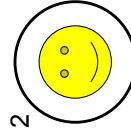
## Glide plane

glide plane of motif



Screw axis

2<sub>1</sub>

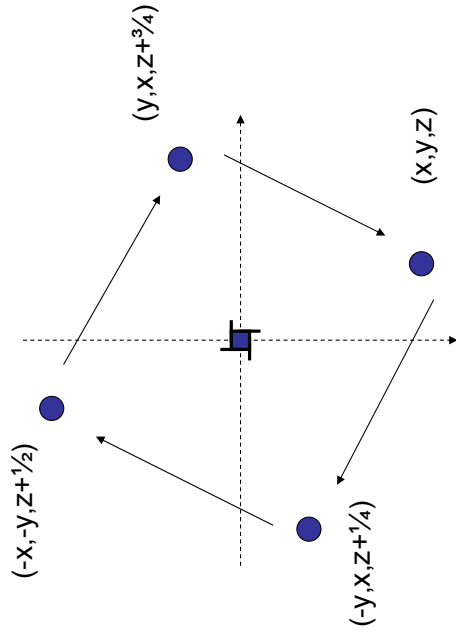


a

Glide mirror plane



4<sub>1</sub>



$$\{4|\bar{t}\} = (3 \times 3)R + \bar{t} = Rr + t$$

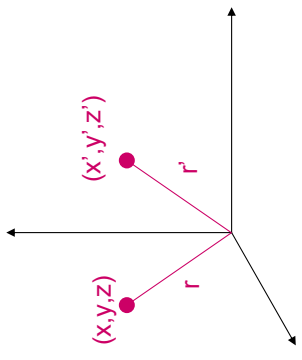
$$\{4|\bar{t}\}^4 = \{1|\bar{t}\}$$

# Point groups

## Pointgroups

- A characteristic collection of symmetry elements
- The symmetry elements has origo as common point
- Symmetry elements and point group symbol:  
Two schemes:  
Schönflies  
Hermann Mauguin
- Illustrated in form of stereographic projection





$$r' = R \cdot r$$

R is a symmetry operator

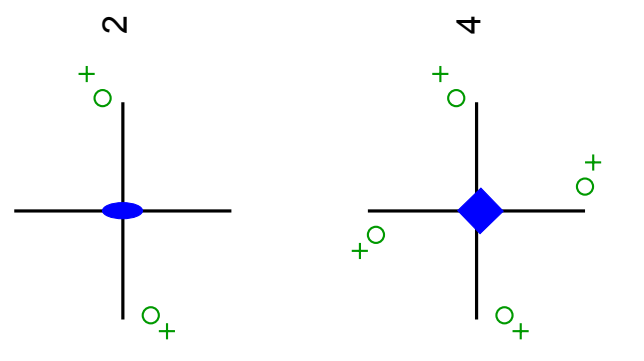
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Symmetry operations:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

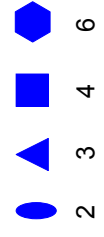
Identity: **I**

$$a_{ij} = 0 \\ a_{ii} = 1$$



Rotation:  $n, C_n$

+ rotation axis [uvw]  
 $n$ [uvw] or  $C_n$ [uvw]

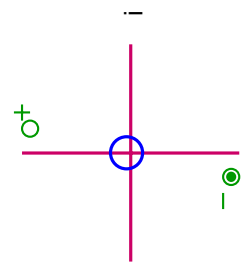


$$\{2[001]\}(xyz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

$$\{4[001]\}(xyz) = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -y \\ x \\ z \end{bmatrix}$$

Inversion / centrosymmetry:  $\bar{1}$  i

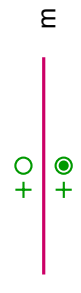
$$\{\bar{1}(i)\}(x, y, z) = (-x, -y, -z)$$



Right hand becomes left hand

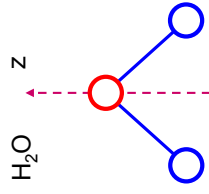
Mirrorplane: m

$$\{m[010]\}(x, y, z) = (x, -y, z)$$



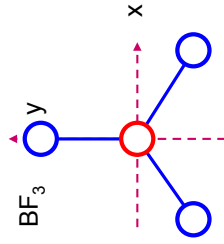
m is defined from the normal of the plane

Rotation axis



$C_2^z$  2

Vertical mirrorplane



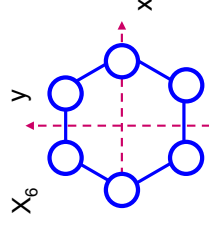
$C_3^z$  3

Horizontal mirrorplane  
Vertical mirrorplane

Other symmetry elements

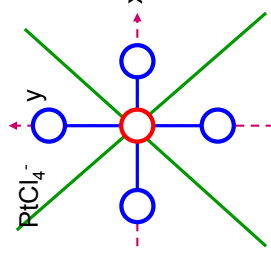
Other symmetry elements

Rotation axis



$C_6^z$  6

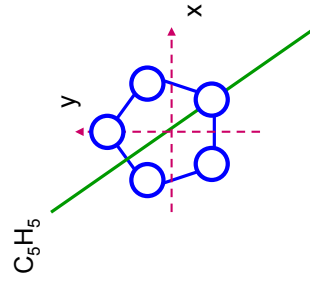
Two-fold axis  
Mirror planes  
Inversion center



$C_4^z$  4

$C_2$  axis  
Mirror planes  
Inversion center

Rotation axis



$C_5^z$  5

5  $C_2$  axis  
Mirror planes

Rotation axis

Other symmetry elements

Triclin system

1 and  $\bar{1}$  does not imply any restrictions for a,b,c or  $\alpha,\beta,\gamma$

Point group with elements:  $\bar{1}$  I, I, i

If a 2-fold axis is added, then the system becomes:

**Monoclinic system**

with the symmetry operations 2 ( $C_2$ ) or  $\bar{2} \equiv m$  ( $\sigma_h$ )

2 I,  $C_2$   
m I,  $\sigma_h$

Presence of further 2 or m is a criteria for an orthorhombic system

What about m normal to 2?

It does not change the criteria for a,b,c or  $\alpha,\beta,\gamma$  and is hence possible.

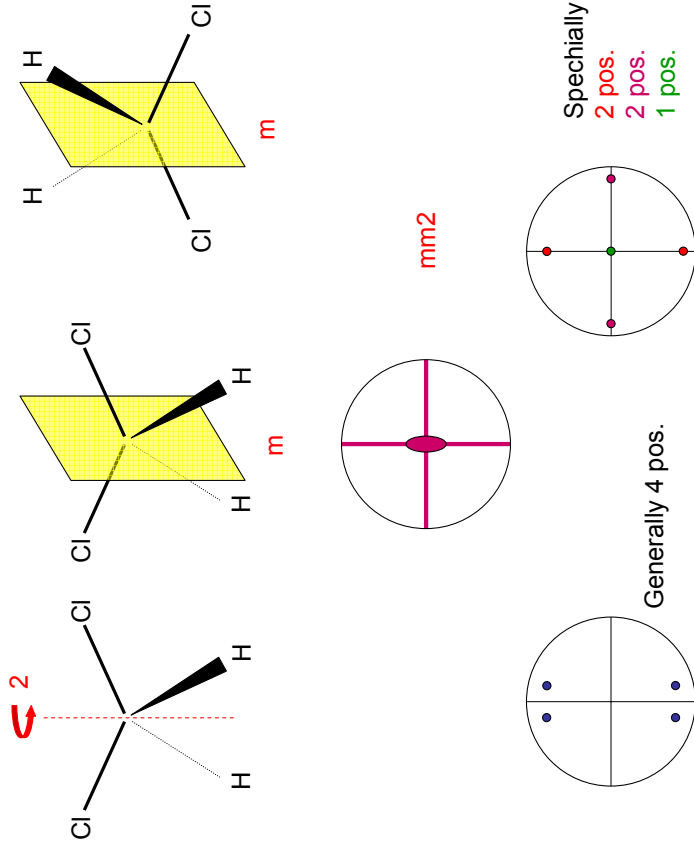
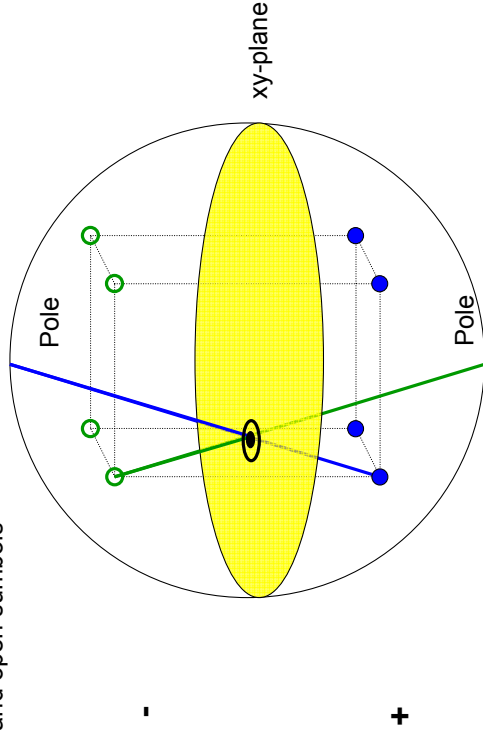
$$\{m[001]\}\{2[001]\} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \{\bar{1}\}$$

$2/m$  centrosymmetric, with the operations: I,  $C_2$ ,  $\sigma_h$ , i

Left hand rule for x,y,z  
Highest rotation axis || z

## Stereographic projection

- The crystal is surrounded by a sphere
- We are interested in the projected surface in a xy-plane through the sphere
- The projected point is determined by the intersection of a connection line from the point of interest to the pole of the opposite side.
- The two halves of the spheres are noted by assigning + and – and to use filled and open symbols



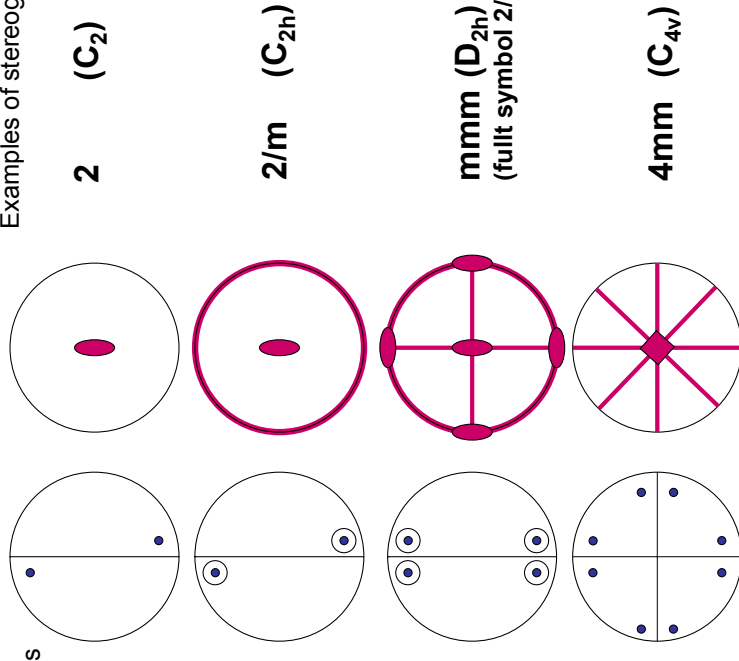
## Symmetry operations

- ◆ Mirrorplane  $m$
  - ◆ Rotationaxis  $n$  (2, 3, 4, 6)
  - ◆ Inversionaxis  $\bar{n}$  ( $\bar{1}$ ,  $\bar{2}$ ...)
  - ◆ Sentrosymmetry  $\bar{1}$
  - ◆ Glidemirrorplane  $n, d, a, b, c$
  - ◆ Screwaxis  $2_1, 3_1, \dots 6_3$
- Pointgroup symmetry
- Special symmetry operations

Examples of stereograms of point groups

Points

Symmetry operations



### Point groups:

A crystallographic pointgroup is a selection of symmetry elements that can operate on a three dimensional lattice. This is only met by 32 pointgroups.

#### Crystal system Crystallographic point group

Triklinic	1, $\bar{1}$
Monoklinic	2, m, 2/m
Orthorhombic	222, mm2, mmm
Tetragonal	4, $\bar{4}$ , 4/m, 422, 4mm, $\bar{4}2m$ , 4/mmm
Trigonal	3, $\bar{3}$ , 32, 3m, $\bar{3}m$
Hexagonal	6, $\bar{6}$ , 6/m, 622, 6mm, $\bar{6}m2$ , 6/mmm
Cubic	23, m3, 432, $\bar{4}3m$ , m3m

Of these are 11 centrosymmetric and 21 non-centrosymmetric.

### Point groups:

A crystallographic pointgroup is a selection of symmetry elements that can operate on a three dimensional lattice. This is only met by 32 pointgroups.

#### Crystal system Crystallographic point group, full symbol

Triklinic	1, $\bar{1}$
Monoklinic	2, m, 2/m
Orthorhombic	222, mm2, 2/m2/m2/m
Tetragonal	4, $\bar{4}$ , 4/m, 422, 4mm, $\bar{4}2m$ , 4/m2/m2/m
Trigonal	3, $\bar{3}$ , 32, 3m, $\bar{3}2/m$
Hexagonal	6, $\bar{6}$ , 6/m, 622, 6mm, $\bar{6}m2$ , 6/m2/m2/m
Cubic	23, 2/m $\bar{3}$ , 432, $\bar{4}3m$ , 4/m $\bar{3}$ 2/m

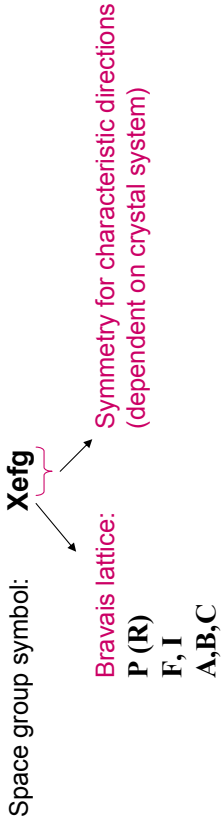
Of these are 11 centrosymmetric and 21 non-centrosymmetric.

	Triclinic	Monoclinic	Tetragonal
X			
$\bar{X}$			
$X+\bar{1}$			
X2		Orthorhombic	
Xm			
$\bar{X}m$			
$X2+\bar{1}$			

	Trigonal	Hexagonal	Cubic
3			
$\bar{3}$			
32			
3m			
$\bar{3}m$			
3m			

# Romgruppe

There are 230 space-groups!



Symmetry operations **without** translation:

- Inversion  $-1, \bar{1}$
- Rotation  $n$
- Mirror  $m$
- Rotation-inversion  $\bar{n}$

Symmetry operations **with** translation:

- Screw-axis  $n_m, 2_1, 6_3, \text{etc.}$
- Glideplane  $a, b, c, n, d$

Non-symmorphic space groups (157 groups)

7 Crystal systems

14 Bravais lattices

32 Point groups



230 Space groups

In order to identify the pointgroup of a space group one must:  
 Change symbols for symmetry elements **with** translation with  
 corresponding symbol for symmetry elements **without** translation

Viz.

$n_m \rightarrow n$  for a screwaxis  
 $a, b, c, d$  or  $n \rightarrow m$  for glide plane

Example:

$P6_3/mmc \rightarrow 6/mmm$   
 $Pnma \rightarrow mmm$

Symmetry planes      Symbol      Translation

Mirror      m      none

Axial glide      a      a/2

                         b      b/2

                         c      c/2

Diagonal glide      n      (a+b)/2, (b+c)/2, (a+c)/2

                         (a+b+c)/2 for cubic and tetragonal only

Diamond glide      d      (a±b)/4, (b±c)/4, (a±c)/4

                         (a±b±c)/4 for cubic and tetragonal only

**$P4/m$**

No. 83

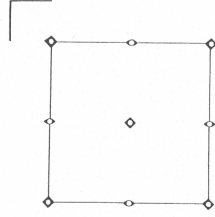
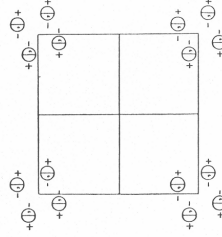
**$C4h$**

$P4/m$

$4/m$

Tetragonal

Patterson symmetry  $P4/m$



Origin at centre ( $4/m$ )

Asymmetric unit  $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1$

Symmetry operations

- (1)  $\bar{1}$  0,0,0
- (2)  $2$  0,0,z
- (3)  $4^+$  0,0,z
- (4)  $4^-$  0,0,z
- (5)  $\bar{1}$  0,0,0
- (6)  $2$  x,y,0
- (7)  $4^+$  0,0,z; 0,0,0
- (8)  $4^-$  0,0,z; 0,0,0

CONTINUED

Generators selected (1);  $r(1,0,0)$ ;  $r(0,1,0)$ ;  $r(0,0,1)$ ; (2); (3); (5)

Positions

- 8 I (1) x,y,z (2) x,y,z (3) y,x,z (4) y,x,z
- (5) x,y,z (6) x,y,z (7) y,x,z (8) y,x,z

Coordinates

- 4 k m.. x,y,1/2 y,x,1/2 y,x,1/2 y,x,1/2
- 4 j m.. x,y,0 x,y,0 y,x,0 y,x,0
- 4 i 2.. 0,1,z 0,1,z 0,1,z 0,1,z
- 2 h 4.. 1,1,z 1,1,z 1,1,z 1,1,z
- 2 g 4.. 0,0,z 0,0,z 0,0,z 0,0,z
- 2 f 2/m.. 0,1,1 1,0,1 1,0,1 1,0,1
- 2 e 2/m.. 0,1,0 1,0,0 1,0,0 1,0,0
- 1 d 4/m.. 1,1,1 1,1,1 1,1,1 1,1,1
- 1 c 4/m.. 1,1,0 1,1,0 1,1,0 1,1,0
- 1 b 4/m.. 0,0,1 0,0,1 0,0,1 0,0,1
- 1 a 4/m.. 0,0,0 0,0,0 0,0,0 0,0,0

Symmetry of special projections

- Along [001]  $P4$
- $a = a$   $b = b$   $c = c$
- Origin at 0,0,0

Maximal non-isomorphic subgroups

- I (2)P4 1,2;3,4
- (2)P3 1,2;7,8
- (2)P2/m 1,2;5,6

Ita none

Itb (2)P4/m ( $c = 2c$ ); (2)C4/c ( $a = 2a, b = 2b$ ); (P4/m); (2)F4/m ( $a = 2a, b = 2b, c = 2c$ ); (4/m)

Maximal isomorphic subgroups of lowest index

Itc (2)P4/m ( $c = 2c$ ); (2)C4/m ( $a = 2a, b = 2b$ ); (P4/m)

Minimal non-isomorphic supergroups

- I (2)P4/m m; (2)P4/m c; (2)P4/m b m; (2)P4/m a c
- II (2)F4/m

Along [100]  $P2/m$

$a = a$   $b = b + c$   $c = c$

Origin at x,x,0

**$C2/c$**

No. 15

**$C2h$**

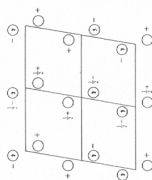
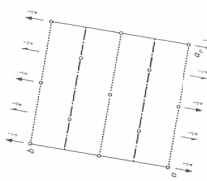
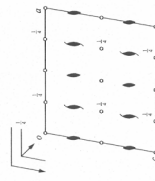
$C12/c1$

$2/m$

Monoclinic

Patterson symmetry  $C12/m$

UNIQUE AXIS  $b$ , CELL CHOICE 1



Origin at  $\bar{1}$  on glide plane  $c$

Asymmetric unit  $0 \leq x \leq 1; 0 \leq y \leq 1; 0 \leq z \leq 1$

Symmetry operations

- For (0,0,0)+ set
- (1)  $\bar{1}$
- (2)  $2$  0,y,1/2
- (3)  $\bar{1}$  0,0,0
- (4)  $c$  x,0,z
- For (1/2,1/2,0)+ set
- (1)  $\bar{1}$  (1/2,1/2,0)
- (2)  $2$  (0,1/2,0)  $\bar{1}$ , y,1/2
- (3)  $\bar{1}$  (1/2,1/2,0)
- (4)  $n$  (1/2,1/2)  $\bar{1}$ , z,1/2

**CuO**

$a = 465$  pm,  $b = 341$  pm,  $c = 511$  pm,  $\beta = 99.5^\circ$

Spacegroup  **$C2/c$**

Cu in  **$4c$**

O in  **$4e$**   $y = 0.416$

Crystal system:  $a \neq b \neq c$ ,  $\alpha = \gamma = 90^\circ$ ,  $\beta \neq 90^\circ$

Bravais-lattice: **C** monoclinic, side centered

Corresponding crystallographic point group:  **$2/m$**

CONTINUED

Generators selected (1); (1,0,0); (0,0,1); (1,1,0); (2); (3)

Positions  
Multiplicity  
Site symmetry  
Site symmetry

8 f 1 (1) x,y,z (2) x,y,z+1/2 (3) x,y,z+1/2 (4) x,y,z+1/2

Reflection conditions  
General:  
hk: h+k=2n  
0k: k=2n  
hk0: h+k=2n  
0k0: k=2n  
00l: l=2n  
00l: l=2n

Special: as above, plus  
no extra conditions  
hk: k+l=2n  
hk: k+l=2n  
hk: l=2n

Along [100] p 2g m  
a'=1/2 b'=c'  
Origin at x,0,0

Symmetry of special projections  
Along [001] c 2n m  
a'=a b'=b  
Origin at 0,0,z

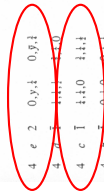
Maximal non-isomorphic subgroups  
I (1)C1 (C2) (1)C2 (C2)  
IIa (2)P1/2c1 (P2/c) 1;2;3;4  
IIb none

Maximal isomorphic subgroups of lowest index  
Iic (3)C1/2c1 (b=3b) (C2/c); (3)C1/2c1 (c=3c) (C2/c); (3)C1/2c1 (d=3a or a=3a, c'=a+c or a'=3a, c'=a+c) (C2/c)

Minimal non-isomorphic supergroups  
I (2)C2cm; (2)Cmc; (2)Cccm; (2)Ccc; (2)Fdd; (2)Fbam; (2)Fba; (2)Fcc; (3)P3; (3)C2/c

II (2)F1/2m1 (C2/m); (2)C1/2m1 (2c'=c) (C2/m); (2)P1/2c1 (2a'=a, 2b'=b) (P2/c)

O  
Cu



CuO  
a = 465 pm, b = 341 pm, c = 511 pm, β = 99.5°  
Spacegroup C2/c  
Cu in 4c  
O in 4e y = 0.416

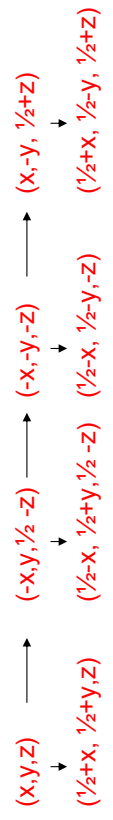
Crystal system: a ≠ b ≠ c, α = γ = 90°, β ≠ 90°

Bravais-lattice: C monoclinic, side centered

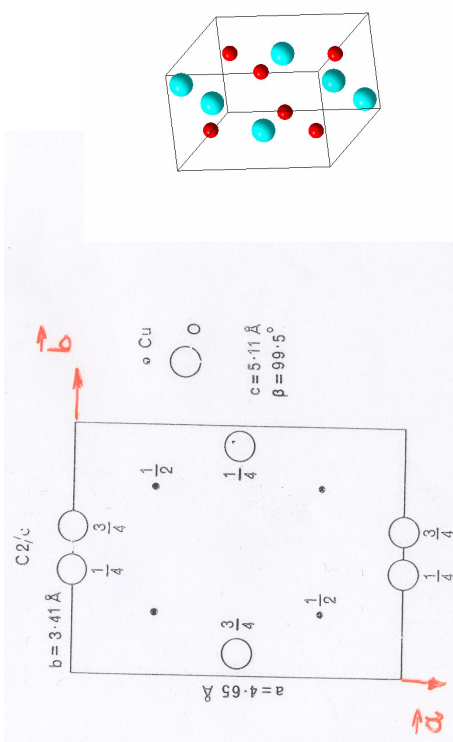
Corresponding crystallographic point group: 2/m

Atom coordinates: Cu 1/4, 1/4, 0  
O 0, 0.416, 1/4

Symmetry operations on a general position:



CuO



The crystal structure of tenorite, CuO. The two upper diagrams are the conventional diagrams for the monoclinic space group C2/c. The lower diagram is a plan of the structure of CuO on (001).

Cu: 1/4, 1/4, 0 etc.  
O: 0, y, 1/4 mod  
y = 0.416 (eksperimentelt)

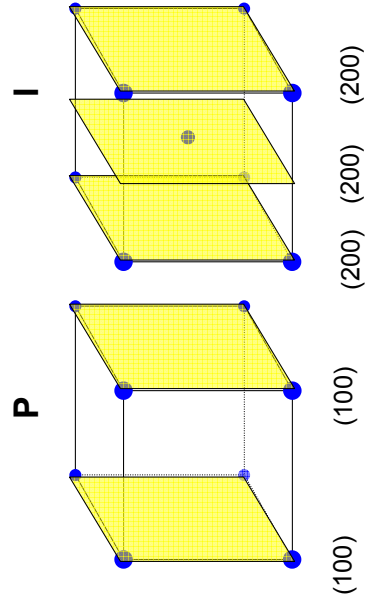
# Millerplan

## Crystal plane and crystal directions

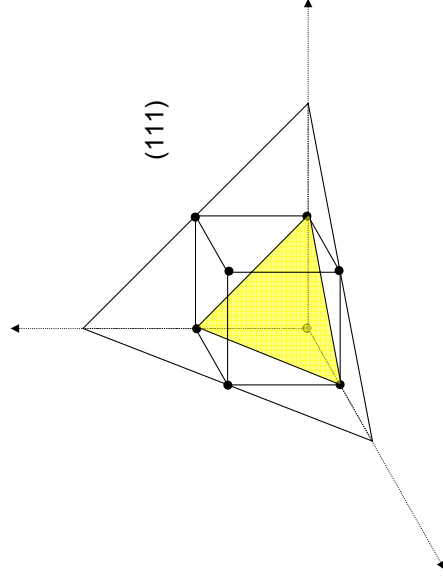
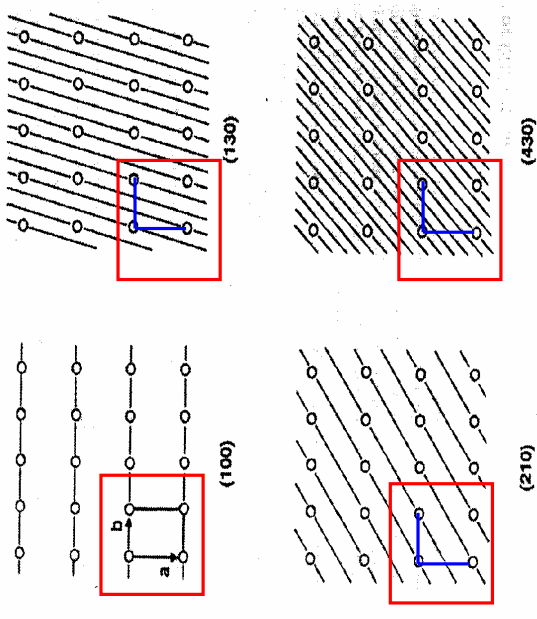
- A plane  $(h\ k\ l)$
- A set of equivalent planes  $\{h\ k\ l\}$
- A direction  $[h\ k\ l]$
- A set of equivalent directions  $\langle h\ k\ l \rangle$

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

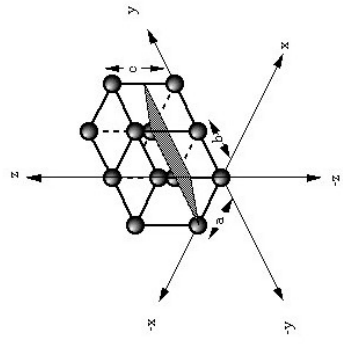
e.g. fcc  $\langle 111 \rangle$   
 $[111]$   $[\bar{1}11]$   $[\bar{1}\bar{1}1]$   $[1\bar{1}\bar{1}]$   
 $[\bar{1}\bar{1}\bar{1}]$   $[11\bar{1}]$   $[1\bar{1}1]$   $[\bar{1}1\bar{1}]$



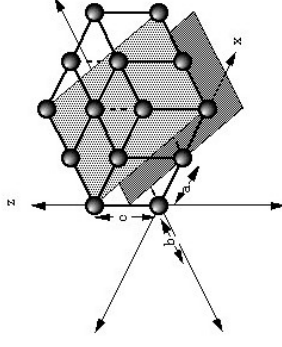
## Miller indices, 2D



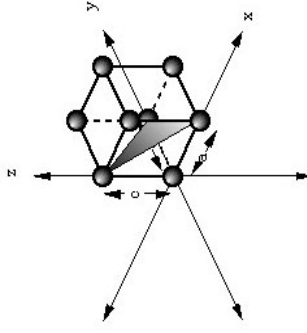




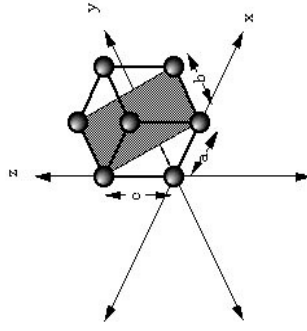
intercept length	a	b	c
reciprocal	$\frac{1}{a}$	$\frac{1}{b}$	$\frac{1}{c}$
cleared fraction	1	0	2
Miller indice	$(\bar{1}02)$		



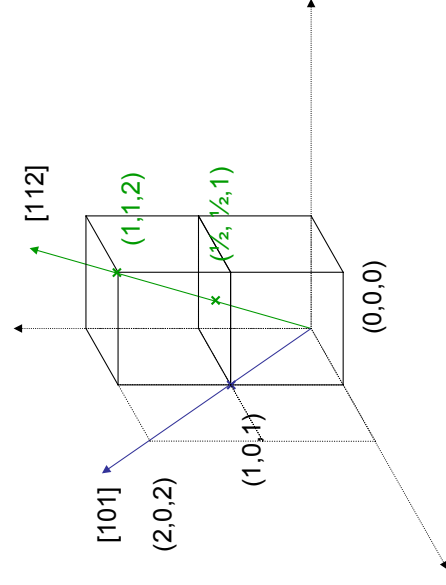
intercept length	a	b	c
reciprocal	$\frac{1}{a}$	$\frac{1}{b}$	$\frac{1}{c}$
cleared fraction	1	0	2
Miller indice	$(102)$		



intercept length	a	b	c
reciprocal	$\frac{1}{a}$	$\frac{1}{b}$	$\frac{1}{c}$
cleared fraction	1	1	1
Miller indice	$(111)$		



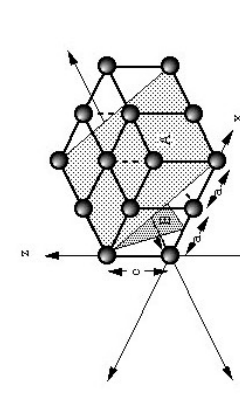
intercept length	a	b	c
reciprocal	$\frac{1}{a}$	$\frac{1}{b}$	$\frac{1}{c}$
cleared fraction	1	0	1
Miller indice	$(101)$		



Directions

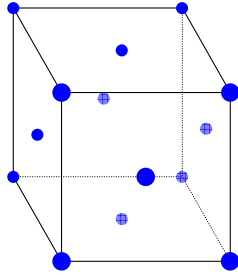
$$[\frac{1}{2}0\frac{1}{2}] = [101] = [202] = n[101]$$

Parallel directions have same index

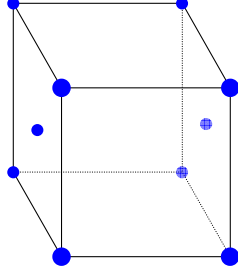


	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	$\infty$	2	$\frac{1}{2}$	$\infty$	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	$(102)$			$(201)$		

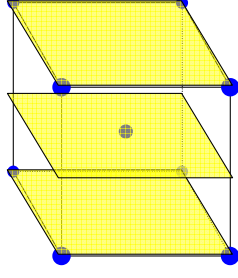
F



C



I



(100) (200)

Conditions for Bragg reflections.

- hkl;
- $h+k = 2n$
- $k+l = 2n$
- $l+h = 2n$
- all odd
- all even

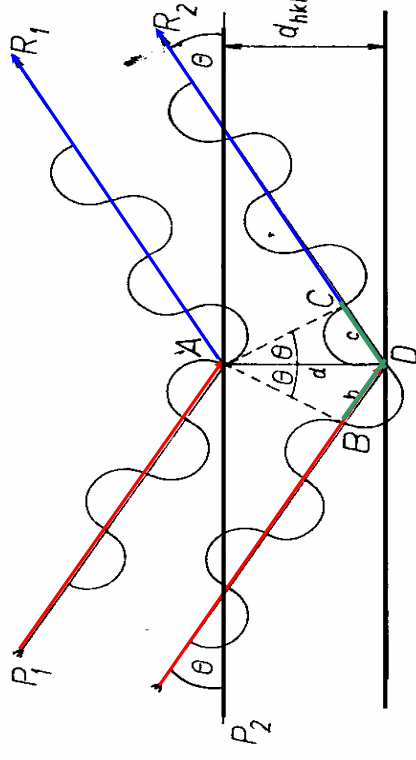
$$h+k+l = 2n$$

$$h+k = 2n$$

P lattice has no conditions

In addition to this, there will be effects from: screw axis and glide planes.

## Braggs lov



$$BD = d \sin \theta \quad DC = d \sin \theta \Rightarrow BDC = 2d \sin \theta = n\lambda$$

$$\lambda = 2d_{hkl} \sin \theta$$

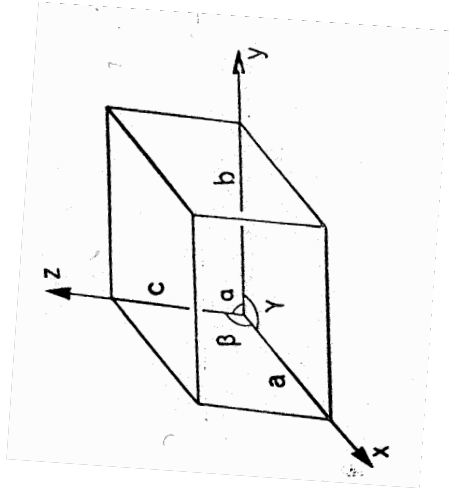
## Density

- Experimental (pyknometric)
- Calculated; X-ray density based on the assumption that the unit cell is known or that a model exists
- Wetting
- Pores in the material

$$\rho_{\text{X-ray}} > \rho_{\text{exp.}}$$

$$\rho_{\text{X-ray}} = \left( \frac{m}{V} \right)_{\text{unitcell}} = \frac{\text{Formula weight} \cdot \text{number of units / cell}}{\text{Unitcell volume} \cdot N_A}$$

# Røntgentetthet



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

# Endring av enhetscelle

## Density and defects

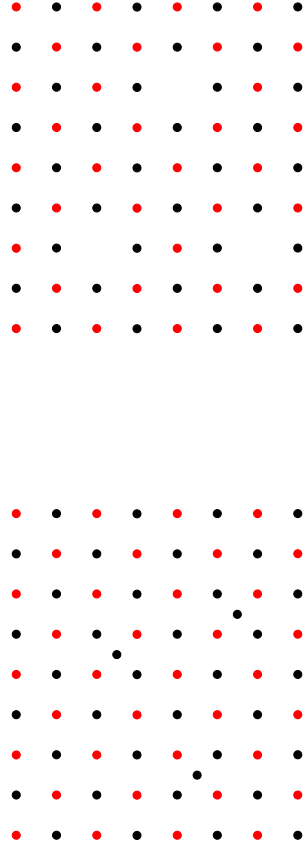
$\rho_{obs}$

- V unitcell; is determined experimentally
- Formula weight

$\rho_{calc}$



Model assumptions:  
 $A/B < 1$

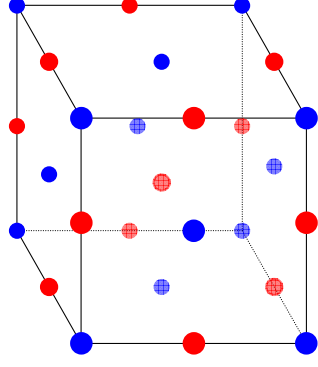


$AB_{1+y}$

$A_{1-x}B$

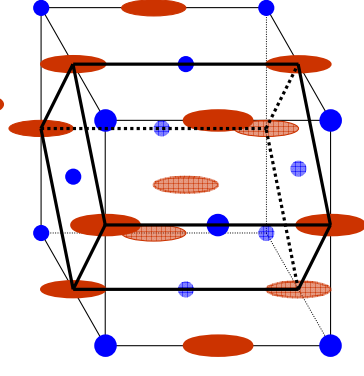
$\rho(\text{interstitial B}) > \rho(\text{perfect}) > \rho(\text{vacant space A})$

● NaCl

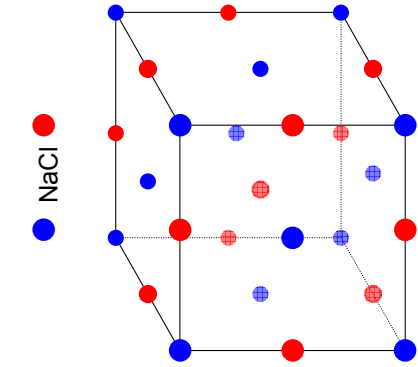


Cubic  
 $z = 4$

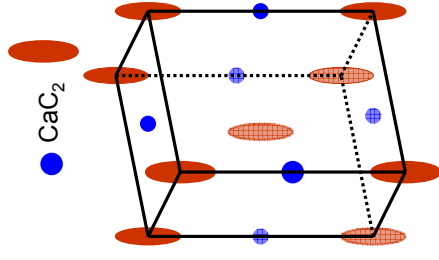
●  $CaC_2$



Non-cubic

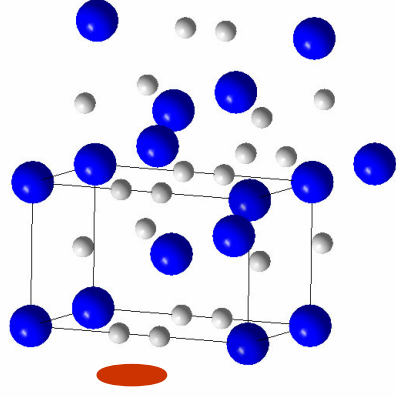


Cubic  
Z = 4

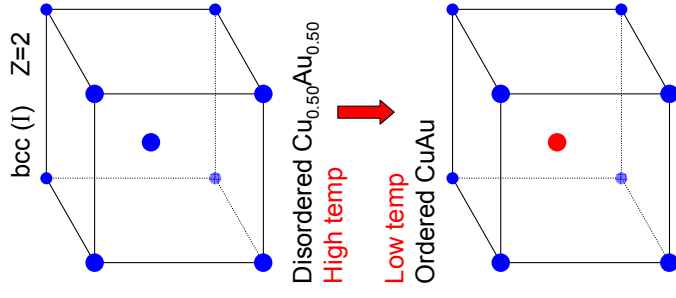
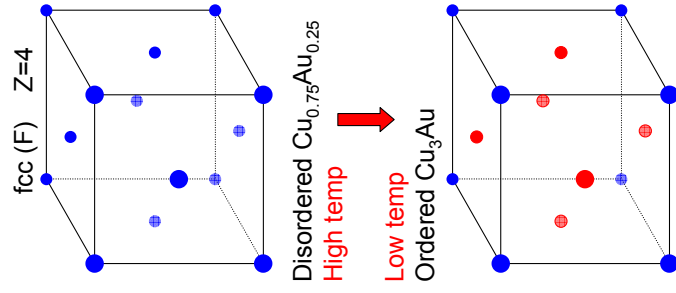
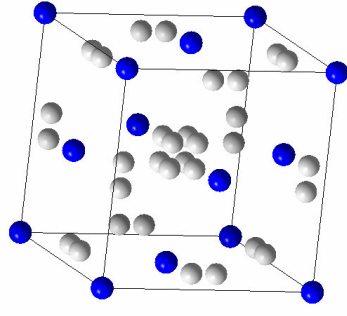


Non-cubic  
Tetragonal  
Z = 2

CaC<sub>2</sub> (tt)

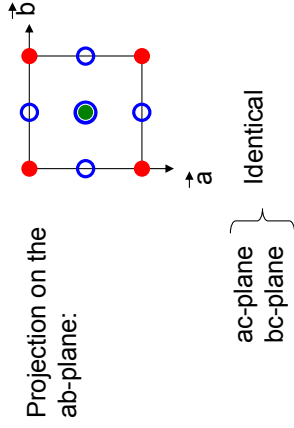
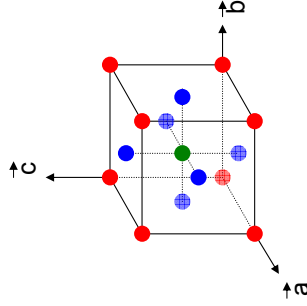


CaC<sub>2</sub> (ht)



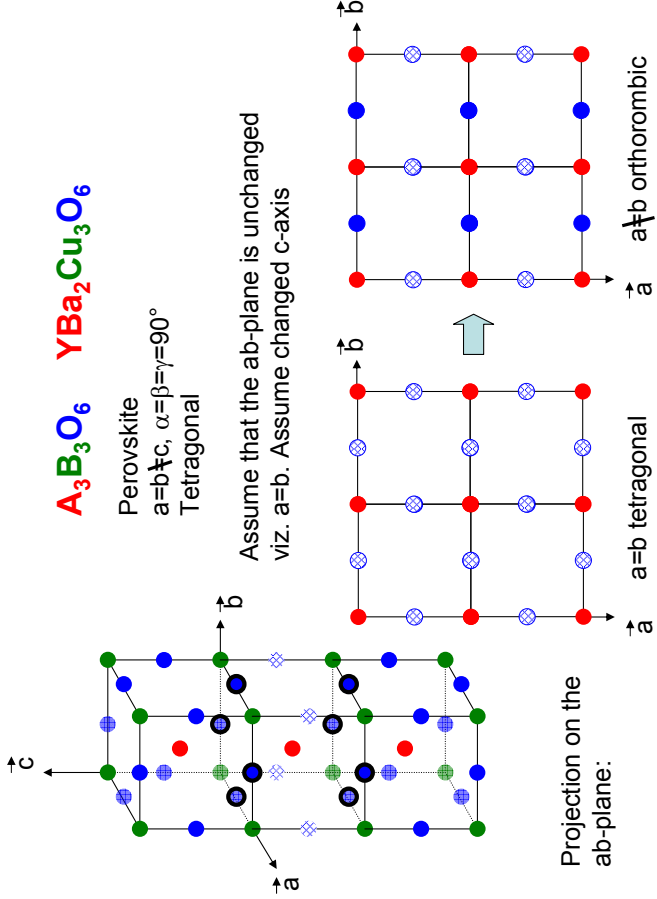
ABO<sub>3</sub>

Perovskite  
a=b=c, α=β=γ=90°  
cubic



Cell dimensions are determined by:  
A-O-A

# Kulepakking



Atoms as spheres:

- ions
- metal atoms
- molecules

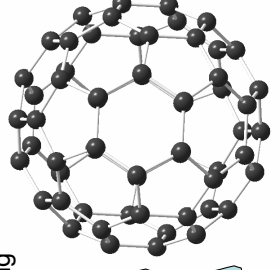
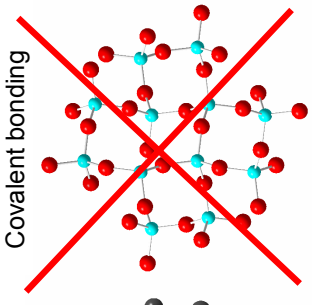
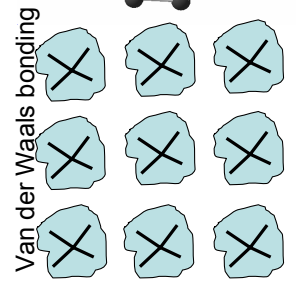
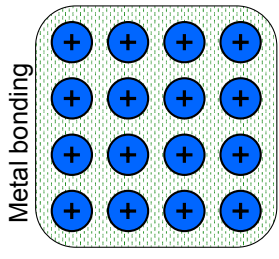
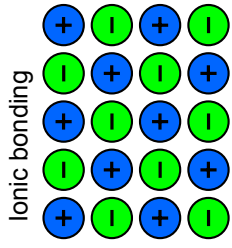


Table 1.2 Types of solids

Type	Units present	Characteristics	Examples	Approximate cohesive energy, $\text{kJ mol}^{-1}$
Ionic	Positive and negative ions	Brittle, insulating and fairly high melting	NaCl LiF	795 1010
Covalent	Atoms (bonded to one another)	Hard, high melting and nonconducting (when pure)	Diamond SiC	715 1010
Metallic	Positive ions embedded in a collection of electron 'gas'	High conductivity	Na Fe	110 395
Van der Waals (Molecular)	Molecules or atoms	Soft, low melting, volatile and insulating	Argon $\text{CH}_4$	7.6 10
Hydrogen-bonded	Molecules held together by hydrogen bonds	Low melting insulators	$\text{H}_2\text{O}$ (ice) HF	50 30

## 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.

AB.....	hcp	hexagonal close packed
ABC.....	ccp	cubic close packed
AA.....		primitive hexagonal packing

Closest (densest) packing of spheres:

74% of the volume is filled by the spheres



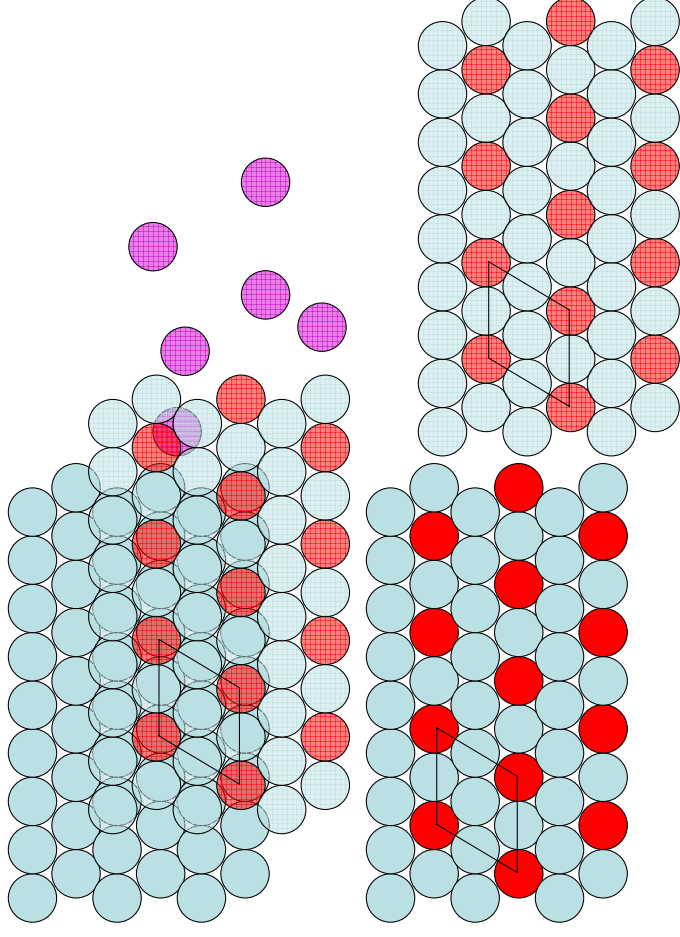
26% voids / vacant space

The voids/holes will have different appearance:

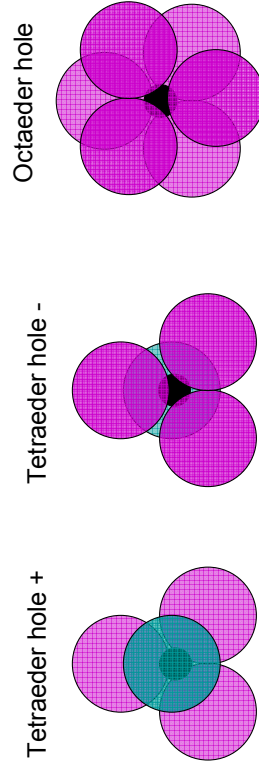
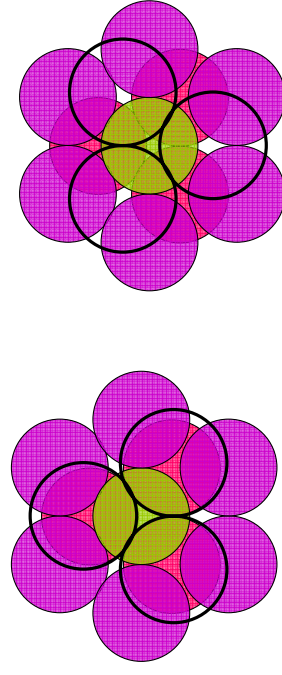
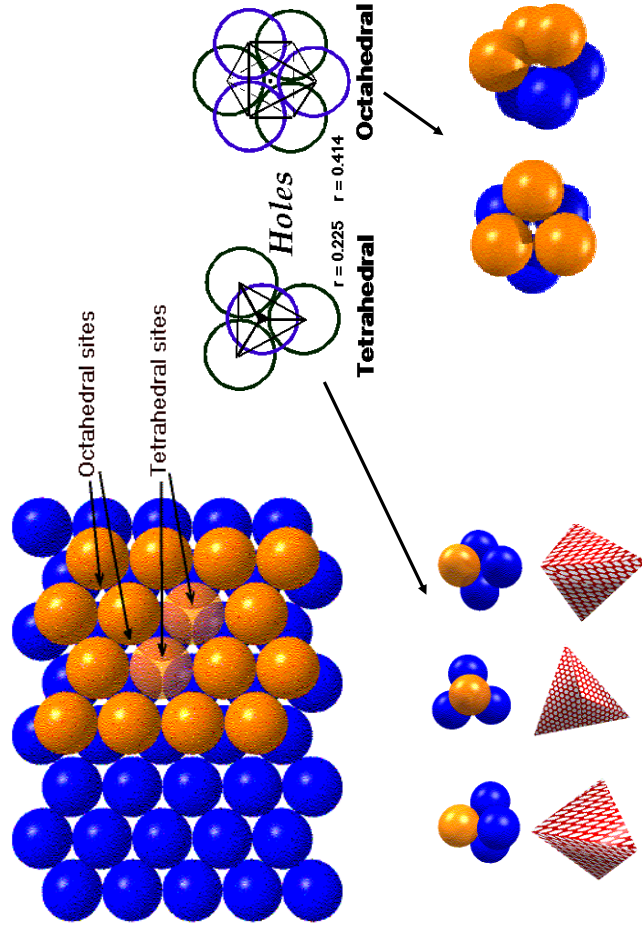
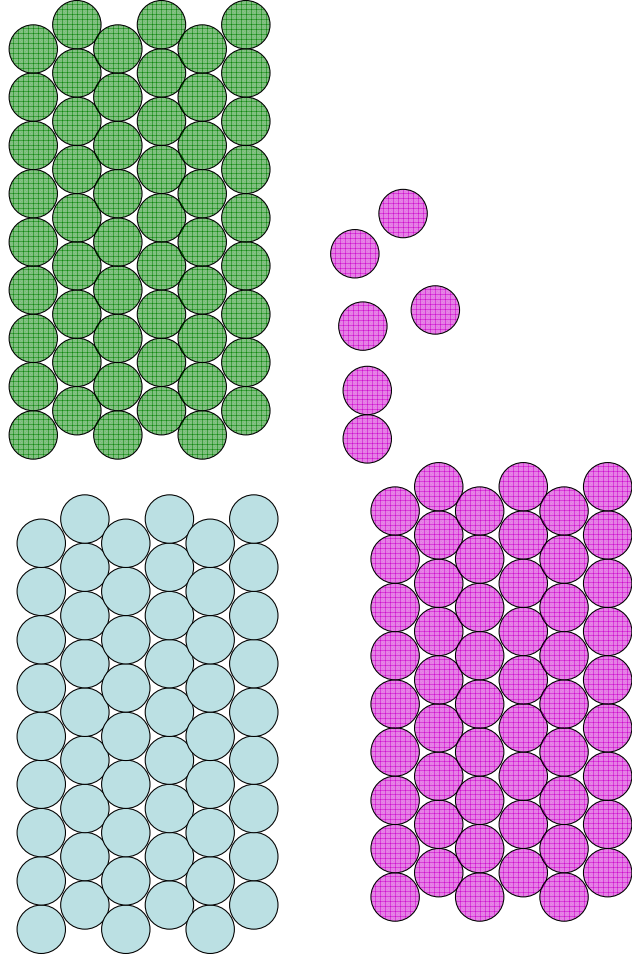
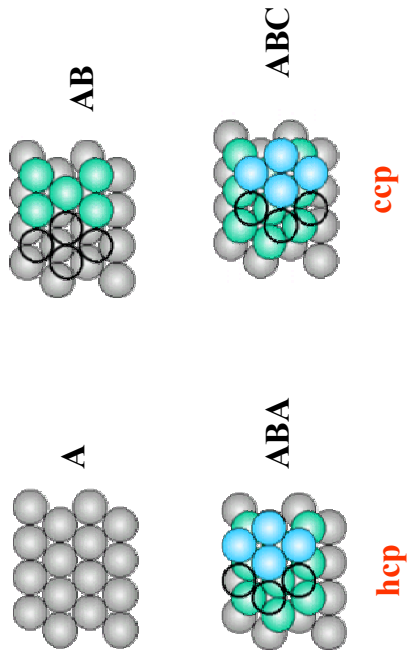
- Octahedral shape
- Tetrahedral shape
- (Trigonal prismatic holes)
- (Trigonal bipyramidal holes)

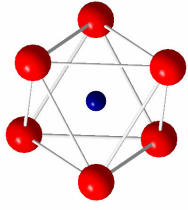
The voids/holes may be filled with atoms

- of the same type as the packing spheres
- of different type



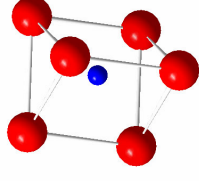
# Dense sphere packing





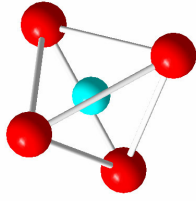
Octahedra holes

**CN = 6**



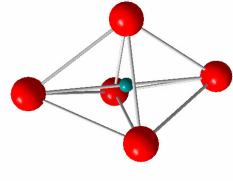
Hexagonal packing (AA...)  
Trigonal prismatic holes

**CN = 6**



Tetrahedra holes

**CN = 4**



Hexagonal closepacked (AB..)  
Trigonal bipyramidal

**CN = 5**

*Type of hole*  
Trigonal prismatic  
Tetragonal  
Octahedral

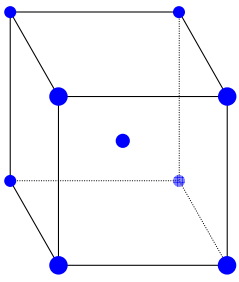
*Number*  
2N  
2N  
N

*Max. radius*  
0.528  
0.225  
0.414

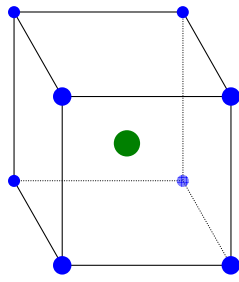
# Plussering

## bcc, fcc, ccp

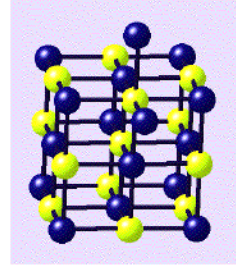




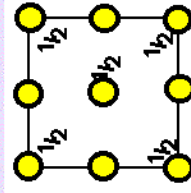
bcc, cubic, I-centered  
 $(0,0,0) + (1/2, 1/2, 1/2)$   
 CN = 8



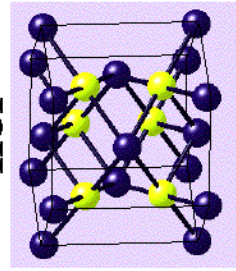
CsCl-type structure, CN = 8  
 M in  $(0,0,0)$   
 X in  $(1/2, 1/2, 1/2)$   
 Not I-centered,  $\rightarrow$  P



CCP



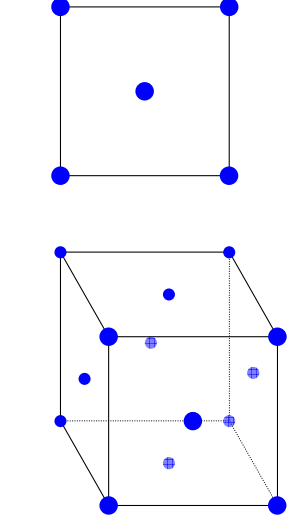
Location of  
**OCTAHEDRAL**  
 Interstitial  
 Holes  
 1 per sphere



HCP



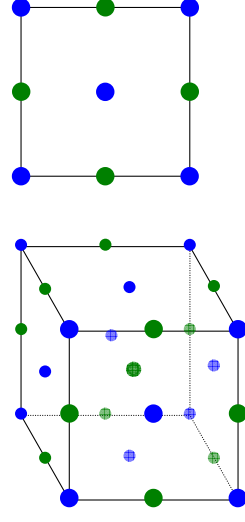
Location of  
**OCTAHEDRAL**  
 Interstitial  
 Holes  
 1 per sphere



fcc, Cubic F-centered  
 lattice

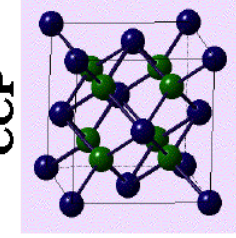
Structure = lattice +  
 basis (motif)

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

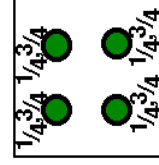


NaCl-type structure =  
 cubic + basis

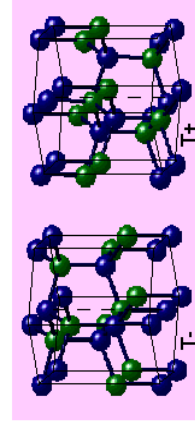
F-centered lattice:  
 Na in  $(0,0,0)$   
 Cl in  $(1/2,0,0)$



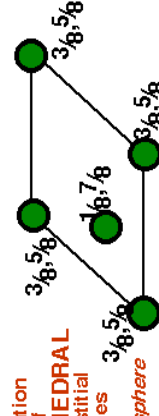
CCP



Location of  
**TETRAHEDRAL**  
 Interstitial  
 Holes  
 2 per sphere

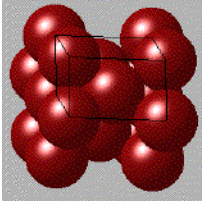


HCP



Location of  
**TETRAHEDRAL**  
 Interstitial  
 Holes  
 2 per sphere

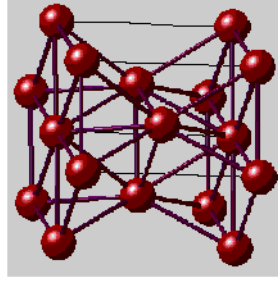
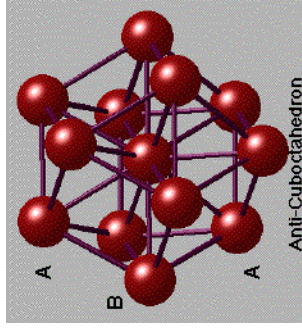
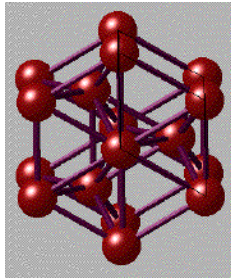
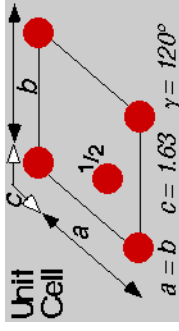
## hcp (hexagonal close packed)



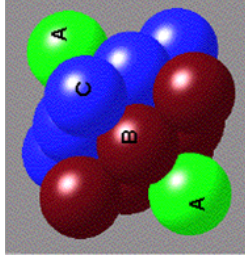
$Z = 2$

2 atoms in unitcell:

$(0, 0, 0), (2/3, 1/3, 1/2)$



## ccp (cubic close packed)

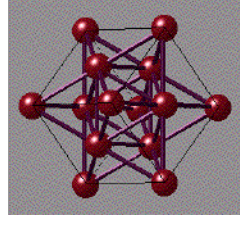
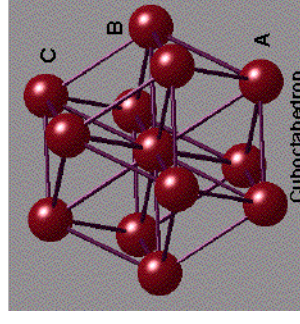
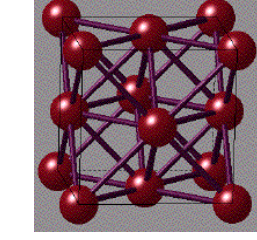
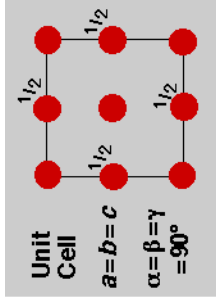


$Z=4$

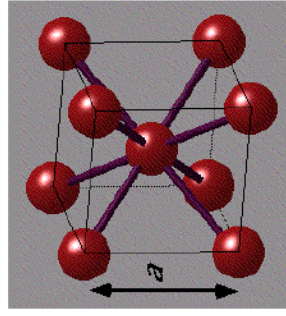
4 atoms in unitcell:

$(0, 0, 0) (0, 1/2, 1/2)$

$(1/2, 0, 1/2) (1/2, 1/2, 0)$

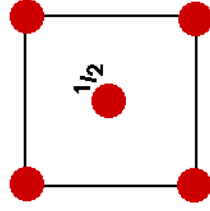


## bcc



Body-Centred Cubic

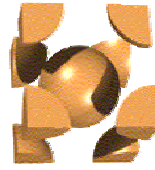
**BCC**



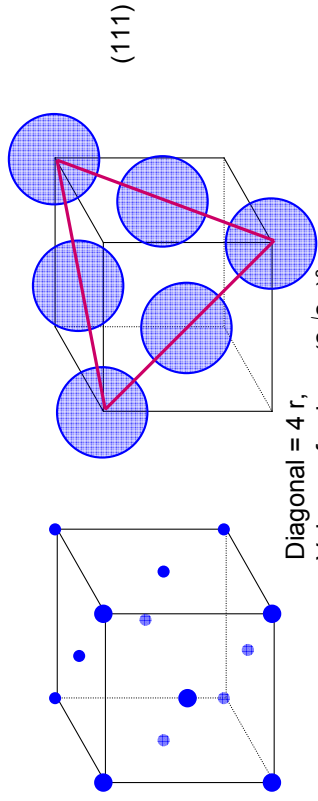
$Z=2$

2 atoms in unitcell:

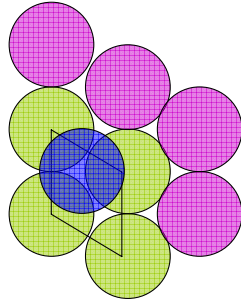
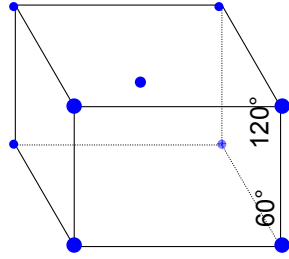
$(0, 0, 0) (1/2, 1/2, 1/2)$



# Hull



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



## 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

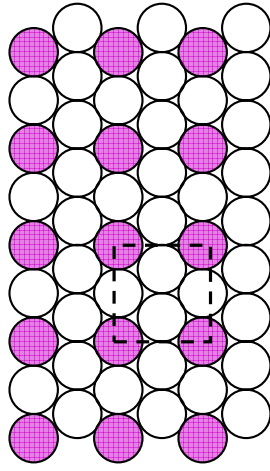
# Strukturen für Kugelpackung

## Structure (types) derived from dense closepacking of spheres

### Principle:

- 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**



**B** Filling of holes (interstitial positions)

$AB_n$     $M_mX$   
 X = Packing sphere

Filling degree	$AB_n$	$M_mX$	Spherepacking	hcp	
All octaederholes		AB	MX	NaCl	NIAs
All tetraederholes		$AB_2$	$M_2X$	$CaF_2$	
$1/2$ tetraederholes	AB	MX	ZnS(bl.)		ZnS(wu.)
$1/2$ octaederholes	$AB_2$	$M_{1/2}X$	$CdCl_2$		$CdI_2$ , $Cd(OH)_2$
$1/3$ octaederholes	$AB_3$	$M_{1/3}X$	$CrCl_3$		$BiI_3$ , $\beta$ - $ZrCl_3$

**C**

Mixed spheres in dense packed layers  
 + filling of interstitial holes

A, B   cations  
 X   anion

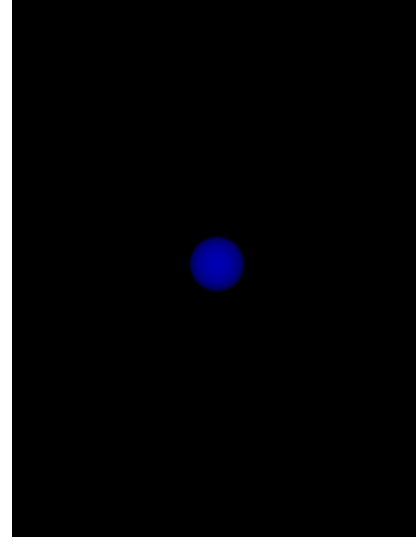
A and X of similar size  
 B is so small that it fits into octaeder holes

$AX_3$  densepacked layers

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

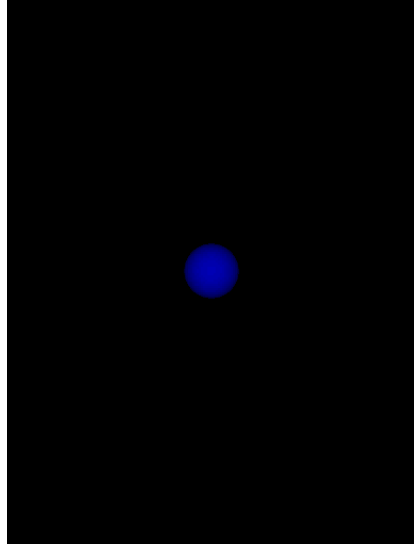
$ABX_3$    perovskite type structure

# Perovskite

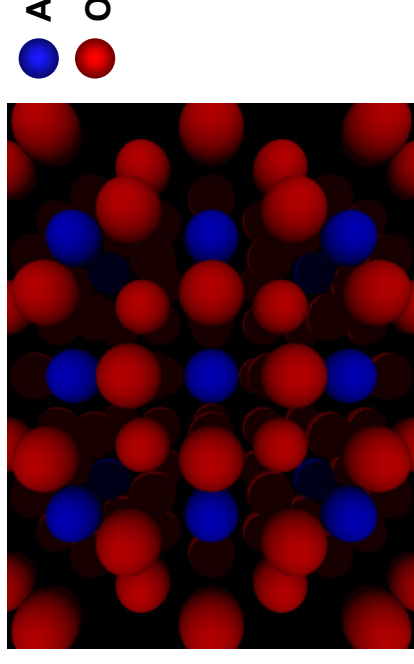


**A**

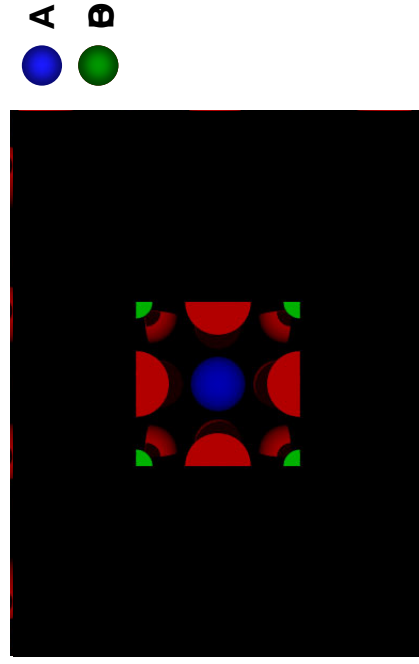
# Perovskite



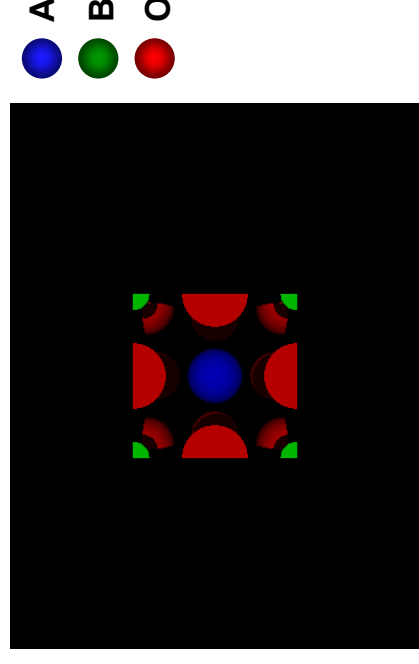
# Perovskite



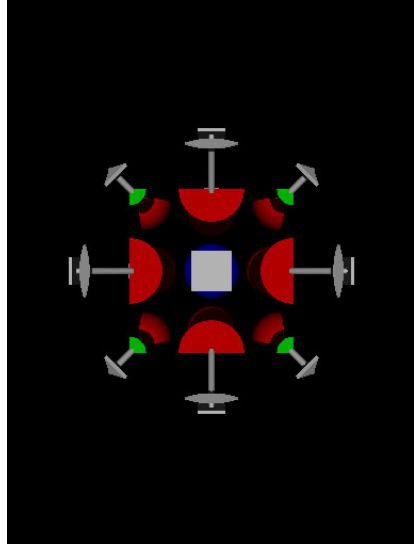
# Perovskite



# Perovskite

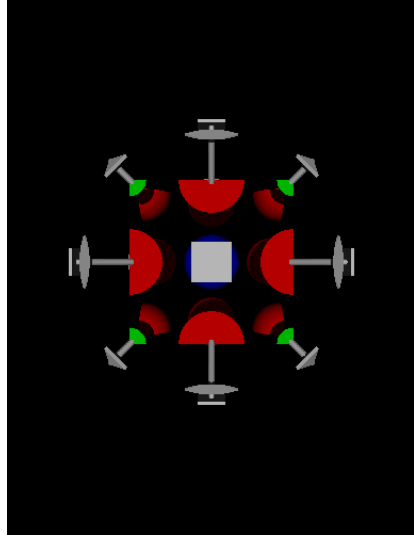


# Perovskite



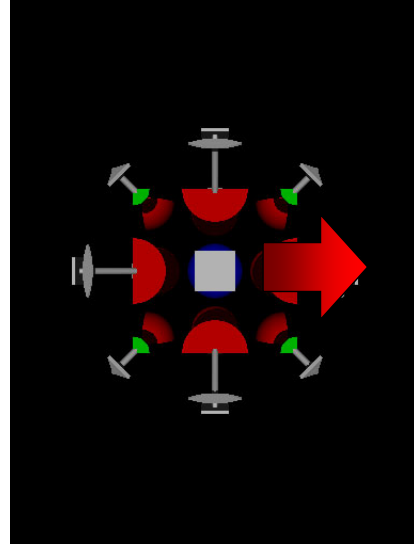
A B O

# Perovskite



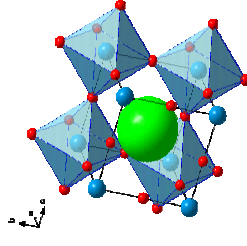
A B O

# Perovskite



A B O

Interesting properties



## Property

Insulator  
High-K dielectric  
Semiconductivity  
Half metallicity

## Compound examples

LaGaO<sub>3</sub>, LaAlO<sub>3</sub>, LaCrO<sub>3</sub>, LaFeO<sub>3</sub>  
BaTiO<sub>3</sub>, Ba<sub>2</sub>EuZrO<sub>5.5</sub>, CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>  
LaMnO<sub>3</sub>, PbCrO<sub>3</sub>, RTiO<sub>3</sub> (R = La...Tm)  
LaBaMn<sub>2</sub>O<sub>5.5</sub>, YBaMn<sub>2</sub>O<sub>5.5</sub>  
Sr<sub>2</sub>FeMoO<sub>6</sub>, Ba<sub>2</sub>FeMoO<sub>6</sub>, Ca<sub>2</sub>FeMoO<sub>6</sub>,  
Ca<sub>2</sub>FeReO<sub>6</sub>

Metallic conductivity LaNiO<sub>3</sub>

Superconductivity YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, HgBa<sub>2</sub>CuO<sub>4</sub>, La<sub>1.5</sub>Nd<sub>0.5</sub>CaBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-z</sub>,  
Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10-d</sub>, HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub>

Colossal

magnetoresistance A<sub>0.3-0.7</sub>MnO<sub>3</sub> (A = Ca, Sr, Pr, Pb)

Multi ferroics BiMnO<sub>3</sub>, BiFeO<sub>3</sub>,

Ferroelasticity LaCoO<sub>3</sub>

Ferromagnetic SrRuO<sub>3</sub>, LaMnO<sub>3.15</sub>, La<sub>1-x</sub>Ca<sub>x</sub>MnO<sub>3</sub>, Sr<sub>1-x</sub>LaMnO<sub>3</sub>

Anti ferro BiMnO<sub>3</sub>, LaFeO<sub>3</sub>, LaMnO<sub>3</sub>

Piezoelectricity PbZr<sub>0.47</sub>Ti<sub>0.53</sub>O<sub>3</sub>

Spin glass CaRuO<sub>3</sub>

Multi valence

materials Ca<sub>3</sub>Co<sub>2</sub>O<sub>6</sub>, Sr<sub>4</sub>Fe<sub>4</sub>O<sub>11</sub>, YBaMn<sub>2</sub>O<sub>5.5</sub>

# Polyederpakking

## Space filling of polyhedra

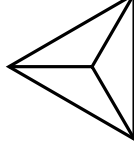
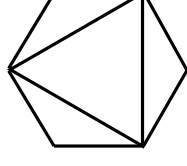
Structures can be described as connections of polyhedra that share:

- Corners
- Edges
- Faces

The polyhedra are simplified for visual clarity.

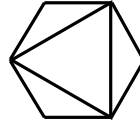
Type of polyhedra:

- Tetrahedra
- Octahedra
- Trigonal prismatic
- ...

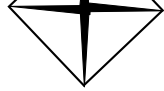


Basically the same types of polyhedra as mention for sphere packing

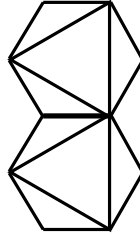
## Limited units, Octahedra



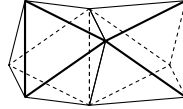
Isolated octahedra



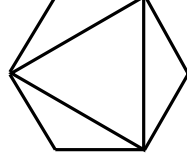
Dimer



Dimer



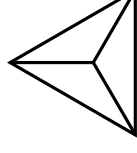
Dimer



Octahedra

Connected by:

- Corners
- Edges
- (Faces)



Tetrahedra

Connected by:

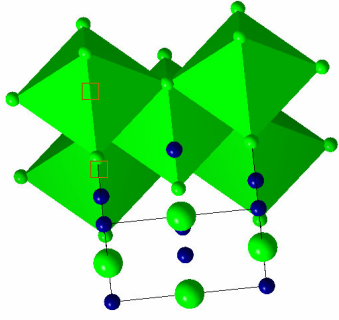
- Corners
- (Edges)

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



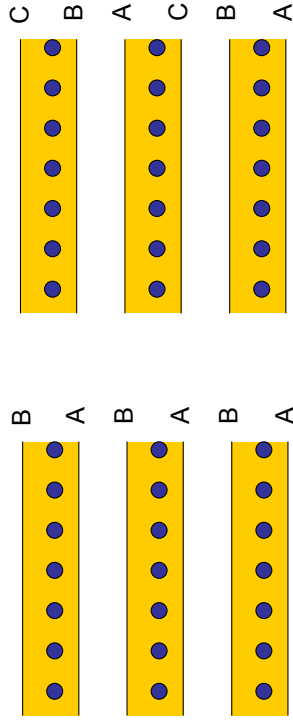


NaCl  
NaCl<sub>6</sub>, C1Na<sub>6</sub>



# CdI<sub>2</sub>

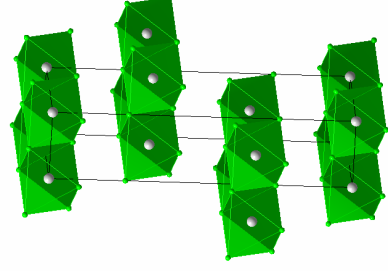
## CdCl<sub>2</sub> / CdI<sub>2</sub> type structures



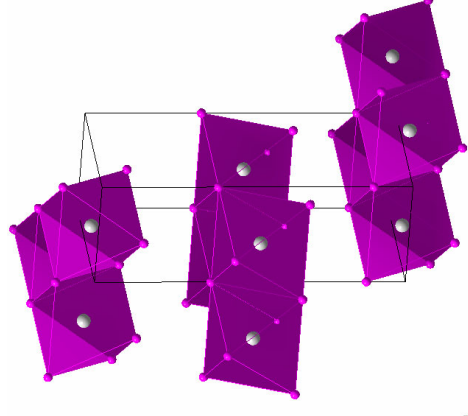
**Within the layers: CdX<sub>6</sub>-octahedra**  
**Between the layers: only van der Waals interactions**

Polymorphs:  
 in 2-dimensions -> same structure with strong bonds  
 different repetition in the 3rd direction, can have weak bonds

CdCl<sub>2</sub>



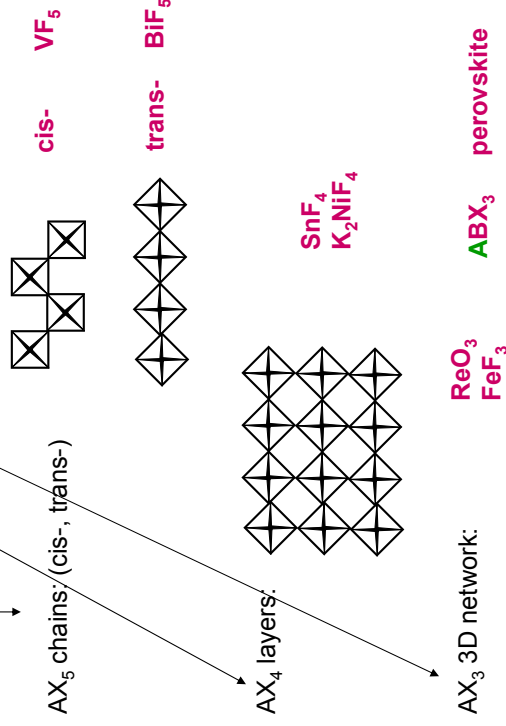
CdI<sub>2</sub>



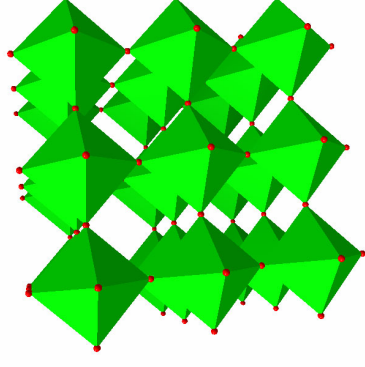
## Infinite systems; octahedra by cornersharing

Number of corners shared in a given octahedra:

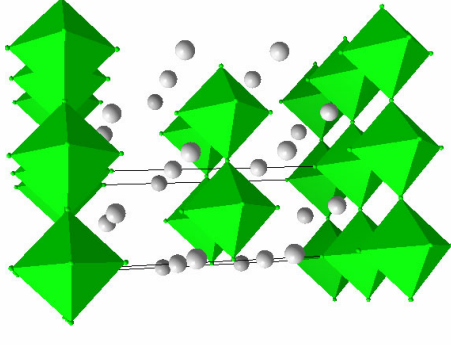
2, (3), 4, (5), 6



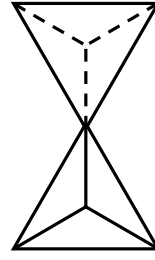
ReO<sub>3</sub>



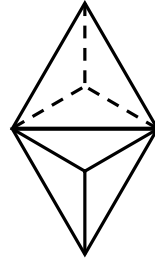
K<sub>2</sub>NiF<sub>4</sub>



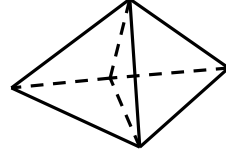
## Polymerization of MX<sub>4</sub> tetrahedra



Corner sharing:  
 $d(M-M) = 2 \cdot d(M-X)$   
 2.0 only observed for SiO<sub>4</sub>  
 Si<sup>4+</sup> - Si<sup>4+</sup> repulsions



Edge sharing:  
 $d(M-M) = 1.16 \cdot d(M-X)$



Face sharing:  
 $d(M-M) = 0.67 \cdot d(M-X)$

## Structures based on tetrahedra

No. shared vertices only shared, Vertices common to two tetrahedra

shared vertices

Formula

Type of complex

Examples

1	A <sub>2</sub> X <sub>7</sub>	Finite molecule or pyro ion	Cl <sub>2</sub> O <sub>7</sub> , S <sub>2</sub> O <sub>7</sub> <sup>2-</sup> , etc.
2	(AX) <sub>3</sub> <sub>n</sub>	Cyclic molecule, or meta-ion infinite chain	S <sub>3</sub> O <sub>9</sub> , Se <sub>4</sub> O <sub>12</sub> , (PnCl <sub>2</sub> ) <sub>n</sub> (P <sub>4</sub> O <sub>12</sub> ) <sup>4-</sup> , (Si <sub>3</sub> O <sub>9</sub> ) <sup>6-</sup> , (SO <sub>3</sub> ) <sub>n</sub> , (PO <sub>3</sub> ) <sub>n</sub> <sup>-</sup>
3	(A <sub>2</sub> X <sub>5</sub> ) <sub>n</sub>	Finite polyhedral, double chain, layer or 3D structure	P <sub>4</sub> O <sub>10</sub> Al[AlSiO <sub>5</sub> ] P <sub>2</sub> O <sub>5</sub> , Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> P <sub>2</sub> O <sub>5</sub> , La <sub>2</sub> [Be <sub>2</sub> O <sub>5</sub> ]
4	(AX) <sub>2</sub> <sub>n</sub>	Layer, double layer, or 3D structure	HgI <sub>2</sub> (red) CaSi <sub>2</sub> Al <sub>2</sub> O <sub>8</sub> (hexag.) SiO <sub>2</sub> structures, GeS <sub>2</sub>

Vertices common to three tetrahedra

3 (AX)<sub>2</sub><sub>n</sub>

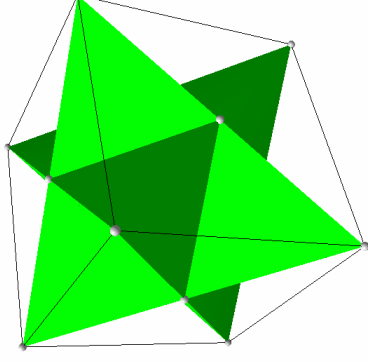
Infinite layer

AlOCl, GaOCl

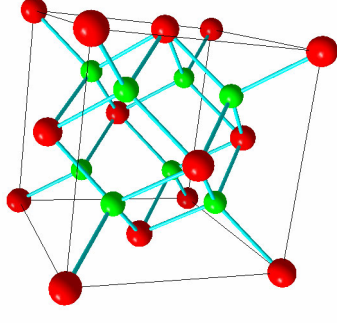
## Structures based on tetrahedra

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	$Li_2O$ , $F_2Ca$
<i>Vertices and edges shared</i>			
	$(AX)_n$	Double layer	$La_2O_3$ , $Ce_2O_2S$ , $U_2N_2Sb$
	$(AX)_n$	3D structure	$\beta$ -BeO

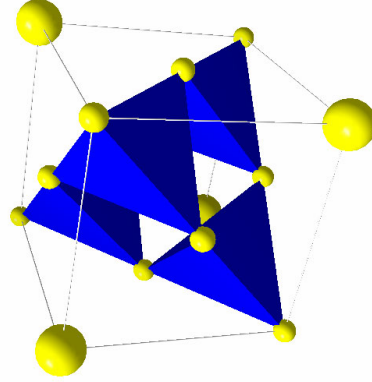
$CaF_2$   
 $FCa_4$  - tetraheda



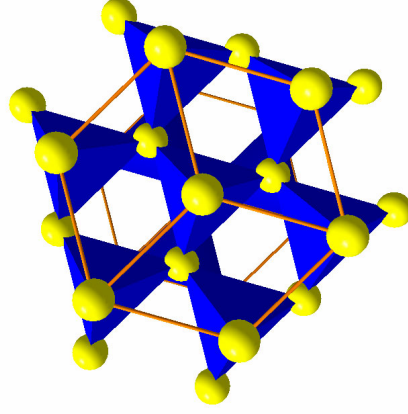
$Na_2O$   
 $NaO_4$  - tetraheda



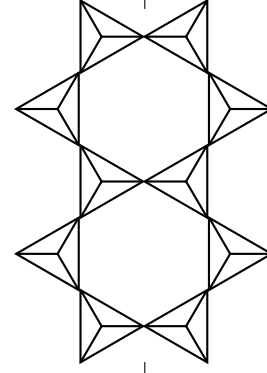
Sink blende  
 $ZnS_4$ ,  $SZn_4$



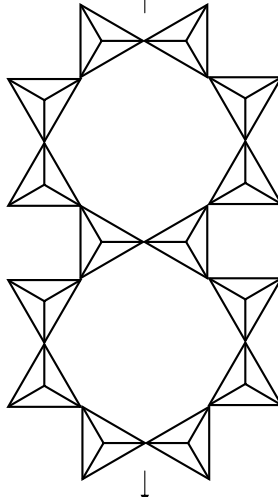
Wurtsitt  
 $ZnS_4$ ,  $SZn_4$



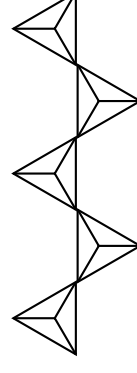
$A_4X_{11}$



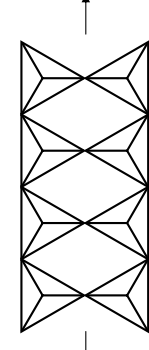
$A_6X_{17}$



$AX_3$



$A_2X_5$



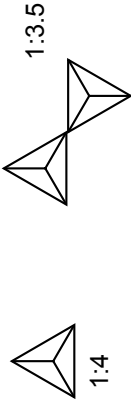
## Silicates:

SiO<sub>4</sub> tetrahedra

Corner (vertex) sharing, never edge or face (too strong Si<sup>4+</sup>-Si<sup>4+</sup> repulsions)

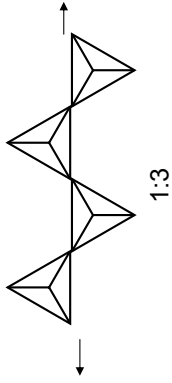
Only two SiO<sub>4</sub> tetrahedra share a common corner

Bridging oxygens count 1/2  
Non-bridging count 1



Rings  
Double rings  
Layer  
Double layer  
3D

1:3  
1:2.5  
1:2.5  
...  
1:2



# ZnS

## ZnS

Structural polymorphs:

Zink blende  
Wurstitt

Stable at normal P, T  
Stable at T > 1020 °C at P = 1 atm

Metastable at RT, but transforms by crushing

Thermodynamics  
Kinetics

Zink blende  
ccp  
1/2 tetrahedra holes filled

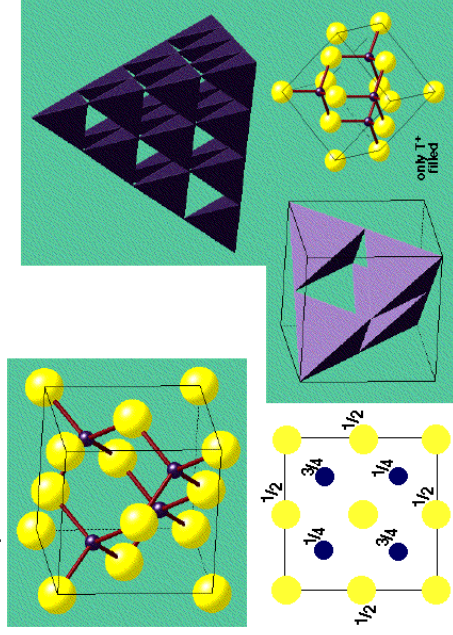
Wurstitt  
hcp  
1/2 tetrahedra holes filled

Relation between chemical formula and silicate anion structure.

Si:O ratio	Number of oxygens per Si		Type of silicate anion	Examples
	bridging	non-bridging		
1:4	0	4	isolated SiO <sub>4</sub> <sup>4-</sup>	Mg <sub>2</sub> SiO <sub>4</sub> , olivine, Li <sub>4</sub> SiO <sub>4</sub>
1:3.5	1	3	dimer Si <sub>2</sub> O <sub>7</sub> <sup>6-</sup>	Ca <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , rankinite, Sc <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> , thortveite
1:3	2	2	chains (SiO <sub>3</sub> ) <sub>n</sub> <sup>2n-</sup>	Na <sub>2</sub> SiO <sub>3</sub> , MgSiO <sub>3</sub> pyroxene
1:2.5	3	1	rings, eg Si <sub>3</sub> O <sub>6</sub> <sup>6-</sup> Si <sub>6</sub> O <sub>18</sub> <sup>12-</sup> infinite sheets (Si <sub>2</sub> O <sub>5</sub> ) <sub>n</sub> <sup>2n-</sup>	CaSiO <sub>3</sub> , BaTiSi <sub>3</sub> O <sub>9</sub> , benitoite Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> beryl Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
1:2	4	0	3D framework SiO <sub>2</sub> <sup>†</sup>	

\* CaSiO<sub>3</sub> is dimorphic. One polymorph has Si<sub>3</sub>O<sub>6</sub><sup>6-</sup> rings. The other polymorph has infinite (SiO<sub>3</sub>)<sub>n</sub><sup>2n-</sup> chains.  
† The three main polymorphs of silica, quartz, tridymite and cristobalite each have a different kind of 3D framework structure.

### ZnS Zinc Blende (Sphalerite)



CCP S<sup>2-</sup> with Zn<sup>2+</sup> in half Tetrahedral holes (only T+ {or T-} filled)

Lattice: fcc

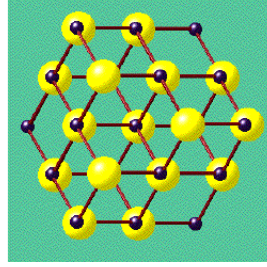
4ZnS in unit cell

Motif: S at (0,0,0); Zn at (1/4, 1/4, 1/4)

Coordination: 4:4 (tetrahedral)

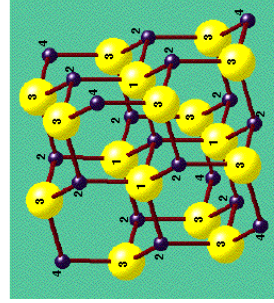
Cation and anion sites are topologically identical

### PLAN VIEWS



Zinc Blende

CCP ABC repeat  
HCP AB repeat  
COORDINATION ENVIRONMENTS



Zinc Blende

4 Nearest Neighbours (Tetrahedral)

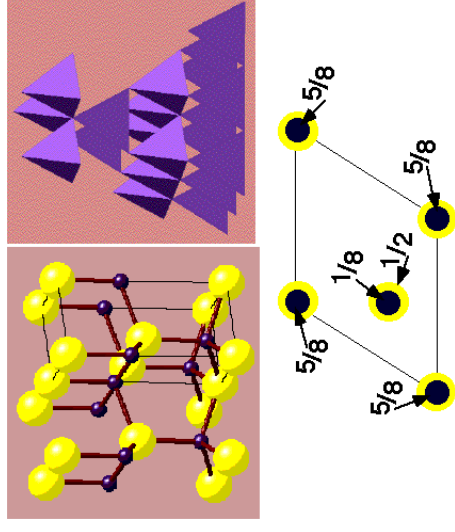
12 Next-Nearest Neighbours

6 Anti-Octahedral

6 Anti-Octahedral

Very different Next-Nearest Neighbour Coordinations & beyond

### ZnS Wurtzite



HCP S<sup>2-</sup> with Zn<sup>2+</sup> in half Tetrahedral holes (only T+ {or T-} filled)

Lattice: Hexagonal - P

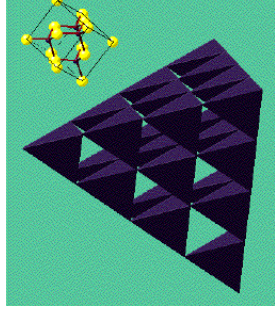
a = b, c Å (8/3)a

Motif: 2S at (0,0,0) & (2/3, 1/3, 1/2); 2Zn at (2/3, 1/3, 1/8) & (0,0,5/8)

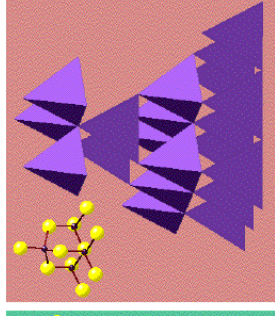
2ZnS in unit cell

Coordination: 4:4 (tetrahedral)

### POLYHEDRAL REPRESENTATIONS



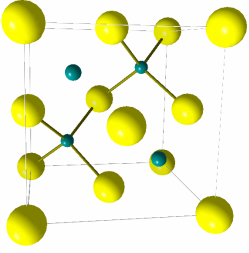
Zinc Blende



Wurtzite

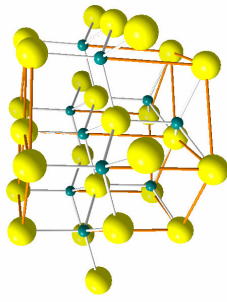
Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

Zink-blende



ZnS<sub>4</sub>-tetrahedra  
Diamond type structure if Zn = S  
Non-centrosymmetric

Wurtsitt

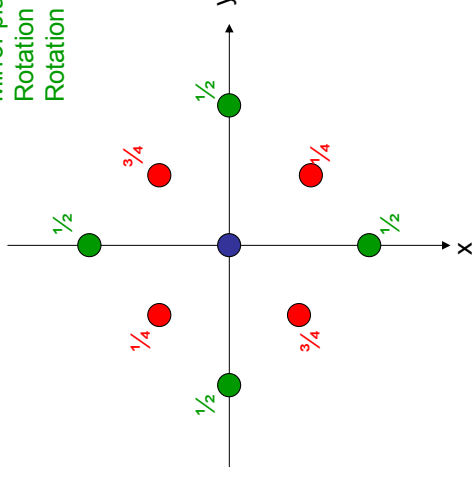


ZnS<sub>4</sub>-tetrahedra of + type

### Point symmetry

S in (0,0,0)

Check for:  
Inversion  
Mirror planes  
Rotation axis  
Rotation inversion axis



Cubic crystal system: Xabc

a = along <100>

b = along <111>

c = along <110>

a) 2, -2, 4, -4 ?

b) 3, -3 ?

c) 2, -2 (=m) ?

-43m

ZnS – wurtsitt

Z = 2 pr. hexagonal unit cell

Other related structures:

MX

MM'X<sub>2</sub>

M<sub>2</sub>M'M''X<sub>4</sub>

ZnO

LiGaO<sub>2</sub>

Li<sub>2</sub>BeSiO<sub>4</sub>

LiPO<sub>4</sub>

...

Polymorph

Allotrope modifications

Polytypes

ZnS (blende), ZnS (wurtsitt)

Diamond, graphite, C<sub>60</sub>

CdCl<sub>2</sub>, CdI<sub>2</sub>

...ABC...

vs.

...AB...

...ABCA...

vs.

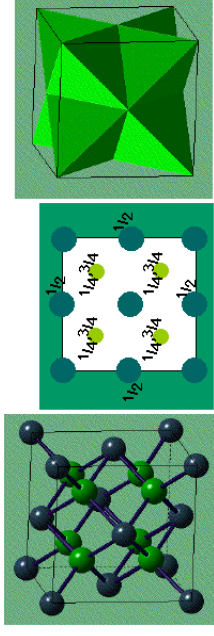
...ABAC...

vs.

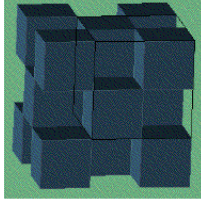
...AVACB...

?

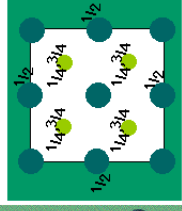
# CaF<sub>2</sub>



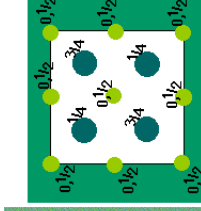
FCa<sub>4</sub> Tetrahedra



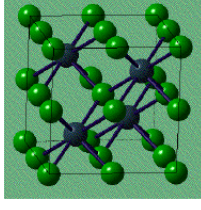
CaFg Cubes



Plan view



Plan view



*Fluorite B-cell*

CCP Ca<sub>2</sub>+ with F- in all Tetrahedral holes

Lattice: fcc

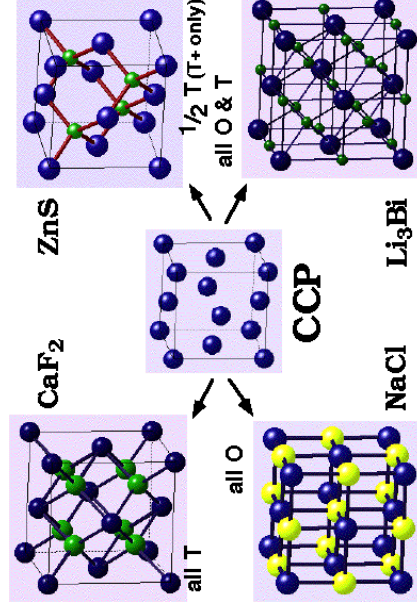
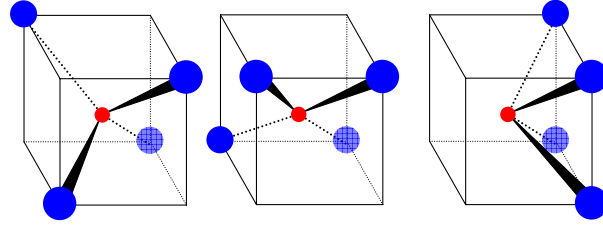
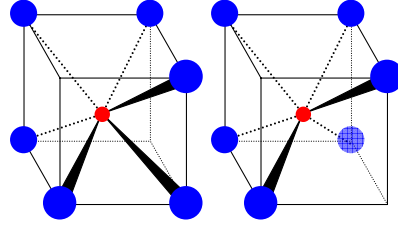
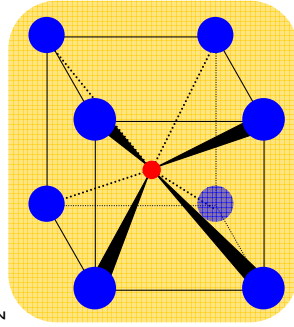
Motif: Ca<sub>2</sub>+ at (0,0,0); 2F- at (1/4, 1/4, 1/4) & (3/4, 3/4, 3/4)

4CaF<sub>2</sub> in unit cell

Coordination: Ca<sub>2</sub>+ 8 (cubic) ; F- 4 (tetrahedral)

In the related Anti-Fluorite structure Cation and Anion positions are reversed

CaF<sub>2</sub>



### NiAs Nickel Arsenide

HCP As with Ni in all Octahedral holes

Lattice: Hexagonal - P

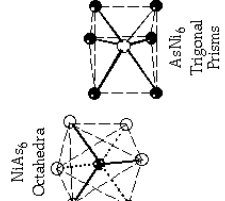
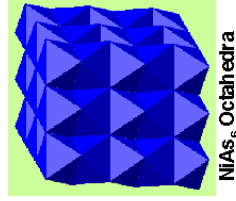
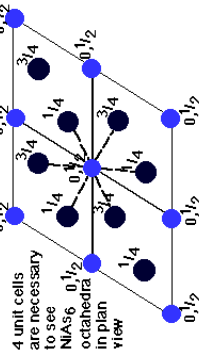
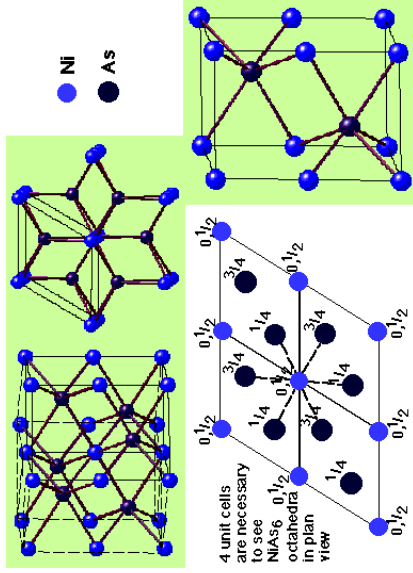
$a = b, c \neq a$

Motif: 2Ni at (0,0,0) & (0,0,1/2)

2As at (2/3, 1/3, 1/4) & (1/3, 2/3, 3/4)

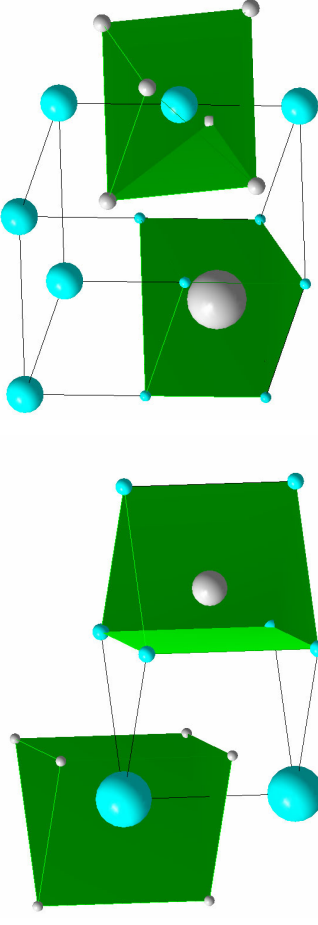
2NiAs in unit cell

Coordination: Ni 6 (octahedral) : As 6 (trigonal prismatic)



WC  
WC<sub>6</sub>, CW<sub>6</sub> trigonal prismatic

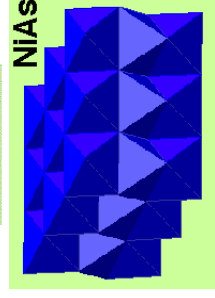
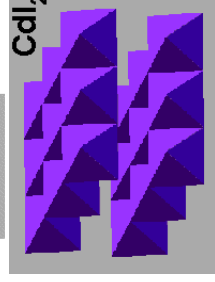
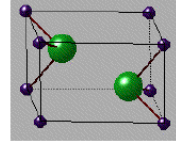
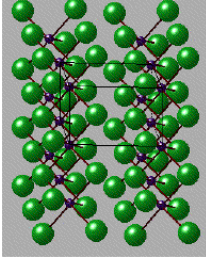
NiAs  
NiAs<sub>6</sub> octahedra  
AsNi<sub>6</sub> trigonal prismatic



100

100

### CdI<sub>2</sub> Cadmium Iodide



Lattice: Hexagonal - P

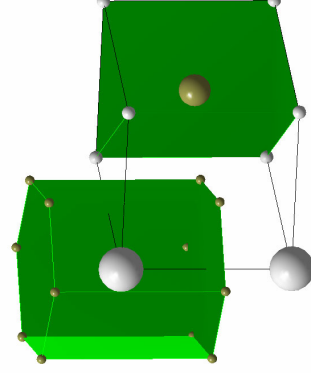
Motif: Cd at (0,0,0); I at (2/3, 1/3, 1/4) & (1/3, 2/3, 3/4)

1CdI<sub>2</sub> in unit cell

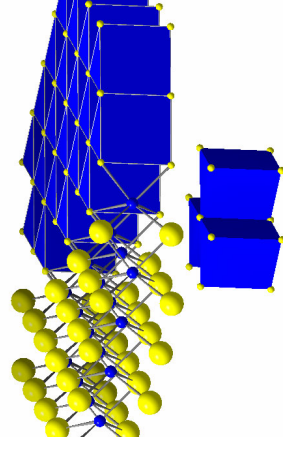
Coordination: Cd - 6 (Octahedral) : I - 3 (base pyramid)

AIB<sub>2</sub> hexagonal prismatic  
AIB<sub>12</sub> hexagonal prismatic  
BAI<sub>6</sub> trigonal prismatic

MoS<sub>2</sub> trigonal pyramidal  
SMO<sub>3</sub> trigonal pyramidal  
MoS<sub>6</sub> trigonal prismatic

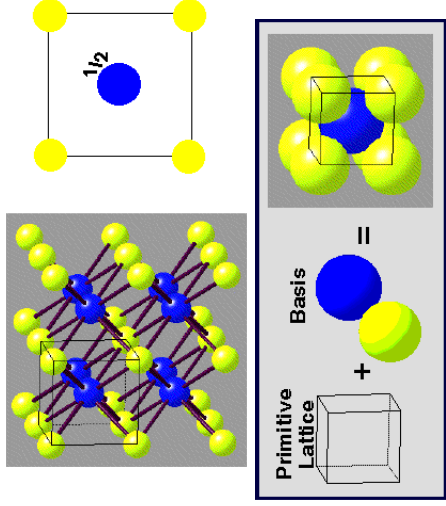


100



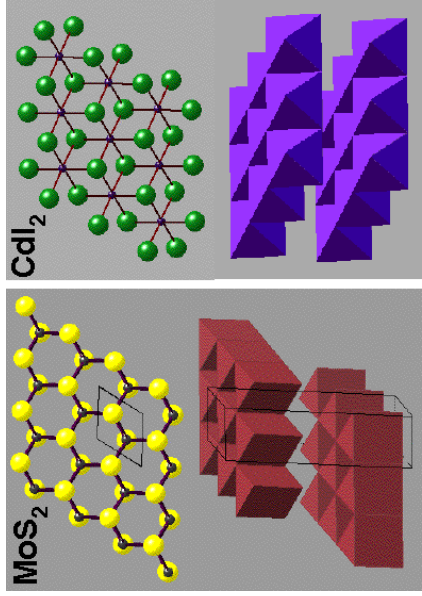


### CsCl Cesium Chloride



- Lattice: Cubic - P (N.B. **Primitive!**)
- Motif: Cl at (0,0,0); Cs at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
- 1CsCl in unit cell
- Coordination: 8:8 (cubic)
- Adoption by chlorides, bromides and iodides of larger cations, e.g. Cs<sup>+</sup>, Tl<sup>+</sup>, NH<sub>4</sub><sup>+</sup>

### MoS2 Molybdenite



**Note:** Hexagonal layers of S atoms are NOT Close-packed in 3D  
**Lattice:** Hexagonal - P  
**Motif:** 2Mo at  $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$  &  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$   
 4S at  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{8})$ ,  $(\frac{2}{3}, \frac{1}{3}, \frac{3}{8})$ ,  $(\frac{1}{3}, \frac{2}{3}, \frac{5}{8})$  &  $(\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$   
 2MoS2 in unit cell  
**Coordination:** Mo 6 (**Trigonal Prismatic**) : S 3 (base pyramid)

### MoS2 Molybdenite

