Symmetry

Crystal systems

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

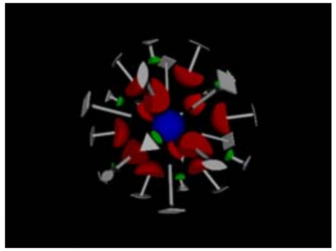


Table 1.1 *The seven crystal systems*

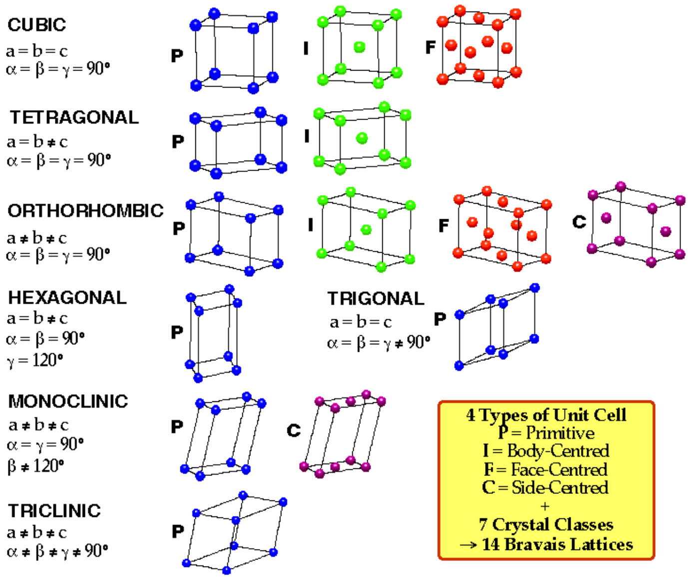
Crystal system	Unit cell shape†	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$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

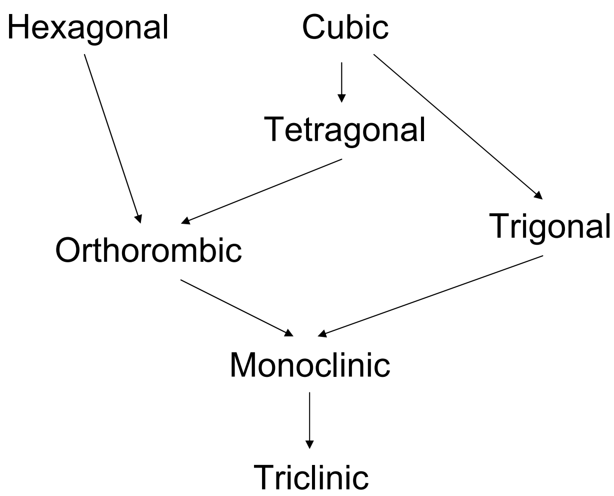
* Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with *b* as the unique axis and the other with *c* defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90^\circ, \gamma \neq 90^\circ$.

† The symbol ≠ means 'not necessarily equal to'. 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 unitcell the symmetry of the condensed material is described fully.

Bravais Lattices

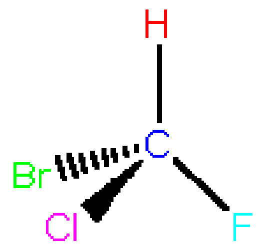




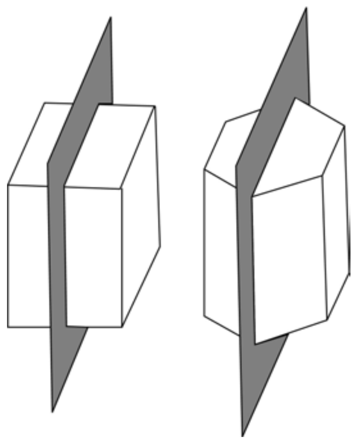
Symmety operations

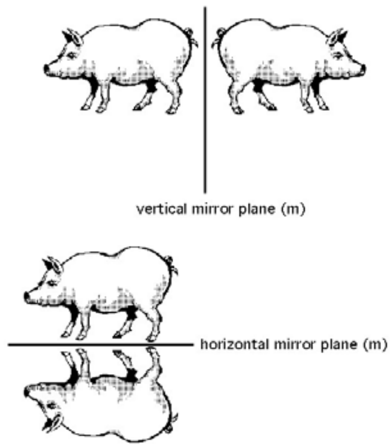
◆ Identity	*i*	Pointgroup symmetry
◆ Mirrorplane	*m*	
◆ Rotationaxis	*n (2,3,4,6)*	
◆ Invertionaxis	$\bar{n}$ ($\bar{1}$,$\bar{2}$…)	
◆ Sentrosymmetry	$\bar{1}$	Spechial symmetry operations
◆ Glidemirrorplane	*n, d, a, b, c*	
◆ Screwaxis	$2_1, 3_1, ..6_3$	

Identity *i*



Mirrorplane *m*

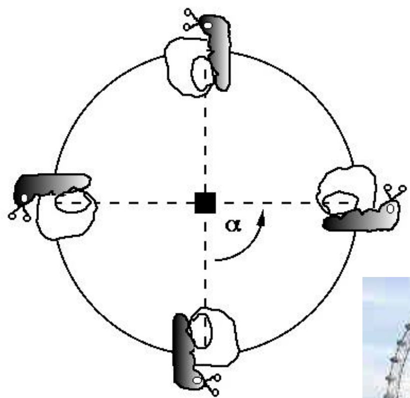


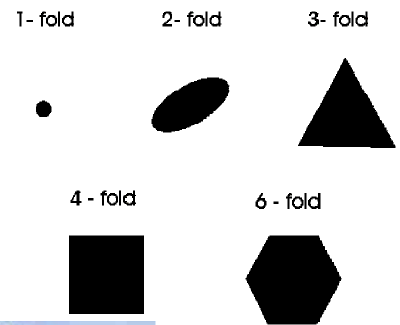


Rotationaxis n

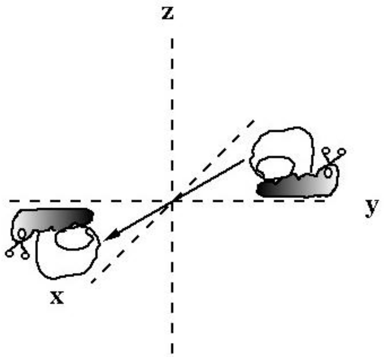
4-fold rotation axis

$\alpha = 360/n$





Inversionaxis $\bar{n}$



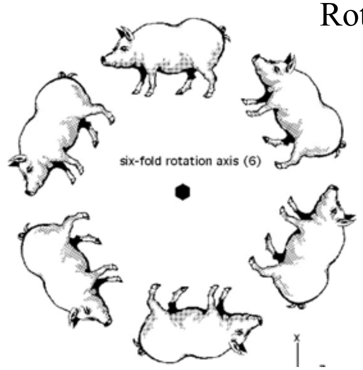
Rotation + inversion

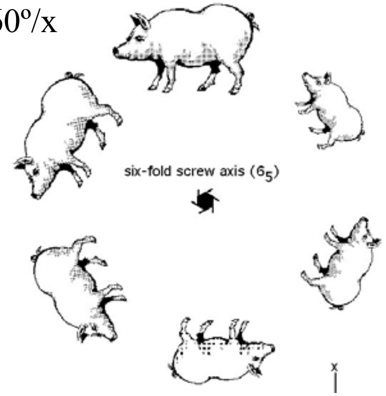
$\alpha = 360^o/n$

Screw axis, X_y

Translation: y/x

Rotation: 360º/x

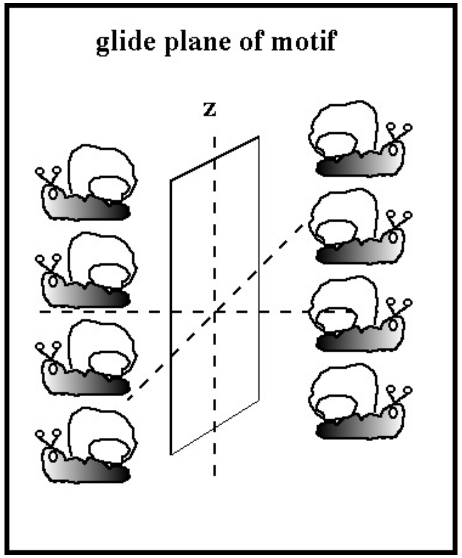


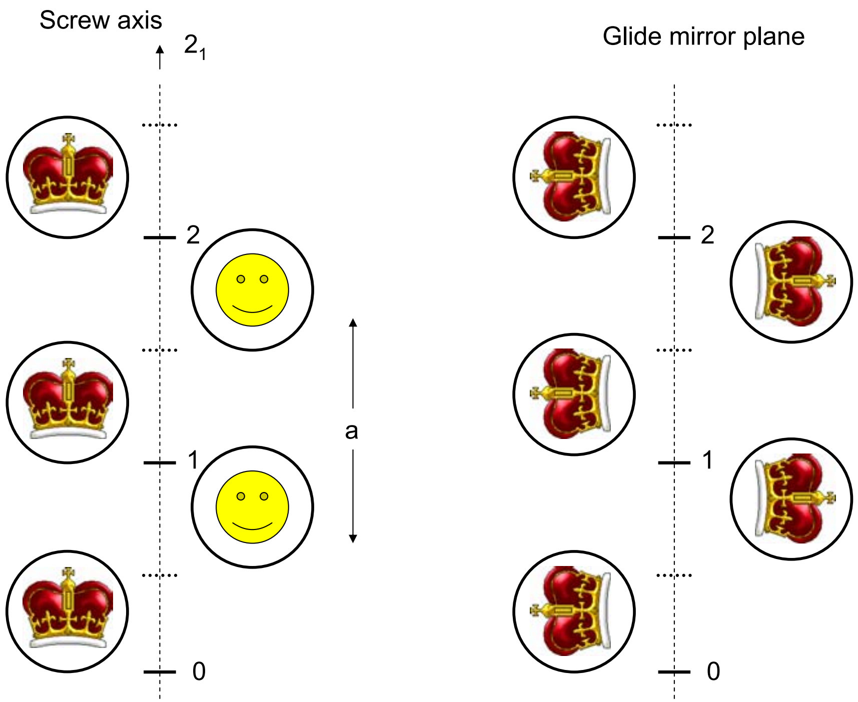


ordinary 6-fold rotation axis

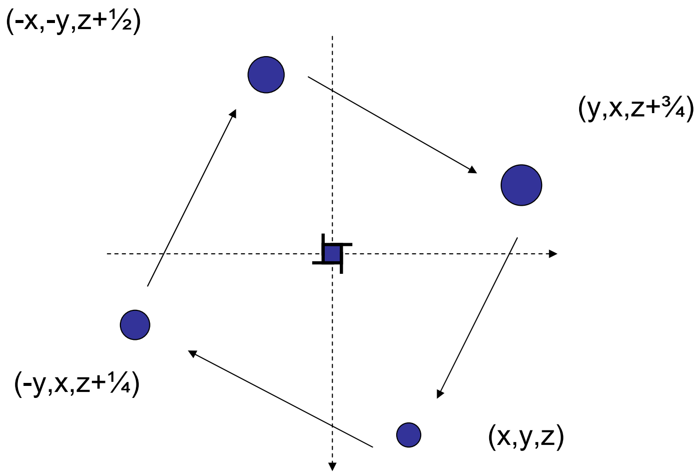
screw rotation axis 6_5

Glide plane



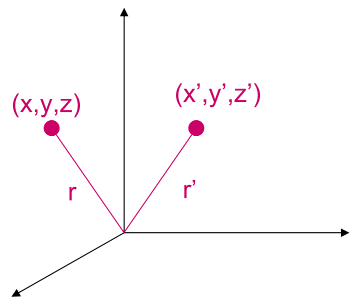


4_1



$$\{4\,|\,\vec{t}\} = (3\times3)r + \vec{t} = Rr + t$$

$$\{4\,|\,\vec{t}\}^4 = \{1\,|\,\vec{t}\}$$



r' = R·r

R is a symmetry operator

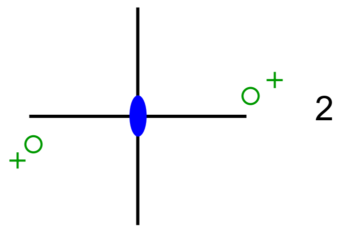
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Symmetry operations:

Identity: **I** $a_{ij} = 0$, $a_{ii} = 1$ $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

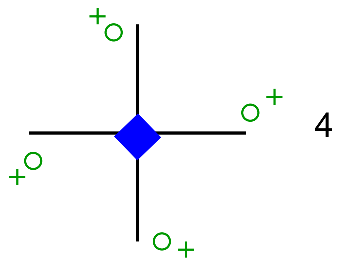
Rotation: n, C_n

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



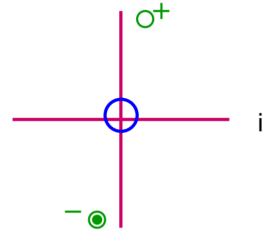
$$\{2[001]\}(xyz) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix}$$

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



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

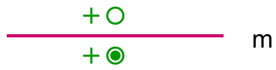
$$\{\bar{1}(i)\}(x,y,z) = (-x,-y,-z)$$



Right hand becomes left hand

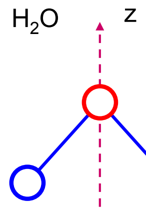
Mirrorplane: m

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



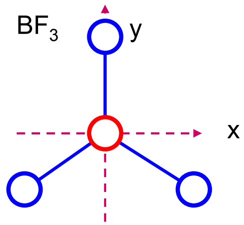
m is defined from the normal of the plane

Rotation axis | **Other symmetry elements**



C_2^z **2**

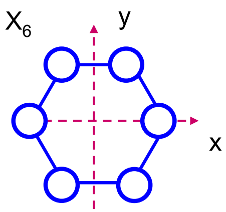
Vertical mirrorplane



C_3^z **3**

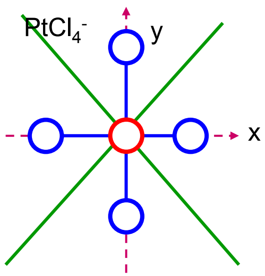
Horizontal mirrorplane
Vertical mirrorplane

Rotation axis | **Other symmetry elements**



C_6^z **6**

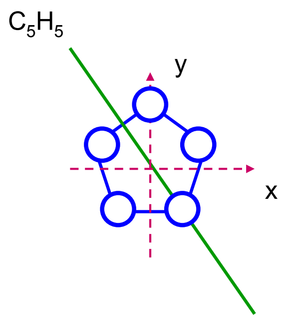
Two-fold axis
Mirror planes
Inversion center



C_4^z **4**

C_2 axis
Mirror planes
Inversion center

Rotation axis | **Other symmetry elements**



C_5^z **5**

5 C_2 axis
Mirror planes

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

Pointgroups

- A chracteristic collection of symmetry elements
- The symmetry elements has origo as common point
- Symmetry elements and point group symbol:

Two schemes:

Schönflies	σ, C_n
Hermann Mauguin	*m*, *n*

- Illustrated in form of stereographic projection

Triclin system

1 and $\bar{1}$ does not imply any restrictions for a,b,c or α,β,γ

Point group with elements:

1 **I**
$\bar{1}$ **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 (σ_h)

2 **I, C_2**
m **I, σ_h**

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

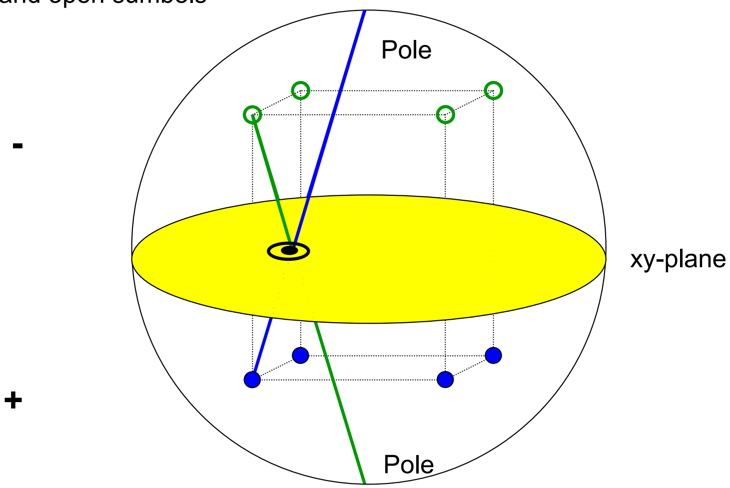
What about m normal to 2?
It does not change the criteria for a,b,c or α,β,γ and is hence possible.

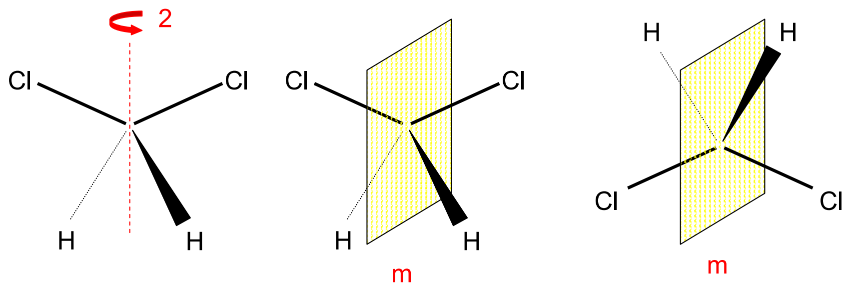
$$\{m[001]\}\{2[001]\} = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{bmatrix}\begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{bmatrix} = \begin{bmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1\end{bmatrix} = \{\bar{1}\}$$

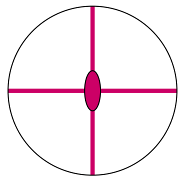
2/m sentrosymmetric, with the operations: I, C_2, σ_h, i

Stereographic projection

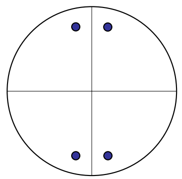
- The crystal is surrounded by a sphere
- We are interested in the projected surface in a xy-plane through the sphere
- The projected point is determined by the intersection of a connection line from the point of interrest to the pole of the opposite side.
- The two halves of the spheres are noted by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



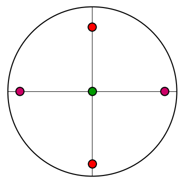




mm2



Generally 4 pos.



Spechially
2 pos.
2 pos.
1 pos.

Symmety operations

- Mirrorplane — *m*
- Rotationaxis — *n (2,3,4,6)*
- Invertionaxis — $\bar{n}$ ($\bar{1}$,$\bar{2}$…)
- Sentrosymmetry — $\bar{1}$

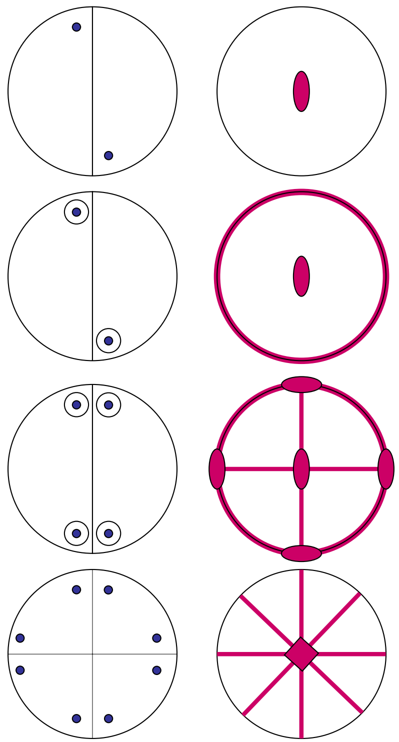
} Pointgroup symmetry

- Glidemirrorplane — *n, d, a, b, c*
- Screwaxis — 2_1, 3_1, ..6_3

} Spechial symmetry operations

Examples of stereograms of point groups

Points — Symmetry operations



2 (C_2)

2/m (C_{2h})

mmm (D_{2h})
(fullt symbol 2/m 2/m 2/m)

4mm (C_{4v})

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,-1
Monoklininc	2, m, 2/m
Orthorombic	222, mm2, mmm
Tetragonal	4, -4, 4/m, 422, 4mm, -42m, 4/mmm
Trigonal	3, -3, 32, 3m, -3m
Hexagonal	6, -6, 6/m, 622, 6mm, -6m2, 6/mmm
Cubic	23, m-3, 432, -43m, m-3m

Of these are:
11 centrosymmetric
21 non-centrosymmetric
10 polar
11 enantiomorphic (chiral)

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Trigonal	3, -3, 32, 3m, -32/m
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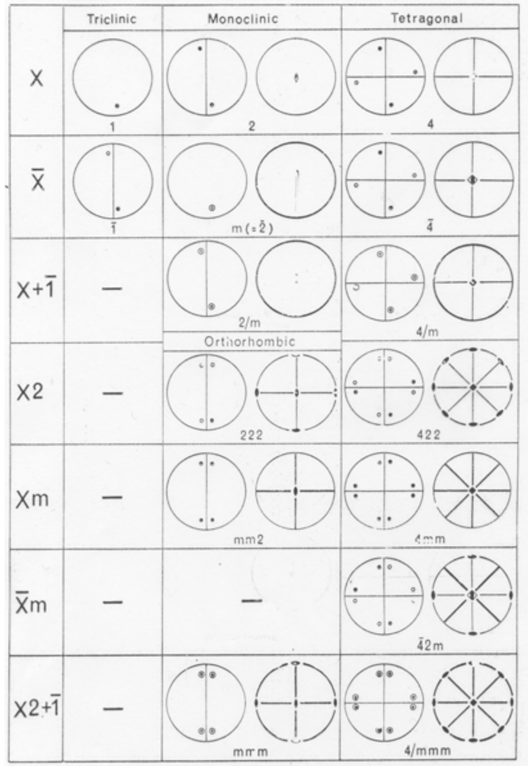
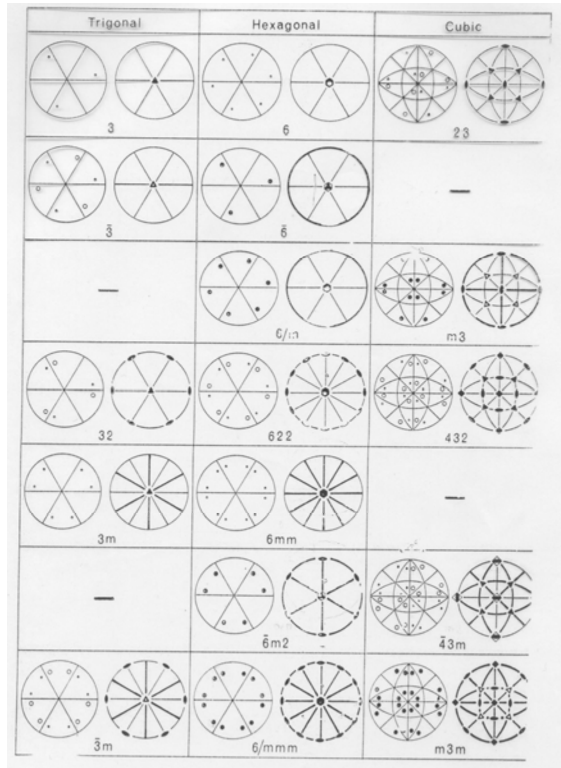




There are 230 space-groups!

Space group symbol: **Xefg**

Bravais lattice:
P (R)
F, I
A,B,C

Symmetry for characteristic directions (dependent on crystal system)

Symmetry operations **without** translation:

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

Symmorfe space groups (73 groups)

Symmetry operations **with** translation:

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

Non-symmorfe space groups (157 groups)

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

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 -> n for a screwaxis
a,b,c,d or n -> m for glide plane

Example:

$P6_3/mmc$	$6_3/mmc$	→	6/mmm
Pnma	nma	→	mmm

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

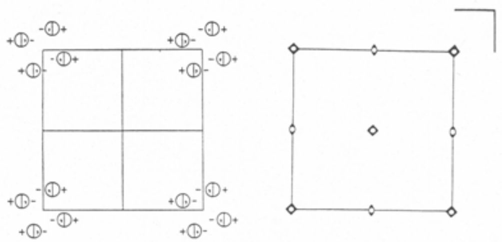
Crystal system: $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$

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

Corresponding crystallographic point group: 2/m

$P\,4/m$ C_{4h}^1 $4/m$ Tetragonal

No. 83 $P\,4/m$ Patterson symmetry $P\,4/m$



Origin at centre ($4/m$)

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le \frac{1}{2}$; $0 \le z \le \frac{1}{2}$

Symmetry operations

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

CONTINUED No. 83 $P\,4/m$

Generators selected (1); t(1,0,0); t(0,1,0); t(0,0,1); (2); (3); (5)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
8	l	1	(1) x,y,z (5) $\bar{x},\bar{y},\bar{z}$	(2) $\bar{x},\bar{y},z$ (6) $x,y,\bar{z}$	(3) $\bar{y},x,z$ (7) $y,\bar{x},\bar{z}$	(4) $y,\bar{x},z$ (8) $\bar{y},x,\bar{z}$	no conditions
							Special:
4	k	m..	$x,y,\frac{1}{2}$	$\bar{x},\bar{y},\frac{1}{2}$	$\bar{y},x,\frac{1}{2}$	$y,\bar{x},\frac{1}{2}$	no extra conditions
4	j	m..	$x,y,0$	$\bar{x},\bar{y},0$	$\bar{y},x,0$	$y,\bar{x},0$	no extra conditions
4	i	2..	$0,\frac{1}{2},z$	$\frac{1}{2},0,z$	$0,\frac{1}{2},\bar{z}$	$\frac{1}{2},0,\bar{z}$	hkl : $h+k=2n$
2	h	4..	$\frac{1}{2},\frac{1}{2},z$	$\frac{1}{2},\frac{1}{2},\bar{z}$			no extra conditions
2	g	4..	$0,0,z$	$0,0,\bar{z}$			no extra conditions
2	f	$2/m$..	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$			hkl : $h+k=2n$
2	e	$2/m$..	$0,\frac{1}{2},0$	$\frac{1}{2},0,0$			hkl : $h+k=2n$
1	d	$4/m$..	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$				no extra conditions
1	c	$4/m$..	$\frac{1}{2},\frac{1}{2},0$				no extra conditions
1	b	$4/m$..	$0,0,\frac{1}{2}$				no extra conditions
1	a	$4/m$..	$0,0,0$				no extra conditions

Symmetry of special projections

Along [001] $p\,4$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at 0,0,z

Along [100] $p\,2mm$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at x,0,0

Along [110] $p\,2mm$
$\mathbf{a}'=\frac{1}{2}(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$
Origin at x,x,0

Maximal non-isomorphic subgroups

I [2]$P\,4$ 1; 2; 3; 4
[2]$P\,\bar{4}$ 1; 2; 7; 8
[2]$P\,2/m$ 1; 2; 5; 6

IIa none

IIb [2]$P\,4_2/m$ ($\mathbf{c}'=2\mathbf{c}$); [2]$C\,4/a$ ($\mathbf{a}'=2\mathbf{a}, \mathbf{b}'=2\mathbf{b}$)($P\,4/n$); [2]$F\,4/m$ ($\mathbf{a}'=2\mathbf{a}, \mathbf{b}'=2\mathbf{b}, \mathbf{c}'=2\mathbf{c}$)($I\,4/m$)

Maximal isomorphic subgroups of lowest index

IIc [2]$P\,4/m$ ($\mathbf{c}'=2\mathbf{c}$); [2]$C\,4/m$ ($\mathbf{a}'=2\mathbf{a}, \mathbf{b}'=2\mathbf{b}$)($P\,4/m$)

Minimal non-isomorphic supergroups

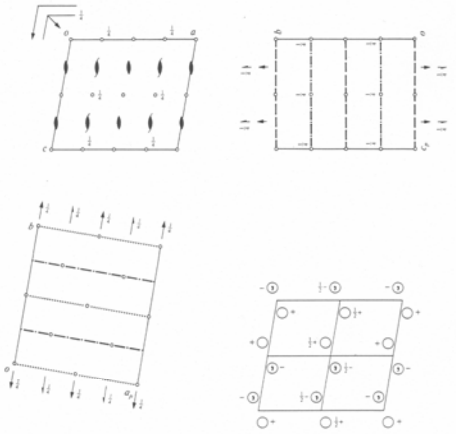
I [2]$P\,4/mmm$; [2]$P\,4/mcc$; [2]$P\,4/mbm$; [2]$P\,4/mnc$

II [2]$I\,4/m$

$C\,2/c$ C^6_{2h} $2/m$ Monoclinic

No. 15 $C\,1\,2/c\,1$ Patterson symmetry $C\,1\,2/m$

UNIQUE AXIS b, CELL CHOICE 1



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

Asymmetric unit $0 \le x \le \frac{1}{4};\ 0 \le y \le \frac{1}{2};\ 0 \le z \le \frac{1}{2}$

Symmetry operations

For (0,0,0)+ set

(1) 1 (2) 2 $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,0,z$

For $(\frac{1}{2},\frac{1}{2},0)$+ set

(1) $t(\frac{1}{2},\frac{1}{2},0)$ (2) $2(0,\frac{1}{2},0)$ $\frac{1}{4},y,\frac{1}{4}$ (3) $\bar{1}$ $\frac{1}{4},\frac{1}{4},0$ (4) $n(\frac{1}{2},0,\frac{1}{2})$ $x,\frac{1}{4},z$

CONTINUED No. 15 $C\,2/c$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},0)$; (2); (3)

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates (0,0,0)+ $(\frac{1}{2},\frac{1}{2},0)$+				Reflection conditions
					General:
8 f 1	(1) x,y,z	(2) $\bar{x},y,\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y},z+\frac{1}{2}$	$hkl: h+k=2n$; $h0l: h,l=2n$; $0kl: k=2n$; $hk0: h+k=2n$; $0k0: k=2n$; $h00: h=2n$; $00l: l=2n$
					Special: as above, plus
O 4 e 2	$0,y,\frac{1}{4}$	$0,\bar{y},\frac{3}{4}$			no extra conditions
4 d $\bar{1}$	$\frac{1}{4},\frac{1}{4},\frac{1}{2}$	$\frac{3}{4},\frac{1}{4},0$			$hkl: k+l=2n$
Cu 4 c $\bar{1}$	$\frac{1}{4},\frac{1}{4},0$	$\frac{3}{4},\frac{1}{4},\frac{1}{2}$			$hkl: k+l=2n$
4 b $\bar{1}$	$0,\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$			$hkl: l=2n$
4 a $\bar{1}$	0,0,0	$0,0,\frac{1}{2}$			$hkl: l=2n$

Symmetry of special projections

Along [001] $c2mm$ — $a'=a_p$ $b'=b$ — Origin at $0,0,z$

Along [100] $p2gm$ — $a'=\frac{1}{2}b$ $b'=c_p$ — Origin at $x,0,0$

Along [010] $p2$ — $a'=\frac{1}{2}c$ $b'=\frac{1}{2}a$ — Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2]$C121(C2)$ (1; 2)+
[2]$C\bar{1}(P\bar{1})$ (1; 3)+
[2]$C1c1(Cc)$ (1; 4)+

IIa [2]$P12/c1(P2/c)$ 1; 2; 3; 4
[2]$P12/n1(P2/c)$ 1; 2; (3; 4)+$(\frac{1}{2},\frac{1}{2},0)$
[2]$P12_1/n1(P2_1/c)$ 1; 3; (2; 4)+$(\frac{1}{2},\frac{1}{2},0)$
[2]$P12_1/c1(P2_1/c)$ 1; 4; (2; 3)+$(\frac{1}{2},\frac{1}{2},0)$

IIb none

Maximal isomorphic subgroups of lowest index

IIc [3]$C12/c1$ ($b'=3b$)($C2/c$); [3]$C12/c1$ ($c'=3c$)($C2/c$); [3]$C12/c1$ ($a'=3a$ or $a'=3a, c'=-a+c$ or $a'=3a, c'=a+c$)($C2/c$)

Minimal non-isomorphic supergroups

I [2]$Cmcm$; [2]$Cmca$; [2]$Cccm$; [2]$Ccca$; [2]$Fddd$; [2]$Ibam$; [2]$Ibca$; [2]$Imma$; [2]$I4_1/a$; [3]$P\bar{3}12/c$; [3]$P\bar{3}2/c1$; [3]$R\bar{3}2/c$

II [2]$F12/m1(C2/m)$; [2]$C12/m1$ ($2c'=c$)($C2/m$); [2]$P12/c1$ ($2a'=a, 2b'=b$)($P2/c$)

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

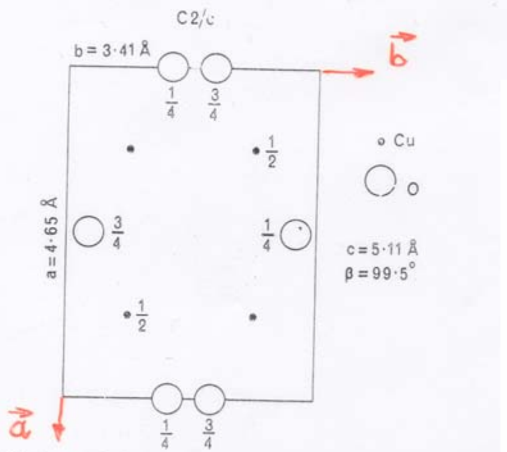
Atom coordinates:		
	Cu	¼, ¼, 0
	O	0, 0.416, ¼

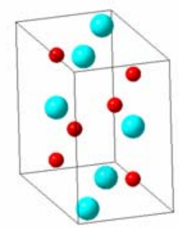
Symmetry operations on a general position:

(x,y,z) → (-x,y,½ -z) → (-x,-y,-z) → (x,-y, ½+z)

↓ (½+x, ½+y,z) ; ↓ (½-x, ½+y,½ -z) ; ↓ (½-x, ½-y,-z) ; ↓ (½+x, ½-y, ½+z)

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 : ¼, ¼, 0 etc.

O : 0, y, ¼ med y = 0.416 (eksperimentelt)

Density

•Experimental (pyknometric)

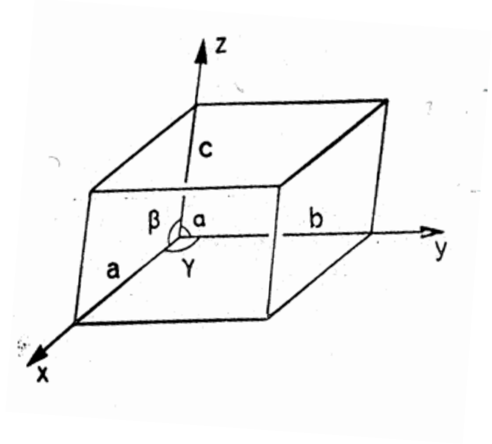
•Wetting

•Pores in the material

•Calculated; X-ray density
based on the assumption that the unit cell is known or that a model exists

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

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



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

Density and defects

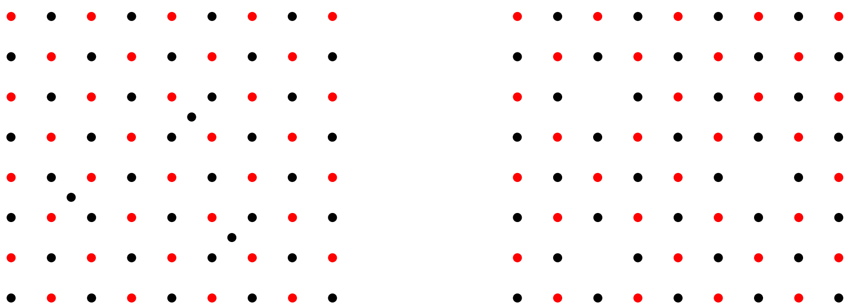
ρ_{obs}

ρ_{calc}

•V unitcell; is determined experimentally
•Formula weight

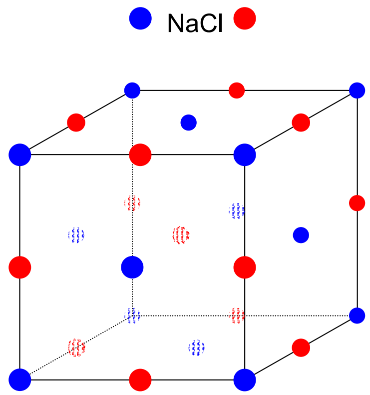
↓

Model assumptions:
A/B < 1

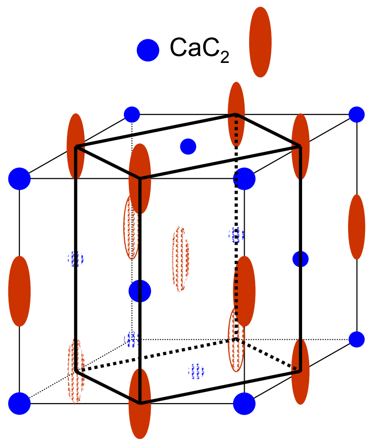


AB_{1+y} $\qquad$ $A_{1-x}B$

ρ(interstitial B) > ρ(perfect) > ρ(vacant space A)

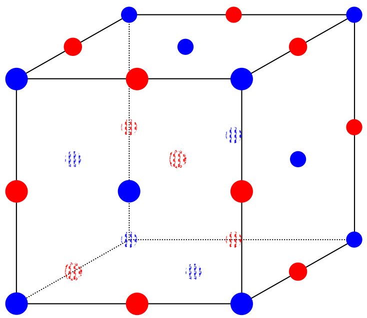


Cubic
z = 4



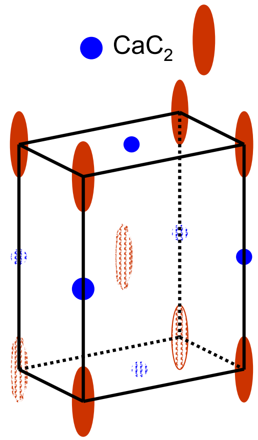
Non-cubic

NaCl



Cubic
z = 4

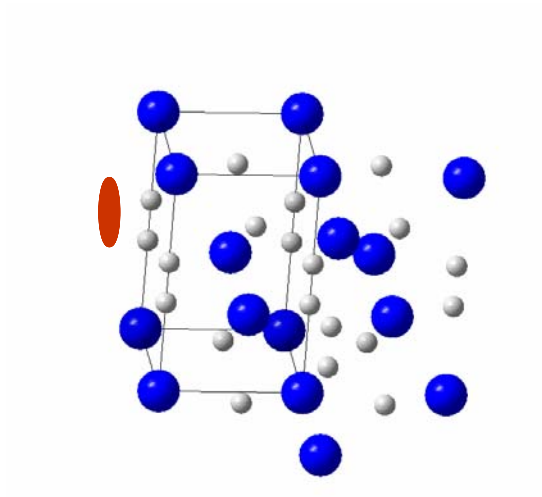
CaC_2



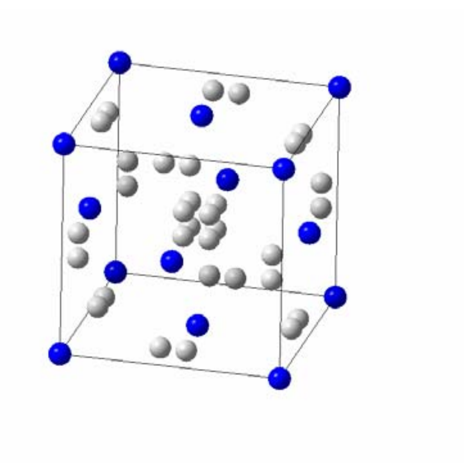
Non-cubic

Tetragonal
z = 2

CaC_2 (lt)



CaC_2 (ht)



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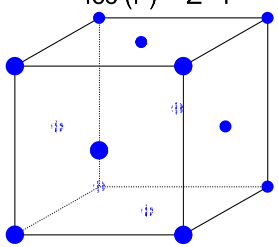
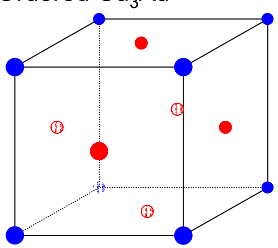
fcc (F) Z=4

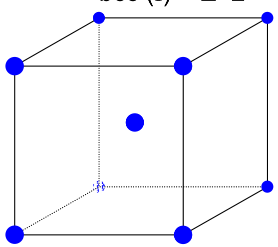


Disordered $Cu_{0.75}Au_{0.25}$
High temp

Low temp
Ordered Cu_3Au

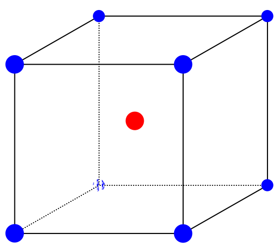


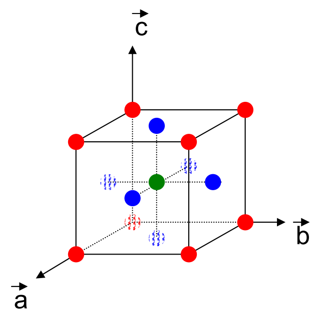
bcc (I) Z=2



Disordered $Cu_{0.50}Au_{0.50}$
High temp

Low temp
Ordered CuAu

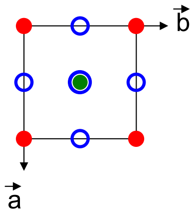




ABO_3

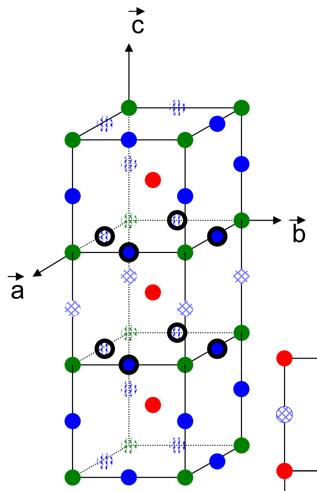
Perovskite
a=b=c, $\alpha=\beta=\gamma=90°$
cubic

Projection on the ab-plane:



Cell dimensions are determined by:
A-O-A

ac-plane
bc-plane } Identical



$A_3B_3O_6$ $YBa_2Cu_3O_6$

Perovskite
$a=b\neq c$, $\alpha=\beta=\gamma=90°$
Tetragonal

Assume that the ab-plane is unchanged viz. a=b. Assume changed c-axis

Projection on the ab-plane: